MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

PRODUCTION AND CHARACTERIZATION OF LOW MASS HIGH TEMPERATURE RESISTANT POLYMER-BASED ADVANCED COMPOSITE MATERIAL

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Ph.D. THESIS

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MARMARA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

DÜŞÜK KÜTLELİ YÜKSEK SICAKLIK DAYANIMINA SAHİP POLİMER BAZLI İLERİ KOMPOZİT MALZEMENİN ÜRETİM VE KARAKTERİZASYONU

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ABSTRACT

PRODUCTION AND CHARACTERIZATION OF LOW MASS HIGH TEMPERATURE RESISTANT POLYMER-BASED ADVANCED COMPOSITE MATERIAL

This study presents heat-resistant polyimide based advanced composite sandwich panels consisting of carbon fiber reinforced PI matrix thermoset and thermoplastic advanced composite laminates (outer faces) and PI foams (core materials). CF-reinforced thermoset and thermoplastic PI matrix advanced composite laminates were manufactured by synthesizing various PI precursors. These precursors were synthesized as poly (amic acid), poly (ester amine) salt and poly (amic acid) ammonium salt. By using these PI precursors, thermoplastic and thermoset advanced composite faces were obtained. The poly (amic acid) ammonium salt precursor resin was applied as a novel method for manufacturing these advanced composites. The thermoplastic composite obtained from the ammonium salt precursor exhibited superior mechanical properties and enhanced thermal properties in comparison to the other advanced composites in this study and those in the literature. On the other hand, the thermosetting composites exhibited highly enhanced storage modulus values up to 400 ˚C and outstanding thermal stability. The thermosetting composite that was obtained from the nadic anhydride terminated poly (amic acid) precursor exhibited high mechanical properties besides its thermal properties. These two advanced composites became prominent and were used for outer faces of the heat resistant sandwich composites. The heat resistant sandwich composites had also two kinds of core materials with low densities. Isocyanate-based PI foams were synthesized and used as core materials. These foams presented different compressive properties. In addition to this, thermosetting adhesive polyimide precursor resin was synthesized to bond these produced outer faces and cores. These sandwiches exhibited high compressive and flexural properties.

ÖZET

DÜŞÜK KÜTLELİ YÜKSEK SICAKLIK DAYANIMINA SAHİP POLİMER BAZLI İLERİ KOMPOZİT MALZEMENİN ÜRETİM VE KARAKTERİZASYONU

Bu çalışmada, karbon fiber takviye edilmiş termoset ve termoplastik poliimid matriksli ileri kompozit laminatlar (dış yüzeyler) ve poliimid köpüklerden (çekirdek malzemeleri) oluşan yüksek ısı dirençli poliimid bazlı gelişmiş tabakalı kompozitler sunulmaktadır. CF takviyeli ileri kompozitlerin imalatında çeşitli sentezlenen öncü poliimid reçineleri kullanılmıştır. Bu öncü PI reçineleri, poli (amik asit), poly (ester amin) tuzları ve poli (amik asit) amonyum tuzları olarak sentezlendi. Poli (amik asit) amonyum tuz öncü PI reçinesinden elde edilen CF takviyeli ileri seviye kompozit imalatı yeni bir metot olarak uygulandı. Bu metottan elde edilen CF takviyeli termoplastik poliimid kompozit, bu çalışmadaki ve literatürdeki diğer gelişmiş kompozitlere kıyasla üstün mekanik özellikler ve gelişmiş termal özellikler sergiledi. Diğer yandan CF takviyeli termoset PI matriksli ileri kompozit malzemeler 400 ˚C'e kadar oldukça gelişmiş depolama modülü ve olağanüstü termal kararlılık sergilemiştir. Bunlara ek olarak, nadik anhidrid sonlu poli (amik asit) PI öncü reçinesinden elde edilen CF takviyeli termoset kompozit ise, bahsedilen termal özelliklerin yanı sıra bu çalışmadaki ve literatürdeki diğer gelişmiş kompozitlere kıyasla üstün mekanik özellikler sergiledi. Bu iki gelişmiş termoplastik ve termoset kompozit diğer kompozitler arasından öne çıktı ve ısı dirençli tabakalı kompozitler için yüzey malzemesi olarak kullanıldılar. Isı dirençli tabakalı kompozitlerde aynı zamanda iki çeşit düşük yoğunluklu kor malzeme kullanıldı. Bu kor malzemeler için izosiyanat bazlı poliimid köpükler sentezlendi. Bu poliimid köpükler farklı seviyede basma özellikleri sergilediler. Bunlara ek olarak bu iki malzemeyi birleştirerek tabakalı yapıyı elde etmek için termosetleşebilen poliimid öncü yapıştırıcı reçine sentezlendi. Ortaya çıkan ısı dirençli tabakalı yapılar yüksek seviyede basma ve eğme dayanımları sergilediler.

CLAIM OF ORIGINALITY

When reviewing the literature, there have been few reports about heat-resistant sandwich composite structures in the literature for the applications above 200 or 250 ˚C. In the literature, it is possible to find separate studies focusing solely on PI foams or fiber reinforced PI-based composites. However, the literature is very poor in terms of the availability of heat-resistant sandwich structures. The literature has only presented Ogasawara'study about heat resistant sandwich structures that consisting of CF reinforced thermoset polyimide matrix composite face and carbon foam core for the applications above 250 ˚C. Sandwich structure composites are very important materials for aviation, aerospace and defence industries in terms of their higher compression and flexural forces and lower densities because of core materials. In this study, heat-resistant sandwich structure composites that consisting of PI based outer faces and core materials were prepared. While outer faces were CF reinforced thermoset and thermoplastic PI matrix advanced composites, the core materials were isocyanate based PI foams. For the advanced composite faces, various PI precursors were synthesized and prepregs were prepared by using these precursor resins. These precursors were poly (amic acid), polyester amine salts and poly (amic acid) ammonium salts. The poly (amic acid) ammonium salt precursor was applied as a novel method for manufacturing CF-reinforced PI matrix advanced composites. The advanced thermoplastic composite obtained from the poly (amic acid) ammonium salt precursor exhibited superior mechanical properties and enhanced thermal properties (near the thermal properties of thermoset advanced composites) in comparison to the other advanced composites in this study and those in the literature. Moreover, the thermoset advanced composite from obtained NA terminated PAA precursor exhibited superior thermo-mechanical properties besides improved mechanical properties when compared to the other advanced composites in this study and those in the literature. For core materials, two kinds of isocyanate based PI foams with low densities were prepared such as 15 and 50 kg/m^3. These foams were entegrated to the advanced composite faces with curing the synthezied PI precursor adhesive resin and heat-resistant advanced sandvich structure composite panels were manufactured. These sandwiches presented improved compressive and flexural properties besides their low densities and thermal properties.

SYMBOLS

A : Cross sectional area

Å : Angstrom

b : Width of tested beam

bar : Unit of pressure

c : Core thickness

˚C : Centigrade degree

COOH : Carboxylic acid

Cu-Kα : X-ray energy frequently used on labscale x-ray instruments

d : Depth of tested beam

E : Elasticity modulus

E′ : Storage modulus

E″ : Loss modulus

k : Reaction rate constant

K : Kelvin

m : Tangent to the initial straight-line portion of the load-deflection curve

mPa.s : Millipascal second

Mn : Number averaged molecular weight

Mw : Weight averaged molecular weight

n : Repeating unit of polymerization

n : Mole ratio

N : Force (Newton)

pKa : The negative log of the acid dissociation constant

ppm : Parts per million

P : Load on tested beam

s : Second

S : Slope of the initial linear portion of the load deflection curve ($\Delta P/\Delta u$)

Tan δ : Loss modulus to storage modulus in DMA

T_d : Initial decomposition temperature in TGA

T_{d5} : 5% weight decomposition temperature in TGA

T_{d10} **:** 10% weight decomposition temperature in TGA

Tg **:** Glass transition temperature

Tm **:** Melting temperature

u **:** Displacement of the loading block

V0 **:** Rating value obtained from by UL94 non-flammability test

V1 **:** Rating value obtained from by UL94 non-flammability test

V2 **:** Rating value obtained from by UL94 non-flammability test

Wt % **:** Weight percentage

W **:** Watt

Θ **:** Reflections from planes set at theta angle during XRD test

λ **:** Energy of Cu-Kα corresponds to an x-ray wavelength of 1.5406 Å

σ **:** Stress

σ_F **:** Facing bending stress

ABBREVIATIONS

ATI : Acetylene terminated imides

BTDE : BTD-dimethyl ester

BMI : Bismaleimide

BTDA : 3,3′,4,4′-Benzophenone-tetracarboxylic dianhydride

BPADA : Bisphenol A dianhydride

BPDA : Biphenyl dianhydride

CHP : 1-Cyclohexyl-2-pyrrolidinone

CF : Carbon fiber

CAI : Compression after impact

CFRP : CF reinforced PI matrix composite

CNT : Carbon nanotubes

CSUS : Core shear ultimate strength

DO : Dopamine hydrochloride

DMAc : Dimethylacetamide

DMF : Dimethylformamide

DMSO : Dimethyl sulfoxide

DSC : Differential scanning calorimetry

DMA : Dynamic mechanical analysis

DMBZ : 2,2'-Dimethylbenzidine

DCC : N,N-Dicyclohexylcarbodiimide

DADPS : 4,4-Diamino diphenyl sulfone

DMF : Dimethylformamide

DMDA : 2,2’-Dimethyl-1,3-(4-aminophenoxy)propane

DCT : Damping coefficient

DTA : Differential thermal analysis

FBS : Facing bending stress

FT-IR : Fouirer transform infrared spektrofotometre

GPa : Gigapascal

GPC : Gel permeation chromatography

GO : Graphene oxide

h : Hour

Hz : Hertz

HRACS : Heat resistant advanced sandwich composite panel

IDT : Initial decomposition temperatures

Kj : Kilojoule

KPa : Kilopascal

L : Length of support span of flexural test machine

LOI : Limiting oxygen index

MPa : Megapascal

Min : Minute

MDA : 4,4'-Methylene dianiline

MW : Multiwall

MetOH : Methanol

NA : Nadic anhydride, 5-Norbornene-2,3-dicarboxylic anhydride

NMP : N-methylpyrrolidone

NMR : Nuclear magnetic resonance

ODA : 4,4'-Diamino diphenyl ether

ODPA : 3,3′,4,4′-Oxydiphthalic anhydride

PA : Phthalic anhydride

PDA :1,3-phenylene diamine

PI : Polyimide

PMR : Polymerization of monomeric reactant

PAA : Poly (amic acid)

PMDA : Pyromellitic dianhydride

PAAS : Poly (amic acid) ammonium salt

PEPA : Phenylethynylphthalic anhydrides

PAI : Poly (amide imide)

PAPI : Polyaryl polymethylene isocyanate

PMI : Poly (methacryl imide)

PEAS : Poly (ester amine) salt

PETI : Phenyl ethynyl terminated imide

PAE : Poly (amic ester)

PP : Polypropylene

PEPA : 4-Phenylethynyl phthalic anhydride

PMDI : Polymeric diphenylmethanediisocyanate

PETI : Phenyl ethynyl terminated imide

PMDA : Pyromellitic dianhydride

rpm : Revolutions per minute

RT : Room temperature

SEM : Scanning electron microscopy

T : Core shear ultimate strength

TMS : Tetramethyl silane

TDA : 4,4'-thiodianiline

TCC : Thermal conductivity coefficient

THF : Tetrahydrofuran

TGA : Thermogravimetric analysis

TEA : Triethylamine

UV : Ultraviole

XRD : X-ray diffraction

4-BDAF : 2,2-Bis(4-(4-aminophenoxy)phenyl) hexafluoropropane

6FDA : 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride

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1. INTRODUCTION

1.1. Polyimide Materials

Aromatic polyimides (PI) are one of the very important kind of high-performance engineering plastics. These PIs exhibit much enhanced properties such as high glass transition temperature, non-flammability, excellent electrical and thermo-mechanical stability, high mechanical properties, high chemical resistance and adhesive properties [1]. These enhanced properties allow polyimide materials using in optoelectronic applications, gas separation applications, superhydrophobic and chemical resistant coatings and films, photocatalysts for hydrogen generation, aerospace and advanced composites [2, 3].

In industry, there are two kinds of PIs that have been used commercially. These are thermoplastic and thermoset PI materials. Thermoplastic PIs are generally obtained by condensation reaction of dianhydrides and diamines. Thermoset PI materials obtain crosslinking with some reacting groups that terminated polymer chains such as phenylethynyls, vinyls, nadics, acetylenes or phenylethynyls. Thermoplastic and thermoset PIs are prepared with using similar condensation reactions. Firstly various PI precursors with or without end cappers have been synthesized for thermoplastic and thermoset PI materials. Reactive end capper terminated PI precursors can present network structures with curing between 270-350 ˚C by means of the additon of these reactive groups [4]. Some of these thermoplastic and thermoset polyimides are commercially termed as Kapton®, PMR-15, PMR-II, LARC, DMBZ-15 Vespel®, ULTEM, Avimid N®, Skybond® or UltradelTM. These materials were applied to flexible circuits, flexible connectors, chip carriers and interconnects for electronic industry. In aerospace industry, they can be used as wire insulation, motor wire windings, electrical switches, structural adhesives, covering for fuel tank. They have been also used as advanced composites for wings and airframes of military aircraft, nacelles and parts close to aircraft engines such as external nozzle flaps, inner and outer ducts, swirl frames, reverser stang fairings, ultra-high-speed fan blades and shuttle orbital aft body flaps. Moreover, PIs have been used as ion thruster beam shields for the flights of space shuttles. On the other hand, PIs have been even used for pacemakers and eye lens implants in medical industry. These PIs have been synthesized by using various methods.

1.2. Polyimide Synthesis

PIs are synthesized by using various synthesis methods according to application areas of PIs such as foams, coatings, films, nanocomposites and fiber reinforced advanced composites. In this section, these synthesis methods will be explained and discussed.

1.2.1. Polyimide synthesis from poly (amic acid) precursor by using conventional two-step method

The most common and known synthesis method is two-step method with poly (amic acid) (PAA) precursor. DuPont solved the infusibility and insolubility problem of aromatic PIs and presented the synthesis approach of Kapton as shown in Figure 1.1. In this synthesis approach, 4,4'-diamino-diphenyl ether (ODA) and pyromellitic dianhydride (PMDA) was used as diamines and dianhydrides monomers and these monomers reacted each other in an aprotic solvent such as dimethylacetamide (DMAc) in order to obtain PAA. These PAA precursors were soluble and convertible to PIs.

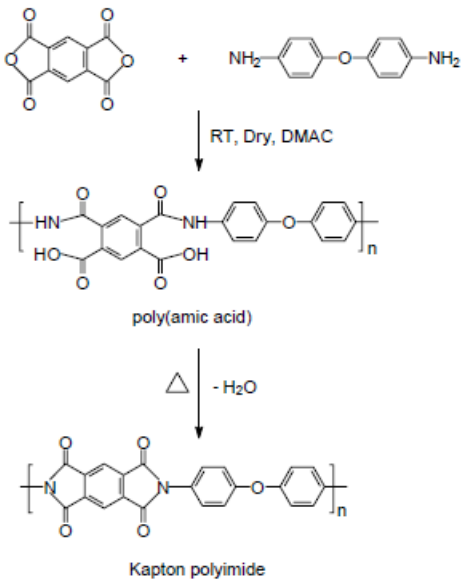


Figure 1.1 Synthesis scheme of Kapton commerical PI material [5]

1.2.2. Synthesis of poly (amic acid)

PAAs are obtained by reaction of a diamines and a dianhydride with a polar aprotic solvent such as DMAc, dimethylformamide (DMF), N-methylpyrrolidone (NMP), and tetrahydrofuran (THF) below room temperature or in an inert gas condition. A

nucleophilic reaction is occurred between the amino groups and the carbonyl groups on the anhydride monomer and then the anhydride ring is opened during the obtaining of repeating units of the PAA. This reaction is a reverse reaction but the kinetic of the forward reaction is much higher than the reverse at the synthesis period of PAA. However, there is a different situation available in the acylation reaction of amine. The forward reaction is second order reaction in this synthesis period of PAA to PI. This reaction is exothermic reaction therefore the reaction should be occurred at low temperature to obtain high molecular weight [6]. Moreover, there is also an important factor to determing the progress rate of the PAA reaction. Nitrogen atom on amino group presents strong nucleophilicity and carbonyl group on dianhydride presents strong electrophilicity. These similar interactions between electrons forward PAA reaction. However, nucleophilicity of the diamine is much more effective than electrophilicity of carbonyl group belonging to the dianhydride for the acylation of the PAA. The higher nucleophilicity of the diamine is the higher reactivity for the acylation of the PAA. The reactivity of diamines determines with the value of pKa which is termed as Hammett relation [7]. This value presents the basicity level of diamines. However, very high basicity prevents to react diamines to dianhydrides, presents tendency to formation of ionic salts. Thus, COOH groups on PAA form ionic bonding with diamines with very high basicity such as aliphatic diamines. The optimum value pKa of diamines should be ranging from 4.5 to 6 [8]. The very low pKa value of diamines cause not to react with dianhydrides due to the poor nucleophilic ability. On the other hand, the electron affinity of anhydrides affect to reaction rate. By increasing in electron affinity of anhydrides increases the acylation rate of PAA. In previous studies, Ea values of various dianhydrides were measured and observed for the effects on the acylation reaction of 4,4’-diaminodiphenyl ether [9]. Besides the monomer reactivities, type of solvents is very important and critical for polymerization. Polar aprotic solvents have tendency to occur strong hydrogen bondings with carbonyl groups on anhydrides and they have major role to move the equilibrium of the reaction to producing PAA. Therefore reverse reaction can be minimized due to the polar aprotic solvents during the occurring of PAA. Polar aprotic solvents are generally used in synthesis reactions of PAAs. In literature, the rate of PAA formation was observed with using polar aprotic solvent with different levels such as THF, acetonitrile, DMAc [10]. The ranking in the rate of PAA formation was THF< acetonitrile < DMAc. On the other hand, these are various minor side reactions during the synthesis of PAAs. These reactions have present importance at

certain conditions. For example, when diamines with low reactivity or low concentrations are available, the acylation reaction will be relatively slow. Figure 1.2 shows various reaction pathways possible to propogate PAA formations and the rate constants of them are given in Table 1 [11].

While k_1 reaction presents acylation of the equilibrium reaction for the formation of PAA, k_1 presents deacylation of that of equilibrium reaction. It is well known that PAA has tendency to occur hydrolytic degredation at even room temperature. A low amount of anhydride was always available in an equilibrium condition of PAA solution. However, this low amount plays major role for hydrolytic degredation of PAA. Water causes to hydrolize anhydride groups forming an ortho dicarboxylic group. The pathway of K_3 shows this forming in Figure 1.2. The high nucleophilicity of water and strong acid-base interactions in polar solvent drive these polymerization reactions. The effects of water on molecular weight of PAA during polymerization were observed in literature and documented [12]. Water can be available as impurity in solvent or monomers. Mostly, purification processes were carried out to eliminate water. For solvent purification, some chemical groups were used to purify the solvent. After this process solvent is termed as dry solvent. In terms of monomers, especially anhydride powders have low moisture resistance. For this reason, they are generally exposed to vacuum process in mild conditions befor using. In PAA solution, a small amount of water molecules occur by converting amic acids to imides as k_2 pathway shown in Figure 1.2. This occurrence is lower at ambient temperature but is significant to prevent water to react adversely due to the cause of gradual decrease in molecular weight in long period [13]. Frost and Kesse [14] studied on water effect on PAA in polar aprotic solvent by at the duration long period. They carried out their observation by using PMDA and ODA to obtain a 11% DMAc PAA solution at 35℃. It was observed that approximately 20 % of the amic acid groups on polymers were imidized after 21 days and 0.19% water in solvent was observed at the same time. When considering of long term storage of PAA, PAA precursor solutions have to be stored in refrigerated conditions in order to obtain higher molecular weight and high quality poliimides.

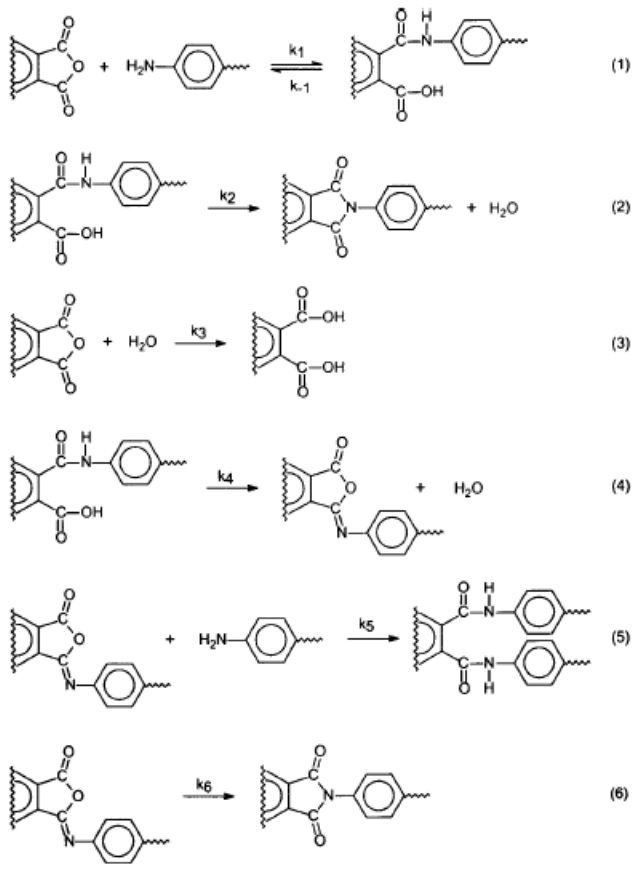


Figure 1.2. Main reaction pathways of poly amic acid [15]

1.2.3. Thermal imidization method by using poly (amic acid) precursor

There are two major pathway reactions converting from PAA to PI in thermal imidization process. The major pathway reaction occurred by heating gradually PAA to 250-300 ˚C. This temperature changes according to glass transition temperature (Tg) and thermal stability of the polymer. During the imidization process of PAA, evoparation of solvent and water resuting from imidization occur. While the nucleophilic attack of the nitrogen atom on amide group makes nucleophilic attack to carbon atom on carboxylic acid group and acylation forming imide bonding occur, elimination of water come true. And this water evaporates by heating of the polymer. As mentioned, there are two amic acid cyclization mechanisms that was emphasized by Harris [16] as shown in Figure 1.3 The major differences between two pathway reactions are lack of ^{1}H proton and the occurrence of N=C bonding. The pathway 1 in Figure 1.3 is more possible to occur due to the belonging to more nucleophilic potential than amide bonding. The low dissociation constant of amide in Table 1.1 confirm this situation [17, 18, 11].

Table 1.1. Reaction rate constant values in Figure 1.2 [11]

Reaction	Rate Constant
Hydrolysis (k_3)	10^{-1}-10^{-2}
Isoimide Formation (k_4)	
Diamide Formation (k_5)	
Propagation (k_1)	0.1-0.5
Depropagation (k_{-1})	10^{-5}-10^{-6}
Isomerization (k_6)	-
Spontaneous Imidization (k_2)	10^{-8}-10^{-9}

Thermal imidization is very proper and effective to obtain films, coatings, fibers and powders because it is easy to remove solvent and by-products. However, the shrinkage stress must be minimized by controlling the curing regime. Otherwise, the film cracking occurs during the thermal imidization due to the shrinkage stress. In curing regime, excess solvent should be removed below 150 °C for first stage. Most of the solvent is evaporated in this stage. After the first stage, a ramp is carried out above Tg of the polymer for second stage. High amount of imidization occurs at the proper temperature of this stage. Considering curing shrinkage, optimum temperature should be applied to polymer. The conversion of PAA to PI after the curing process is varied from 92 to 99 %. It is thought that this ratio is maximum to obtain with thermal imidization. Due to the kinetic interruption effect, 100% conversion of PAA to PI can not be provided at at 300°C and more above temperatures [16]. Residual amic acid groups can be avaliable after the complete imidization process due to the kinetic interruption. These residual groups are hydrolytically unstable in resulting PI. Their concentrations varied from 1% to 8% decrease the hydrolytical stability of resulting PI [20].

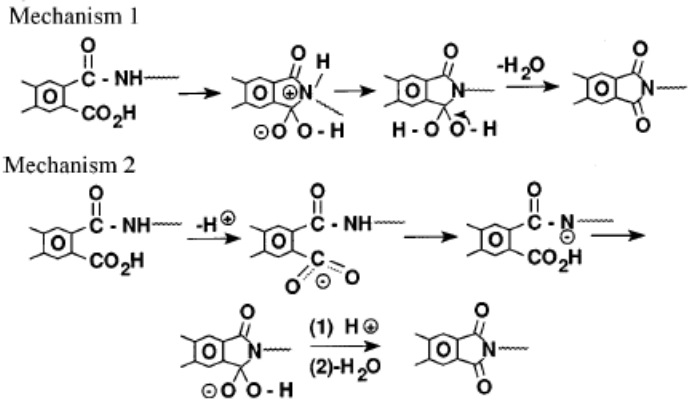


Figure 1.3. Two major mechanism of polyimide formation [16]

On the other hand, thermal imidization includes in side reactions that can affect the properties of resulting PIs. For this reason, PIs obtained from thermal imidization present different properties those obtained from chemical imidization.

For insoluable PIs, molecular weight decreases in the first imidization stage between 100-250 ˚C due to the depolimerization reaction. But this situation is not observed for soluble PIs confirming by FT-IR [21,22,24]. However, the decreased molecular weight is recovered gradually at high temperatures. These side reactions can cause to crosslinking of the chains. Amine terminated imide chains can crosslinked with the other imide chains by the attack of ended amino groups to carbonyl groups on imide structure. This attack provides the imine formation besides the crosslinking [24, 25]. Raman spectroscopy confirms this situation [26]. However, a recent study present that the amine terminated chains with low molecular weight can provide considerable crosslinking and considerable amount of imine formation. The chain length affects this behavior adversely [27]. On the other hand, isoimide formation is another type of side reaction. It can be easiliy thermal imidized at high temperatures.

1.2.4. Chemical imidization of poly (amic acid) precursor

In imidization of poly (amic acid) precursor by chemically, acylation of PAA to PI was promoted by using dehydrating agents in the temperature range of 20 and 80 °C. Acid anhydrides are generally used as dehydrating agents such as benzoic anhydride, propionic anhydride, n-butylric anhydride, acetic anhydride. This is effective for both soluble and insoluble PIs [28, 29]. Besides the dehydrating agents, tertiary amines are used as amine catalysts such as trialkylamines groups, methylpyride, N-methylmorpholine, lutidine, pyridine. The properties of resulting PIs present variability according to type of dehydrating agents, kinds of repeating monomer unit and reaction temperature. For instance, trialkylamines results high molecular weight PIs due to their high pK_a (>10.65).

However, heteroaromatic amines catalysts such as 2-methylpyridine, isoquinoline and pyridine with moderate basicity (5.2 < pKa < 5.7) also present high molecular weight PIs [30]. On the other hand, isoimide formation is a kind of side reaction, as mentioned. PAAs can substantially convert to isoimides by using acetyl chloride or N,N-dicyclohexylcarbodiimde (DCC) as a dehydrating agents [31]. Moreover, when pyridine is used as catalyst, it provides a mixture of isoimide and imide formation [32]. Considering the triethylamine instead of pyridine, isoimide formation is emitted and imidization occurs in substantially faster rate of reaction [31]. A study was carried out by using benzophenone tetracarboxylic dianhydride/9,9-fluorenedianiline in literature and this study presented that the most effective ratio of catalyst (cyclizing agents) was determined as in range of 4-9 moles for per repeating unit of PAA. Moreover, the period of imidization reaction is become shorten (from 15 h to 2h) by increasing temperature from room temperature (RT) to 100 ˚C [33]. Figure 1.4 shows an imidization reaction with dehydrating agent and catalyst. While acetic anhydride was used as dehydrating agent and pyridine was used as catalyst. During this imidization reaction there are two pathway of reactions to occur imide groups. Pathway A presents the reaction directly from PAA to PI. Pathway B presents the reaction from PAA to amide-iminol form and this groups then convert to isoimide. However, pathway B is very unstable and reversible. Isoimide and amide-iminol forms are available in the same media. Although, these forms are converted to imide groups by thermal imidization, chemical imidization includes back reactions of isomerization. Thus, isoimide and imide forms are available in same media. However, if catalyst with higher basicity or stronger amine is used such as triethylamine, the acetate ion of isoimide converts to acetate formation. Thus, acetate formation drives the reaction to imide and imide groups exist as stable in the solution [34]. As mentioned, chemical imidization does not involve depolimerization reactions in contrast to thermal imidization. Therefore molecular weight of the polymer does not change and remains constant [35]. Due to the high cost, complex process and low process capability for commercial implementations, thermal imidization is still more preferable than chemical imidization.

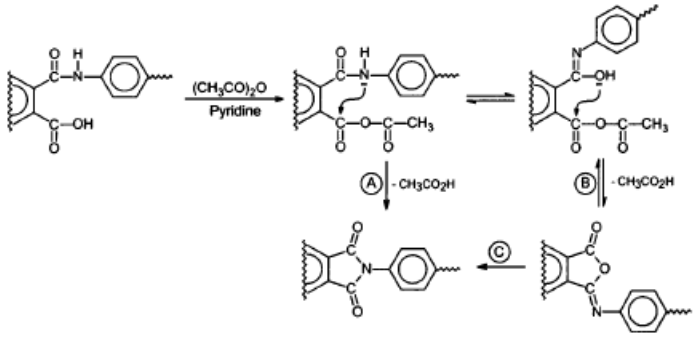


Figure 1.4. Imidization reaction with acetic anhydride and pyridine [11,33]

Due to the the complexity and high cost of process, commercial implementations do not generally prefer to imidize of PAA.

1.2.5. Solution imidization from poly (amic acid) precursor at high temperature

While PIs prepared by thermal imidization method as solid state exhibit infusibility, low processability and insolubility [36], high temperature solution imidization overcome these disadvantages. This method presents cyclodehydration of PAA in the presence of an azeotropic agent by heating in a solvent with high boiling point such as 160-200 ˚C [17, 37, 38]. When compared to thermal imidization, the reactions that were not desired such as hydrolytic degredation and isoimide, were not observed in solution due to the high mobility of chains and low process temperature.

1.2.6. One-step solution imidization from poly (amic acid) precursor at high temperature

Diamine and dianhydrides were exposed to imidization by one-step solution imidization from poly (amic acid) precursor at high temperature. Soluable PIs can be obtained by using this method. This method is carried out at temperatures of approximately 140 ˚C with a solvent with a high boiling point or a mixture of these solvents.This reaction allow the imidization reaction to occur very rapidly. The high boiling solvents generally used for this method are polar aprotic amide solvents, m-cresol, chlorophenols, trichlorobenzenes, o-dichlorobenzene, chloronaphthalene, benzonitrile, and nitrobenzene. 1-cyclohexyl-2-pyrrolidinone (CHP), o-dichlorobenzene, toluene were generally used as co-solvents to remove water that occur by imidization by azeotroping [39-42]. In this synthesis method, the obtaining of high molecular weight PAA is not required because amic-acid groups is

very unstable at high temperatures and has a short-life. Amic-acid intermediate groups are still available but they are in very low quantity due to the fact that they rapidly convert to imide or amide and anhydride groups [43, 44]. On the other hand, imidization reaction was catalyzed by acid in most of literature [45, 46]. However, Kreuz et al. [47], showed that tertiary amines as catalyst could be used for thermal imidization. For this reason, tertiary amines that could be used in high boiling solvent such as quinolone are used in high temperature solution imidization method in m-cresol solvent. On the other hand, other tertiary amines and dialkylaminopyridines can be used as effective catalyst in dichlorobenzene [48-50]. This method provides an imidization conversion of 100%. There are no detected by-products such as amic acid, isoimide groups after the synthesis. The difference in properties of PIs obtained from this synthesis and conventional two-step methods derived from these mentioned explanations [39, 51]. When considering one of other advantages of that method, it provides higher molecular weight for polyimides with monomers having hard to polymerize due to having of groups sterically and electronically hindered. Therefore, these polyimides can be prepared with melt polycondensation by using extrusion molding method. These products have high thermal products such as Tm is around 300°C and Tg is around 250°C [52].

1.2.7. Polyimide synthesis from poly (amic acid) derivatives

It is well known that PAA is very sensitive to hydrolytic degredation. These side reactions substantially decrease the molecular weight of PAA and resulting PI [53]. It is thought that hydrolytic degredation proceed with acid catalyzed formation of anhydride instead of hydrolysis of amide bonding as shown in Figure 1.5. [11] Therefore, in order to stop hydrolytic degredation, PAA derivatives have been used to prevent the proton transfer from the acid linkage. COOH (carboxylic acid) on these PAA derivatives has been blocked to be occurred salt, ester and amide linkage. Poly (ester amine) salts, poly (amic ester) and poly (amic ammonium) salts have been important intermediate precursors to be converted to PIs. These derivative precursor present high hydrolytic stability and poly (amic ester)s have been easily precipitated in order to store for very long period. The ester and amide derivatives of PAAs are stable and prevent the carboxylate anion. However, ionic salts on repeating units on PAA increase the viscosity of PAA. Poly amic acid ammonium salt (PAAS) solution has very high hydrolytic stability that the viscosity of it remains constant after even 90 days. Moreover, poly amic ester has capabability to

hydrolytic degredation. Because COOH groups on PAA backbone can be blocked with methanol and trietylamine groups. This situation substantially improved hydrolytic degredation resistance.

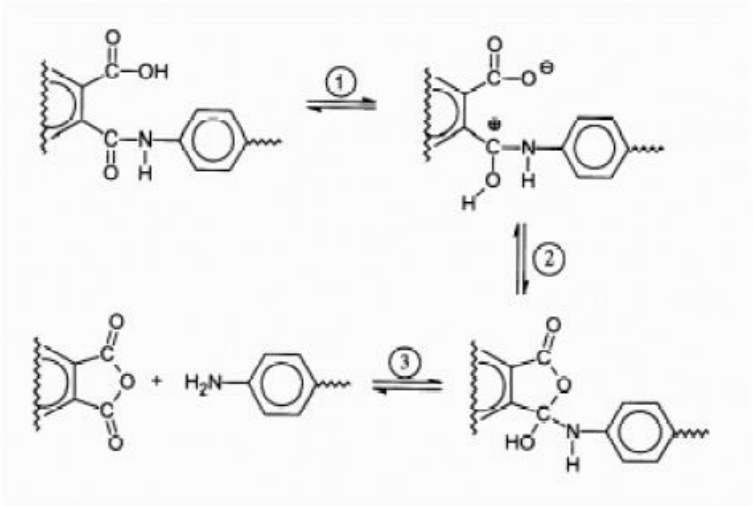


Figure 1.5. Hydrolysis degredation reactions of poly (amic acid) [11]

These high stabilities are required for some applications such as microelectronics and advanced composites. Also, high storage capability makes the cost lower. Especially, PAA derivatives such as poly (amic ester) photocurable polyimides have been often used for photocurable polyimides. Derivatized PAA can be prepared by two kinds of synthsis methods. One of them is derivatization of COOH groups on PAA such as ester or amide salts. The other method is derivatization of monomer used and this monomer is polymerized. The curing regime is poly (amic ester) to imidized has some differences such as slowly heating and curing higher than 200 ˚C.

1.2.8. Polyimide synthesis from polyisoimide precursors

Polyisoimide is another precursor to obtain PI. Although it has important advantages, it is not commonly used to synthesize PI. They have lower melt viscosities, glass transition temperatures than resulting PIs. Because they have characteristic bondings showing lower symmetrically and regularity [54]. They are also soluble and high processible. These properties present ease of implementations for some applications such as fiber reinforced advanced materials and rod like polyimides. On the other hand, the key difference between polyisoimide precursors and the others is not to be occured any molecules such as water during the imidization. Especially, this point is very important to obtain fiber reinforced

advanced composites without voids. There are little researches about this point. In this regard, polyisoimides are synthesized from PAA precursor and they conver to PI by thermally. Dehydrating agents such as acetic anhydrides having fluorine molecules together with triethylamine groups, acetyl chloride, N,N dicyclohexylcarbodiimide (DCC). These dehydrating agents were used to for synthesizing polyisoimides in high yields [30, 31, 55]. This resulting polyisoimide is heated above 250 ˚C for thermal imidization. On the otherhand, polyisoimides can be converted to poly (amic ester) by reacting alcohol and then thermally imidized at high temperatures [56]. Moreover, polyisoimides can be reacted with amine functional groups like the reaction of polyisoimide and alcohol and as a result of this reaction poly (amic amide) occurs shown as Figure 1.6 [57].

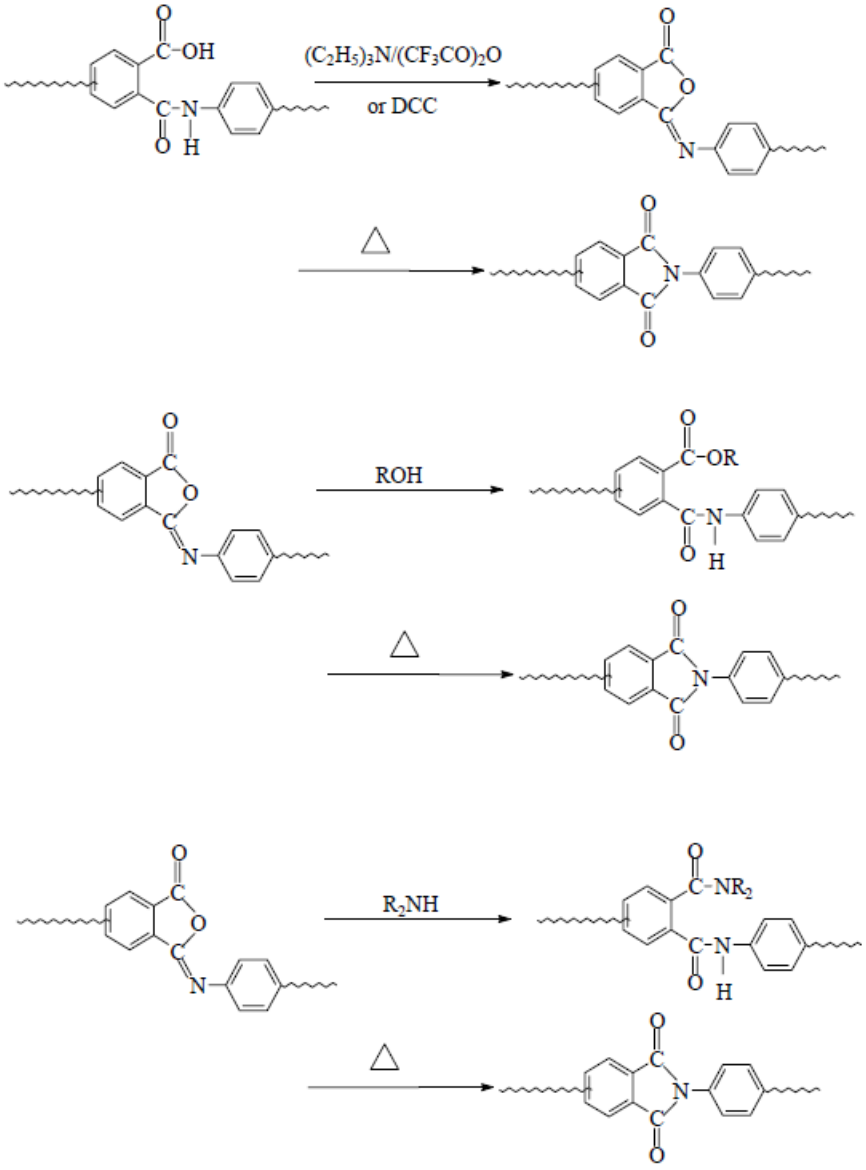


Figure 1.6. Synthesis of polyimides from polyisoimide precursors [57]

1.2.9. Polyimide synthesis from poly (amic ester) precursors

This method is also termed as ester-acid route because the anhydrides are derivatized as diacid-diester with using alcohol. In this synthesizing method, first anhydrides react with alcohol to open the ring and be occurred diacid-diester groups. These resulting diacid-diester groups react with diamines and poly (ester amine) salts occur. When exposed to mild temperature conditions, poly (amic ester) obtained. These precursors can tolerate the disadvantages of water presence in reactor media and solvent [58, 59].

During the esterification process, the anhydrides were reacted with alcohol in excess methanol at 60-70 ˚C for 2 h. And then excess alcohol is removed and ester-acid groups were reacted with diamines in a solution with polar aprotic solvent. Finally poly (amic ester) precursor is obtained. This precursor can be imidized with high temperature solution or thermal imidization methods. It is found out that ester-acid groups are converted to anhydride groups at elevated temperatures and then these resulting anhydrides were reacted diamines to occur poly (amic acid) [58, 60].

1.2.10. Polyimide synthesis from diamines and tetracarboxylic acids

This synthesis is used to obtain high molecular weight aliphatic-aromatic polyimides. Aliphatic diamines and aramotaic tetracarboxylic monomers were reacted each other to occur salts similar to the synthesis of nylon. This synthesis method is shown in Figure 1.7. These salts are expose to thermal imidization above 200 ˚C and under high pressure.

In another issue, these salts convert to poly (amic acid) and polyimide at the same time at high temperatures. Thus, the imidization reaction was occurred very rapid [61].

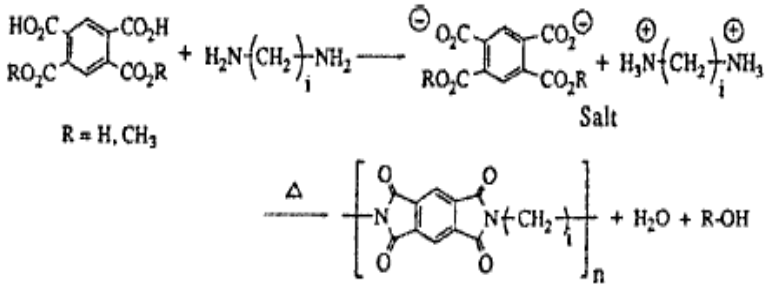


Figure 1.7. The synthesis from tetracarboxylic acids and diamines [61]

They have some advantages compared to PAA precursors in terms of one-step melt polymerization. Their melt viscosities are lower at heating stage. Moreover, their reaction

stability and purification capability is very higher than PAA precursors.

1.2.11. Synthesis of polyimides by using diisocyanate and dianhydride monomers

Isocyanates and phtalic anhydrides reactions are well known to occur PIs [62]. This reaction without a catalyst become forward an intermediate with seven membered cyclic and then carbon dioxide releases by occurring resulting PI [63] as shown in Figure 1.8.

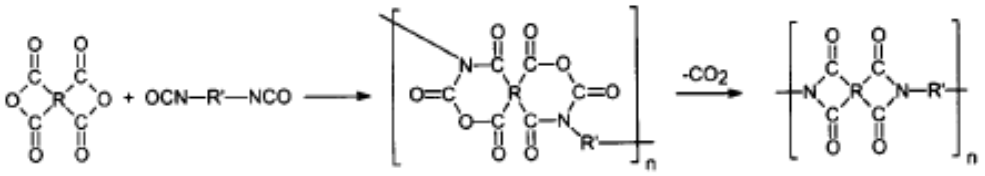


Figure 1.8. The synthesis from anhydrides and diisocyanates including seven membered intermediate

Aliphatic isocyanates react faster with aromatic anhydrides than aromatic isocyanates. Aromatic isocyanates require a longer periods to be cured at 180 ˚C. These reactions can be accelerated with catalysts such as alkali metal alcoholates, tertiary amines and alcohol. On the other hand, water with proper amount can behave as catalyst in reaction period. Its catalytic behavior also increased with dipolar amide solvents. They react with isocyanates to occur amine groups and the resulting amine groups react with dianhydrides to obtain polyimides. These reactions increased the rate of imidization. However, side reactions derived from presence of water can be occurred such as hydrolysis of anhydrides though the reaction of water and isocyanate is much faster than that of anhydrides and water [64]. This synthesis method has been generally used for preparing of polyimide foams due to the releasing of carbondioxide as blowing agent.

1.2.12. Poly (ether imide) synthesis from nucleophilic aromatic substitution reactions

This synthesis method is similar to synthesis of poly (ether ketone)s [65] and poly (ether sulfone)s [66]. Halo and nitro substituted aromatic groups are very reactive by means of imide groups and they present nucleophilic aromatic substitution with bisphenol salts in polar aprotic solvent. Therefore aromatic ether bondings occur as a result of these reactions [67-69]. The scheme of this method is shown in Figure 1.9. Halo and nitro substituted aromatic imide groups are more reactive those of sulfone and ketone groups.

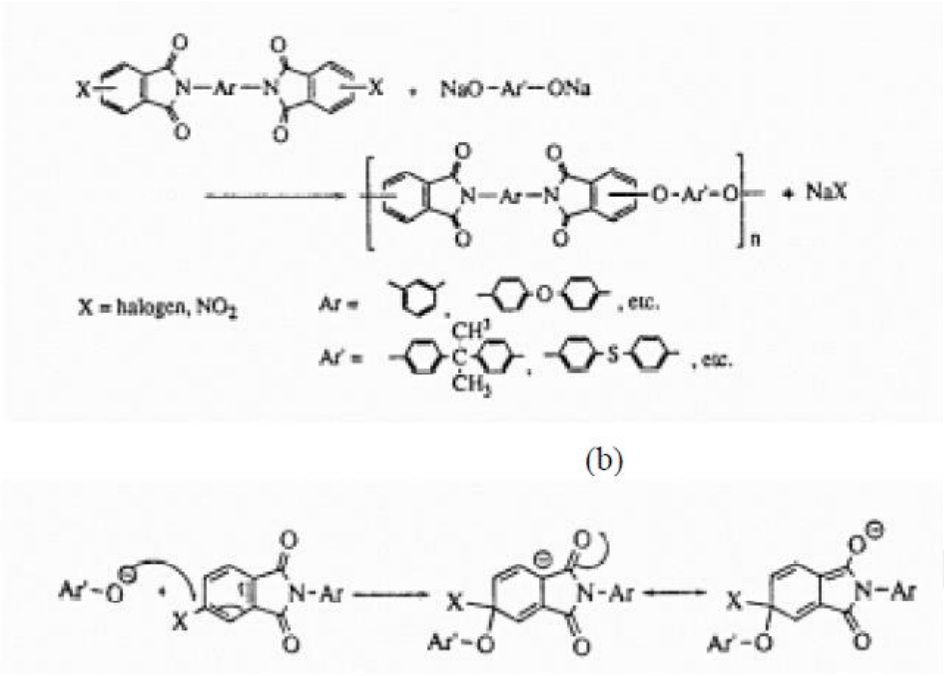


Figure 1.9. Polyetherimides from bisphenol salts and halo substituted diimide monomers [70]

1.2.13. Preperation of crosslinked polyimides by termination of the chains with reactive end cappers

Polyimide chains can be terminated by reactive end cappers such as maleic anhydride, nadic anhydride, phenylethynyl, acetylene. These precursors were crosslinked with reverse Diels Alder reaction at temperatures above 270 ˚C [71].

1.3. Characterizations Related with Polyimide Synthesis

1.3.1. Molecular weight measurements

Average molecular weight can be measured by size exclusion chromatography or gel permeation (GPC) as Mw and Mn, light scattering photometry as Mw, membrane osmometry as Mn [72].

Average molecular weight distribution and the measurement of average molecular weight are very important on behalf of polyimides. Molecular weight and its distribution affect the physical, mechanical and thermal properties. For this reason, controlling molecular weight is very important. Especially for PIs, it is hard to control molecular weight and distribution, end cappers were used for terminating chains. Therefore, crosslinking, bonding of linear or entaglements of chains can be prevented by these end cappers such as phtalic anhydride. PI precursors without end cappers presented uncontrolled molecular

weight. Optimum molecular weight is critical for obtaining of desired enhanced properties.The adjusting of desired molecular weight provides high processability, proper melt viscosity for injection and compression molding processes. Therefore resulting PIs exhibited high thermal stability and mechanical properties with optimum molecular weight and distribution. As end cappers, phtalic anhydrides were used for thermoplastic polyimide materials, some groups such as nadic anhydrides, phenylethynyl, and acetylene were used for thermoset PI materials. End capper for thermoplastic PIs (without non-reactive groups) such as phtalic anhydride provides re-allignment of the chains over a period of time after synthesis or manufacturing process and more effective annealing can be carried out. Full imidized PIs exhibited very high solvent resistance and molecular weight of them can not be measured. The measurement datas of molecular weight for fully imidized PIs can be only taken from the PI precursors such as PAA, PAA derivatives. However these values are not certain to discuss and evaluate molecular weights because of the possibility of degredation of PAA or PAA derivatives chains (unstable reactions) and crosslinking during the imidization reactions. On the other hand, molecular weight of soluble PIs can be easily measured characterization methods as mentioned. However, some polyimides with rigid aromatic rings can be soluble in polar aprotic amide solvents and GPC is not enough to characterize these PIs due to the strong interactions between the chains and solvents. Konas et al. [73,74] solved this problem by adding electrolyte in NMP such as LiBr or P_2O_5. This strong interaction was also suppressed with THF and chloroform solutions. As stationary phase crosslinked polystyrene was used and calibration was carried out according to polystyrene.

1.3.2. Structural characterization

In the synthesis of PI, there are various reactions occurred, as mentioned above. These reactions are observed in two sections such as “from monomers to precursors” and “from precursor to PI”. The formations and reagents of reactions are determined by various spectroscopies such as Fourier Transform Infrared (FTIR), Raman, and UV and ^{1}H, ^{13}C, ^{15}N and ^{19}F NMR spectroscopies. The reaction process can be understanded by these spectroscopies. Imidization can be easily confirmed by FTIR spectroscopy with characteristic peaks derived from absorbtions or vibrations of bondings such as imide, amic acid, anhydride, amine, isoimide. Quantitative and qualitative measurements can also be carried out by FTIR spectra. Some possible absorbtions of FTIR during the formation

of PI is shown in Table 1.2. [6,75,76]. The highest peak belonging to C=O symmetrical stretching of imide bonding occurs at at 1720 cm^{-1} but there is another high peak at 1720 cm^{-1} belonging to C=O groups of COOH on the amic acid. For this reason, 1780 cm^{-1}, 1380 cm^{-1} and 725 cm^{-1} bands should be used in order to characterize imide groups.

On the other hand, NMR spectroscopy gives more detail results about polymers according to signal intensity of protons. For example, ^{1}H NMR shows broad proton signal intensity of COOH in range of 12.5 and 13.5 and showed sharp proton signal intensity of NH on amide groups in range of 10 and 11 in order to characterize the PAA. Moreover, conversation from PAA to PI can be determined from the proton signals from COOH. These signals disappear at the high temperature due to the imidization of PAA [77]. There are different reaction possibilities during the thermal and chemical imidization as mentioned such as side reactions, hydrolytic degredations, imidizations and isomerizations. ^{13}C-NMR is also very useful to use for discussing of the ring opening of anhydrides. Formation ratio of isomerization and poly (amic acid) can be estimate by signal intensities of C=C and C-C bondings determined by ^{13}C-NMR under various conditions [78, 79]. The chemical shifts derived from the different reactivity of anhydrides and diamines can be investigated by ^{5}N, ^{1}H and ^{5}N-NMR spectra [80]. By using ^{5}N-NMR, diamine reactivities can be discussed and investigated. On the other hand ^{19}F-NMR is useful method to determining fluorine containing monomers [81].

Table 1.2. Infrared absorbtion bands imide and related compounds [6, 75, 76]

Structures	Absorbtion band	Origin	Intensity
Aromatic Imides	1720	C=O symmetric	very small
	1780	C=O asymmetric	small
	725	C=O	small
	1380	C-N	-
Isoimides	1795-1820	Iminolactone	small
	1700	Iminolactone	medium
	921-934	Iminolactone	very small
Amic acids	2900-3200	COO-H, HN-H	medium
	1710	C=O on COOH	small
	1660	C=O on CONH	small
	1550	C-NH	medium
Anhydrides	1820	C=O	medium
	1780	C=O	small
	720	C=O	small
Amines	3200 (two bands)	NH_2 asym&sym.	broad

1.3.3. Thermal characterization

Thermal characterization is very critical to evaluate thermal properties of PIs. Aromatic PIs especially exhibit very outstanding thermal and thermal-oxydative stability. It is well known that rigid aromatic rings increased the thermal stability of polymers. These structures also gain PIs high mechanical and physical properties. Moreover, PIs have high thermo-mechanical properties. These enhanced properties are very suitable for advanced composites used in critical and aerospace applications. These composite resins have very high durable at temperatures as high as 371 ˚C for long period. Moreover, a study on aromatic PIs was carried out to be measured long term thermal stability for 60000 hours at 177 ˚C. In aerospace applications, advanced materials such as PIs are needed that can respond to high thermo-mechanical properties as mentioned. Thermal properties were characterized by various methods such as thermogravimetric analysis (TGA), dynamic

mechanical analysis (DMA), differential scanning calorimetry (DSC) and the other viscoelastic measurements [82, 83]. Among these methods, DMA and TGA are often used to determine thermal stabilities of PIs. While TGA is based on losing of weight with increasing temperature, DMA is based on changing storage modulus with increasing temperature. These methods can be carried out in different atmosphere such as nitrogen and air. The analysis applied in air atmosphere represents thermo-oxydative resistance and that of nitrogen atmosphere represents thermal degredation of material. The weight loss of 5% is ciritical value in order to proceed the functionality of polyimide for non-load bearing implementations. Polyimides applications such as coatings, films and adhesive are not structural materials. Polyimides were reinforced fiber materials to use as structural materials in various industries and sectors. Fiber reinforced polyimides are very critical materials that exhibit so enhanced mechanical and thermal properties. They are exposed to dynamic and static loadings at various changing temperatures. Thermal stability of polymers is very concerned with their molecular structure. Molecular structure are substantially affected by using monomers such as diamine-dianhydrides or diisocyanate-dianhydrides. Moreover thermoset or thermoplastic structures affect the thermal stabilities of polymers and thermoset structures present much more enhanced thermal stability than thermoplastic ones.

For instance, Figure 1.10 shows that thermal stability of some anhydrides used for PIs. Polyimides with these anhydrides and a certain diamine were exposed to isothermal analysis at 400 ˚C in air. The thermal stability relation of these anhydrides was given in Figure 1.10 [84].

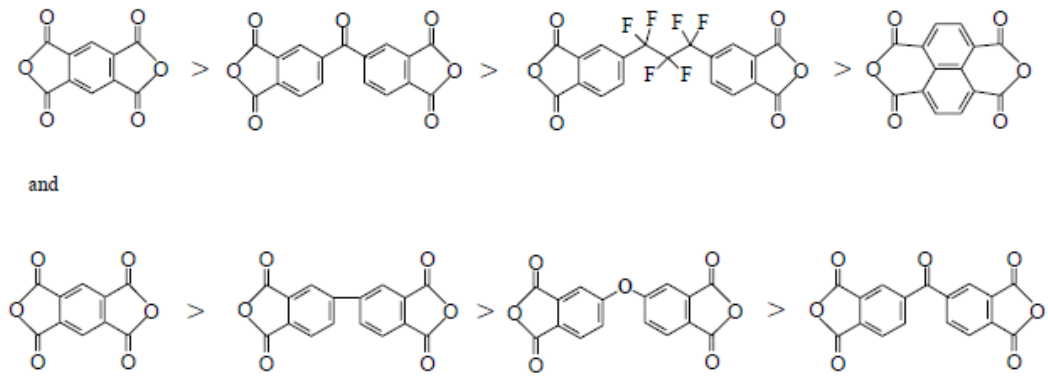


Figure 1.10. Thermal stability relations between some dianhydrides used in polyimides [15]

Ketone group containing polyimide structures exhibit lower thermal stability than those having completely aromatic systems [85]. When considering the effect of monomer

structure on crosslinking reactions, the used diamines for polyimides presents more affect on thermal stability than the dianhydride structures [82]. The groups near diamines are sensitive to react due to the having of high electron densities. Moreover, the diamines with high electron density tend to exposing oxidation than those with lower electron density. This thermal stability was measured by using different diamines for polypyromellitimides at 400 ˚C. These diamines are lined up according to X bridge on diamine in order of X: $C(CF_3)_2$ > SO_2 >CH_2 > CO > SO> O [84, 86, 87]. On the other hand, CH_2 linkage on polyimide is first oxidized and converted to CO unit by thermo-oxidative degredation. Aliphatic units containing polyimides are more sensitive to oxidation than aromatic polyimides. They decompose easily and more quickly at lower temperatures compared to aromatic ones.

The end group of polyimide has very important role in thermal stability. If a non-reactive end capper is used for terminating chains, thermal stability of polyimide will be more enhanced. It is important that molecular weight should not be decreased to less than optimum level for high thermal stability.Therefore, these end cappers prevent polyimides to terminate with diamine and dianhydride groups. Phatalic anhydride is one of important non-reactive end cappers. And diamines also present low melt stability hence thermal oxidative resistance is also low in the presence of high diamine functionality at the stage of melting. This situation was confirmed by crystallization, melt rheological experiments or TGA [88, 89]. Anhydrides functionality terminated chains are a little more thermal resistance than the diamine ones but they can not compared to non-reactive end groups. At elevated temperatures, anhydrides exposed to degredation by first hydrolysis and then at decarboxylation or thermally induced decarbonylation [82, 90]. Polyimides were also terminated by reactive end capper for preparing thermosetting polyimides. And these thermosetting curing mechanism is based thermal degredation of reactive end capper. For instance, nadic anhydride reactive end capper terminated polyimides are crosslinked by reverse Dielse Alder reaction at high temperatures. Some reactive end cappers terminated imide oligomers are given in Figure 1.11.

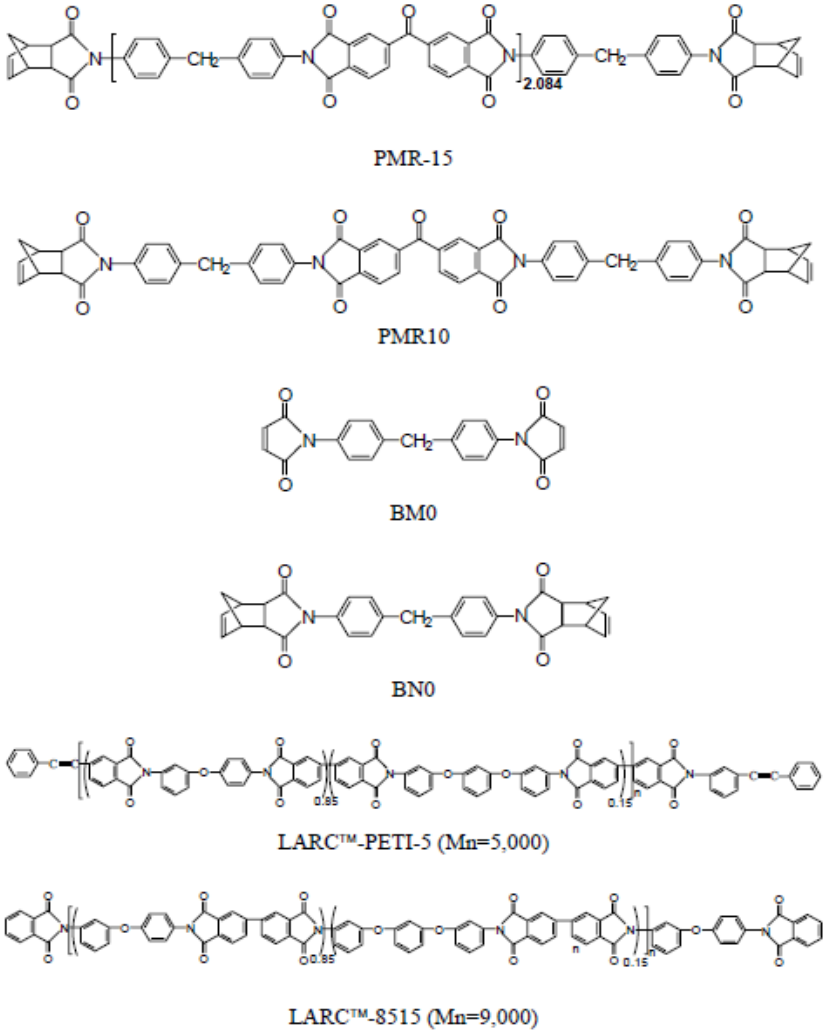


Figure 1.11. Some reactive end capper terminated imide oligomers [15]

1.3.4. Solution and melt processability

PIs have outstanding properties but they can not be taken place in most of applications because of the insoluble and infusible structures. Their rigid structure has very high glass transition temperature and very high melting point with high crystallinity. Therefore they have low melt viscosity and very low capability to process. It can not reach enough melt follow hence crosslinkings and decomposition of polyimides can occur. For these reasons, moldability and processability should be increased in order to obtain polyimide materials with complex shape [91]. On the other hand, these strong interactions between structures on polyimide chains prevent the solubility adversely. Therefore high polar aprotic solvents with high boiling point have to be used for solving these rigid imide structures. These solutions are used in high solvent ratios such as 80% and 90 wt %. Moreover, it is hard to

remove these solvents from these solutions due to their high boiling point. In order to overcome these drawbacks and obtain more flowable and soluable PI structures, many studies are carried out. For instance, Dupont invented a technology to manufacture a soluable and moldable PI powders. These PIs (Vespel) were synthesized to use ODA and PMDA. These particulate powders were entegrated into a mold and heate to 300 ˚C for 10 min to melt [92, 93]. This procedure has been used in various researches in literature.

In order to improve melt flowability and solubility of PIs, some approaches are taken place in literature. In order to decrease the interactions of molecular structures and stiffness of polymer backbone, some flexible bridges or linkages, angular and unsymmetrical structures are taken place on polyimide backbones. Moreover, a large pendant groups on polymer backbone prevent the symmetry of the structures and minimize the chain interactions on polymer backbone. Figure 1.12 showed some bridges or linkages that can be used on polyimide backbones in order to obtain these purposes as mentioned above [58, 94, 95].

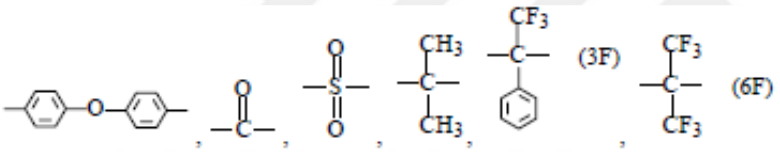


Figure 1.12. Some flexible linkage on polyimide chains [96]

There is another approach to obtain excellent solubility and melt processability. This approach is preparing reactive end capper terminated imide oligomers. These imide oligomers are crosslinked at high temperatures by means of these reactive end capper. Therefore thermosetting polyimides are obtained. The Tg and stiffness values of these thermosetting polyimides are also so enhanced.

1.4. Polyimides as Resin Matrices for Advanced Composites

1.4.1. Advanced materials

It is well known that composite means a new complete material that occurred from fibers or particles embedded into a matrix. A composite is consitituted two materials that eliminate their deficient and presented a new improved material. The term of “advanced material” that composite material with very high properties prepared from using high performance fibers as reinforcing material such as boron, carbon and aramid.

Currently, the most used matrix materials are epoxy-based systems. These polymer matrix systems have very high processability and very improved mechanical properties. However, epoxy matrix composites can not be used at high temperatures above 177 ˚C. This situation has been limited their usage in critical area of aerospace industry. Fiber materials can be obtained as woven fabrics or unidirectional tapes. These fabrics or tapes are impregnated into matrix resin and prepreg are prepared by hot-melt or solution coating before the manufacturing process. Moreover, powder impregnation has been carried out in recent works. These powders are melt and melt resin is comingled into fibers. In hot-melt prepreg method, a thin film is prepared between rollers at desired thickness. These thin film resins and reinforcing fibers are passed between heated rollers to impregnate the fibers with the resins. Therefore prepregs are obtained. In solvent coating method, fibers are dipped into the solution resin and hold in room temperature or mild condition with or without vacuum pressure in order to remove excess solvent. Impregnated prepregs were wrapped between release films. This method is generally used for woven fabrics. The physical properties of prepregs plies are very important to obtain desired mechanical properties. Prepregs should be enough tackiness. The shelf life of pregreg should be enough. Resin in prepregs should not be lossed their properties in process period. After obtaining of these prepregs plies of prepregs were stacking to occur a component in desired design. There are two kinds of manufacturing process in literature. These are autoclave and compression molding. In compression molding process, solvent minimizing and consolidating of stacked plies of prepregs process is firstly carried out with heating with or without vacuum pressure in furnace. And then consolidated prepreg is taken place in compression molding. In this stage, prepregs are hot pressed in open or close molds with desired design. In autoclave process, a large heated pressure vessel is used and vacuum bagging is applied with pressure in this vessel. Prepregs are heated with applying of high pressure and vacuum simultaneously. Autoclave method has been useful and convenient to lower void ratio in fiber reinforced composites. The presence of low void ratio is very important to obtain improved mechanical properties. Moreover, cure cyles is very important to obtain high mechanical properties.The most important reasons of the using advanced composites are the high specific stiffness and strength values and they have substantial potential for manufacturing with lower component cost. Up to till, epoxy composite systems have been widely used and manufacturing technology is suitable with epoxy systems. However, these systems can not be used as long term above 130 ˚C and

application areas is limited at high temperatures. Aerospace industry required advanced materials with high heat resistant and high mechanical properties. Some important examples are military aircraft components, missiles and aero-engines. To meet these requirements, lots of studies have been applied on fiber reinforced advanced composites with PI matrix.

1.4.2. Polyimide composites

Due to the outstanding properties of PIs, PIs as matrix have been excellent candidate for advanced composites. Besides high chemical resistance, low dielectric coefficient and very high mechanical properties, they present very high thermal stabilities and thermo-mechanical properties. These properties are very suitable for critical materials of civil or military aerospace industries. They present high performance at high temperatures or in cryogenic conditions. These PI matrices have been also used as adhesive materials. These adhesive materials present high adhesive performance and present very importance for high temperatures applications. PIs have also high thermo-oxidative, glass transition temperature and melting point and permeability. In the light of these informations, PI matrix advanced composites are key materials. Figure 1.13 shows high temperature usage capability of some polymer matrices in advanced composites such as conventional epoxy, bismaleimide and PI. As shown in Figure 1.13, PIs have the highest usage temperatures for short and long periods.

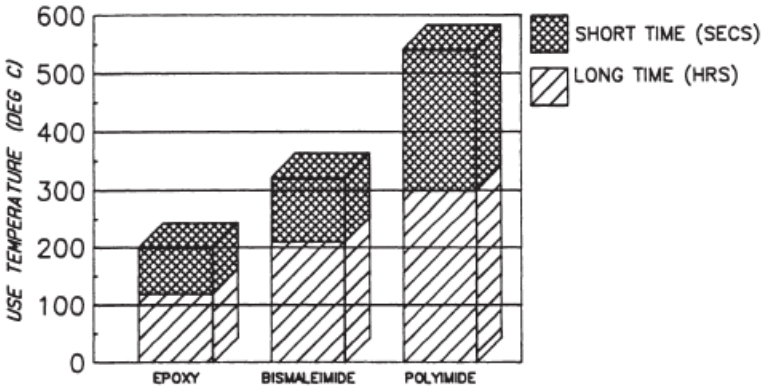


Figure 1.13. The high temperature usage capability of some polymer matrices of advanced composites

1.4.3. Thermosetting polyimide resins

Aerospace industry has required advanced resins with high mechanical and thermal performance. In recent year, the requirement on polyimide resins have been substantially increased instead of phenolics, unsaturated polyesters and epoxies for various applications such as matrices of advanced composite and adhesives. Thermosetting PI resins have low molecular weight and they are used PI precursors such as poly (amic acid), poly (ester amine) salt or poly (amic ester) salt. While these precursors are impregnated into fibers for advanced composites, those are applied onto interfaces of two components as adhesives. These precursors are then cured and crosslinked at high temperatures. Because of the low molecular weight, these thermosetting PI resin is termed as oligomer. These thermosetting imide oligomer is terminated reactive and capper such as nadic anhydride, phenylethynyl or acetylene. These reactive groups have double or triple bondings between carbons and crosslinked by reverse Diels Alder reaction at high temperatures. The reactive groups can be also incorporated as pendant on polymer backnones. Thermosetting PI precursors have lower molecular weight than thermoplastic PI precursors. For this reason, the processability of thermosetting PI precursors is higher than the thermoplastic ones. The thermosetting ones present lower viscosity value, too. The thermoplastic PI precursors have been also terminated by non-reactive end capper such as phtalic anhydride in order to obtain high processability, mechanical and thermal properties. However, thermosetting PI matrix advanced composites present higher mechanical and thermal properties than those with thermoplastic PI matrix. Thermosetting PIs can be used for solvent resistance, high modulus in lots of applications such as structural composites in aerospace, electrical and electronical insulators, thermal insulator materials [9, 97]. The properties of PIs can be substantially varied by means of selecting different diamines, dianhydrides and end capper monomers. Moreover, the properties of thermosetting PIs can be varied by changing molecular weight and crosslinking density. There are different end groups to be used for crosslinking. Thermosetting PIs have been classified according to the structures of these end groups. Some of these common end groups are shown in Figure 1.14.

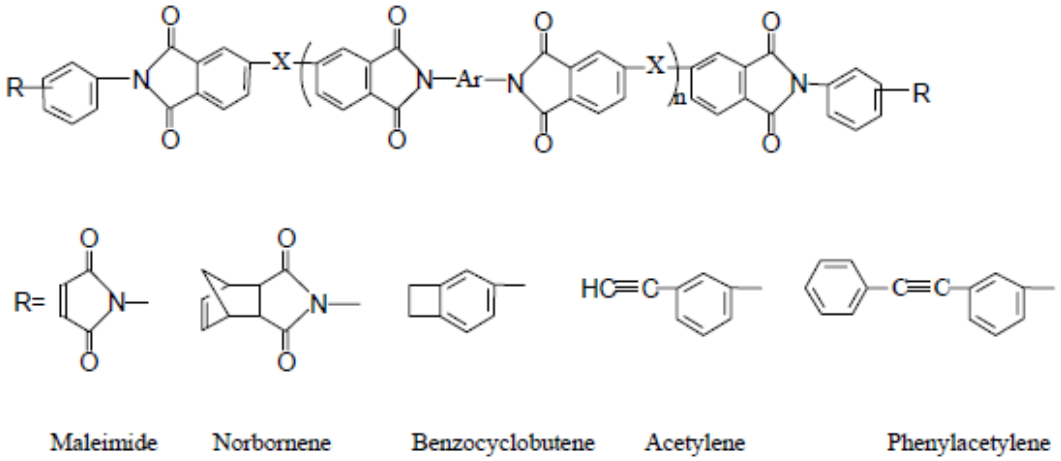


Figure 1.14. Some common reactive end cappers for polyimides [15]

1.4.3.1. Thermosetting imide matrices functionalized with maleimide

Maleimide functionalized imide oligomer is one of matrices used for advanced composites. They have very high processability and good balanced properties in terms of mechanical, thermal and electrical properties. Morever, bismaleimides or n-substituted maleimides can be cured at lower temperatures than 250 ˚C like high performance epoxies and under low vacuum level [97]. These resins have been also used in electronic industries for printed circuit boards and multilayers besides advanced composites.

1.4.3.2. Synthesizing of thermosetting bismaleimide matrices

Bismaleimide (BMI) has been synthesized as monomeric or oligomeric with low molecular weight in various levels. However, BMIs have been mostly prepared without using anhydride monomer. They are prepared by reacting of inexpensive diamines and maleic anhydrides. These BMIs present high thermal performances. By addition of anhydrides and increasing of molecular weight, the mechanical properties of BMIs increase. Figure 1.15 shows the synthesizing of BMIs. The synthesis is carried out by means of a catalyst such as triethyl amine in presence of acetic anhydride [9, 97, 98]. However, the yield of BMI is investigated as low ratio in range of 65-75% after the purification process [99]. Because there are many side reactions occurred during the chemical imidization. Sauers [100] found that during the occurring of bismaleimide isoimide moieties with high ratio were formed as intermediates and they are unstable phases with rearranging continuously to maleimide groups. It was determined that these unstable behavious were derived from acetate ion catalysis. Using high ratio catalysts

occured maleimides with high purity and low isoimide impurity groups were found in synthesis solution. When acetic anhydride is presence, the other by-product is acetanilides that occurred in high ratios with very low or no concentrations of acetate ions [99]. In addition to these side reactions, the by-products of Michael adducts are formed during the chemical imidization. This reaction is formed between acetic acid and maleimide groups. High ratio of catalyst causes the forming of Michael adducts and acetanilides groups. For these reasons, thermal imidization for BMI synthesis is more proper to obtain low solvent cost, high yield and reduce by-products amounts. Thermal imidization of bismaleic acids are applied in presence of azeotropic solvents [101, 102].

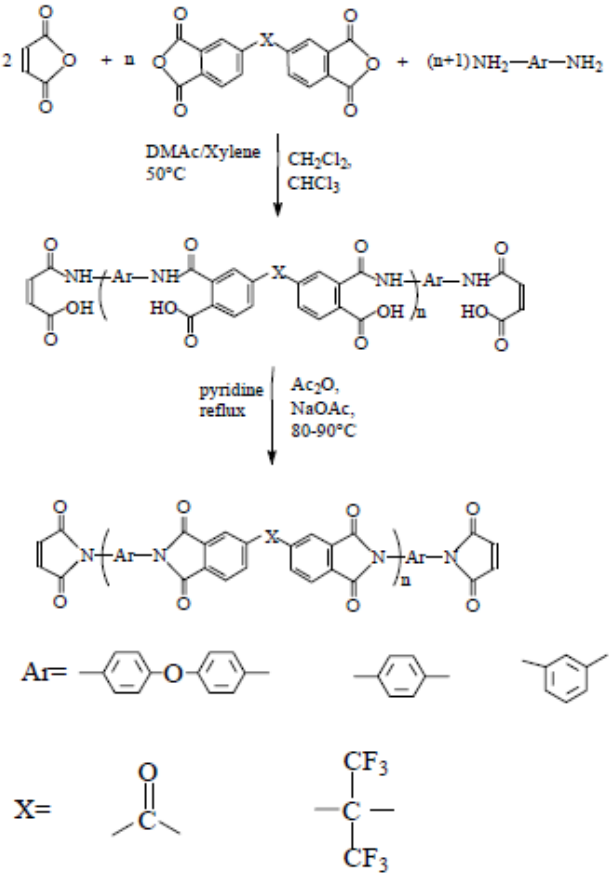


Figure 1.15. The synthesis of bismaleimide resins [9, 97, 98]

In another issue, bismaleimide resins have been synthesized as higher molecular weight for adhesives, molding and advanced composite applications. In synthesis procedure, diamine terminated chains are prepared and endcapped by maleic anhydrides. Anhydrides are used in various molar ratios to obtain higher molecular weight than simple bismaleimides. These intermediate resins are thermally cured at 250 ˚C for 1 h. The resulting bismaleimides present higher thoughness than simple bismaleimides. On the

other hand, maleic anhydride end capped amide-imide oligomers can be synthesized by using trimellitic anhydride and cured by thermal imidization [103].

Bismaleimide was chemically imidized in some researches [104]. Acetic anyhydride and sodium acetate were used for chemical imidization of bismaleimides in high purity. The sulfone ether backbone prevents the high solubility of bismaleic acids. By using common organic solvents the solutions with high solids can be processed. After the curing, bismaleimide presents high glass transition temperature and high thermo-mechanical values. These results can be changed by the molecular weight between the crosslinking bonds. In another research, a hydroxylphenyl maleimide was used. The hydroxylphenyl maleic acid and diglycidylbisphenol-A epoxy resin were reacted with using catalyst and another class of bismaleimide was obtained [105,106].

1.4.3.3. Thermosetting imide matrix functionalized with nadic anhydride

Nadic anhydride functionalized imide structures have been drived forward PMR type resins. PMR means polymerization of monomeric reactants. In this method, monomers are obtained as salt and these repeating salts occured the polymers. These salts are terminated by nadic anhydride groups. The resuting salts were firstly amidized at 80-150 ˚C and then imidized at 150-240 ˚C. These nadic anhydride terminated imide oligomers were crosslinked at temperatures in range of 270-350 ˚C. This crosslinking mechanism is provided by reverse Diels Alder reaction. Among PMR type polyimide resins, PMR-15 that have molecular weight of 1500 g/mol, is invented by Serrafini [107] in 1973 and is still the most favoured resin for advanced composites. In order to synthesize PMR-15, 4,4'-methylene dianiline (MDA) as diamine and 3,3′,4,4′-Benzophenone-tetracarboxylic dianhydride (BTDA) as dianhydride were used for polymer backbone. 5-Norbornene-2,3-dicarboxylic anhydride (NA, nadic anhydride) was used as reactive end capper to be crosslinking imide oligomers. The mole ratios of these components were adjusted to 2.000:3.087:2.087 (BTDA: MDA: NA). The polymer backbone is in situ synthesized and then crosslinked. During the synthesis, BTDA and NA monomers are esterifed at 60 ˚C for 2 h in methanol and convert to ester acids. These ester acids were reacted with MDA at room temperature in methanol solvent or polar aprotic solvent. After these reactions, poly (ester amine) salts (PEAS) were occurred. In order to manufacture advanced composites, these salts are easily impregnated into the fibers due to the low viscosity and prepregs are obtained. After the exposing to heating, amidization and subsequently imidization were

occurred. At higher temperatures and high pressures crosslinked reactions were provided and the advanced composite were prepared. Figure 1.16 shows the synthesis of PMR-15 resin. After applying poly (ester amine) salts monomers into fibers and obtaining enough tackiness of plies, these wetted woven or unidirectional tapes were wrapped between release films. Therefore prepregs are obtained. These prepregs are exposed to solvent removing process and subsequently heated to 150-200 ˚C for amidization by in situ condensation reaction and then partly imidization. Thus nadic anhydride terminated prepolymers are occurred into the fibers. These consolidated fibers and prepolymers components are cured at higher temperatures in range of 250-350 ˚C and fiber reinforced thermosetting PI matrix advanced composite is prepared.

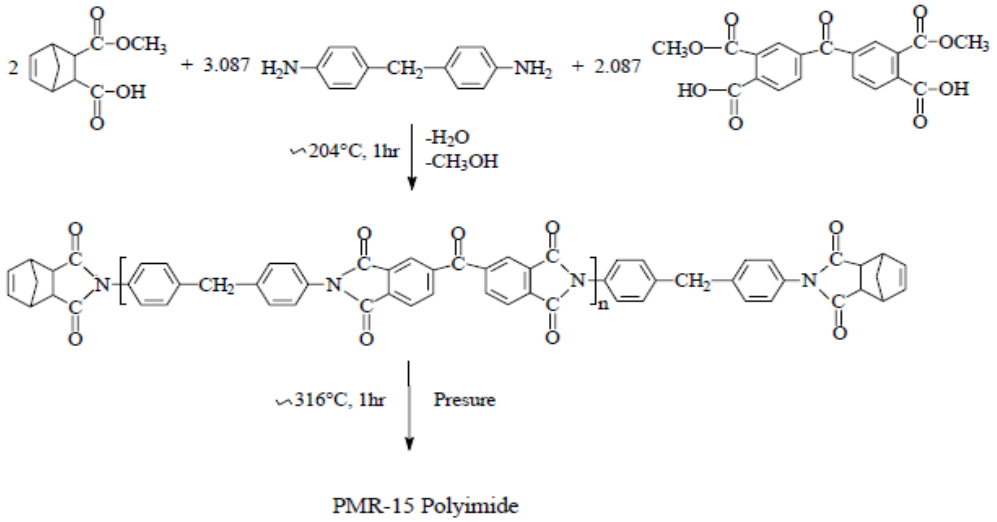


Figure 1.16. The synthesis of PMR-15 resin [15]

PMR-15 has high processibility, excellent mechanical and thermal properties. They can be used at high temperatures in range of 288-316 ˚C for long periods (1000-10000 h according to usage temperatures). However, there are lots of factors limiting their usage potential. Evaporating molecules and solvents and low resin flowability prevent the manufacturing of thick and complex shape products. Microcracking occurrence during the manufacturing is disadvantages for stress-crack resistance. PMR-15 composites present low toughness values. Thermal stability of PMR-15 substantially decreases above 316 ˚C. Moreover, MDA monomer used as diamine is unhealthy and toxic. In order to solve these problems, the other PMR type resins were synthesized. To increase the thermal and thermo-oxidative stability fluorine containing monomers replaced for PMR type composites and these advanced composites present excellent results at higher temperatures than 316 ˚C. While fluorine containing PMR type resins are termed as

second generation PMR resins, those without fluorine groups are termed as first generation PMR resins. These second generation PMR type advanced composites can not present as high as first generation PMR type advanced composites. For example, 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) can be used instead of the other anhydrides such as BTDA in PMR-15 to obtain second generation PMR type resins. This second generation advanced composite with 6FDA is termed as PMR-II. On the other hand, different diamines can be used instead of MDA due to its toxic structure. For example Chuang et al. [108] synthesized a new PMR type resin that is termed as DMBZ-15, 2,2'-dimethylbenzidine (DMBZ) was used instead of MDA in the structure of PMR-15. Moreover DMBZ-15 presented higher thermal and mechanical properties. However, thermal properties of DMBZ-15 were lower than the second generation PMR type advanced composites.

1.4.3.4. Acetylene functionalized imide oligomers

Acetylene functional groups can be entegrated imide matrices as end capper, pendant groups. Thes groups are reactive groups and provide to crosslinking of polymer chains at high temperatures. These groups terminated PIs was first used by the Hughes Aircraft Company and this imide product that terminated these groups are termed as Thermid 600 (no longer available) [109, 110]. A kind of Thermid 600 imide oligomer is shown in Figure 1.17.

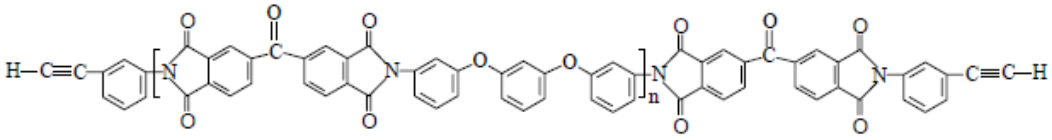


Figure 1.17. Acetylene terminated imide oligomer (Thermid MC-600) [109, 110]

These materials are obtained by the reaction of aromatic tetracarboxylic acid dianhydride and aromatic diamines in polar aprotic solvents such as DMAc, DMF or NMP. After that, the end cap monomer, ethynylsubstituted aromatic amine, was added into the solution and reacted the prepolymer for occurring of ethynylsubstituted aromatic amine terminated amic acid oligomer. These oligomers are then converted to acetylene-terminated imide oligomer structure by thermal or chemical imidization. The molecular weight of the resulting imide oligomer can be adjusted with changing of the stoichiometry of the reactant monomers. There are different ethynyl based end cappers used for various thermosetting imide oligomer resins such as 3-(3’-ethynyl-phenoxy) aniline, 3-

ethynylaniline and 4-ethynylaniline [110, 111]. During the thermal imidization, 4-ethynylaniline groups cause to convert the acetylenic groups to acetyl groups by the hydration with water [112]. For preventing this situation, benzenic trimmers and naphthalenic dimers are protected from monofunctional curing products by various chemical methods. Thermal curing have become forward various structures such as dimers, naphthalenes, cyclooctatetrenes, benzenes and polymeric materials. Acetylene terminated imides (ATIs) do not produce volatile by-products during the curing at 200 ˚C or higher temperatures. The properties such as mechanical properties, thermo-oxidative stability, dielectric properties are very sensitive to process parameters and polymer structures. They can be easiliy changed by the polymer backbone structure, crosslinking density, curing regime and conditions. Moreover, the curing of ATIs is hard to carry out due to the narrow heating range. The first stage of mentioned curing process occur very rapidly because there is no occurred sterically barrier to proceed the free radical mechanism [97]. In order to overcome these problems, Landis and Baselow [113] prepared acetylene terminated isoimide precursor resin. It is well known that isoimide has been converted to imide at the melting stage. Isoimide oligomers were processed at 250 ˚C and presented more improved flow properties compared than imide oligomers. This situation was derived from lowering of uncured Tg and therefore a wider processing window in curing regime was obtained. Acetylene terminated isoimide oligomer presented higher process capability than ATIs. However, the cured material obtained from the isoimide oligomer exhibited lower mechanical and thermal properties due to having lower Tg value of the uncured material. A commercial material that is termed as Thermid FA-700, was produced by this isoimide method. The problem of lower properties was solved by incorporating 6FDA monomer into the isoimide precursor backbone. The structure of Thermid FA-700 is shown in Figure 1.18. This material exhibited high cured Tg.

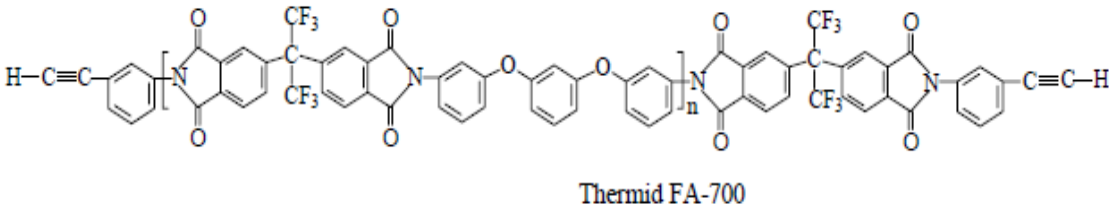


Figure 1.18. Acetylene terminated fluorinated imide oligomer obtained from isoimide precursor (Thermid FA-700) [109, 110]

1.4.3.5. Phenylethynyl functionalized imide oligomers

As mentioned, narrow processing window of curing regime is problem to prepare the acetylene terminated imide oligomers. To overcome this problem, various end cappers have been also used such as phenylvinylacetylene, propargyl, phenyl diacetylene [145-147]. The acetylene end cappers with phenyl groups increase substantially the Tg value of resulting imide due to the retarding of end group reactions. Phenyl groups on the end cappers provide sterically obstacles to occur the end group reactions. And the end group reactions at the higher temperatures allow removing the high boiling residue solvents before the curing point. Therefore more improved material is obtained due to the much lower voids in resulting imide material. Reserachers synthesized 4-phenylethyl phthalic anhydride that is low toxic and easy to synthesize, to terminate imide oligomer [114-118]. PEPA terminated imide oligomers presented higher thermo-oxidative stability [118]. In order to synthesize the phenylethynylphthalic anhydrides, 4-iodo or bromphthalic anhydride has been reacted with a kind of phenylacetylene. It was investigated that electron withdrawing resulting from phenyl ring affect the curing temperature [119, 117] and it was obtained higher Tg value. The phenylethynyl terminated imide oligomers present high thermal stability, Tg, moisture resistance. These thermoset oligomers have exhibited higher fracture toughness than the other thermoset polyimides. Their elongation ratios have been as those of thermoplastics [117-120]. The properties of the thermoset PIs obtained from phenylethynyl terminated imide oligomers depend on the prepolymer structure, prepolymer chain length and curing conditions of process [121]. The flow parameter is very important for resins. This property can be adjusted by flexible monomers on backbone or chain length. Moreover crosslink density changes the properties. It can be changed by polymer chain length, stoichiometric ratio and adding functional groups on backbones to react [122]. Although the phenylethynyl cure reaction

could not be exactly understanded, it has been well known that free radical mechanisms are effective for the curing mechanism [116, 123, 124].

1.4.4. Thermoplastic polyimide matrix resins

These type PIs are also termed as linear PIs and include only condensation polymerization mechanism. At first stage, thermoset PI resins were synthesized by condensation polymerization. However, they were crosslinked by the reactive functional groups end capped or on the polymer backbone after the imidization.

Thermoplastic PI resins have been generally synthesized from various diamines and dianhydrides in polar aprotic high boiling solvent such as NMP, DMAc, DMF. However, these type solvents have been made process capability low due to the difficulty of solvent removal. These solvents have high interactions with the polyimide structure. For this reason, during the removal, solvent can be evaporated with a mount of resin and it can also be residue in curing material. Residual solvent has caused high void raito in main material. In this regard, some approaches were developed and commercialized in order to these drawbacks. These developed and commercialized approaches were given in sub-headings.

1.4.4.1. Skybond and pyralin thermoplastic resin systems

Sybond and Pyralin systems are similar systems. While BTDA monomer has been used for Skybond systems, PMDA monomer has been used for Pyralin systems. These systems were manufactured by Monsanto and Dupont. As mentioned, these systems were based on BTDA and PMDA with various diamines. These systems are used in NMP solvent and impregnation into fibers was applied with NMP solvent. However these systems caused high void raito in advanced composite materials. These ratios have been reached up to 10%. Currently, these systems have been used and various studies have been carried out in order to minimize these high void ratios such as the changing and obtaining curing regime more slowly. These polyimide systems have been used in temperature range of 200-250 ˚C.

1.4.4.2. Avimide KIII and Avimide N thermoplastic resin systems

These class polyimides were invented by Dupont. Avimide KIII that was prepared for is the last version of Avimide K series. These systems have been inclusive of the Advanced Tactical Fighter of USA. First, the high void ratio and low prossesibility problems of

these systems have been almost minimized and overcome. The one of application areas has been wing skins of airplanes. According to Boeing report, thermoplastic advanced composite prepared from using this Avimide system has been used in their wing skins. Avimide KIII has been synthesized by PMR based synthesis approach. Carbon fiber (CF) reinforced advanced thermoplastic composites by using this resin system have exhibited compression after impact strength (CAI) values [56, 57]. Moreover, it exhibited high Tg values approximately 250 ˚C and the advanced composite from this system can be used in long-term applications for 200 ˚C. It is well known that PMR approach has presented a kind of monomeric solution. PMR approach has been carried out in NMP solvent for Avimide systems. Moreover, changing and optimizing molecular weight and cure cycle has been presented higher processability. On the other hand, in order to obtain higher thermal and thermal-oxydative stability Avimid N was also synthesized as thermoplastic resin. The difference of this new Avimid system has been usage of 2,2-bis(3,4dicarboxyphenyl) hexafluoropropane as fluorinated monomer. The composites obtained from Avimid N were manufactured by compression molding with the pressure of 17 MPa and the composites exhibited outstanding thermo-mechanical properties. The Avimid N film presented 360 ˚C of Tg and outstanding thermo-mechanical retention at 371 ˚C in air or nitrogen conditions [125]. However, Avimide N has low flow properties for fiber reinforced advanced composites and high interactions with polar aprotic solvents. For these reasons, significant processing problems were observed in the manufacturing of the advanced composites obtained from this fluorinated system. However, the higher microcracking resistance than PMR-15 composites besides outstanding thermal stability has become forward Avimide N system. For complex part, chopped CF was used to reinforce Avimide N matrix [126]. These properties of Avimide N and their composites make the components very proper to use in jet-engine applications.

1.4.4.3. Partially fluorinated thermoplastic polyimide resin systems

Fluorinated monomers have been used to obtain higher thermo-oxidative and thermal stability. Moreover, 2,2-Bis(4-(4-aminophenoxy)phenyl)hexafluoropropane (4-BDAF) that was invented by TRW, was used to toughen PMR-15 instead of MDA monomer. 4-BDAF was used with PMDA monomer and this PI matrix has been one of promising partially fluorinated thermoplastic resins. CF reinforced advanced composite were

manufactured by using this PMDA/4-BDAF based resin and obtained excellent thermal stability. This composite was exposed to high temperature at 357 ˚C under a compressed air with 4 atm for 100 h and very low weight loss such as 8% was obtained. PMDA/4-BDAF based composites have been exhibited a Tg of 430 ˚C. However processability of these fluorinated systems has a major drawback. These systems have been mostly used as coatings for PMR-15 composites for especially complex parts.

1.4.4.4. LaRC-TPI thermoplastic resin systems

This thermoplastic system was invented by NASA Langley Research Center and this system has been primarily thought as adhesive resin. This system has been constituted with BTDA and 3,3'-diaminobenzophenone monomers. It has been also suitable for advanced composite systems because it has exhibited high Tg values of 250 ˚C and high toughness value. However, there are significant drawbacks to manufacture such as high melt viscosity and solvent removal problem. A few researches were carried out to solve these problems. For instances, Pratt et al. [127] used resins with lower molecular weight and additives of imide. Therefore they obtained optimum melt viscosities and this revised system presented high quality advanced composites. Hartness [128] synthesized this LarC-TPI polyamic acid solution system in diglyme solvent and this revised system was impregnated into CF. Poor consolidation was obtained because of the low melt flow of resin. For this reason, Hartness developed powder impregnation of this system with using proper process. High quality composites were prepared by this powder impregnation prepreg method. Sherman [129] used special polymerization and imidization methods to obtain controlled molecular weights and distributions. Morever, semi interpenetrating networks and acetylene terminated chains were obtained and high quality composites were obtained. This version of LaRC-TPI is termed as “Durimid”, belonging to Roger Corporation.

1.4.4.5. Matrimid 5218 thermoplastic resin systems

That system was developed by Ciba-Geigy and has been constituted with BTDA and 5(6)-amino-l-(4-aminophenyl)-1,3-trimethylindane. During the manufacturing it has been completely imidized. However, due to the low solubility this system can be used for a certain applications. The prepreg process was applied with butrolactone. Composites have been manufactured by compression molding with pressure of 100 psi at 316 ˚C. They

have exhibited high fracture toughness values and high Tg value of 280°C. This type advanced composite can be used at 230°C.

1.4.4.6. Poly (ether imide) thermoplastic resin systems

Poly (ether imide) system is a special class for engineering thermoplastics. They have good balanced properties and high process capability. This material have become forward by General Electric. Ultem 1000 is a class of poly (ether imide) invented by General Electric, has been used as a matrix of glass fiber reinforced composites. This composite has exhibited Tg value of 220 °C and good mechanical properties [130]. However, its usage for aerospace industry is restricted due to its low solvent resistance. For this reason, General Electric cooperated with American Cyanamid to solve this mentioned solvent resistance problem. They developed a new prepreg system with a new poly (ether imide) that was chemically modified. This class of poly (ether imide) has been termed as Cypac. This modified poly (ether imide) matrix composite has exhibited high solvent resistance besides same maintained process capability. Cypac has overcome some drawbacks of Ultem 1000 [131]. Cypac has exhibited no degredation when exposed to the chemical fluids such as LP-4 jet fuel, Skydrol hydraulic fluid and methyl ethyl ketone solvents. It has also showed outstanding toughness and good mechanical properties up to 148 °C.

1.4.4.7. Poly (amide imide) thermoplastic resin systems

Poly (amide imide) (PAI) is a class of high performance thermoplastic engineering polymer. This class has been mostly used in several industry as thermoplastic engineering material such as adhesives, electrical wire enamel and various injection-moulding and extrusion products. This class was invented by AMOCO and its comerical name is “TORLON”. AMOCO was developed another class of PAI for composite applications and this class PAI matrix composites are termed as TORLON-C. PAI is synthesized by reaction of trimellitic dianhydride and an aromatic diamine. After the synthesis, both amide and imide groups are taken placed on the polymer backbone according to AMOCO. These groups cause high temperature stability and high toughness. This resin can be impregnated into fibers or fabric by applying appropriate processes and then can be moulded by compression or autoclave processes. These composites, TORLON-C, present high Tg value of 277 °C, improved impact resistance and high thermal properties. However, TORLON-C composites have high moisture absorbtion. This drawback

decreases its usage temperature [132].

1.4.5. Polyimide resins to use as carbon fiber sizing agent

Sizing has been performed to CFs in order to protect the fibers towards damage and increase the interactions. It also presents strong bondings between fibers and matrix. Most of fibers that aim for high temperature composite have been generally sized with 1-1.5% wt. of epoxy resin. However, there are significant questions available about epoxy size of fibers that used in high temperatures. The thermal stability of PI sizing agent should be suitable with the PI matrix. Luippold [133] investigated the sizing effects on different fibers of PMR-15 and LaRC 160 matrices. He compared the properties of epoxy sized fibers to those fibers sized with PI sizing agents such as PI03, Celanese, and Thermid AL600 after the exposure of the sized fibers to 316 °C for 1600 h. Both fibers exhibited similar results. It was thought that the exposure to 316 °C for long term degredated PI matrix. It was also noticed that Thermid Al600 sized fibers exhibited better properties than P103 sized ones. Moreover, T40R fiber sized PMR-15 composites showed better thermal-oxydative properties than the pure composites of PMR-15 composites.
In the light of all these informations, Table 1.3 shows the thermosetting and thermoplastic resins as matrix used for fiber reinforced advanced composites in literature and the comparision of the properties of these advanced composites obtained from those resin.

Table 1.3. Comparison of the properties of some thermoplasitc and thermosetting PI matrix advanced composites in literatute

CF-reinforced Composites	V391/Hitex 46 8B unitape	PMR15 /Celion 3K 8 HS fabric	LaRC-160 /Celion 3K 3 HS fabric	PMR II-50 /Celion 6000 unitape	Thermid 600/ Hercules HTS unitape	LaRC-TPI/ Hercules AS4	Cypac 7005/AS4 fabric	Torlon-C /Celione 6000 unitape	Avimid KIII/ AS4 unitape	Avimid N/ HTS unitape
Tg (°C)	263	345	340	370	354	250	225	243	251	355
Flexural Strength/Modulus (MPa/GPa)										
23 (˚C)	1765/169	845/66	814/66	1840	1346/1				1619/124	1207/104
150 (˚C)										
177 (˚C)	841/159									
288 (˚C)		697/59	562/59							
316 (˚C)					1021/8					
343 (˚C)				593						
Short Beam Shear (MPa)										
23 (˚C)	124	69	46	112	86	95	66	110	95	52
150 (˚C)						73	41			
288 (˚C)		48	34							
343 (˚C)				46						
Compressive										
Strength/Modulus (MPA/GPa)										
23 (˚C)							503/-		994/-	
150 (˚C)							414/-			
343 (˚C)										
References	[134]	[135-140]	[141-143]	[144]	[145]	[127-129]	[130,131]	[132,146]	[145,147]	[145,147]

1.5. Polymer Foams

Foams are termed as cellular materials because their microstructures involve in lots of cells. The size of these cells can be at level of millimeter, micron or nanometer. Moreover, these cells can be prepared as open or closed cells for thermal and sound insulation. Foam material can be natural or synthetically such as sea foam, wood, bone, peanuts, honeycomb, styrofoam or the other polymer foams. Polymer foams are good balanced density and properties and become forward among the other materials. A material with cellular structure gains important improvements and contributions to the pure materials such as thermal and acoustic insulation, high permeability, very low density, high strength to weight ratio and high surface area.

Wood and bone were used cellular materials by prehistoric man and requirements have increased in progress of time. Therefore new foam materials have been found. Moreover, a variety of foam materials have been manufactured by developing technology. Polymer technology and synthesis developments in 19th and 20th century have exhibited various polymer based foams and cellular materials and these polymer foams as thermoplastic and thermoset materials have been used in various applications [148]. Melt thermoplastic foams have high processibility due to the converting solid to liquid and they have wide range of properties. The properties of polymer foams can be varied by using various chemical monomers and synthesis methods. Melt thermoplastic foams have been generally prepared by incorporating blowing agents into the melt physically or chemically. Polyethylene, polypropylene and polystyrene thermoplastic foams present low process cost and are cheap source materials. Foaming process of these thermoplastic polymers are applied with by saturating of a volatile blowing agent into the polymer melt and proper conditions are produced to occur nucleation and growth of bubbles. An inert gases such as nitrogen or carbon dioxide can be exposed to the melt physically or the chemical agents to degredate and their by-products can be evaporated in suitable condition of foaming process.These chemical and physical methods become forward foam materials. On the other hand, some molecules such as carbon dioxide resulting from chemical reactions during the polymer synthesis occurs polymer foams like polyurethanes that widely used and isocyanate based polyimides. These foaming processes can be termed as in-situ foaming process. The one of important thermoplastic polymer foaming process is twin screw extruder with blowing of organic volatiles into the polymer melt under pressure. By means of this method the gas is supersaturated into the melt. After the nucleation and

growth of bubbles desired expansion of polymer is provided and finally thermoplastic resin was rapid cooled. If thermoset polymer foam is produced, curing agent shoud be incorporated into the melt at the final stage [149].

1.5.1. Polyimide foams

PI foams have outstanding thermal properties such as thermal and thermo-oxydative stability, thermal insulation as well as flame resistance. Moreover, they present high mechanical properties, toughness and resilience values.Therefore they have been used for aerospace, building applications. In summary, thermal and mechanical properties have been generally better than the other polymer foam materials such as polyurethane, polystyrene, epoxy [150]. Due to the low weight, thermal resistance character, high thermal and acoustic insulation properties, these PI foams are also used for aircraft, spacecraft, marine, high-speed trains, missiles and military applications.

In order to prepare PI foams, various synthesis methods are available. In terms of synthesis, PI foam manufacturing is classified as diamine based and isocyanate based method. Diamine based methods includes a variety of PI precursors such as poly (amic acid), poly (ester amine) salt, poly amic ester powders or solutions with very low solvent ratio. Diamine based foaming process does not include complex reactions like isocyanate based PI foams.

As additive, only surfactant can be adequate to prepare PI foam. Moreover, the cells in the foam are generally occured by removing solvent with high or low boiling point during heating and thermal imidization process [150]. For example, Cano [149] prepared PI foams from poly (amic acid) precursor powders and manufactured PI foam and microspheres by heating these powder precursors and thermally imidization. Diamine based PI foams are generally prepared by two-step method. First, aromatic diamine and aromatic dianhydrides or dianhydride derivative react with each other in polar aprotic solvents or alcohols in order to obtain precursors. These precursors can be powders or solutions with very low solvent amount. In the second stage these precursore are exposed to heating of 200 ˚C and above in a furnace therefore foaming and thermal imidization are provided [151-153]. On the other hand, isocyanate based foaming process is termed as one-pot method. In this method, CO_2 molecules release after the polymerization reaction of dianhydrides and diisocyanates such as polyaryl polymethylene isocyanate (PAPI). The releasing of CO_2 molecules is very important occurrence for foaming process. Moreover,

important additives such as surfactant, catalysts and accelerators are incorporated into the process during the polymerization reaction in order to obtained PI foams including homogeneous size and distribution of cells and with desired properties. The process of iscocyanate based PI foams has easy to carry out but the amount and priority order of additives in the process is very important to obtain the product with desired properties. Moreover, isocyanate based foaming process can be manufactured with much lower cost than diamine based PI foams. Moreover, its production technology is simple and present efficient manufacturing cycle. It is also proper to prepare low-density foams. However, the properties of isocyanate based PI foams have important drawback to use in critical applications for high temperatures such as 250 ˚C and above. A variety of by-products occur by side reacitons in the isocyanate based PI foaming process. These remained by-products in final PI foams substantially cause to decrease the thermal properties. Researches have continued to minimize these side reactions to occur by-products that decrease the thermal properties. Diamine based PI foams have been generally used for the applications with high temperatures of 250 ˚C and above, especially in aerospace industry. In current, aerospace industry has been quickly developing and the requirements of these PI foams with heat resistance have been increased. There is being extensive researches about soft, flexible and rigid PI foams carried out [154].

1.5.2. Diamine based PI foams prepared by poly (amic acid) and poly (ester amine) salts precursors (two-step method)

Aromatic diamines and aromatic dianhydrides are reacted each other in polar aprotic solvent in order to poly (amic acid) precursor. However, this precursor does not have adequate solid content for foaming process. PIs obtained from aromatic diamines and aromatic dianhydrides have rigid and strong bonding interactions. In order to solve these rigid and strong bonding interactions and in order to proceed the polymerization reaction without hydrolitic degredation, strong polar aprotic solvents with high boiling point such as NMP, DMAc and DMF are preferred. However, after the obtaining poly (amic acid) precursors it is hard to remove these solvents from the solution. To increase the solids content of the poly (amic acid) precursor solution, strong vacuum should be applied by exposure to mild temperature without conversion to imide groups. This process should be carried out in moulds or as in-situ application. At the second stage, heating was applied to the precursor solution for foaming and thermal imidization. The thermal imidization and

foaming process occur at 200 and above 200 ˚C. In order to make the process easier, poly (ester amine) salt is synthesized as precursor. This method is so suitable for manufacturing of PI foams. Dianhydrides were esterifed by methanol at 70 ˚C for 2 h. After the reflux, esterifed dianhydrides were reacted with diamines in methanol solvent. These resulting poly (ester amine) salts were obtained as powders by removing the solvent at room temperature. Due to the low boiling point of methanol removing process is easy. These poly (ester amine) salts powders are exposed to heating at 200 ˚C and above for foaming and thermal imidization [149].

1.5.3. Isocyanate based PI foams (one-pot method)

Isocyanate-based PI foams have been attracted by researchers due to their low-cost equipment requirements and easy preparation of process. However, by-products derived from side reactions such as uredio groups are detrimental to final product and these side reactions decrease the thermal properties and flame reterdancy. These thermal properties can not meet some requirements in critical applications. Isocyanate groups easily react with amino groups that occured by the reaction of isocyanate and water. As a result of this reaction uredio groups occur as by-products that are undesired [155]. In order to minimize these side reactions, researchers have carried out some studies such as postgrating method. Sun et al. [156] prepared isocyanate based PI foams by post grafting method to overcome the deficiencies of isocyanate based PI foam synthesis process. In this method, a prepolymer was synthesized with PAPI and different amount of dianhydrides and overdose isocyanates to obtain first solution. The second solution was consisted of anhydride derivatives, distilled water, catalyst and surfactant. Second solution was added into the first solution, stirred for a while and foaming process started. There are three stage for occurrence of polymerization and foaming. First, the excess isocyanates on PAPI react both water and anhydride derivatives. As a result of these reactions, it was expected that seven membered ring imide intermediates, amine functional groups, a small amount of ureadio groups during the synthesizing and foaming process. Most of reactions resulted in imide functional groups during synthesis and with exposure to heating at about 180 ˚C after foaming process. Possible reactions in postgrafting method are shown in Figure 1.19.

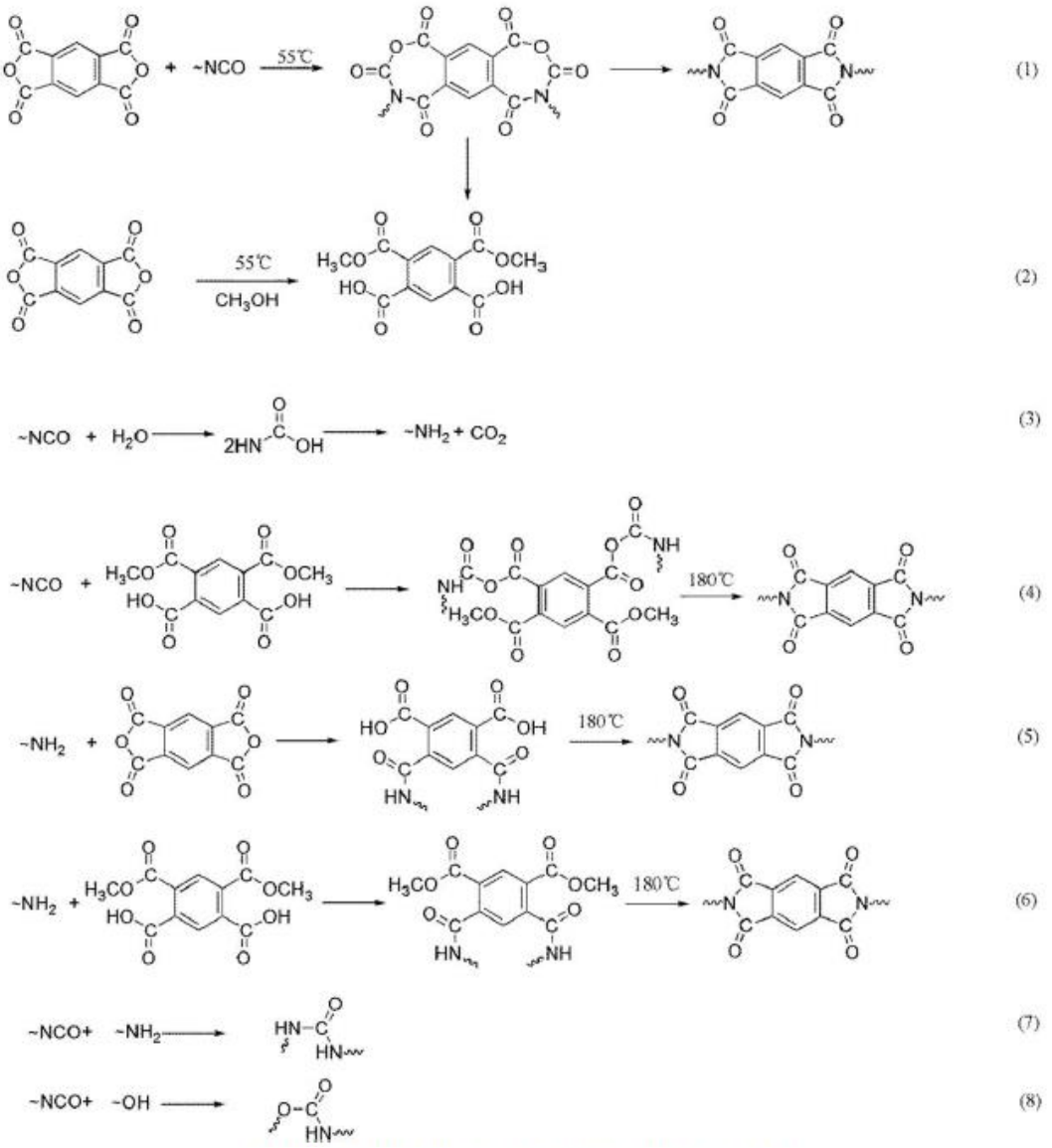


Figure 1.19. Chemical reactions that propable in postgrafting method related with isocyanate based PI foam preparation [156]

Reseachers have continued to study on isocyanate based PI foams due to high their processibility and applicability. PI foams obtained from precursor solutions and powders have encountered important problems about limited applicability. Isocyanated based PI foam process is similar with polyurethane foaming process with two components. Polyurethane foaming process is very widely used. Because of that, isocyanate based PI foaming process can be easiliy entegraded into polyurethane process technology that is widely used in industries and research laboratuaries.

In postgrafting method of isocyanate based PI foams, isocyanate index on PAPI is very important to obtain desired properties. Isocyanate amount affects substantially foaming properties, crosslinking of chains and polymer chain growth. Low amount of isocyanate causes low chain growth, inadequate crosslinking and occurring of inadequate foaming. High amount of isocyanate cause brittleness due to high amount of crosslinking and so many by-products such as carbamide, urea and amino groups. As well known, these by-products groups affect the properties adversely. Moreover, water amount is very efficient to obtain CO_2 as blowing agent in postgrafting method. In addition to these, it can be also behave as catalyst for isocyanate and anhydride reactions resulting with imide groups in another isocyanate based PI foaming processes. On the other hand, amount of catalyst and surfactant groups are also very important for isocyanate based PI foaming processes [156]. Also, poly ethylene glycol is used as assistant additive in order to adjust the amount of closed and open cells in foam product. Poly (ethylene glycol) prevents to escape the occurring organic volatile that provide the foaming of the polymer. Therefore, organic volatile into the cells produced closed cells while escaping of the volatile from the cells occur open cells. As mentioned, isocyanate based PI foam process produced carbon dioxide as blowing agent or foaming agent [156,157].

1.5.4. Thermosetting PI foams functionalized with nadiimide groups

Flexible PI foams have been used in aerospace and aviation industries such as cabin interior trim. However, rigid PI foam has been required for aviation and aerospace industries besides their properties of thermal and acoustic insulation, light weight and high chemical stability in recent years [158,159]. However, rigid PIs with high mechanical properties could not be produced in exact desired properties for especially the applications above 250 ˚C such as structural composite materials. For this reason, researchers have been focused on thermosetting PI foams. For thermosetting PI foams, diamine based foams have been prepared by terminating of the chains with some crosslinking and end capper groups such as nadic anhydiride, phenyl ethynyl monomers. Diamine based PI foam are preferable for the applications used above 250 ˚C. Moreover, diamine based PIs can be crosslinked with more controllability. The crosslinking density can be easiliy adjust by the stochiometry monomers and terminating agents. Moreover, the properties of low water absorbtion, high flame reterdancy and low toxicity are required for aerospace and aviation industries. Especially, as core materials in sandwich structures of radars, rigid PI

foams have been demanded not only the performance of wave transmission or absorbing, high temperature resistance but also certain high mechanical strengths. Up to till, polymethacrylimide (PMI) foams have been used for the related applications. However, these foams can keep up with their mechanical properties up to 210 ˚C. They are not suitable material for the applications above 200 ˚C due to their polyolefin polymer chains. Polyolefin polymer bondings have relatively much weaker than imide bondings in terms of both mechanical and thermal properties [160]. In addition to that, industrial flexible isocyanate based PI foams are not suitable in terms of mechanical and thermal properties for these critical applications [161, 162]. In conclusion, PI foams that can be used above 250 ˚C having high mechanical strengths near PMI foams are urgently required for military and civil aerospace industries.

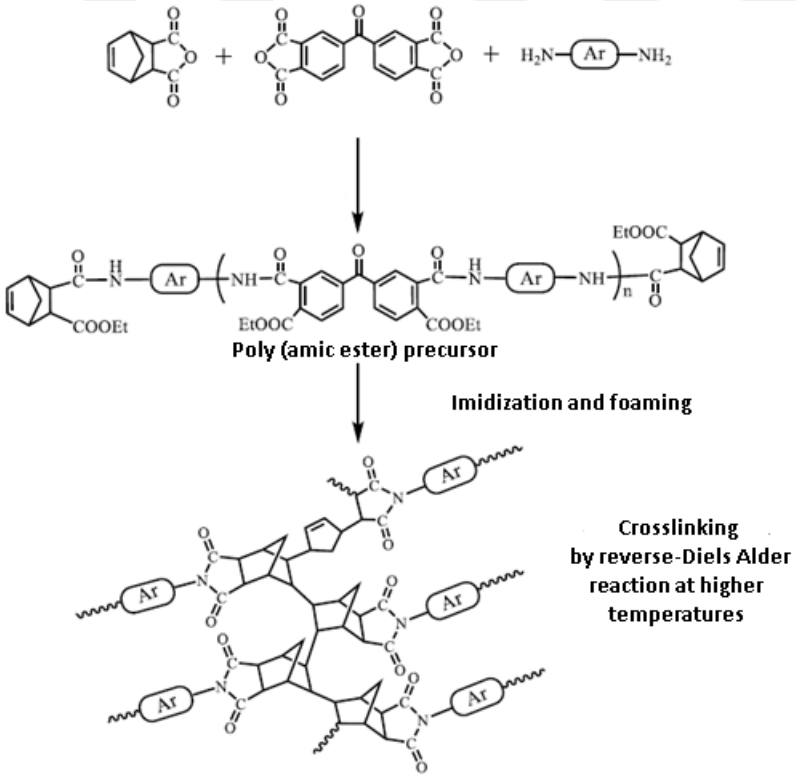


Figure 1.20. The preparation of thermosetting PI foam by using nadiimide functionalized poly (ester amine) powder precursor [163]

Li et. al [163] prepared crosslinked PI foams by using nadic anhydride terminated poly (ester amine) powder precursors as shown in Figure 1.20. In synthesis of this precursor while diaromatic diamine, aromatic dianhydride were used to occur polymer backbone, nadic anhydride was used to provide molecule weight control as end capper and occur the crosslinking of the chains as crosslinking agent. Moreover, the stochiometry of the

monomer reactants was adjusted according to PMR-15. First, the aromatic dianhydride and nadic anhydride were solved and esterified in alcohol at 90 ˚C and then diamine monomers were added slowly at room temperature. The homogeneous solution was occurred and stirred for 2 h. The homogeneous poly (ester amine) precursor solution was obtained. After this reaction, the excess solvent was removed by rotating distillation and powder precursors were resulted. These powder precursors were taken place in a graphite mold and then both imidization, crosslinking of the precursors and foaming process were provided by holding at 280-330 ˚C for 2 h. The obtained PI foams exhibited superior mechanical and thermal properties. The flexural and compressive strengths reached to 1.42 MPa and 0.47 Mpa, respectively. The densities of the resulting PI foams were varied from 40 to 200 kg/m^3. These results were superior to the PI foam and aerogel studies in the literature. These type PI foams present more proper properties for critical and specific applications that required higher mechanical and thermal properties. And these PI foam can be commercially produced for higher temperatures instead of PMI foams.

1.6. Heat Resistant Sandwich Structure Composites

Sandwich structure composites are important and unique materials for aerospace, aviation, marine and automotive industries because of their superior specific bending strength and modulus. These high specific strengths provide them one of the most suitable material class for lightweight and high-strength applications. A sandwich structure composite consist of two thin, strong and stiff faces and a low-density porous core material. Face materials are often obtained from steel, aluminium sheets and fiber reinforced composite laminates. Porous core materials are based on foam, honeycombs, aerogels and natural materials such as balsa wood. These face and core materials should be strongly bonded each other. For this reason, strong adhesive resin should be used and cured between faces and core material. In current, lightweight and high-strength materials have substabtially been demanded for especially aerospace and aviation, automotive, marine industries. Due to their lightweight, high strength and stiffness properties, fiber reinforced polymer matrix composite faces and polymer based porous cores have come to the forefront [157,164]. Epoxy as polymer matrix for fiber reinforced composites has been one of the most widely used in literature. As core materials, polymer foams and honeycombs are most widely used. Moreover, polymer types have generally been such as polypropylene, polyurethane, polyamide. However, these face and core materials can be proper below 200 ˚C. At higher

temperatures these kinds of polymer materials have been exposed to thermal degredation. Moreover, the mechanical properties of them have been substantially decreased [165,166]. Some critical application areas such as spacecrafts, fighter aircrafts, and civil airplanes required the usage of materials above 200 ˚C. The usage of polymer materials is very important for these applications due to their low densities. For instance, the mechanical component or structural parts near aircraft engines (nacelles), the airframes and wings of supersonic aircrafts, missile components and space satellites are some of these critical applications. In terms of the usage in these critical applications, PIs are excellent candidates as polymer matrix. PIs can be prepared as foams and they can be taken place in fiber reinforced composites as matrix [157,164]. Besides composites and foams, PIs can be manufactured as high temperature strong adhesive and microelectronic materials [167]. In the light of these informings, fiber reinforced polyimide based composites as face and polyimide foams as core materials have become forward as heat-resistant materials. By using these components, low-density heat-resistant sandwich structures can be pepared that are very important materials for the above mentioned critical applications. Moreover, high temperature strong adhesive required for these applications and to bond the polyimide based faces and core materials. For this reason PI precursor resins are widely used. These precursors are cured at high temperatures between the faces and core materials in order to obtain sandwich structures. PI precursors have been also used to impregnate fiber woven fabric for obtaining the advanced composites. Polymerization of monomeric reactant (PMR)-type resins are one of most widely used for both adhesives and the preparing of fiber reinforced advanced composites. These type precursors are based on poly (ester amine) salts (PEAS). These monomeric reactants have been easily impregnated into the fabrics and provided ease of process [167, 168]. PEAS can be converted poly amic ester precursor (poly ester amine precursor) by amidization in the temperature range of 80-150 ˚C [169, 170]. Poly (amic ester) precursor can also be applied to fiber fabrics or used as adhesive. Poly amic acid (PAA) that is the conventional precursor, it has been used as an impregnation resin for fabrics and an adhesive. By using these PI precursors fiber reinforced thermosetting and thermoplastic PI matrix composites and adhesives can be manufactured. Reactive end cappers such as nadic anhydride (NA) or phenyl ethynyl terminated imide (PETI) have been generally used for obtaining thermosetting PIs. When considering PI foams, various studies about PI foams are available in literature. These foams have been prepared as isocyanate and diamine based. Poly (ester amine) salt

powder and poly (amic ester) solution precursors have become prominent among diamine based PI foams. Thermoplastic and thermosetting PI foams that prepared by using these diamine based precursors have become forward in terms of their properties. On the other hand, isocyanate based PI foams have been significantly attracted by reseachers due to their ease of process and low-cost production. However, by-products that occurred during the synthesis and foaming process have affected the final product adversely. For this reason researchers have focused on this limitation of isocyanate based PI foams to reach the properties of diamine based PI foams. When considering heat resistant sandwich structures in the light of these informations, fiber reinforced polyimide based advanced composites and PI foams are excellent components to obtain heat-resistant sandwich structure composites. In order to combine these components, high temperature strong adhesive such as the mentioned PI precursors are the most suitable candidate. Figure 1.21 shows a scheme of a general sandwich structure composite.

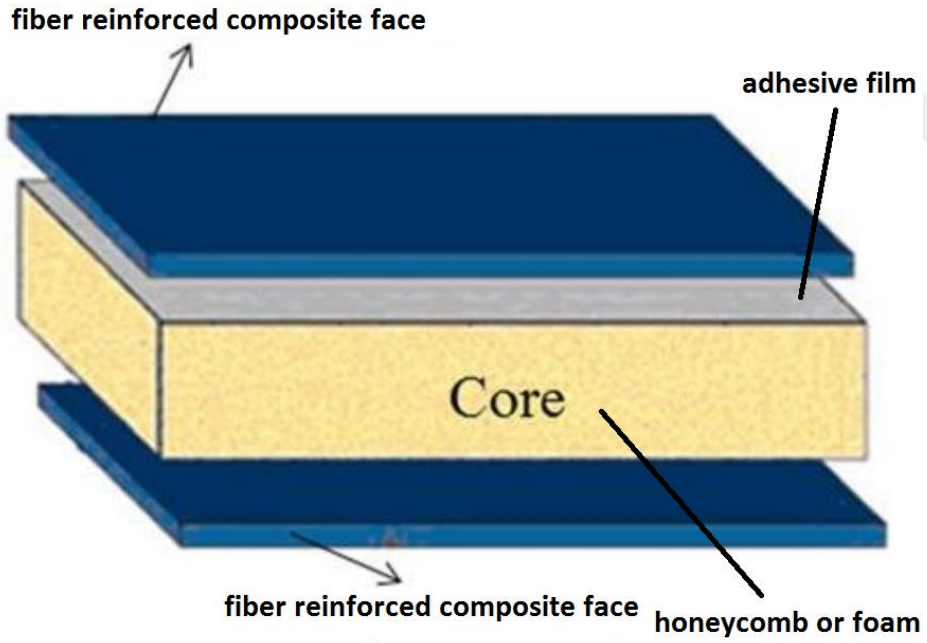


Figure 1.21. The scheme of a sandwich structure composite

Reviewing the literature about heat-resistant sandvich structure composites, there has been few study on heat-resistant sandwich structures. It is thought that this situation is derived from the poor availability of heat-resistant materials such as face sheets, cores, and adhesives [171,157]. Ogasawara et al. [171] has exhibited heat-resistant sandwich composite with CF fiber reinforced thermosetting PI matrix advanced composite faces and commercial carbon foam (GraFoam) core. They used phenyl ethynyl-terminated imide

oligomer (TriA-X) as composite matrix and adhesive film. This oligomer was cured and crosslinked in the reinforcing fabric at high temperatures with pressure. Moreover, it was applied between the faces and the carbon foam core material and cured and crosslinked at high temperatures with little pressure. The flexural force of this heat-resistant sandwich composite presented the value of 305 N. The Tg value of the CF reinforced thermosetting PI matrix advanced composite was 362 ˚C. Moreover, the density of carbon foam was 166 kg/m^3. Another study on heat-resistant sandwich composite was carried out by Camarda [172]. This sandwich composite consisted of graphite-reinforced PI matrix composite faces and a glass-reinforced PMR-15 honeycomb core. They reported the tensile and compressive properties of the final product. Much more studies should be applied on the development of heat-resistant sandwich composites, which have critical application areas for the defense, aviation and aerospace industries.

2. MATERIALS AND METHOD

2.1. Reinforcing Material of Advanced Composites

Epoxy-sized T300 CF fabric of 245 g/m^2 and 2x2 twill weave with a tow size of 3K that was purchased from Toray was used as the reinforcing material.

2.2 Vacuum Infusion Consumable Materials

Prepregs were stacked and consolidated and vacuum bagged on vacuum infusion heating bench. In order to carried out this process, some vacuum infusion consumable materials were used such as vacuum bag, release film, teflon sheet with 2mm, sealing tape, spiral tubing, vacuum tubing and T fitting.

2.3 Teflon Sheet

As vacuum infusion consumable material, teflon sheets with 2mm were used to remove the consolidated pregregs easily and with no damage.

2.4. Chemical Materials

2.4.1. 3,3,4,4-Benzophenone-tetracarboxylic dianhydride (BTDA)

Manufacturer: Sigma Aldrich
Mol. Formula: $C_{17}H_6O_7$
Mol. Weight: 322.22 g/mol
Structural Formula:

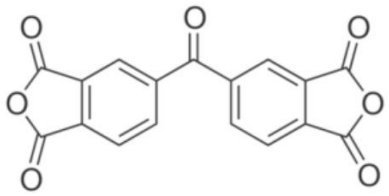


Figure 2.1. The chemical structure of BTDA

The chemical structure of BTDA is shown as Figure 2.1.

2.4.2. Pyromellitic dianhydride (PMDA)

Manufacturer: Sigma Aldrich

Mol. Formula: $C_6H_2(C_2O_3)_2$

Mol. Weight: 218.12 g/mol

Structural Formula:

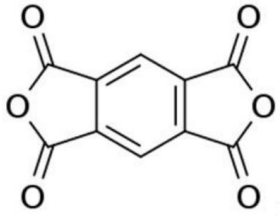


Figure 2.2. The chemical structure of pyromellitic dianhydride

The chemical structure for pyromellitic dianhydride is given in Figure 2.2.

2.4.3. 4,4-Diamino diphenyl sulfone (DADPS)

Manufacturer: Sigma Aldrich

Molecule Formula: $C_{12}H_{12}N_2O_2S$

Molecular Weight: 248.3

Structural Formula:

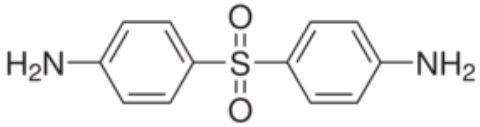


Figure 2.3. The chemical structure of 4,4-diamino diphenyl sulfone

The chemical structure of 4,4-diamino diphenyl sulfone is shown as Figure 2.3.

2.4.4. Dimethylformamide (DMF)

Manufacturer: Sigma Aldrich

Molecule Formula: C_3H_7NO

Molecular Weight: 73.09

Structural Formula:

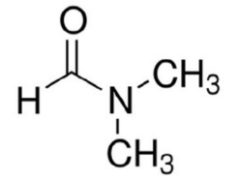


Figure 2.4. The chemical structure of dimethylformamide

The chemical structure for dimethylformamide is given in Figure 2.4.

2.4.5. Triethylamine (TEA)

Manufacturer: Sigma Aldrich

Molecule Formula: $C_6H_{15}N$

Molecular Weight: 101.19

Structural Formula:

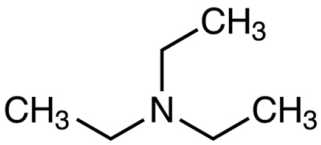


Figure 2.5. The chemical structure of triethylamine

The chemical structure for triethylamine is given in Figure 2.5.

2.4.6. Distilled water

Manufacturer: Marmara University Laboratuary

Molecule Formula: H_2O

Molecular Weight: 18

2.4.7. Surfactant (Tegostab B8522)

Manufacturer: Evonik

It is developed as an additive to use in rigid foam systems which are formulated to obtain high amount of open cell in foam.

2.4.8. Methanol

Manufacturer: Sigma Aldrich

Molecule Formula: CH_3OH

Molecular Weight: 32.04

Structural Formula

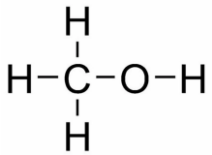


Figure 2.6. The chemical structure of methanol

The chemical structure for methanol is given in Figure 2.6.

2.4.9. 5-Norbornene-2,3-dicarboxylic anhydride (Nadic anhydride)

Manufacturer: J&K Company

Molecule Formula: $C_9H_8O_3$

Molecular Weight: 164.158

Structural Formula

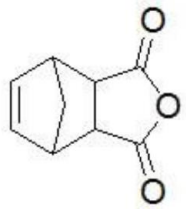


Figure 2.7. The chemical structure of nadic anhydride

The chemical structure for nadic anhydride is given in Figure 2.7.

2.4.10. Polymeric diphenylmethane diisocyanate (PMDI)

Commerical Name: Ongronat 2100

Manufacturer: Borsot Chem.

NCO: 30 - 32 m/m%

Viscosity @25°C: 170 - 230 mPa.s

Functionality: 2.6 - 2.7

Structural Formula:

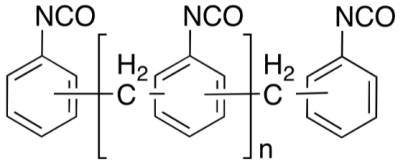


Figure 2.8. The chemical structure of polymeric diphenylmethane diisocyanate

The chemical structure for polymeric diphenylmethane diisocyanate is given in Figure 2.8.

2.5. Experimental Equipment and Methods

2.5.1. FT-IR spectra

Shimadzu brand 8300 model FT-IR Spectra device was used to clarify the synthesized polymer characteristic bondings. The PI matrices of the advanced composites were confirmed by their FT-IR spectra. FT-IR spectrum analysis was also performed for the poly (amic ammonium) salt and poly (amic acid) precursors and their characteristic peaks were compared with each other. Moreover, PI characteristic peaks belonging to the isocyanate-based PI foams were enlightened by FT-IR spectra.

2.5.2. Thermogravimetric analysis (TGA) equipment

Thermal stability value measurement for PI matrices of the advanced composites and isocyanate based PI foams was performed by using TA Instruments Q50 model TGA equipment using the differential thermal analysis (DTA) method. The specimens were analysized starting from 30 ˚C up to 800 ˚C. The heating rate was 10 ˚C / min in the condition of nitrogen atmosphere.

2.5.3. ^{1}H NMR spectra

The chemical structure of poly (amic ammonium) salt precursor was also characterized by H NMR spectra using a Unity Inovr 400 instrument with dimethyl sulfoxide (DMSO) as the solvent and tetramethyl silane (TMS) as a reference.

2.5.4. X-ray diffraction (XRD) analysis

The PI matrices of the PAAS-T, PAA-TS and PAA-T advanced composites were ground for powder X-ray diffraction (XRD) analysis. The powder X-ray diffraction (XRD) studies were carried out by using a Shimadzu-6100 XRD device with Cu-Kα radiation (λ = 1.5406 A) in the 2Θ/Θ mode at RT. The 2Θ scan data were collected at 0.01˚ intervals. The scanning speed was 2˚ (2Θ)/min.

2.5.5. Viscometer device

The apparent viscosity values of the poly amic acid, poly amic acid ammonium salt and NA-terminated poly (amic acid) precursor resins with a solution concentration of 50 wt % were measured with a Brookfield DV-II viscometer at RT.

2.5.6. Dynamic mechanical thermal analysis (DMA)

DMA is a technique that is widely used to characterize properties of a material as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. DMA was conducted with a TA Instruments DMA 2980 dynamic mechanical analyzer. The heating rate was 5 ˚C / and it was applied starting from -150 ˚C up to 400 ˚C. The advanced composite samples and PI foams were run at a frequency of 1 Hz in the dual cantilever bending mode.

2.5.7. Mechanical test equipment

The three-point flexure test was applied for the advanced composite samples to observe flexural strength, flexural modulus and flexural strain results according to the ASTM D790 standard. The tensile test was also applied to the advanced composite samples according to the ASTM D3039 standard in order to observe tensile strength, tensile modulus and tensile strain results. The three-point flexural test was also carried out for the heat-resistant advanced sandwich composite panels (HRACSs) to observe flexural

strength, flexural modulus according to the ASTM D790 standard. The formulations to calculate flexural strength and modulus according to ASTM D790 standard. Moreover, some properties of the HRACSs such as core shear ultimate strength (CSUS) and facing bending stress (FBS) were calculated according to the ASTM C393 standard. In addition of these properties, flatwise compressive strength and modulus of sandwich cores were calculated and evaluated according to according to ASTM C365 standard. On the otherhand, compressive tests of PI foams were carried out according to the ISO 844 standard apart from the sandwich core compressive tests. All these tensile and compressive tests were carried out by using an Instron model 4505 device and Series IX acquisition software. Charpy test with unnotched was carried out for the most prominent two advanced composites, PAAS-T and PAA-TS. This test was applied with an Instron CEAST 9050 Charpy Impact Tester with a 5 J hammer according to EN-ISO 179-1 standard. The CF fabric (2 × 2 Twill) plies were adjusted symmetrically as "0/45/0/45/45/0/45/0" in a multidirectional manner. Flexural and tensile tests for advanced composite faces were applied as five replicated samples. The flexural tests of the heat resistant sandwich composites were applied as three replicated samples. The compression tests of sandwich composites and PI foams were applied as three replicated samples.

2.5.8. UL94 flammability test equipment

UL94 vertical burning tests were carried out in order to observe fire reterdancies and flammability of the PI foams and the prominent advanced composite laminates (PAAS-T and PAA-TS).

2.5.9. The Limiting oxygen index (LOI) test equipment

LOI is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer. This test was used to observe the fire resistance and flammability of the PI foams and the prominent advanced composite laminates (PAAS-T and PAA-TS).

2.5.10. C-Therm TCI 2A conductivity analyzer

The thermal conductivity coefficient and effusivity of the prominent advanced composite laminates (PAAS-T and PAA-TS) and the PI foams that formed the HRACSs were separately measured by a C-Therm TCI 2A conductivity analyzer.

2.5.11. Hydrazine method

The hydrazine method was applied in order to calculate the fiber content in the advanced composites. Small particles of each advanced composite was seperately put in the hydrazine hydrate solution and hold for 5 h at room temperatures. After the holding in room temperatures the solution was heated to boiling temperature and hold for 15 min at the boling temperature of hydrazine hydrate solution. After these procedures, the fibrous residue into the solution was filtered and washed acetone in three times. The filtered and washed fibrous residue was coverted from brownish to black color. This residue was dried in oven and measured its weight. Fiber content of the composites was calculated with the ratio of the fibrous residue to the composite laminate. The carbon fiber content of the advanced composites presented in range of 59–61 wt %.

2.5.12. Scanning electron microscopy (SEM) analysis

Scanning electron microscopy (SEM) analysis was exposed to the advanced composites in order to observe their fracture surfaces and interlaminar combination and compatibility between fiber and matrix after three-point flexural tests. SEM micrographs of the cells into the PI foams were observed by using a JOEL JSM-5910 LV SEM device. The surfaces were coated with a gold layer by vacuum sputtering.

2.5.13. Three-necked round bottom flask with condenser

In order to synthesize the PI precursors such as poly (amic acid), poly (ester amine) salt, poly (amic ammonium) salt and isocyanate based prepolymer in nitrogen atmosphere, three-necked round bottom flask with condenser was used.

2.5.14. Magnetic stirrer

In order to synthesize the PI precursors and isocyanate based prepolymer, magnetic stirrer with heater was used.

2.5.15. Glass cylindrical bar

Glass cylindrical bar was used during the prepreg preparation. It was used to spread and impregnate the poured PI precursor solution onto CF fabric with reciprocating action of the glass cylindrical bar in line.

2.5.16. Teflon roller

Teflon roller was used during the prepreg preparation. It was used by rolling movement with little hand compression on the impregnated CF fabric between the release films in order to increase the impregnation and spreading homogeneity of the PI precursor solution.

2.5.17. Vacuum oven

Vacucell vacuum oven was used during the prepreg preparation. Two-step impregnation was applied for CF fabrics. After first and second impregnation, the excess solvent of the impregnated CF fabrics were removed in mild temperature condition under 0.5 bar vacuum. After the second vacuum process, each ply had adequate tackiness for composite manufacturing process.

2.5.18. Vacuum infusion equipment

Vacuum infusion machine with its consumable materials was used for vacuum bagging process of the stacked composite pregreg plies. During this process, partly curing was provided and the solvent amount was minimized. After the vaccum bagging process with the certain process parameter such as process time, temperatures and vacuum level, a consolidated composite was obtained and this composite was taken place to be further imidized and crosslinked at compression molding at next stage.

2.5.19. Compression molding machine

Consolidated prepregs were hot pressed to obtain the advanced composites by using compression molding with high temperature and pressure.

2.5.20. Furnace with air circulation

Instron furnace was used for the post-curing process of the manufactured advanced composites.

3. RESULTS AND DISCUSSION

3.1 Characterization of Carbon Fiber-reinforced Thermoplastic and Thermosetting Polyimide Matrix Composites Manufactured by Using Various Synthesized PI Precursor Resins

3.1.1. Abstract

Currently, it is important to manufacture thermoplastic advanced composites with high mechanical and thermal properties because of their higher impact resistance than thermoset composites. In this study, carbon fiber (CF)-reinforced thermoplastic and thermosetting polyimide (PI) matrix composites were manufactured by vacuum bagging followed by compression molding. Before the manufacturing process, prepregs were also prepared with various PI precursor resins by using two-step impregnation. These precursors were synthesized as poly (amic acid) (PAA), polyester amine salts (PEAS) and poly (amic acid) ammonium salts (PAAS). The PAAS precursor resin was applied as a novel method for manufacturing CF-reinforced PI matrix advanced composites. The advanced thermoplastic composite obtained from the PAAS precursor (PAAS-T) exhibited superior mechanical properties and enhanced thermal properties (near the thermal properties of thermoset advanced composites) in comparison to the other advanced composites in this study and those in the literature. However, the NA-terminated PAAS precursor (thermosetting PI precursor) did not exhibit a similar effect in terms of mechanical properties. On the other hand, the thermosetting composites exhibited highly enhanced storage modulus values up to 400 °C and outstanding thermal stability at TGA. The thermosetting composite that was obtained from the NA-terminated PAA precursor resin exhibited high mechanical properties besides its thermal properties.

Keywords: poly (amic acid) ammonium salt precursor resin, NA-terminated poly (amic acid) precursor, two-step impregnation, carbon fiber/polyimide composite, high-performance thermosetting and thermoplastic advanced composites

3.1.2. Introduction

Aromatic polyimides are some of the most useful high-performance engineering plastics. Properties of polyimides such as high glass transition temperature, excellent electrical, thermal and mechanical stability, dimensional stability and chemical resistance have been considerably attractive for research and contributed to their wide area of applicability in

engineering [173]. Aromatic polyimides have been used in biochip design,optoelectronic applications, gas separation, coating, superhydrophobic surfaces, photocatalysts for hydrogen generation, aerospace and advanced composites [174,175]. Considering advanced composites, fiber-reinforced polyimide matrix composites have been some of the significant advanced composites. Polyimides as matrices in fiber-reinforced polymer composites with high strength-to-weight ratios at high temperatures have been key materials, especially for aerospace and aviation structures [176,177]. Their major application areas are wings and airframes of military aircraft, parts close to aircraft engines such as nacelles, ultra-high-speed fan blades, inner and outer ducts, swirl frames, reverser stang fairings, external nozzle flaps, and shuttle orbital aft body flaps. Ion thruster beam shields for the flights of space shuttles and as covers of fuel tanks are also some application areas in the aerospace industry. Besides these polyimides are important materials for cryogenic applications in the naval and aerospace industries [174, 178].

In the literature, there have been various studies related to fiber-reinforced polyimide-based thermoplastic and thermoset composites. In these studies, precursor resins were synthesized first, and prepregs were obtained by the impregnation of fiber fabrics. These prepregs were converted to advanced composites by using autoclaving or compression molding [178]. The most common precursor resins that have been used to obtain prepregs are poly (amic acid) (PAA), poly amic ester (PAE) and poly ester-amine salt (PEAS). A review of relevant previous studies was conducted. Accordingly, Lu et al. [179] prepared T300 unidirectional thermoplastic composites with CF-reinforced polyimides and co-polyimides as the matrix. They also obtained both PAA precursors for prepregs and PI films to manufacture advanced composites by hot-pressing at a 2-3 MPa pressure. The PAA precursor resins were synthesized in dimethyl acetamide (DMAc) using 3,4′-oxydianiline (ODA), 3,3′,4,4′-oxydiphthalic anhydride (ODPA), 3,3’,4,4’-benzophenone carboxylic dianhydride (BTDA), bisphenol A dianhydride (BPADA) and biphenyl dianhydride (BPDA) monomers. Phthalic anhydride (PA) was used for end-capping to control the molecular weight. The composite containing BTDA/ODA/PA exhibited a flexural strength value of 536 MPa and a flexural modulus of 95 GPa, while the composite containing BTDA-BPDA (9:1)/3,4 ODA/PA exhibited a flexural strength value of 500 MPa and a flexural modulus of 90.5 GPa. The Tg values of these composites were found in the dynamic mechanical analysis (DMA) as 276 °C and 278 °C, respectively. Su et al. [180] prepared CF-reinforced thermoplastic polyimide-based hierarchical composites with

in-situ-grown carbon nanotubes (CNT) on CF fabric to obtain enhanced fiber-matrix interfacial adhesion. They synthesized a PAA precursor resin containing BPADA and ODA monomers. In order to improve the CF fabric's mechanical properties, they also treated it with a nitric and sulfuric acid solution. While the pure composite (CF/PI) represented a flexural strength with 420 MPa and a flexural modulus with 45 GPa, the CF/PI composites where the carbon nanotubes grew for 40 min (CF/PI-40) represented a flexural strength with 560 MPa and a flexural modulus with 64 GPa. The Tg values obtained in the DMA of CF/PI and CF/PI-40 were 218 °C and 245 °C, respectively. Livengood et al. [181] synthesized PAA precursor resins from BTDA and 2,2'-dimethyl-1,3-(4-aminophenoxy)propane (DMDA) in tetrahydrofuran (THF) / N-Methyl-2-Pyrrolidone (NMP) co-solvent and prepared T650 unidirectional CF-reinforced thermoplastic polyimide matrix composites. They reported that the composite exhibited Tg values varying from 230 °C to 250 °C and storage moduli varying from 210 °C to 220 °C in DMA. Cano et al. [182] synthesized polyimide and co-polyimide thermoplastic resins using ODPA and ODA monomers with the PEAS precursor method. Phthalic anhydride (PA) was also used to control molecular weight as an end capper. The PEAS precursor was formed out of a reaction between an aromatic diamine and diester-diacid monomers. The diamine monomers reacted instantly with the diester-diacid monomers, and chain-like structures (ionic interactions between amine and carboxylic acid groups) with alternate diamine/diester-diacid components occurred in a repeat unit form. These precursor resins were used as the PI matrix for 12K IM7 unidirectional CF-reinforced thermoplastic advanced composites. While the 0° flexural strengths of these composites were in range of 1500-1700 MPa, their 90° flexural strengths were in range of 110-130 MPa.

Serafini et al. [167] invented unidirectional CF-reinforced thermoset PI matrix advanced composites using PEAS precursors with the US patent no 3.745.149 at NASA laboratories. They also obtained chain-like structures with PEAS precursors like Cano et al. [182]. These polymer chains were crosslinked by means of some terminating agents such as nadic anhydride (NA) and phenyl ethynyl (PETI) at high temperatures and pressures. These composites were termed as PMR-type composites. PMR refers to the polymerization of monomeric reactants. Serafini et al. [167] used various diamines and dianhydrides such as BTDA, methylenedianiline (MDA) and 4,4'-thiodianiline (TDA) and pyromellitic anhydride (PMDA) for the production of a polymer backbone. NA was used as a reactive terminating alkyl ester and crosslinking agent. In the synthesis process, the

molecular ratios of the PEASs were varied, and PMR-15 (1500 molecular weight) became prominent in terms of its mechanical and thermal properties. Unidirectional CF-reinforced advanced composites obtained from PMR-15 exhibited high interlaminar strength values in a range of 55-89 MPa. Chuang et al. [168] prepared a high-Tg thermosetting PMR-type polyimide advanced composite. They developed DMBZ-15 by replacing methylenedianiline (MDA) in PMR-15 with 2,2′-dimethylbenzidine (DMBZ). BTDA, DMBZ and NA were used as monomers to synthesize the precursor resin. A CF fabric (T650-35, 8 harness satin weave, UC309 epoxy sizing) was used as the reinforcing material for this thermoset advanced composite. The researchers compared the properties of DMBZ-15 and PMR-15. DMBZ-15 presented a higher Tan δ Tg value and a higher onset temperature of the storage modulus ($E^{'}$) than PMR-15. While the onset temperature and Tan δ Tg value of DMBZ-15 were 409 ˚C and 425 ˚C, those of PMR-15 were 345 ˚C and 375 ˚C, respectively. Moreover, while the flexural strength and modulus of DMBZ-15 were 1027 MPa and 58 GPa at room temperature (RT), the flexural strength and modulus of PMR-15 were 1030 MPa and 58 GPa at RT, respectively. Ogasawara et al. [171] developed a new heat-resistant sandwich structure including a thermoset advanced composite face obtained from a novel phenyl ethynyl-terminated imide oligomer (TriA-X). This thermoset advanced composite presented a Tg value of 362 ˚C.

In the literature, in-situ-grown carbon nanotubes on CF and multiwall (MW) carbon nanotubes have been used to increase the interfacial combination between the CF and PI matrices of CF-reinforced polyimide composites. Ogasawara et al. [183] dispersed MW carbon nanotubes into phenyl ethynyl-terminated polyimide resin (TriA-PI; thermosetting polyimide) and obtained a thermoset polyimide with excellent mechanical properties and processability, as well as a high glass transition temperature. Chen et al. [184] prepared carbon fiber - multi-scale carbon nanotube hybrids using a chemical method followed by the hot-press technique to ameliorate the interfacial combination between the CF and PI matrix.

In addition to these viewpoints in the literature, there has been other PI precursor available for synthesis for various purposes. This precursor is poly (amic acid) ammonium salt (PAAS) that has been used in some applications such as thin films, hybrid films and interlayers in the literature. PAASs have been prepared by blocking the COOH groups with triethyl amine monomers to facilitate the formation of ammonium salts on the polymer backbone. Cai et al. [185] prepared PI films from PAAS precursors with

improved thermal stability and mechanical properties. They also reported that PAASs had excellent hydrolytic stability, and their mechanical properties barely decreased after 90 days. Because of the allowing of long storage periods at RT, these precursors attract much interest. They are an excellent candidate due to their potential practical applications. Ke et al. [186] used a PAAS solution (1 wt % solid) to size the T700 carbon fiber. They toughened the thermosetting polyimide composite. The compression after impact (CAI) value of the carbon fiber-reinforced PI composite increased from 175 MPa up to 190 MPa. Iroh and Jordan [187] prepared CF (T650-42)/ PMR-15 composites containing thermoplastic polyimide interphase coatings obtained from a PAAS solution. They used the monomers of BTDA/ODA-PDA (1,3-phenylene diamine) to synthesize the PAAS solution (1% solid). The deposition of the interphase on CF was performed using the galvanostatic method by passing a certain current. The flexural strength of the composites increased in the presence of the interphase coatings. Facinelli et al. [188] synthesized PAASs and reported that PI synthesized from PAAS had a higher molecular weight than conventional PAA, as well as improved thermal and mechanical properties. They also mentioned General Electric's ULTEM, which is a thermoplastic polyimide with an excellent combination of thermal stability, mechanical properties and processability. In addition to these, they reported that PAASs could make excellent fiber sizing media, subsequently to be imidized to yield tough, relatively water insensitive, fiber-matrix interphase layers [188, 130]. Facinelli et al. [188] emphasized their interest in exploring these positive aspects of PAASs for composite applications.

The objective of this study is to develop CF fabric (T300)-reinforced thermoplastic and thermosetting PI matrix advanced composites by using various synthesized PI precursor resins as PAA, PEAS and PAAS. The most original aspect of this study is the use of a PAAS precursor for producing CF-reinforced PI matrix advanced composites. PAAS precursor resin was applied as a novel method for manufacturing CF-reinforced PI matrix advanced composites. Advanced thermoplastic composite obtained from the PAAS precursor (PAAS-T) exhibited superior mechanical properties and enhanced thermal properties (near the thermal properties of thermoset advanced composites) compared to the other advanced composites in this study and literature. It is important to manufacture thermoplastic advanced composites with high mechanical and thermal properties nowadays because of their higher impact resistance than thermoset ones. This is an important improvement in terms of CF-reinforced PI matrix thermoplastic advanced

composites. However, the NA-terminated PAAS precursor (thermosetting PI precursor for manufacturing PAAS-TS) did not exhibited the same effect in terms of mechanical properties. On the other hand, the advanced thermoset composites exhibited highly enhanced thermo-mechanical properties at around 400 °C. The advanced thermoset composite that was obtained from the NA-terminated PAA precursor resin (thermosetting PI precursor resin for manufacturing PAA-TS) exhibited enhanced mechanical properties besides its outstanding thermal properties. Moreover, the PIs obtained from the PAA precursor presented slightly higher thermal stability compared to the PIs obtained from the PAAS precursor although those that were obtained from the PAAS precursor resin presented enhanced thermal stability. Still, the thermoplastic advanced composite obtained from the PAA precursor resin (PAA-T) exhibited very low mechanical properties compared to that obtained from the PAAS precursor resin. It was thought that PAAS precursors could substantially increase processing capability. Moreover, PAAS has unique properties such as making excellent fiber sizing media, fiber-matrix interphase layers, being relatively water insensitive and having high hydrolytic stability. It is well-known that high hydrolytic stability provides storage capability for precursor resins at RT for long periods. It is thought that prepregs obtained using PAAS precursors with high-temperature solvents can also be stored at RT for long periods. As another issue, two different solvents as methanol and dimethylformamide (DMF) were used for the PEAS precursor resins. It is known that different solvents affect the molecular weight and properties of PIs. Therefore, the effects of PEAS precursors obtained from DMF and methanol solvents on the properties of CF-reinforced thermosetting and thermoplastic PI matrix advanced composites were investigated. BTDA and DADPS were determined as the monomers for the synthesized polymers, and NA was used as the terminating agent and crosslinker. It is thought that DADPS would make considerable contributions to thermal and mechanical properties. It was used instead of the MDA monomer of the PMR-15 composite due to the toxic structure of MDA. The properties were also compared to PMR-15 composites besides composites in other studies in the literature. Regarding the manufacturing process, CF-reinforced thermoset and thermoplastic PI matrix composites have been usually manufactured by autoclaving or compression molding. The prepreg preparation period takes as much time as 8 and 12 h for maturation after the impregnation step. The impregnation process has been generally carried out in the literature by the immersion of the CF fabric into the solution with the dip tank method [180,182,189]. This impregnation

process takes a long time. As mentioned above, Su et al. [180] synthesized a PAA precursor resin containing BPADA and ODA monomers in DMF. They immersed the CF fabric into the solution in a dipping tank for 12 h and put it into a vacuum oven to evaporate the excess solvent. This procedure was repeated for three times. Lan et al. [189] fabricated prepregs for CF (T800H)-reinforced thermoset polyimide matrix advanced composites by impregnation into the solution in a dipping tank. These wetting fibers were kept for 12 h at 60 ˚C for maturation. Our study presents two-step impregnation followed by solvent removal in a vacuum oven in a short time during the preparation of the prepregs. The prepared composites were mechanically characterized by flexural and tensile tests. The Charpy test was also carried out to investigate impact resistance for the most prominent thermoset and thermoplastic advanced composites, PAAS-T and PAA-TS. Thermo-gravimetric analysis (TGA) was applied to measure thermal stability of the specimens. For certain frequencies, dynamic mechanical thermal analysis (DMA) was carried out to observe the alteration of the modulus with an increase in the temperature. The Tan δ peaks of the advanced composites were also investigated by DMA. H NMR spectral analysis was carried out at RT by using the Unity Inovr 400 instrument with dimethyl sulfoxide (DMSO) as the solvent. Tetramethyl silane (TMS) was used as a reference. The H NMR spectral results confirmed the chemical structure of PAAS. FT-IR analysis was carried out for the PI matrices of all composites, as well as the PAAS and PAA precursor resins. XRD (X-ray diffraction) analysis was performed for investigating the degree of crystallinity or amorphousness of the microstructures of the PI matrices obtained from the PAAS, PAA and NA-terminated PAA precursor resins. Measurements of apparent viscosity were also performed for the PAAS, PAA and NA-terminated PAA precursor resins.

3.1.3. Experimental

3.1.3.1. Materials

3,3,4,4-Benzophenone-tetracarboxylic dianhydride (BTDA), 4,4 diamino diphenyl sulfone (DADPS), dimethylformamide (DMF), triethyl amine (TEA) and methanol were purchased from Sigma-Aldrich. 5-Norbornene-2,3-dicarboxylic anhydride (nadic anhydride, NA) > 97.0% was purchased from J&K Company. T300 carbon fiber fabric (CF) of 245 g/m^2, 2x2 twill weave with a tow size of 3K that was purchased from Toray was used as the reinforcement material.

3.1.3.2. Preparation of PI precursor resins

3.1.3.2.1. Preparation of PI precursor resins for thermoplastic advanced composites

Four different synthesis methods were carried out, and CF fiber-reinforced composites were termed according to these synthesis methods. The PAA precursor resin, PAAS precursor resin and two different PEAS precursor resins were prepared. While one of the PEAS precursor resins was synthesized in the DMF solvent, the other one was synthesized in the methanol solvent. The CF-reinforced thermoplastic PI matrix composites (CFTC) synthesized from these precursor resins were termed as PAA-T, PAAS-T, PEASD-T and PEASM-T. Some explanations about the sample codes of the manufactured PI composites are given in Table 3.1. The thermoplastic precursor resins were prepared as 50 % wt. solids. No dilution or evaporation of the solvent was carried out before the prepreg impregnation step. All reactions were completed in a flask with three necks and a round-bottom. It was also entegrated with a magnetic stirrer, condenser and thermometer. These reactions were applied in a controlled N_2 atmosphere. All PI thermoplastic precursors were synthesized according to the stoichiometry of an equimolar amount of the dianhydride monomer (BTDA) and diamine monomer (DADPS).

3.1.3.2.2. Preparation of PAA precursor resin

This precursor was synthesized using the conventional PAA synthesis method. First, the DADPS and DMF were charged into the flask. The DADPS and DMF were stirred for 30 min at RT. Then, an equimolar amount of the dianhydride monomer (BTDA) was gradually added to the contents in the flask and stirred for 12 h at RT. After stirring the BTDA and DADPS, the PAA precursor resin was obtained as a clear viscous liquid.

3.1.3.2.3. Preparation of PEAS precursor resin in DMF solvent

This precursor was firstly formed from the reaction of the BTDA dissolved in a mixture of DMF and methanol. MeOH was used for the esterification, and the MeOH reacted with BTDA stoichiometrically in the DMF solvent. This solution was kept at 70°C for 2 h to convert the BTDA into BTD-dimethyl ester (BTDE). The DADPS was then gradually added to the BTDE solution and stirred for 12 h at RT. The PEAS precursor resin in the DMF solvent was obtained as a clear viscous liquid.

Table 3.1.1. Information and explanations about the advanced composites

Synthesis Method	Solvent	Composite Type	Composite Code
Poly (ester amine) salt method	DMF	Thermoplastic	PEASD-T
		Thermoset	PEASD-TS
Poly (ester amine) salt method	Methanol	Thermoplastic	PEASM-T
		Thermoset	PEASM-TS
Poly (amic acid) method	DMF	Thermoplastic	PAA-T
		Thermoset	PAA-TS
Poly (amic ammonium) salt method	DMF	Thermoplastic	PAAS-T
		Thermoset	PAAS-TS

3.1.3.2.4. Preparation of PEAS precursor resin in methanol solvent

This precursor was firstly formed from the reaction of the BTDA dissolved in only the methanol solvent. The MeOH reacted with the BTDA stoichiometrically in the excess methanol solvent. This solution was kept at 70°C for 2 h to convert the BTDA into BTDE. The DADPS was gradually added to the BTDE solution and stirred for 12 h. The PEAS precursor in the methanol solvent was obtained as a clear viscous liquid.

3.1.3.2.5. Preparation of PAAS precursor resin

The difference of this method from the conventional PAA precursor method is the addition of triethyl amine (TEA) monomers into the PAA precursor solution. The synthesis scheme of the PAAS precursor is presented in Figure 3.1. The PAA solution was vigorously stirred at RT for 2 h after the addition of the TEA monomers. The amounts of the TEA monomers were adjusted to block the COOH groups on the PAA chain. Thus, ammonium salts formed along the polymer chains in the solution. The PAAS precursor resin was obtained as a clear viscous liquid.

3.1.3.2.6. Preparation of PI precursor resins for thermoset advanced composites

The same synthesis methods as the precursor resins of the thermoplastic PI composites were carried out, and the CF fabric-reinforced PI matrix thermoset advanced composites were termed according to these synthesis methods. In these methods, NA was used as the end capper and to provide the crosslinking of the polymer chains at high temperatures. The molar ratio of the monomers was adjusted according to the stoichiometry of 2NE/(n + 1) DADPS /n BTDE as well. The "n" value was 2.087. This ratio belonged to the PMR-15 precursor resin that had a molecular weight of 1500 [6]. The crosslinking of the NA-terminated precursor resins was facilitated with the reverse Diels-Alder reaction at a high temperature (above 300 °C) and by applying a high pressure during the manufacturing process [190, 191]. The synthesis schemes of the PEASM-TS and PAA-TS are given in Figures 3.2 and 3.3., respectively. These precursor resins were prepared as 50 wt % solids.

3.1.3.3. Prepreg fabrication

The prepreg fabrication step involved two-step impregnation by a glass cylindrical bar followed by solvent evaporation in a vacuum furnace at mild temperatures and under a vacuum. Figure 3.4 presents the preparation scheme of the prepregs. The CF fabric was cut into six equal pieces so that the dimensions of each piece would be 15 cm x 15 cm before the impregnation process. Each CF fabric piece was laid down on the polypropylene (PP) film. The precursor resins that were prepared were poured onto the CF fabric as four columns at equal distances, and they were spread onto the fabrics by the glass cylindrical bar. The resin was impregnated into the fabrics homogeneously with the reciprocating action of the glass cylindrical bar in line. After the first impregnation step, the wet CF fabrics on the PP film were subjected to vacuum at a mild temperature in order to evaporate the excess solvent. While the precursor resin using the DMF solvent was evaporated at 60 °C and 0.5 bar in vacuum for 1 h, the precursor resin using the methanol solvent was evaporated at 40 °C and 0.5 bar in vacuum for 30 min. After the removal of the solvent in the wet CF fabrics, the second impregnation step was carried out by turning the CF fabrics upside down on the PP film, followed by pouring the resin, spreading it with the reciprocating action of the glass cylindrical bar again. Vacuum evaporation was carried out again in the same conditions as before. Finally, the CF fabric was taken out of the vacuum oven, wrapped with the PP film and kept for 30 min. The prepregs obtained adequate tackiness for composite manufacturing.

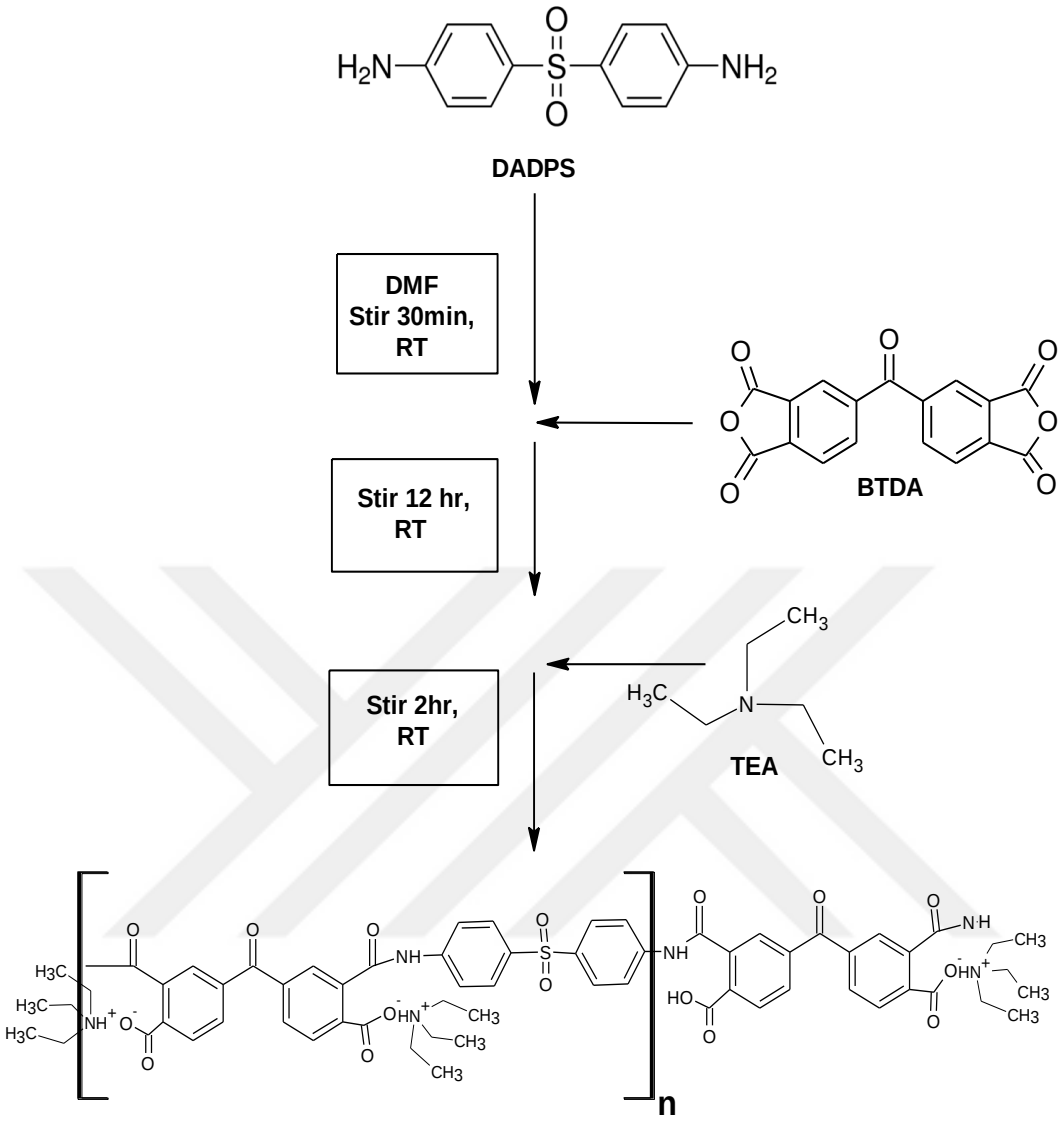


Figure 3.1.1. The synthesis scheme of the PAAS-T precursor resin

3.1.3.4. Composite manufacturing

Figure 3.5 presents the detailed process scheme of the composite manufacturing step. The manufacturing of the composites included two stages. The first stage included vacuum bagging on the vacuum infusion heating bench. The other one involved the compression molding process including high-temperature curing and high-pressure application.

3.1.3.4.1. Vacuum bagging process

Each prepreg laminate was separated from the PP release films and overlapped with each other on the Teflon surface of the vacuum infusion heating bench. Moreover, each prepreg was overlapped onto each other by applying hand force by a Teflon roller. All overlapped prepregs were placed between thin Teflon films in the vacuum infusion system. The prepregs were vacuum-bagged and heated with the vacuum infusion heating bench to minimize the solvent and consolidate the prepregs by partial imidization.

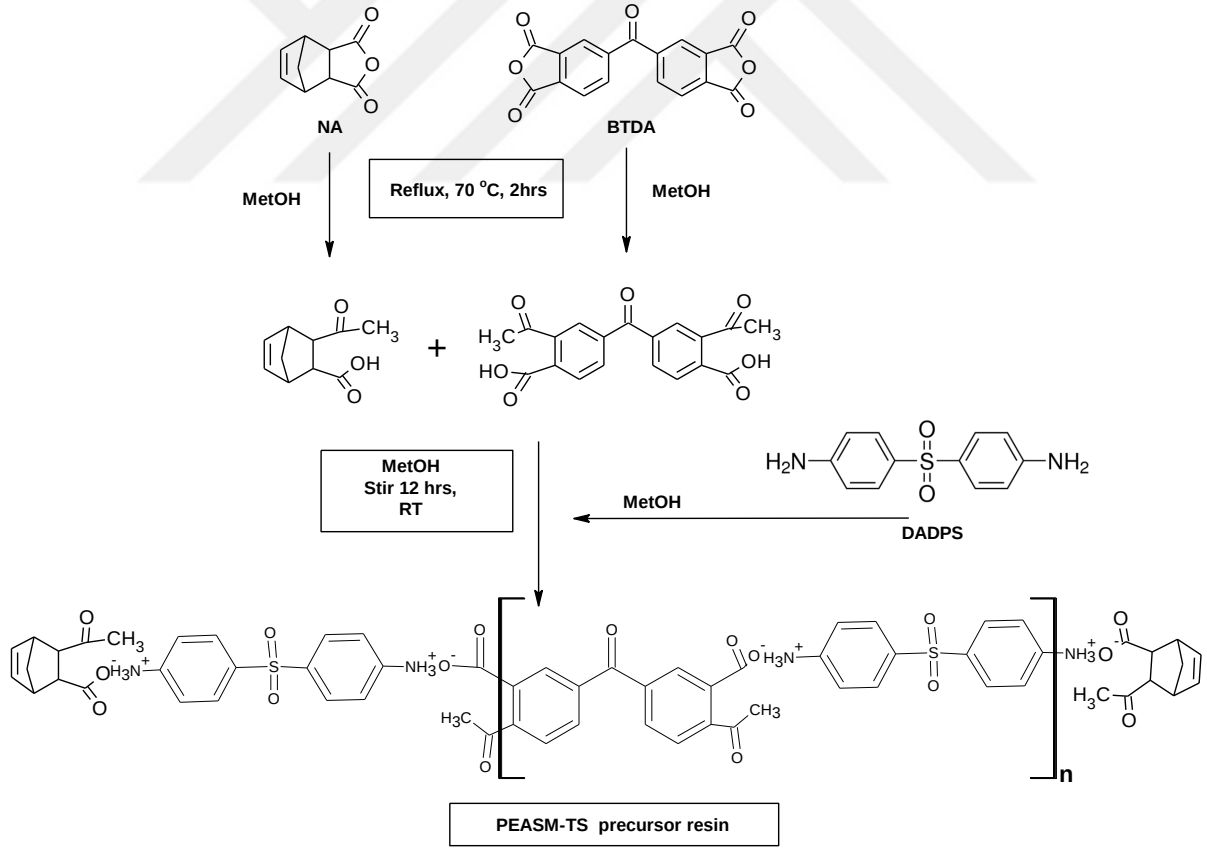


Figure 3.1.2. The synthesis scheme of the PEASM-TS precursor resin

A pressure load of 0.2 bar was also applied on the overlapped prepregs at higher temperatures during the vacuum-bagging process. Process parameters such as time and temperatures were determined according to the type of solvent based on the boiling

temperature.

3.1.3.4.2. Process parameters of vacuum-bagging process

The prepregs impregnated from the precursors containing the DMF solvent were firstly exposed to near-full vacuum and kept at 60 °C for 30 min. Then a pressure load of 0.2 bar was applied on the prepregs, followed by keeping them at 140 °C and 150 °C for 1 h. When the process was completed, the heater was turned off, and the prepregs were allowed to cool slowly for 2 h under near-full vacuum. The prepregs impregnated from the precursors containing the methanol solvent were firstly exposed to near-full vacuum and kept at 40 °C for 30 min. Then, a pressure load of 0.2 bar was applied on the prepregs, followed by keeping them at 120 °C for 2 h. When the process was completed, the heater was turned off, and the prepregs were allowed to cool slowly for 2 h under near-full vacuum.

3.1.3.4.3. Compression molding process

After the cooling period of the vacuum bagging process, the prepregs were removed from the vacuum bag on the vacuum infusion heating bench, and the Teflon films were easily taken from top and bottom of the consolidated prepregs. These intermediate products were put between steel plates covered with aluminum foil. These steel plates were placed on the lower mold half at 175 °C, and the upper mold half was closed with a pressure of 30 bar. When the molds were closed, the process temperature was immediately reduced to 160 °C. As soon as the temperature decreased to 160 °C, it was adjusted to 330 °C. The temperature was increased from 160 °C to 330 °C in 1h and kept at 330 °C for 30 min. After the process was completed, the heater of the compression molding setup was turned off, and the products were cooled under pressure. Finally, the composite laminates were post-cured at 330 °C for 4 h in an air-circulation furnace. The thermoset advanced composites were termed as PAA-TS, PAAS-TS, PEASD-TS and PEASM-TS as given in Table 3.1.

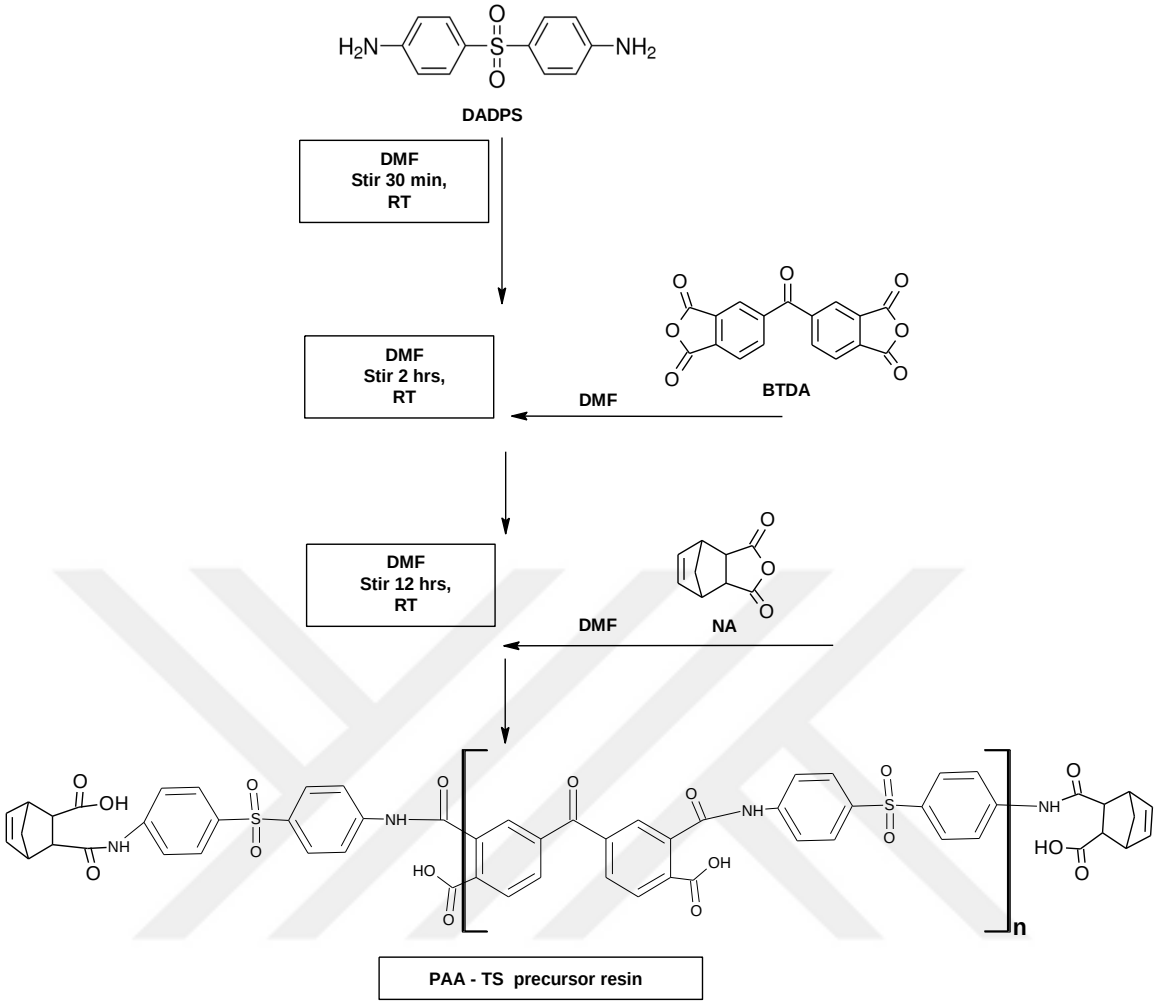


Figure 3.1.3. The synthesis scheme of the PAA-TS precursor resin

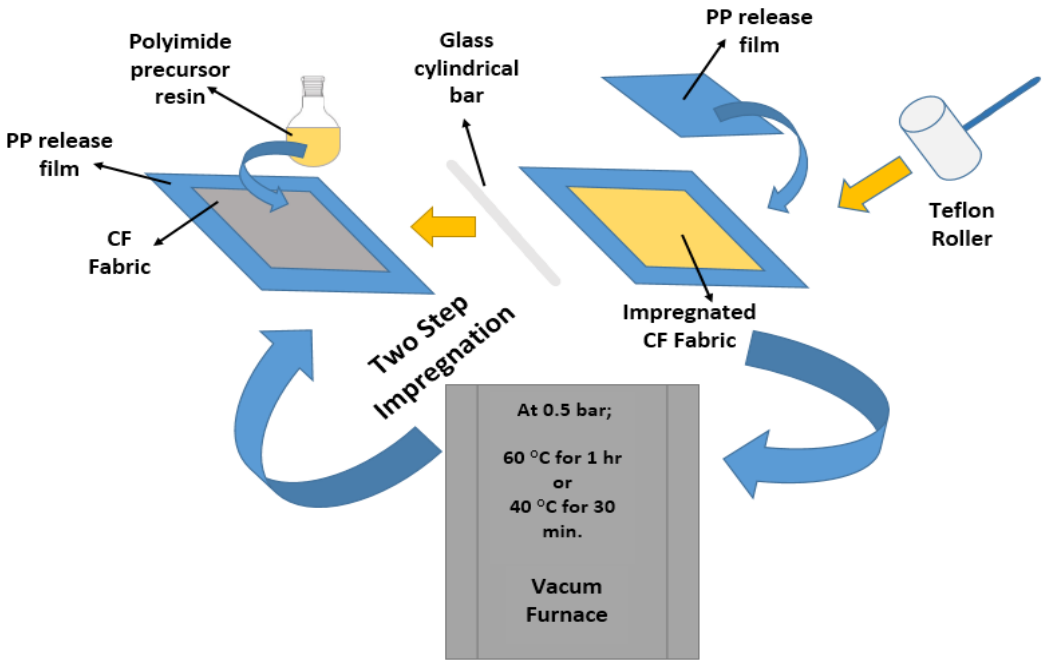


Figure 3.1.4. The preparation of the prepregs with two-step impregnation in the vacuum oven

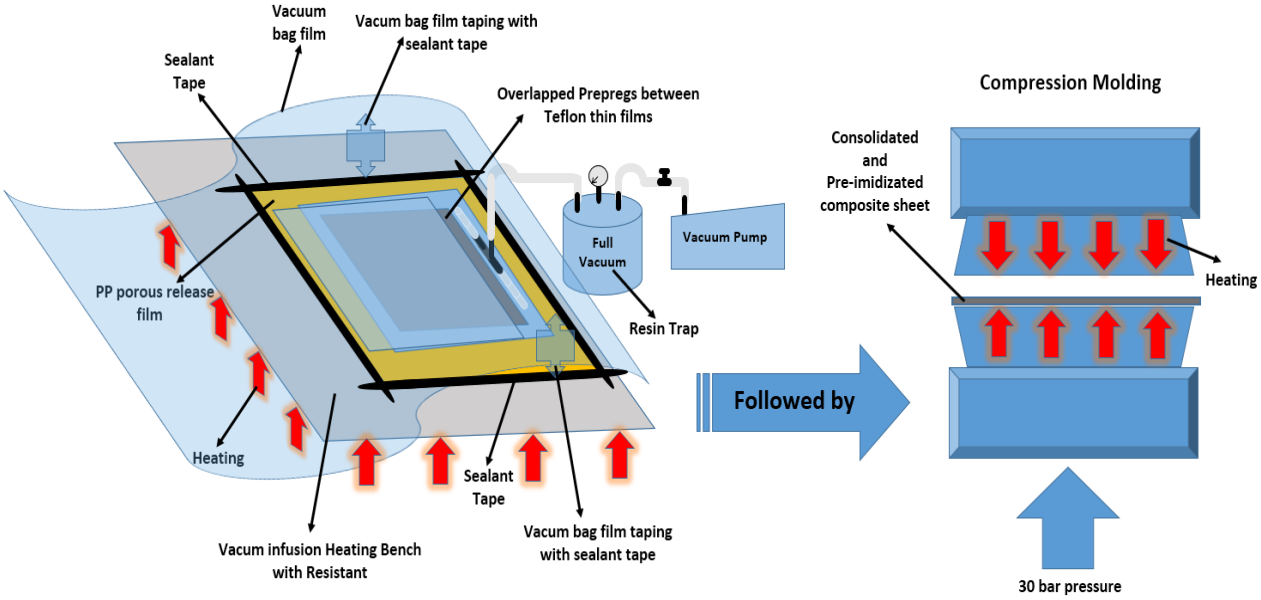


Figure 3.1.5. The detailed process scheme of composite manufacturing

3.1.3.5. Measurements

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the PIs were recorded using a Shimadzu 8303 FTIR Spectrometer. The PI matrices of the advanced composites were confirmed by their FTIR spectra. FTIR spectrum analysis was also performed for the PAAS and PAA precursor resins. The characteristic peaks of the PAAS and PAA precursor resins were confirmed based on their FTIR spectra. H-NMR spectra were also analyzed for PAAS at RT using a Unity Inovr 400 instrument with dimethyl sulfoxide (DMSO) as the solvent and tetramethyl silane (TMS) as a reference. The chemical structure of the PAAS was confirmed. TGAs of the PIs were performed using a TA Instruments Q50 model TGA device using the differential thermal analysis (DTA) method. The samples were run from 30 °C to 800 °C. This heating rate was 10°C / min in nitrogen atmosphere. The samples of TGA and FT-IR were prepared as free films according to the composite manufacturing process parameters. The PI matrices of the PAAS-T, PAA-TS and PAA-T were ground for powder X-ray diffraction (XRD) analysis. The powder X-ray diffraction (XRD) studies were carried out by using a Shimadzu-6100 XRD device with Cu-Kα radiation (λ = 1.5406 A) in the 2Θ/Θ mode at RT. The 2Θ scan data were collected at 0.01˚ intervals. The scanning speed was 2˚ (2Θ)/min. The apparent viscosity values of the PAA, PAAS and NA-terminated PAA precursor resins with a solution concentration of 50% wt. were measured with a Brookfield DV-II viscometer at RT. DMA is used to observe thermo-mechanical properties of a material in different frequencies. Heating rate was 5°C / min and it was applied starting from -150°C up to 400°C. The composite samples were run at a frequency of 1 Hz in the dual cantilever bending mode. The three-point flexure test, based on the ASTM D790 standard, was used to evaluate flexural strength, flexural modulus and flexural strain. The tensile test, according to the ASTM D3039 standard, was used to evaluate tensile strength, tensile modulus and tensile strain of the composites. The flexural and tensile tests were conducted using an Instron model 4505 device and the Series IX acquisition software. Charpy impact tests were performed by an Instron CEAST 9050 Charpy impact tester with a 5 J hammer. The advanced composite laminates with un-notched and rectangular shapes were prepared at dimensions of 15x45 mm according to the EN-ISO 179-1 standard. The CF fabric (2x2 Twill) of the advanced laminates was cut symmetrically in “0/45/0/45/45/0/45/0” in a

multidirectional manner. This test was performed for the most prominent products among the thermoset and thermoplastic advanced composites, PAAS-T and PAA-TS. In order to calculate the fiber content of the final products, the hydrazide method was used for 0.4-0.6 g of the advanced composite laminates that were treated with hydrazine hydrate at RT for 5 h. Next, the temperature was gradually raised to boil the solution for 10 min. After cooling down to room temperature, the fibrous residue was exposed to filtration process followed by washing with acetone. And then, it was exposed to evaporating in an oven until it reached a constant weight. If the fiber was brownish in color, these fibers would be treated again with hydrazine hydrate until the fiber had an almost normal black color. The fiber content of the composites was determined according to the ratio of the fibrous residue to the composite laminate. The composites contained 59-61 wt % CF. Scanning electron microscopy (SEM) analysis was performed using a JOEL JSM-5910 LV device to investigate the fracture surfaces of the composites after the flexural tests. The surfaces were coated with a gold layer by vacuum sputtering.

3.1.4. Results and discussion

The characterization for the PI matrice structures of all advanced composites were confirmed based on their FT-IR spectra. Figures 3.6 and 3.7 demonstrate the characteristics of the absorptions of the synthesized polyimides. The peaks of C=O symmetric stretching vibration at around 1785 cm^{-1} and C=O asymmetric stretching vibration at around 1718 cm^{-1} were observed. C–N stretching vibrations were observed at around 1356 cm^{-1}.

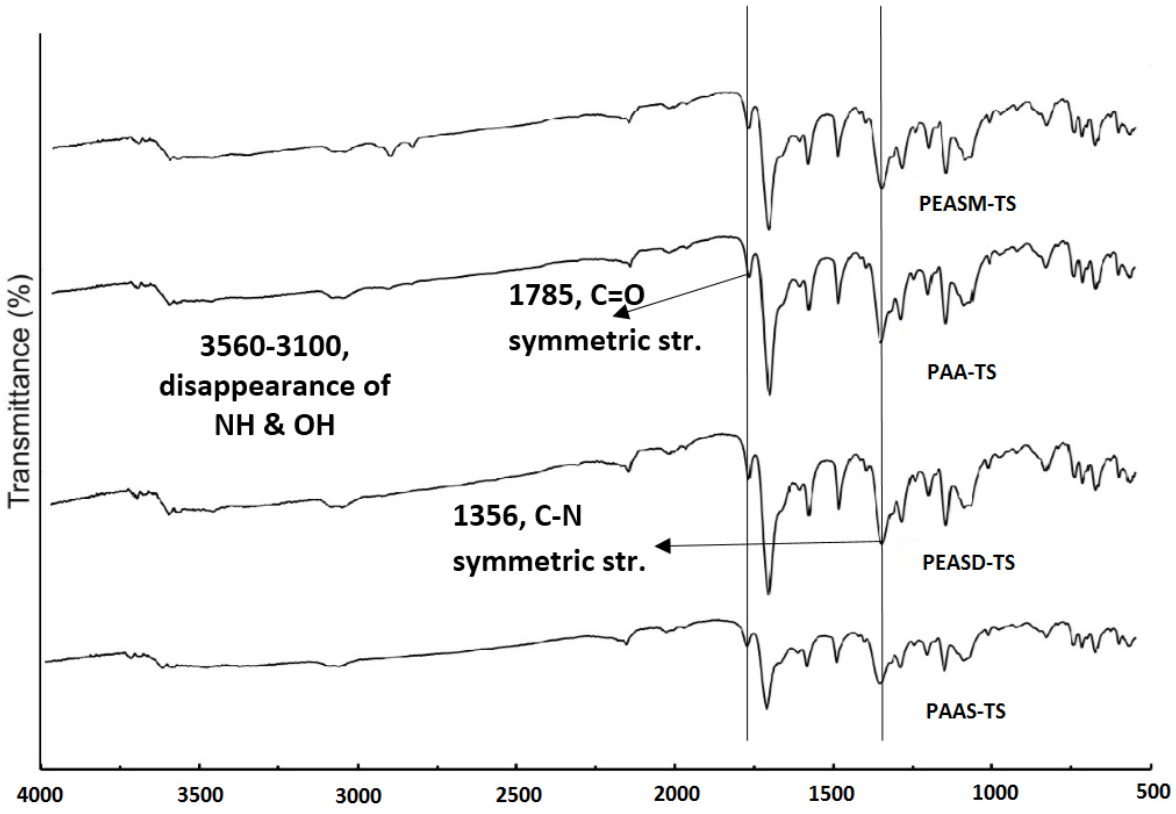


Figure 3.1.6. The FT-IR results of the thermosetting PI matrices

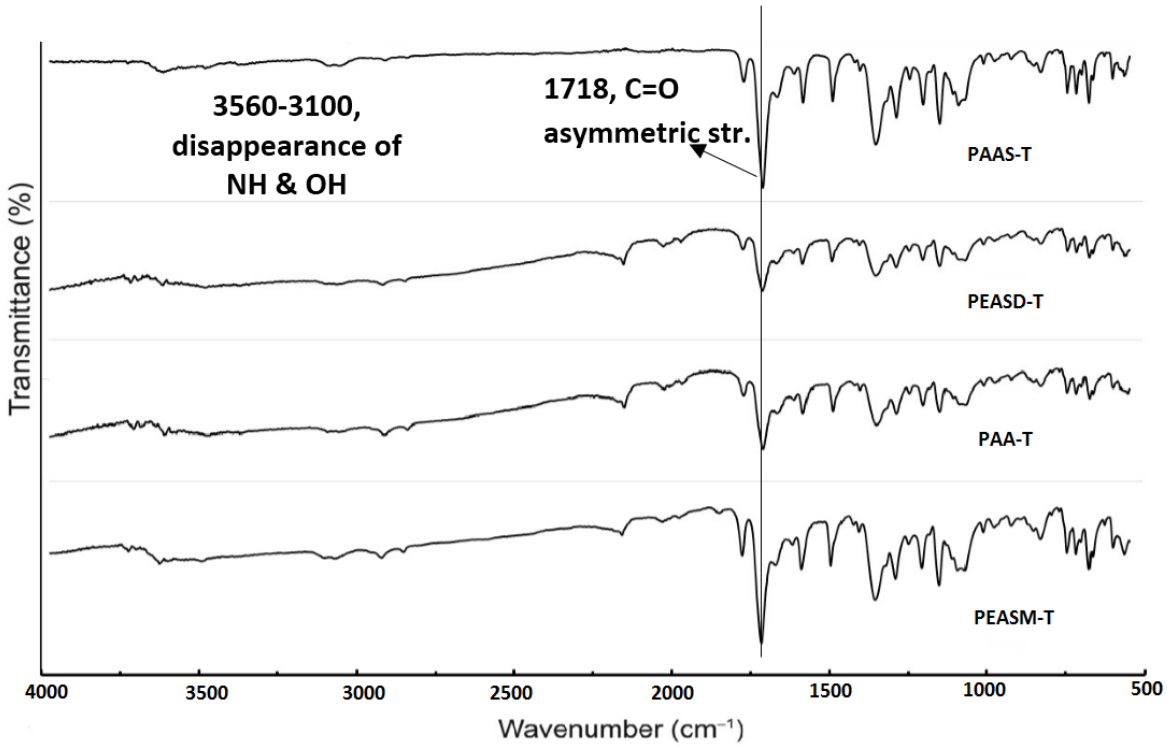


Figure 3.1.7. The FT-IR results of the thermoplastic PI matrices

Moreover, the characterization peaks of the PAA and PAAS precursor resins were prominent as shown in Figure 3.8. While -CO-N amide carbonyl stretching was at around 1660 cm^{-1}, -NH-&-OH- peaks were observed between 3560 cm^{-1} and 3100 cm^{-1}, as expected. The C=O acid stretching vibrations at around 1715 cm^{-1} disappeared for PAAS because of the blocking of COOH groups with the TEA monomers. The chemical structure of PAAS was explained in detail with the results of its ^{1}H NMR spectrum analyses. The ^{1}H NMR spectra of PAAS is shown in Figure 3.9., where it is compared to the results of PAA and TEA in the literature. The ^{1}H NMR spectra have presented the protons of $-CH_2$ and $-CH_3$ groups of TEA as 2.44 ppm and 0.95 ppm, respectively, in the literature. These peaks of the TEA in PAAS chemically shifted to 3.06 or 3.09 ppm and 1.21 ppm due to the shielding effect of the $–COO^{-}H^{+}$ protons in PAAS. A similar result was observed by Cai et al. [185]. Other protons ranging from 7 to 8 ppm were attributed to aromatic groups in the chemical structure of PAAS. Moreover, the comparison of the ^{1}H NMR spectra of PAAS to PAA in the literature revealed that the sharp peak of NH ranging from 10 to 11 ppm and the broad peak of COOH at around 13 ppm belonging to the chemical structure of PAA disappeared [185, 192].

CF fabric (T300)-reinforced thermoplastic and thermoset polyimide matrix composites were manufactured in this study. A bidirectional CF woven fabric (2x2 twill) was used as

the reinforcement material. While woven fabrics are generally bidirectional, unidirectional CF have one direction. For this reason, composites reinforced with unidirectional CF fiber have exhibited much higher (0°) strength and (0°) modulus than ones reinforced with woven fabrics. However, applications with complex design have always required woven fabric such as twill, plain and harness-satin CF patterns. Gao et al. [178] investigated the high-temperature mechanical properties of CF (MT300)-reinforced PMR polyimides. KH420 is a PE-(phenyl ethynyl) end-capped PMR precursor resin that is included in PDA (66 wt %)-ODA and MDA monomers. The authors prepared both unidirectional and "+45°/0°/90°/-45°/0°" multidirectional laminates in order to compare the properties of them to each other. While the 0° flexural strength of the unidirectional composite laminate was presented as 1428 MPa, the 0° and 90° flexural strength values of the multidirectional composite laminate were presented as 292 MPa and 209 MPa, respectively.

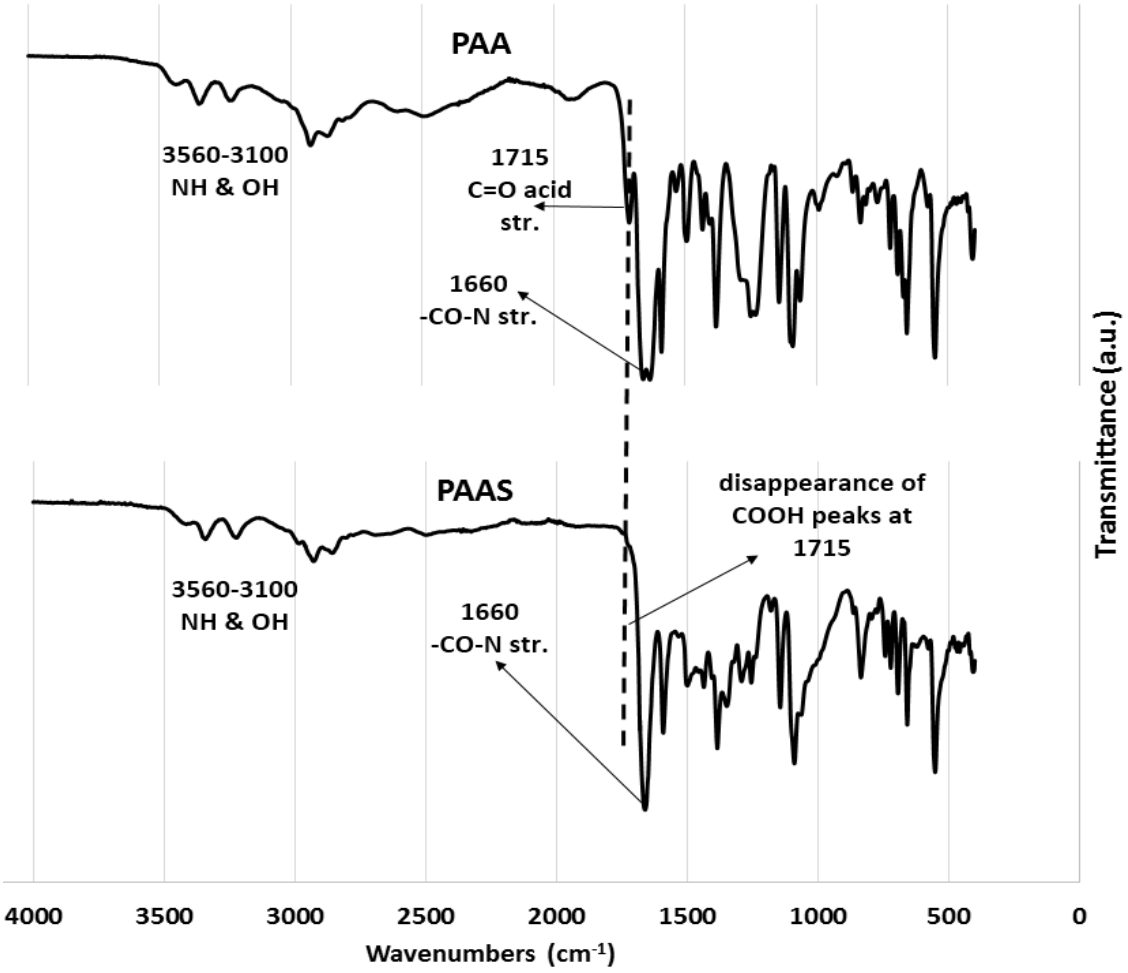


Figure 3.1.8. The FTIR spectra of the PAA and PAAS precursor resins

The advanced composites in this study were manufactured from CF fabric-reinforced

prepregs. In order to prepare these prepregs, three different PI precursor resins as PAA, PEAS and PAAS were used. While the PEAS precursors were prepared in both DMF and methanol solvents, the PAA and PAAS precursors were obtained using the DMF solvent. In the literature, there have been various composite manufacturing studies from PAA and PEAS precursors. However, PAAS precursors have not been used for fiber-reinforced composite applications. In this study, using PAAS precursor resins, CF-reinforced thermoplastic and thermoset PI matrix advanced composites (PAAS-T and PAAS-TS) were manufactured. Although both composites presented enhanced results, mechanical properties of the thermoplastic composite was interestingly superior to all composites in this study. PAAS-TS also presented lower levels of improvement in its properties than the other thermoset advanced composite obtained using the NA-terminated PAA precursor resin (PAA-TS). For this reason, this study also presents a comparison of CF-reinforced advanced PI composites prepared by various PI precursor resins to each other and those reported in other studies in the literature. The monomers that were used in the synthesis of the precursor resins in this study were similar to those used in the PMR-15 resin, except for DADPS. It is well-known that PMR-15 has been shown to have high processability, mechanical and thermal properties. CF fabric-reinforced PMR-15 composites have been synthesized from BTDA and MDA monomers. NA has been used as a terminating and crosslinking agent for PMR-15. The molar ratio of PMR-15 has been adjusted according to the stoichiometry of 2NE/(n + 1)MDA/n BTDE. PMR-15 resins have a molecular weight of 1500. This composite presents optimal mechanical and thermal properties with a molecular weight of 1500, as well as high processability. Nevertheless, MDA is a highly toxic monomer. In this study, DADPS was used instead of the MDA monomer due to the dangerous effects of MDA for human health and the objective of obtaining CF-reinforced polyimide matrix advanced composites with higher Tg values and thermo-mechanical properties. It is well-known that DADPS has been used for various applications due to its very high thermo-mechanical properties [169]. Nonetheless, it was thought that DADPS would reduce processability in comparison to composites with MDA monomers [176, 169]. Therefore, two-step impregnation was carried out during the prepreg preparation process. The prepreg preparation process included two-step impregnation and maturation under vacuum in a vacuum furnace. Maturation in the vacuum oven took a much shorter time than the conventional maturation process that includes keeping the material at RT for long durations such as 8 and 12 h or longer [168,180,189]. After the prepreg preparation

step, this study was completed by the vacuum-bagging process followed by compression molding. Finally, the composites were exposed to post-curing at 330 °C for 4 h in an air-circulation furnace.

The mechanical properties of all advanced composites were observed based on flexural and tensile tests as shown in Table 3.2. The stress-strain curves of these tests are also shown in Figures 3.10 and 3.11. The thermoset advanced composites generally exhibited superior mechanical properties to the thermoplastic advanced composites, except for PAAS-T. However, the mechanical properties of PAAS-T were interestingly the highest among all composites. This composite displayed highly enhanced values as a flexural strength of 940 MPa and a flexural modulus of 97 GPa. Among the thermoplastic composites, PAA-T exhibited the lowest results as a flexural strength of 153 MPa and a flexural modulus of 25 GPa. After PAAS-T, PEASM-T presented the highest flexural strength, and PEASD-T presented the highest flexural modulus. The flexural strength of PAAS-T was 161% higher than that of PEASM-T and 514% higher than that of PAA-T. Moreover, the flexural modulus of PAAS-T was 42% higher than that of PEASD-T and 280% higher than that of PAA-T. Among the thermoset composites, PEASD-TS gave the lowest results with a flexural strength of 440 MPa and a flexural modulus of 60.9 GPa. PAA-TS provided the highest flexural strength and modulus as 921 MPa and 73.3 GPa, respectively. In the comparison of PAAS-T to the other thermoset composites, the flexural strength of PAAS-T was 113% higher than that of PEASD-TS and 2% higher than that of PAA-TS. Moreover, the flexural modulus of PAAS-T was 32% higher than that of PEASD-TS and 59% higher than that of PAA-TS. On the other hand, the flexural strength of PAAS-T was 41% higher than that of PAAS-TS, and its modulus was 40% higher than that of PAAS-TS. As mentioned, PAAS-TS and PAAS-T were prepared using the same precursor resin (poly amic acid ammonium salt precursor), and these ammonium salts were obtained by blocking COOH groups on PAA ionically. However, PAAS-T was prepared using the thermoplastic composite precursor resin, and it was synthesized with the stoichiometry of an equal molar ratio as mentioned. Additionally, PAAS-TS was prepared using the thermoset composite precursor resin, and it was synthesized by using NA as the terminating agent and crosslinker. The molecular ratio of PAAS-TS was also adjusted according to the stoichiometry of 2NE/(n + 1)DADPS/nBTDE like the other thermoset composite precursor resins in this study. The value of “n” has been selected as 2.087. This value was used to synthesize the thermoset composite precursors in this study.

Thus, it was expected that the molecular weight of the thermoset composite PI precursors would be lower than the molecular weight of the thermoplastic composite PI precursors in this study [178, 180].

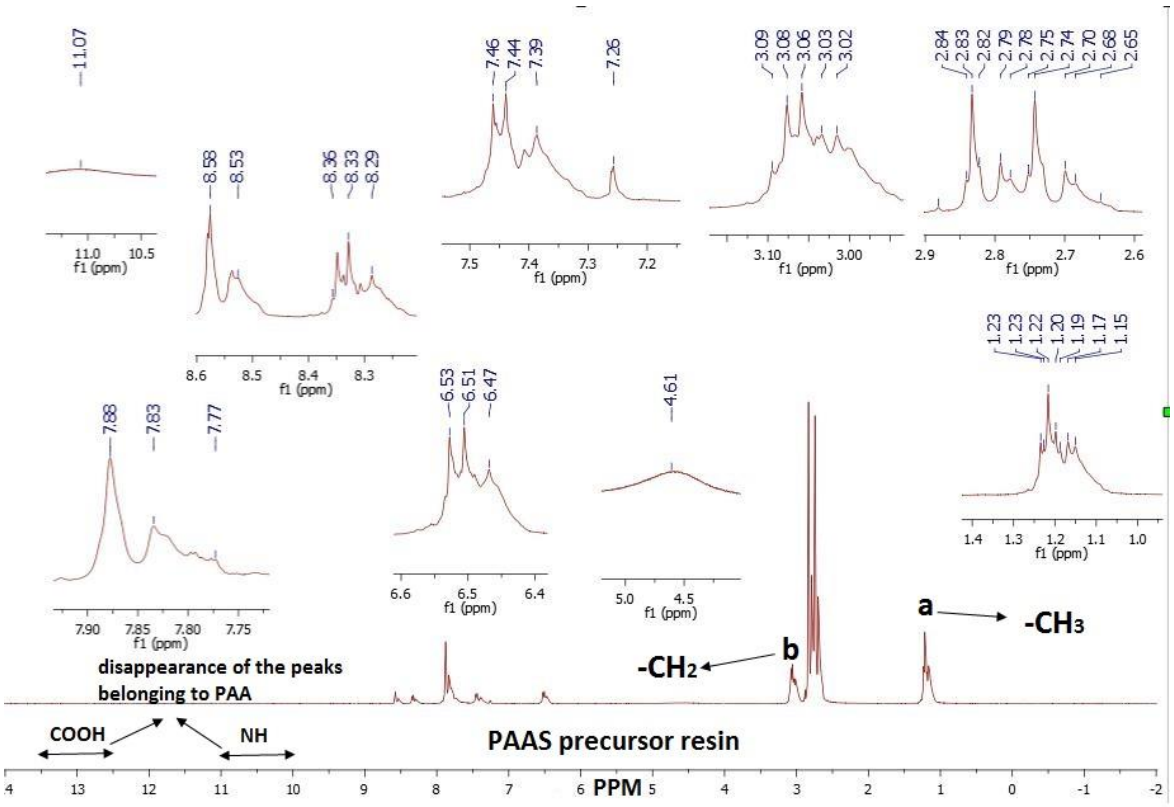


Figure 3.1.9. The ^{1}H NMR spectra of PAAS

In general, thermoplastic composite PI precursor resins are expected to have a higher molecular weight than thermoset composite PI precursors to obtain enhanced mechanical and thermal properties. Yuan et al. [192] synthesized both thermoplastic and thermoset PI films using 4-phenylethynyl phthalic anhydride (PEPA; reactive end capper) and phthalic anhydride (PA)-terminated PAA precursors. The properties of the PIs obtained from PA-terminated PAA precursor resins with higher molecular weights were comparable to those of the PEPA-terminated PAA precursor resins. In our study, while the advanced composites obtained using the PAAS and NA-terminated PAA precursors presented the highest properties, those obtained from the PAA precursor presented the lowest properties. For this reason, the apparent viscosities of the PAA, PAAS and NA-terminated PAA precursors were measured to discuss and compare the molecular weights of these precursors to each other and those reported in other studies in the literature. As expected, the apparent viscosity of the NA-terminated PAA precursor resin was lower than those of

the PAA and PAAS precursor resins. While the NA-terminated PAA precursor resin had an apparent viscosity of 4935 mPas, the PAA and PAAS precursor resins was apparent viscosity values of 5478 and 4938 mPas, respectively. These values are given in Table 3.3. Yuan et al. [192] observed apparent viscosities at varying solution concentrations and molecular weights of PAA precursors. They reported that an increase in solution concentrations and molecular weights resulted in increases in the apparent viscosities of the precursors. While PAA-PA-25 and PAA-PEPA-25 (calculated according to 2500 Mw) with a solution concentration of 30% wt. exhibited apparent viscosities of approximately 2500 mPas, PAA with a solution concentration of 20% wt. exhibited apparent viscosities of approximately 9000 mPas. According to these results, the viscosity of the PAA precursor in our study was lower than the expected value. This situation may be attributed to the synthesis of PAA at a solution concentration of 50%. Indeed, it is well-known that this concentration is kept high to obtain PAA with a high molecular weight. Moreover, the apparent viscosity of the PAAS precursor was a little lower than that of the PAA precursor. It was thought that blocking COOH groups with TEA could have provided higher chain mobility and reduced the apparent viscosity of PAA. It was an interesting finding that although PAA and PAAS had similar apparent viscosity values, PAAS-T presented much higher mechanical properties than PAA-T. As mentioned before, the solutions of PAAS constituted excellent fiber sizing media. Considering that two-step Impregnation was performed in this study, the first impregnation step might have posed a sizing effect for the CF fabric [178, 187]. As another issue, the apparent viscosity should be suitable for the wettability of a CF fabric. Cano et al. [182] presented high-quality CF-reinforced prepregs wetted by PEAS precursor resins which had solids contents of 65 wt % in NMP and apparent viscosity values ranging from 4955 to 9660 mPa.s. If we compare the NA-terminated PAA precursor resin in our study to the PEAS precursor resin in Cano et al.' study, the viscosity value of the NA-terminated PAA precursor resin was suitable for the production of high-quality prepregs and advanced composites. The SEM morphologies and mechanical properties of PAA-TS confirmed this situation.

Powder XRD analysis was performed for the PI matrices of the PAA-TS, PAAS-T and PAA-T materials. The XRD patterns of these PI matrices are shown in Figure 10. The related PI matrices displayed a similar pattern, indicating amorphous polymers. The broad peaks were centered near a 2Θ value of 17˚. However, the PI matrix of PAAS-T had a slightly sharper peak than the other PI matrix. This situation indicated a slightly more

packed nanostructure than the other PI matrices [193]. The angles of the peaks are also shown as angles A, B and C in Figure 3.1.10. According to these angles, the broadest peak belonged to PAA-TS due to its crosslinking structure. It is known that thermoplastic PIs with crystalline and linear imide chain structures could be synthesized by PAAS precursor resin.

Table 3.1.2. Mechanical properties of the advanced composites

Products	Flexural Strength (MPa)	Flexural Modulus (GPa)	Flexural Strain (%)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Tensile Strain (%)
PEASM-T	359	56.9	0.75	174	39	0.59
PAA-T	153	25.5	1.0	134	41	0.24
PEASD-T	285	68.1	0.51	178	47.5	0.39
PAAS-T	940	97	1.06	349	75.3	0.42
PEASM-TS	767	68	1.26	333	56.2	0.58
PAA-TS	921	73.3	1.34	272	72.3	0.36
PEASD-TS	440	60.9	0.8	228	71	0.30
PAAS-TS	663	69.1	1.0	264	71.9	0.34
PEASM-T	359	56.9	0.75	174	39	0.59

General Electric's ULTEM-type thermoplastic was synthesized by this method. In order to block COOH groups, they used base molecules that consisted of various ammonium salts [188, 130]. Therefore, PIs with a crystalline structure and linear chains could be obtained by this method of General Electric. However, high crystallinity peaks belonging to the PI matrix of PAAS-T were not observed in this study. This situation could be attributed to the curing regime at a high temperature (300 and 330 ˚C) and the synthesis of the PAA precursor resin. Facinelli et al. [188] synthesized PA end-capped PAAS, and melt imidization was performed at 250 °C and 300 °C for 30 min to obtain crystalline and

linear PIs. In this study, PAAS was synthesized stoichiometrically without an end capper. Hence, it was thought that PAAs with uncontrolled molecular weights were obtained in this study. This situation could prevent the degree of the crystallinity of PAAS [192]. At high curing temperatures above 300 ˚C, PAAs without end cappers could be crosslinked between polymer chains. This behavior also causes a more amorphous structure [188,192]. In another issue, the increase in the crystallinity for PAAS-T could increase interfacial area between fibers and matrix and contribute to improve the properties.

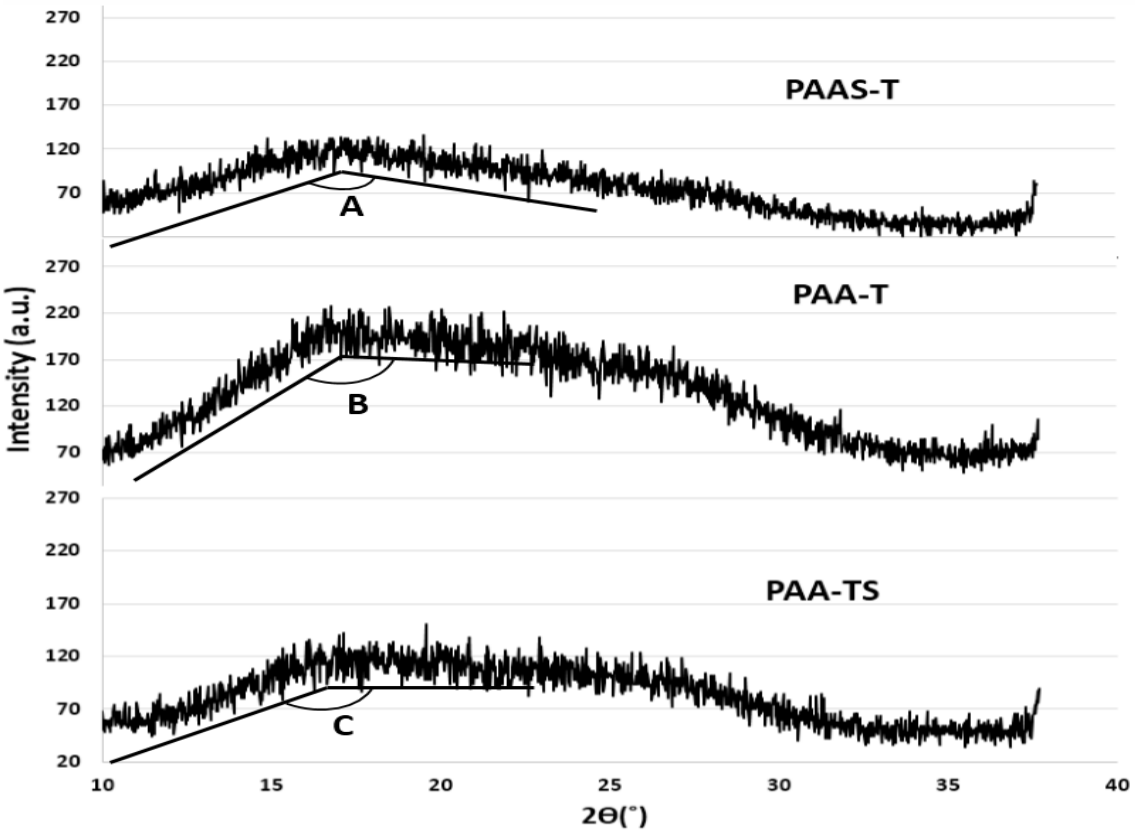


Figure 3.1.10. The X-ray diffraction analysis of the PI matrices of PAAS-T, PAA-T and PAA-TS

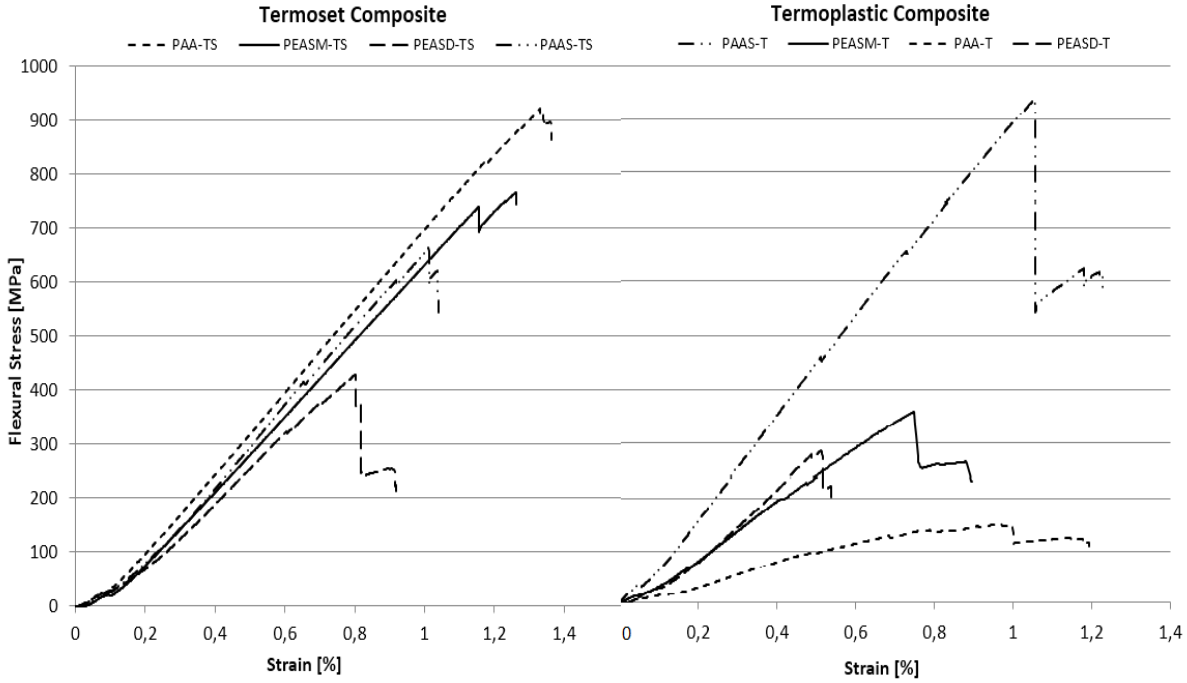


Figure 3.1.11. The average flexural stress-strain curves of the advanced composites

In the literature, tensile tests have been performed in a few studies for fiber-reinforced PI matrix composites.

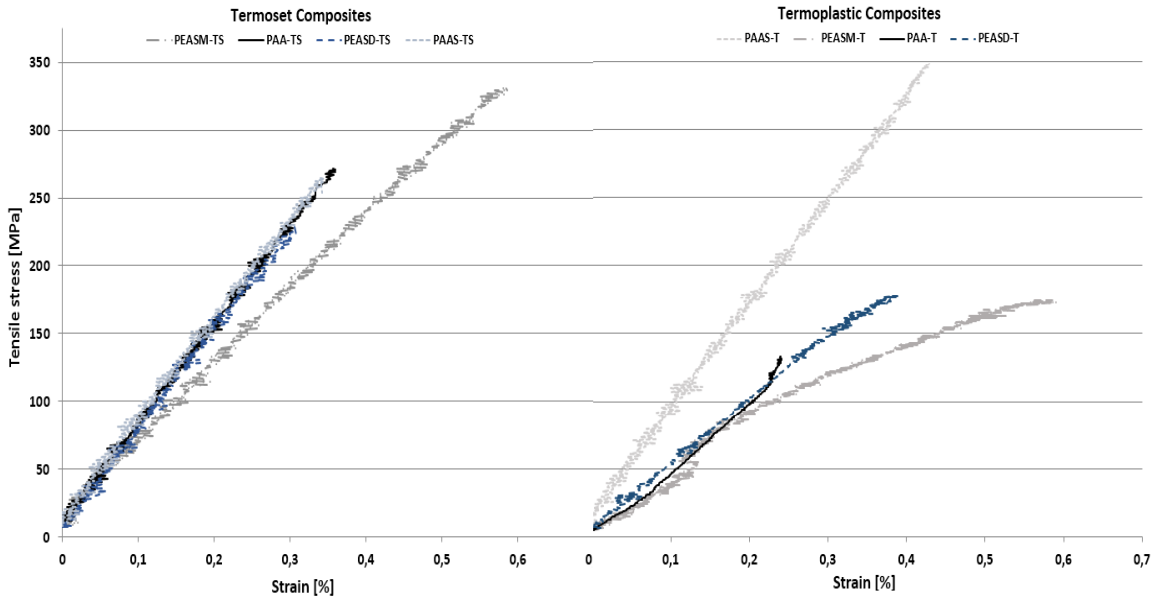


Figure 3.1.12. The average tensile stress-strain curves of the advanced composites

This study also presented the tensile test and flexural test results of the thermoplastic and thermoset advanced composites. In the analyses, it was observed that the results had a similar trend with the flexural results. The tensile results of the thermoset composites exhibited higher values than those of the thermoplastic composites, except for the PAAS-T composite. PAAS-T exhibited the highest tensile strength and modulus among all

composites in this study. This composite showed improved values. While the tensile strength was 349 MPa, the tensile modulus was 75 GPa.

Table 3.1.3. Apparent viscosities of some PI precursor resins

Precursor Type	Prominent Product	Apparent Viscosity (mPa.s)
PEASM-T	PAAS-T	4938
PAA-T	PAA-T	5478
PEASD-T	PAA-TS	4935

Similar to the flexural test results, PAAS-T, PAA-TS and PEASM-TS presented the highest tensile results among all composites in this study. On the other hand, PAA-T exhibited the lowest tensile strength of 134 MPa and one of the lowest tensile moduli as 41 GPa with PEASM-T.

Fiber-reinforced polymer matrix thermoset advanced composites generally have superior mechanical and thermal properties than fiber-reinforced polymer matrix thermoplastic advanced composites. However, thermoplastic composites present higher toughness than thermoset composites. For this reason, many studies have been conducted recently about fiber-reinforced polymer matrix thermoplastic advanced composites, especially polymers with high temperature resistance such as polyimides, poly ether ether ketones, and bismaleimides. Therefore, the impact resistance values of the thermoset and thermoplastic advanced composite products with the highest mechanical properties (PAA-TS and PAAS-T) were observed and compared to each other. Both products showed enhanced impact resistance, while thermoplastic one (PAAS-T) presented a higher impact resistance, as expected. While the impact resistance of the PAAS-T composite was 46.6 Kj/m^2, that of the PAA-TS composite was 39 Kj/m^2. These values were given in Table 3.4. This result was also validated with the peak value of Tan δ in DMA. The height of the Tan δ peak in DMA presents the energy absorbance of the product. It is termed as the damping coefficient (DCT). While the DCT of PAAS-T was 0.2, that of PAA-TS was 0.03.

Table 3.1.4. Charpy impact resistance values of PAA-TS and PAAS-T

Product	Charpy Impact Resistance (Kj/m^2)
PAAS-T	46.6
PAA-TS	39

PIs have been reported to exhibit high thermal resistance due to their heterocyclic and rigid structure. TGA is one of the important analyses in the assessment of the thermal stability of PIs. PI films were prepared to carry out TGA in this study. These films were synthesized and cured under the same conditions and process parameters as the advanced composites. The initial decomposition temperature, 10% weight decomposition temperature (T_{d10}) and char yield at 800 °C were observed by TGA as shown in Figure 3.14. All composites presented high thermal stability. The initial decomposition temperatures (IDT) of PAAS-T, PEASM-T, PAA-T and PAA-TS were higher than 500 °C. In general, the IDT values of the thermoplastic PIs were higher than those of the thermoset PIs, except for PAA-TS. PAA-TS presented the highest IDT value as 512 °C. The T_{d10} values of the thermoplastic PIs were also slightly higher than those of the thermoset PIs, except for PAA-TS. PAA-TS presented one of the highest T_{d10} values as 520 °C. The T_{d10} values of five PIs, PAA-T, PEASD-T, PAAS-T, PAA-TS and PEASD-TS, were higher than 500 °C. Unlike the IDT and T_{d10} values, the char yields of the thermoset PIs were generally higher than those of the thermoplastic PIs. On the other hand, PAA-TS also had a different trend, and it showed a slightly lower char yield value than that of PAA-T. The char yield values of all PIs except for PAA-TS were higher than 50%. The highest char yield value was 63% in PEASD-TS, and the lowest char yield value was 48% in PAA-TS. Still, a char yield of 48% can be considered an improved value. In the analyses of the thermal stability of all PIs, it was thought that the DADPS monomer could have contributed positively.

PIs are known to have high performance properties at high temperatures and in cryogenic conditions.

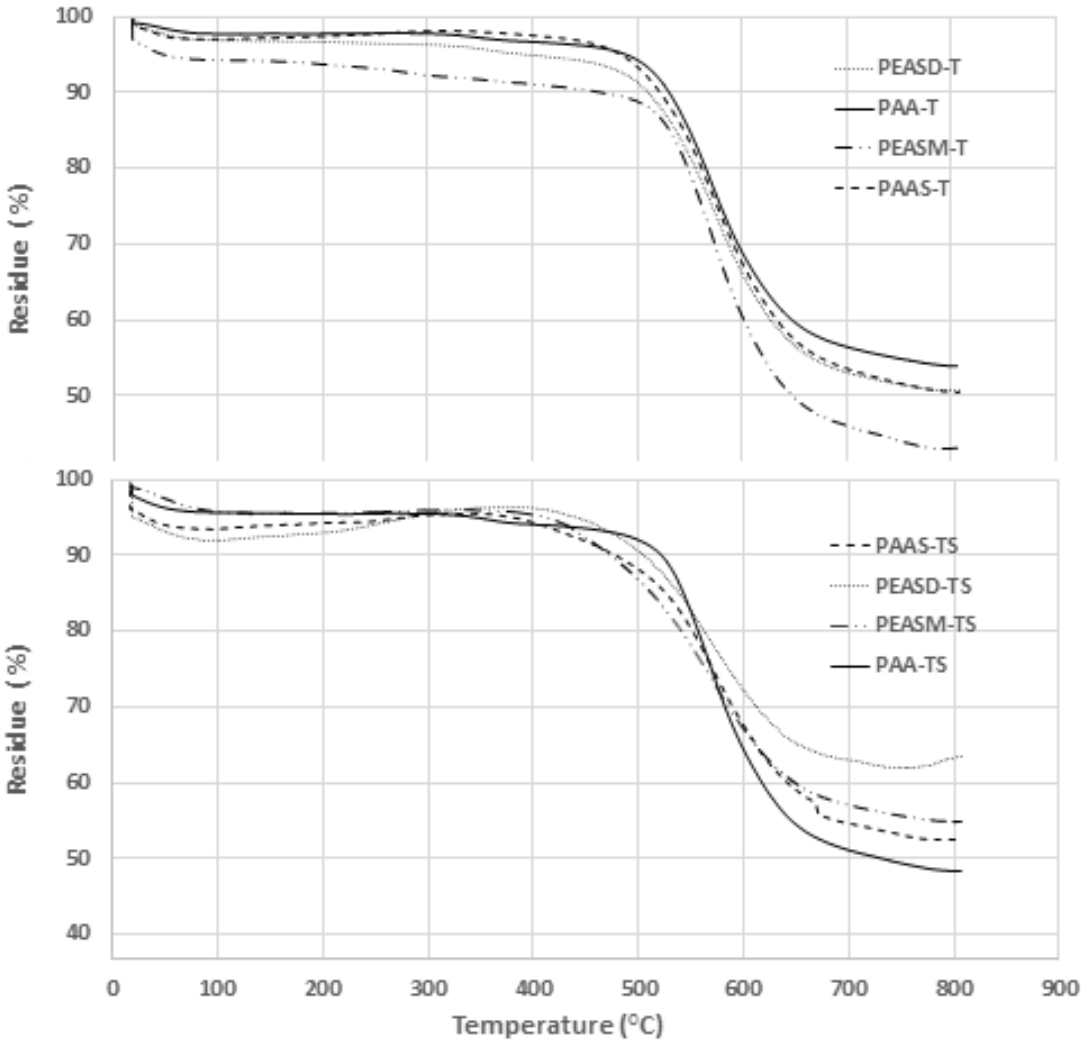


Figure 3.1.13. The TGA results of advanced composites

The composites in our study were exposed to dynamic loads at different frequencies and temperatures. Because of these reasons, the PI composites were characterized by DMA to determine their thermal and mechanical stability values at 1 Hz frequency from -150 °C to 400 °C. The storage modulus (E′), Tan δ curves and values were observed. The onset temperatures of the E′ curves for the advanced thermoset composites were higher than those of the advanced thermoplastic composites. The storage moduli curves of the thermoset composites did not show a considerably sharp decrease. The damping coefficients of Tan δ (DCT) also confirmed this situation. This was because the DCT values for the thermoset composites were as low as 0.03 and 0.04, as shown in Table 3.5. The curves of the E′ and DCT values are presented in Figures 3.14 and 3.15. Damping property can be interpreted with the height of Tan δ peak. The viscoelasticity of the PIs was analyzed by running loss tangent measurements by DMA. Tan δ value can be found by the division of E″ to E′ value. When Tan δ is bigger than 1, materials exhibit behavior like viscoelastic liquid. In addition to this, when Tan δ is lower than 1, they can exhibit behavior like viscoelastic solids [170].

In our study, while the DCT values of the thermoplastic composites varied from 0.09 to 0.20, those of the thermoset composites varied from 0.03 to 0.04. In the comparison of the E′ values at the onset temperatures of the advanced composites to the E′ values at 400 °C, the decreases in the advanced composites can be observed in Figure 3.11. While the decrease in the E′ value of the thermoplastic advanced composites from the onset temperatures to 400 °C varied from 52% to 70%, the decrease in the thermoset advanced composites varied from 0.26% to 0.5%. These results demonstrated the usage possibility of thermoset advanced composites at 400 °C. Moreover, while the decrease of E′ value for the thermoplastic advanced composites from RT to their onset temperatures varied from 5.2% to 14.6%, the decrease in the thermoset advanced composites varied from 4.2% to 11.1%. The elasticity modulus of materials generally increases when their temperature decreased. Thus, materials show brittleness in cryogenic conditions. In order to minimize these adverse conditions for materials, obtaining a small increase or achieving the stability of this modulus for mediums with very low temperatures is important. Considering the E′ values of the advanced composites from RT to -150 °C, all advanced composites exhibited little increase and presented stable behavior, except for PEASD-TS. Accordingly, the E′ value of PEASD-TS showed a slight increase of 10.1%. The increase in the E′ value of the other advanced composites varied from 1.2% to 4.3%. The E′ values of all advanced

composites at different temperatures and DCT values are given in Table 3.5.

While the onset temperatures of E′ exhibited substantial distinct decreases for the thermoplastic advanced composites, the onset temperatures of the thermoset advanced composites had small reductions which were not distinct. The onset temperatures for the thermoplastic composites varied from 272 °C to 304 °C, and the onset temperatures for the thermoset advanced composites ranged from 330 °C to 359 °C. Additionally, the glass transition temperature (Tg) was determined according to the peak on the Tan δ curve. While Tg values of the thermoplastic advanced composites varied from 324 °C to 370°C, and those of the thermoset advanced composites ranged from 352 °C to 412 °C. As shown in Figures 3.14 and 3.15., the advanced composites showed enhanced properties in terms of the onset temperatures of their storage moduli and their Tg values. These values are given in Table 3.6.

In comparison to the results of other studies in the literature, the PAA-TS and PAAS-T presented much more enhanced mechanical and thermal properties.

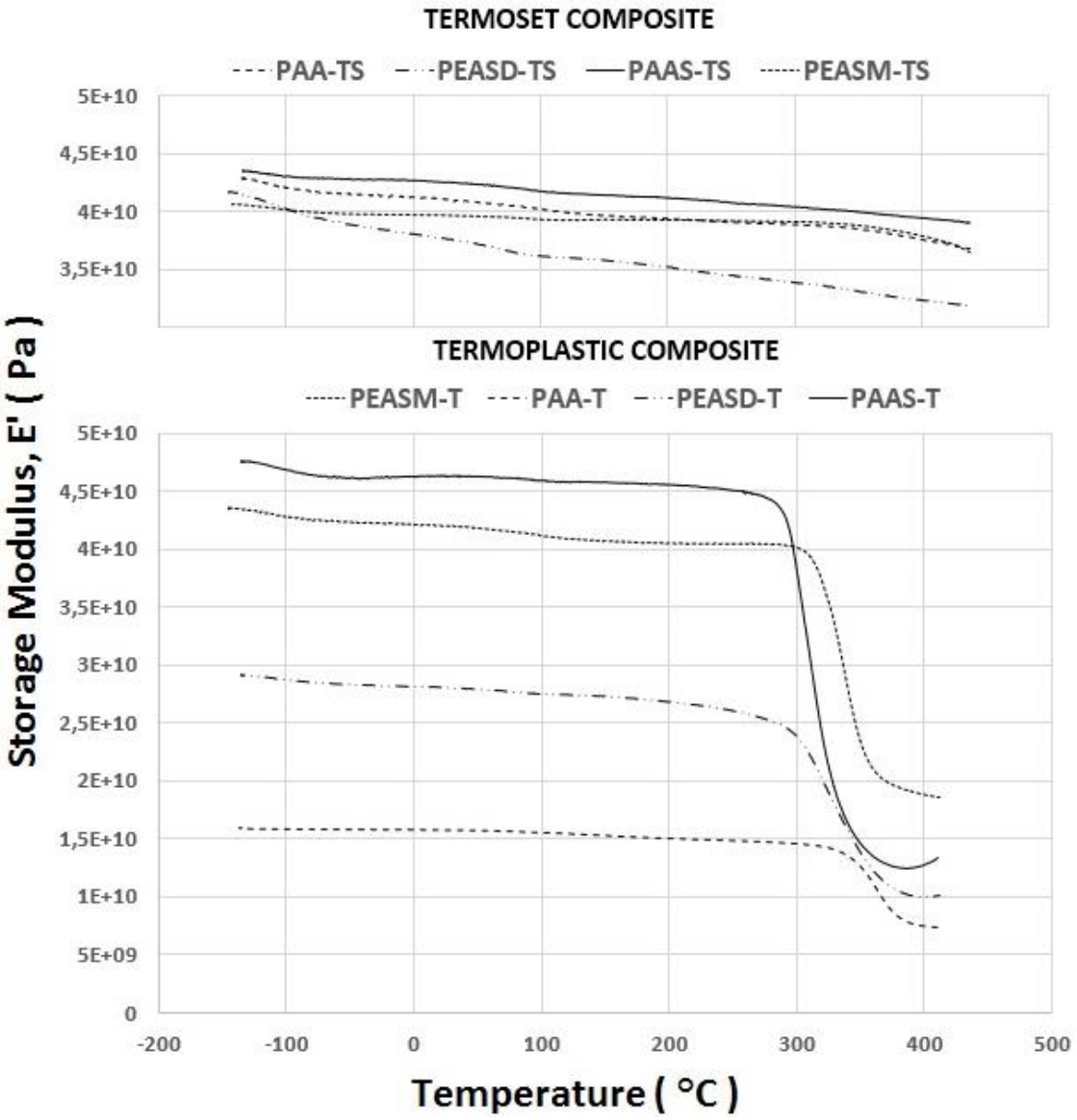


Figure 3.1.14. The storage modulus curves of the advanced composites

Table 3.1.5. DMA results of the advanced composites

Products	Storage Modulus at – 150 °C (Pa)	Storage Modulus at RT (Pa)	Storage Modulus at Onset Temperature (Pa)	Storage Modulus at 400 °C (Pa)	Damping Coefficient (Tan δ)
PEASM-T	4.35 E^{10}	4.19 E^{10}	3.97 E^{10}	1.88 E^{10}	0.11
PAA-T	1.59 E^{10}	1.57 E^{10}	1.34 E^{10}	0.74 E^{10}	0.09
PEASD-T	2.92 E^{10}	2.80 E^{10}	2.53 E^{10}	0.99 E^{10}	0.12
PAAS-T	4.75 E^{10}	4.62 E^{10}	4.33 E^{10}	1.27 E^{10}	0.20
PEASM-TS	4.05 E^{10}	3.97 E^{10}	3.80 E^{10}	3.79 E^{10}	0.04
PAA-TS	4.28 E^{10}	4.10 E^{10}	3.80 E^{10}	3.79 E^{10}	0.03
PEASD-TS	4.14 E^{10}	3.76 E^{10}	3.34 E^{10}	3.22 E^{10}	0.03
PAAS-TS	4.35 E^{10}	4.25 E^{10}	3.96 E^{10}	3.94 E^{10}	0.03

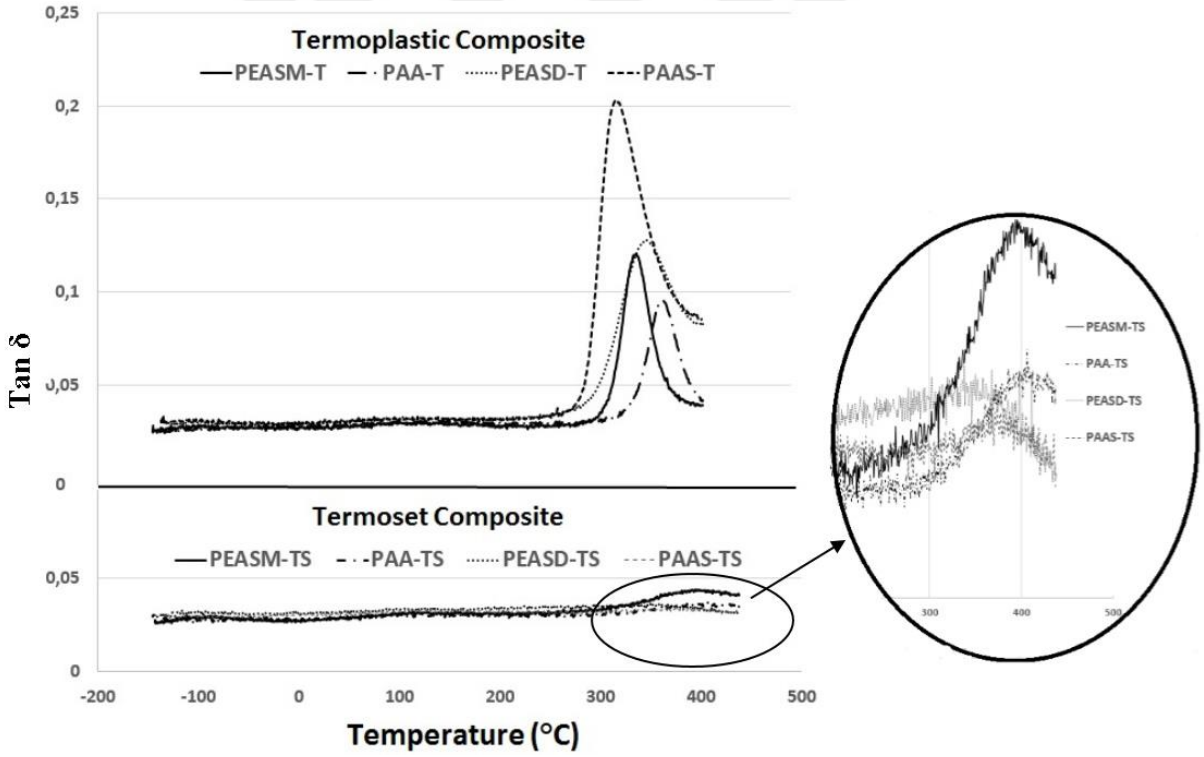


Figure 3.1.15. The Tan δ curves of the advanced composites

Table 3.1.6. DMA and TGA results of the advanced composites

Products	DMA		TGA		
	The Onset Temperature of Storage Modulus (°C)	Tan δ Tg (°C)	Initial Decomposition Temperature (%)	10% Weight Decomposition Temperature (T_{d10}, °C)	Char Yield at 800 °C (%)
PEASM-T	304	345	510	465	43
PAA-T	318	370	510	530	53
PEASD-T	272	354	495	504	50
PAAS-T	288	324	500	522	50
PEASM-TS	352	394 (very small)	446	473	55
PAA-TS	359	412 (very small)	512	520	48
PEASD-TS	325	352 (very small)	455	503	63
PAAS-TS	330	380 (very small)	468	474	52

While the mechanical properties of the PAA-TS and PAAS-T in our study and those in some prominent studies in the literature are given in Table 3.7., the thermal properties of these are given in Table 8. In the literature, CF-reinforced PI matrix thermoset advanced composites have shown much more enhanced thermal and mechanical properties than CF-reinforced PI matrix thermoplastic advanced composites. However, PAAS-T exhibited superior mechanical properties than even thermoset advanced composites in the literature, in addition to thermoplastic advanced composites. Moreover, the thermal properties of PAAS-T got close to those of thermoset advanced composites in the literature. The mechanical properties of PMR-15 invented by Serafini et al. [167] were reported by Miller et al. [194], as presented in Table 3.7. Miller et al. [194] improved the flexural modulus of PMR-15 composites by filling them with expanded graphite. While PAAS-T and PAA-TS showed slightly lower flexural strengths, their flexural moduli were much superior to the results of Miller and Serafini et al. Su et al. [180] prepared CF fabric-reinforced thermoplastic advanced composites with grown carbon nanotubes to improve the interphase of the fiber and matrix. Although they stated improved results, these results were far below the results of PAAS-T in our study. In addition, tensile properties are another important mechanical property, but there have been few studies including the

tensile results of CF-reinforced PI matrix thermoplastic and thermoset composites in the literature.

Parasad [195] manufactured and improved CF fabric (IM7)-reinforced RP46 (a commercial thermosetting PI matrix) matrix thermoset advanced composites with the vacuum assisted resin transfer method (VARTM). RP46 was improved with a PMR polyimide resin system. This new advanced composite represented a tensile strength and modulus with 314 MPa and 62 GPa, respectively. In comparison to the advanced composite they reported, PAAS-T in this study was substantially more prominent in terms of tensile strength and tensile modulus. However, while PAA-TS provided a higher tensile modulus value than that of the composite reported by Parasad, the tensile strength of PAA-TS was slightly lower. On the otherhand, the thermal properties of PAA-TS were much superior to that of the composite reported by Parasad.

If we focus on the thermal properties of CF-reinforced PI matrix advanced thermoset and thermoplastic composites in the literature, CF-reinforced PI matrix advanced thermoset composites have shown more enhanced thermal properties than CF-reinforced PI matrix advanced thermoplastic composites, as expected. This situation can also be observed in Table 3.8. While the Tan δ Tg values of the thermoplastic advanced composites varied from 215 ˚C to 280 ˚C, those of the thermoset advanced composites varied from 355 ˚C to 425 ˚C. Although PAAS-T was a thermoplastic advanced composite, it showed high Tan δ Tg and E' onset temperature values, which were close to those of the thermoset advanced composites. Moreover, PAA-TS presented higher Tan δ Tg and E' onset temperature values than most composites reported in studies in the literature. Chuang et al. [168] improved PMR-15 in terms of thermal properties and presented a new high-Tg PMR-type thermoset advanced composite (DMBZ-15) by using 2,2'-dimethylbenzidine (DMBZ) instead of methylenedianiline (MDA). Although the Tan δ Tg of DMBZ-15 was slightly higher than that of PAA-TS, PAA-TS had a much lower DCT value than DMBZ-15. Thus, PAA-TS showed a very low rate of decrease in the E′ value above the E′ onset temperature. The DCT value also presents the energy absorbance of composites. Accordingly, thermoplastic advanced composites show higher DCT values than thermoset advanced composites. This situation can be observed in Table 8. In our study, the DCT value of PAAS-T was much higher than that of PAA-TS, and the charpy impact resistance value of PAAS-T was more enhanced than that of PAA-TS.

Table 3.1.7. Comparison of the mechanical properties of the advanced composites to the properties of other materials reported in previous studies in the literature

Products	Reference	Product Detail	Flexural Strength (MPa)	Flexural Modulus (GPa)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Advanced Thermoplastic Composite	Lu et al. [7]	CF fabric-reinforced PI matrix composite (CFRP)	500-536	-	-	-
Advanced Thermoplastic Composite	Su et al. [8]	CFRP with carbon nanotubes	450-560	45-64	-	-
Advanced Thermoset Composite	Prasad [29]	CF fabric (IM7)/RP46 (improved PMR polyimide resin) with VARTM	-	-	314	62
Advanced Thermoset Composite	Miller et al. [28]	CFRP with expanded graphite (PMR-15)	875	62	-	-
Advanced Thermoset Composite	Miller et al. [28]	CFRP (PMR-15)	985	53	-	-
Thermoplastic Advanced Composite	This study (PAAS-T)	CFRP by using PAAS precursor resin	940	97	349	75.3
Thermoset Advanced Composite	This study (PAA-TS)	CFRP by using NA-terminated PAA precursor resin	921	73.3	272	72.3

In addition to these results, Qu et al. [196] Su et al. [180] and Xiao et al. [197] conducted studies to obtain PI matrices with high Tg and excellent thermal stability values. Their results provided less improvement compared to the PI matrices obtained from the PI precursors in this study. Table 3.8 presents the TGA values of the PI matrices obtained from the PI precursor resins that were synthesized in this study using the same manufacturing process parameters as those used for the advanced composites. It is known that the PI matrices of fiber-reinforced composites have different properties than pure PIs due to the complex formations at the interphases of fibers and matrices. Nevertheless, these values of pure PI matrices are comparable between each other. The thermal stability of the PI matrix obtained from the PAAS precursor was enhanced, and it was comparable to the PI matrix obtained from the PAA precursor. On the other hand, although PAA-T exhibited very low mechanical properties, its thermal stability improved according to DMA. It was suggested that the PAAS precursor has a very high process capability to manufacture CF-reinforced PI matrix advanced composites. Gu et al. [198] developed a novel PI/clay hybrid nanocomposite using a PAAS precursor resin. They emphasized that the PAAS precursor was impregnated into the silicate layers of clays with a high rate of homogeneity, and this clay was completely dispersed into the PAAS matrix. XRD did not exhibit any peak belonging to clay. They also emphasized that PAA is intertwined with solvents, and these solvents cannot be easily removed from PAA at the curing temperature of PAA. However, this situation was not observed for the PAAS matrix solu

Table 3.1.8. Comparison of the thermal properties of the advanced composites to the properties of other materials reported in previous studies

Products	Reference	Product Detail	T_g[a] (°C)	E′ (°C)	DCT	T_d (°C)	T_5 (°C)	Char Yield (%)
Advanced Thermoplastic Composite	Lu et al. [7]	CF fabric-reinforced PI matrix composite (CFRP)	248-280	-	-	-	-	-
Advanced Thermoplastic Composite	Su et al. [8]	CFRP with in situ grown carbon nanotubes	215-245	210-235	-	475-490	502-519	-
Advanced Thermoplastic Composite	Livengood et al. [9]	Thermoplastic fiber-reinforced PI composites	250	210-220	-	-	-	-
Advanced Thermoset Composite	Serafini et al. [11] (NASA)	CFRP (PMR-15) [11,12]	375	345	-	-	-	-
Advanced Thermoset Composite	Chuang et al. [12] (NASA)	CFRP (DMBZ-15) High Tg PMR type Composite	425	409	0.1			
Advanced Thermoset Composite	Ogasawara et al. [13]	PETI-terminated imide oligomer	362	-	-	-	-	-
Advanced Thermoset Composite	Prasad [29]	CF fabric (IM7)/RP46 with VARTM	355-368	275-305	0.9-0.12	-	-	-
Advanced Thermoset Composite	Qu et al. [30]	Thermoset polyimide matrix with high Tg for CFRP	-	-	-	-	467-470	-
Advanced Thermoset Composite	Chen et al. [23]	CFRP (PMR type composites)	390	361	0.18	-	-	-
Advanced Thermoset Composite	Xiao et al. [31]	Thermoset PIs with excellent thermal and thermo-oxidative stability	-	-	-	455-467	487-494	-
Advanced Thermoset Composite	This Study (PAA-TS)	CFRP by using NA-terminated PAA precursor resin	413	359	0.03	512	520	48
Advanced Thermoplastic Composite	This Study (PAAS-T)	CFRP by prepared PAAS precursor resin	324	288	0.2	500	522	50

T_g[a]; glass transition temperature by DMA, **E′**; onset temperature of the storage modulus, **T_d**; initial decomposition temperature of the PI matrix by TGA, **T_5**; 5% weight decomposition temperature of the PI matrix by TGA

The cross-sections of the advanced composite laminates in the thickness direction were subjected to scanning electron microscopy (SEM) observations after the flexural test. The SEM images of the fractured composite samples after the flexural test are shown in Figure 16. For tensile and compressive sides of the composite, PAA-T presented a huge delaminated area. On the contrary, the fractured specimens of PAA-TS and PAAS-T had much less delaminated areas. These huge delaminated areas in PAA-T sample states weak interfacial bonding of fiber and matrix and the weaker structure and more brittleness of the matrix. On the other hand, PAAS-T and PAA-TS indicated less delaminated areas and matrix cracking, these results cause to improved interfacial bonding that may be restricted by high delamination, fiber pull-out, fiber–matrix debonding [199]. Larger wetting and bonding areas between fiber and matrix were obtained by using PAAS (the precursor of PAAS-T) and NA terminated PAA precursors (the precursor of PAA-TS).

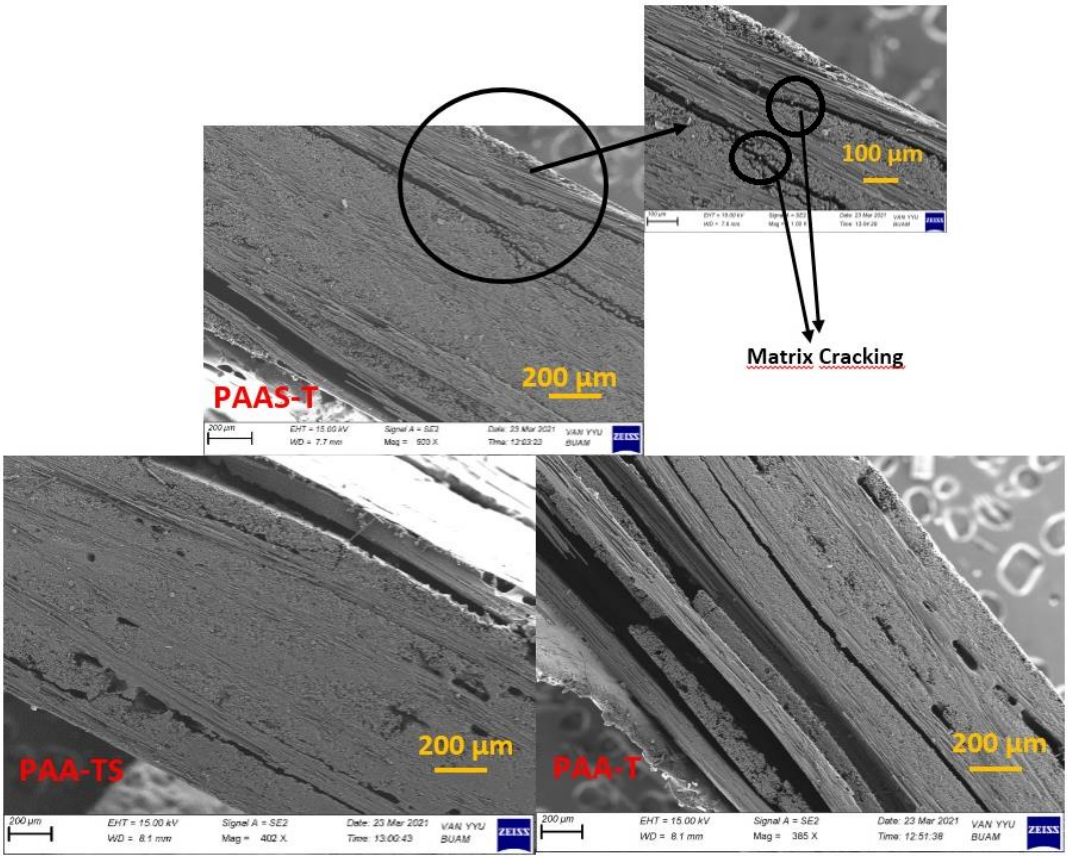


Figure 3.1.16. The SEM images of PAAS-T, PAA-TS and PAA-T after the flexural test

The sizing effect of PAAS precursor could also increase the interface areas. On the otherhand, NA terminated PAA precursor was crosslinked with reverse Diels Alder reaction including opening C=C bonding radicals of NA monomer, as mentioned. Therefore, NA terminated PAA precursor could be crosslinked with CF.

3.1.5. Conclusion

Currently, thermoplastic advanced composites with high performance are an important requirement in various industries such as the aerospace, automotive and marine industries due to their higher impact resistance than thermoset composites. This study prepared CF-reinforced thermoplastic and thermosetting PI matrix composites by using different synthesized PI precursor resins. These composites were obtained from prepregs and manufactured by vacuum bagging and compression molding processes. The prepregs were prepared using the two-step impregnation method with a vacuum oven. The PAAS precursor resin among the synthesized PI precursors, is a novel method in the manufacturing of CF-reinforced advanced PI matrix composites. The advanced thermoplastic composite obtained from the PAAS precursor (PAAS-T) exhibited superior mechanical properties and enhanced thermal properties (near the thermal properties of thermoset advanced composites) compared to the other advanced composites in this study and in the literature. However, the NA-terminated PAAS precursor (thermosetting PI precursor) did not exhibit a similar effect in terms of mechanical properties. PAAS-T had a flexural strength of 940 MPa and a flexural modulus of 97 GPa. It also represented tensile strength and modulus with 349 MPa and 75.3 GPa, respectively. On the other hand, PAA-T (thermoplastic advanced composite obtained from the PAA precursor) presented the lowest mechanical properties although it had more enhanced thermal stability than PAAS-T. It was thought that the PAAS precursor resin could substantially increase the process capability of the PAA precursor for the production of CF-reinforced PI matrix advanced composites. As another issue, the advanced thermoset composites in this study showed highly enhanced thermo-mechanical properties at around 400 °C. The advanced thermoset composite that was obtained from the NA-terminated PAA precursor resin (PAA-TS) had the highest thermo-mechanical properties in this study. Accordingly, PAA-TS that is one of the CF-reinforced PI matrix advanced composites, presented the highest thermo-mechanical-properties in the literature. It presented thermo-mechanical properties comparable to the DMBZ-15 advanced composite. It was thought that DADPS made substantial contributions to the thermal and mechanical properties of advanced composites.

3.2 Mechanical Properties of Heat-resistant Polyimide-based Advanced Composite Sandwich Panels

3.2.1. Abstract

This study presents heat-resistant polyimide (PI)-based advanced composite sandwich panels (HRACS) consisting of CF-reinforced polyimide matrix thermoset and thermoplastic advanced composite laminates (Outer faces) and PI foams (Core materials). For the outer faces, thermoplastic composite laminates were prepared from poly (amic acid) ammonium salt (PAAS) precursor resin, and the thermoset was prepared from nadic anhydride (NA)-terminated poly (amic acid) (PAA) precursor resin. BTDA (3,3,4,4 Benzophenone tetracarboxylic dianhydride) and DADPS (4,4 diaminodiphenyl sulfone) were used as monomers for the polymer backbones. For the thermosetting composite, NA was also used as an end capper and to provide crosslinking of the polymer chains. On the other hand, the HRACSs had two kinds of core materials with different densities and thicknesses. As core materials, isocyanate-based PI foams were used. PMDA (pyromellitic anhydride) and PMDI (polymeric diphenylmethanediisocyanate) were used for the PI foams and the amounts of the additives such as the surfactant, water and triethyl amine. As a result of these variations, different compressive properties and densities were obtained. On the other hand, a PMR-type adhesive PI resin was synthesized in this study. The HRACSs were prepared with the curing and crosslinking of this synthesized PMR-type adhesive PI resin at the interfaces of the outer face and core materials. These HRACSs exhibited outstanding compressive and flexural properties. The flexural force of the HRACSs increased up to 535 N while the composite laminates exhibited values of 197 N and 255 N. The CSUS of HRACSs presented excellent values ranging from 2.61 to 8.70 MPa.

Keywords: Heat-resistant polyimide composite sandwich panels, poly amic acid ammonium salt precursor resin, fiber-reinforced thermoplastic and thermoset polyimide composite, PMR-type PI adhesive resin

3.2.2. Introduction

Composites with a sandwich structure are a special class of composite materials which have become very famous due to their high specific strength and rigidity. The high specific strength of these materials makes them a priority for usage in aerospace, space, automotive and undersea applications. These sandwich panels consist of two rigid, thin, strong faces divided by a porous core material with a lower density. These faces have been generally manufactured from materials like steel, aluminum and composites. Porous core materials have been generally made out of foam, honeycomb and balsa wood. In order to bond these face and core materials to each other, a strong adhesive resin or film can be used [165,166].

Currently, high-strength and lightweight materials have substantially been renowned for especially the aerospace, marine and automotive industries. Therefore, fiber-reinforced polymer-based composite face sheets and polymer-based cores have become prominent because of lightweight and high in-plane and bending stiffness values [165,166]. In literature, while face materials have generally been glass fiber- and CF-reinforced epoxy composites, core materials have been honeycomb (e.g., Nomex TM paper) [165,200] - or polymer-type (e.g., polyurethane and polypropylene foams) foams [200,201]. The maximum service temperature of these polymer-based face sheets and cores are generally well-above 200 °C because of the degradation of the materials and the high extent of decrease in its mechanical properties. However, some critical applications of aerospace structures require highly heat-resistant sandwich structures the service temperature of which exceeds 200 °C. For example, the wing and airframe of supersonic aircraft and the components that are close to the aircraft engine such as nacelles are some of these critical applications. These sandwich structures may also be used in space satellites for exploration in the future. For use in these critical applications, PI materials have been one of the most preferred polymer materials [2,197].Various materials can be also manufactured from PIs including composites, fibers, foams, microelectronic materials and high-temperature adhesives. In this regard, fiber-reinforced advanced composites and high-performance adhesives have been obtained by using PI precursor resins in the literature. PMR (Polymerization of Monomeric Reactant)-type resins have been significant among prominent polyimide resins. These types of resins have been synthesized by using the poly ester-amine salt (PEAS) method [197]. They have been used for the matrix resins of both fiber-reinforced advanced composites and high-performance adhesives. In the

literature, there are various studies on PMR-type polyimide resins in terms of the preparation of advanced composites and adhesives [197]. In addition to PMR-type polyimide resins, poly (amic acid) (PAA) precursor resins have been used for both thermosetting and thermoplastic PI composites. For thermosetting composites, nadic anhydride (NA) or phenyl ethynyl terminated imide (PETI) have been generally used as end cappers and to provide the crosslinking of the polymer chains. Furthermore, there have been various studies on polyimide foams. These foams have been usually prepared as isocyanate-based and diamine-based polyimides based on the synthesis methods used. While diamine-based polyimide foams have exhibited better thermal properties than isocyanate-based ones, isocyanate-based ones have presented easier processability and much lower costs. In light of this information, there have been few reports about heat-resistant polyimide-based sandwich panels in the literature. This is substantially caused by the weak presence of heat resistant materials such as face sheets, cores and adhesives [183]. In the literature, it is possible to find separate studies focusing solely on polyimide foams or fiber-reinforced polyimide-based composites.

Some studies in the literature about fiber-reinforced thermoplastic and thermoset polyimide-based composites are discussed here. Lu et al. [179] prepared T300 carbon fiber (CF)-reinforced polyimide and co-polyimide matrix thermoplastic composites. They synthesized PAA precursor resins in dimethyl acetamide (DMAc). They used oxydianiline (ODA), oxydiphthalic anhydride (ODPA), benzophenone tetracarboxylic dianhydride (BTDA), bisphenol A dianhydride (BPADA) and biphenyl dianhydride (BPDA) for polymer backbones. Phthalic anhydride (PA) was used as the end capper to control the molecular weight. Then, the prepared prepregs and polyimide films were piled up alternately into a die to be molded. A laminated plate was manufactured by using a hot-press machine at a pressure of 2-3 MPa. The composite containing BTDA / 3,4 ODA/PA represented a flexural strength and modulus with 536 MPa and 95 GPa, while the composite containing BTDA-BPDA (9:1)/3,4 ODA/PA represented flexural strength and modulus with 500 MPa and 90.5 GPa. Livengood et al. [181] synthesized a PAA precursor resin from BTDA and 2,2’-dimethyl-1,3-(4-aminophenoxy)propane (DMDA) and prepared CF-reinforced thermoplastic polyimide matrix composites. They used the T650 carbon unidirectional fiber and manufactured the composites with the drum winding method. They reported that the dynamic mechanical analysis (DMA) of the prepared composite exhibited Tg values ranging from 230 °C to 250 °C, and onset temperatures

around 210 °C and 220 °C. Su et al. [180] prepared CF-reinforced thermoplastic polyimide-based hierarchical composites with in situ grown carbon nanotubes on CF fabric to obtain enhanced fiber-matrix interfacial adhesion. They synthesized a PAA precursor resin containing BPADA and ODA monomers. In order to improve the CF fabric's mechanical properties, they treated it with a nitric and sulfuric acid solution. They were hold for 12 h in the PAA solution and followed by holding in an oven at 100 °C. After obtaining prepregs, the composites were manufactured by hot-pressing. While the pure composite (CF/PI) represented flexural strength and modulus with 420 MPa and 45 GPa, the CF/PI composites where the carbon nanotubes grew for 40 min (CF/PI-40) represented flexural strength and modulus with 560 MPa and 64 GPa. The Tg values obtained in the DMA of the CF/PI and CF/PI-40 were 218 °C and 245 °C, respectively.

Serafini et al. [167] invented unidirectional CF-reinforced PMR-type thermoset composites using PEAS precursors with the US patent no. 3.745.149 at the NASA laboratories. PEAS is formed in a reaction between an aromatic diamine and diester-diacid monomers. Firstly, dianhydrides react with alcohol, and diester-diacid monomers occur in the solution. Diamine monomers are added into the diacid-diester solution, and the reaction occurs instantly with the carboxyl groups in the diester-diacid and a chain-like structure with alternate diamine/diester-diacid as a repeat unit form. The monomers in PEAS are connected by ionic interactions between amine and carboxylic acid groups. In this sense, PEAS precursors can be regarded as salt-like [178]. For these reasons, these monomeric salts can be easily impregnated into fiber fabric and subjected to in situ polymerization. They are also crosslinked at high temperatures by means of some terminating monomers such as NA and PETI. Serafini et al. [167] used different diamines and dianhydrides such as BTDA, methylenedianiline (MDA) and 4,4'-thiodianiline (TDA) and pyromellitic dianhydride (PMDA) for the formation of a polymer backbone. NA was used as a reactive terminating alkyl ester and a crosslinking agent. In the synthesis process, NA and BTDA was converted into diacid-diester monomers by the reaction of methanol. The diacid-diesters reacted with MDA monomers, and PEAS was obtained. Additionally, the molecular ratios of the monomers varied, and PMR-15 (1500 Molecular weight) became prominent in terms of its mechanical and thermal properties. Unidirectional prepreg tapes were prepared using the drum winding method. While the composite manufactured by using the PMDA, TDA and NA monomers exhibited an interlaminar strength of 55 MPa, the composite manufactured by using BTDA, MDA and

NA exhibited an interlaminar strength of 89 MPa.

In addition to these viewpoints in the literature, there have been other PI precursors available to be synthesized for various purposes. These precursors are poly (amic acid) alkyl salts (PAASs) that have been used in some applications such as thin films, hybrid films and interlayers in the literature. PAAS can be prepared by blocking the COOH groups on the PAA backbone with triethyl amine (TEA), where ammonium salts can form on the polymer backbone. Cai et al. [185] prepared PI films from PAAS precursors with improved thermal stability and mechanical properties. They also reported that the PAASs had excellent hydrolytic stability, and their mechanical properties almost did not decrease at all after 90 days. Because of their ability to be stored for a long period at room temperature (RT), these precursors attract much interest. They are an excellent candidate with their potential practical applications. Ke et al. [186] used a PAAS solution (1% solid) to size the T700 carbon fiber. They toughened the thermosetting polyimide composite. The compression after impact (CAI) values of the CF-reinforced PI composite increased from 175 MPa up to 190 MPa. Facinelli et al. [188] synthesized PAASs and reported that the PIs synthesized from poly (amic acid) triethylammonium salts had higher a molecular weight than conventional PAA, as well as improved thermal and mechanical properties. They also mentioned General Electric's ULTEM, which is a thermoplastic polyimide with an excellent combination of thermal stability, mechanical properties and processability. In addition to these, they reported that PAASs could make excellent fiber sizing media and subsequently be imidized to yield tough, relatively water insensitive and fiber-matrix interphase layers [188,130]. Facinelly et al. [188] emphasized that they were interested in exploring these positive aspects of PAASs for composite applications.

According to the literature review about isocyanate-based polyimide foams, researchers have generally aimed to improve the properties of isocyanate-based PI foams in two ways [150].

(1) Optimization of the foam preparation technology during the process.
(2) Incorporation of fillers and particulates with small sizes such as vermiculite, fiber felt, graphite, graphene and inorganic additives into the PI foam matrix to improve mechanical properties and thermal stability.

For instance, Yu et al. [202] synthesized a series of isocyanate-based PI foams by the reaction of two different solutions. The effects of different water amounts and the

isocyanate index on the structures were investigated in terms of the physical and mechanical properties of rigid PI foams. The PI foams were prepared at an isocyanate index value of 1.28, and the weight ratios of water (H_2O/PMDA) varied as 5/100, 6/100, 8/100–10/100 and 12/100. While the densities of the foams changed between 119 kg/m^3 to 68 kg/m^3, the compressive strength values varied from 0.86 MPa to 0.29 MPa. Regarding the second way of improving isocyanate-based PI foams, Qin et al. [203] reported the introduction of the dispersed dopamine hydrochloride (Do)@graphene oxide (GO) solution into isocyanate-based PI foams. They improved the properties of the foam matrix and provided better dispersion than graphene.

As mentioned, there have been few studies on sandwich composite panels that have combined fiber-reinforced polyimide-based advanced composites and polyimide foams in the literature. Ogasawara et al. [171] presented the processing and properties of a new heat-resistant sandwich structure that consisted of CF-reinforced polyimide matrix composite face sheets and a carbon foam core. A novel phenyl ethynyl-terminated imide oligomer (TriA-X) was used for both the matrix resin and the film adhesive. The carbon foam (Grafoam) was used as the core material. The CF/TriA-X sandwich panel exhibited a flexural force of 305 N and a core shear strength of 1.1 MPa. Camarda et al. [172] reported a heat-resistant sandwich structure (Celion 6000/PMR-15 Gr/PI composite) consisting of a graphite-reinforced polyimide matrix composite and a glass-reinforced PMR-15 honeycomb. They presented the material's tensile and compressive properties.

In this study, heat-resistant polyimide-based advanced composite sandwich panels (HRACS) with different core thickness were prepared. In these processes, outer faces were obtained from carbon fiber-reinforced polyimide matrix composites. Two kinds of CF-reinforced polyimide matrix composites were prepared for the outer faces as thermoplastic and thermoset. While the thermoplastic composite was prepared from a PAAS precursor resin, the thermoset one was prepared from an NA-terminated PAA precursor resin. As the core materials, two kinds of isocyanate-based polyimide foams with different densities were synthesized by adjusting the process technique. Additionally, a PMR-type PI adhesive resin was synthesized to bond these components for obtaining HRACSs. The HRACSs were mechanically characterized by using the three-point flexural and flatwise compressive test. The flexural and flatwise compressive properties were investigated for the sandwich composites. The mechanical properties of the polyimide foams and the composite laminates were also evaluated separately. Moreover, DMA was carried out at a

certain frequency to observe the alteration of the modulus with an increase in the temperature for the PI foams and the composite laminates.

3.2.3. Experimental

3.2.3.1. Materials

3,3,4,4-Benzophenone tetracarboxylicdianhydride, pyromellitic dianhydride (PMDA), 4,4 diamino diphenyl sulfone (DADPS), dimethylformamide (DMF), triethyl amine (TEA), distilled water, surfactant (Evonik TEGOSTAB B8522) and methanol were purchased from Sigma-Aldrich. 5-Norbornene-2,3-dicarboxylic Anhydride (Nadic anhydride, NA) > 97.0% was purchased from the J&K Company. ONGRONAT 2100 was used as the polymeric diphenylmethane diisocyanate (PMDI) with an average functionality of 2.6-2.7. Epoxy sized T300 carbon fiber (CF) fabric of 245 g/m^2 and 2x2 twill weave with a tow size of 3 K that was purchased from Toray was used as the reinforcing material.

3.2.3.2. Preparation of PI precursor resins

3.2.3.2.1. Preparation of PAAS precursor resin for advanced thermoplastic composite

In order to manufacture the advanced thermoplastic composite, firstly, the PI precursor resin was synthesized, followed by the preparation of the prepreg tape. The PI precursor resin of the advanced thermoplastic composite was PAAS. This advanced thermoplastic composite was termed as PAAS-T. The synthesis scheme of PAAS-T is presented in Figure 3.2.1. The PAAS precursor resin was obtained with the conventional PAA synthesis method followed by the addition of triethyl amine monomers into the PAA precursor solution. The PAAS-T precursor resin was prepared as a 50% wt. solid. No dilution and evaporation of solvent were carried out before the prepreg impregnation period. All reactions were completed in a flask with three necks and round-bottom. It was also entegrated with a magnetic stirrer and condenser. These reactions were applied in a N_2 atmosphere. The PAAS-T precursor resin was synthesized according to the stoichiometry of an equimolar amount of the dianhydride monomer (BTDA) and diamine monomer (DADPS). In detail, first of all, DADPS and DMF were fed into the flask. The DADPS and DMF were stirred for 30 min at RT. Then, an equimolar amount of BTDA was gradually added to the contents in the flask and stirred for 12 h at RT. After stirring BTDA and DADPS, a PAA precursor resin was obtained as a clear viscous liquid. After

this, TEA monomers were added into the PAA solution. This solution was vigorously stirred at RT for 2 hours. The amounts of TEA monomers were adjusted to block the COOH groups completely on the PAA chain. Therefore, ammonium salts formed along the polymer chains in the solution. The PAAS-T precursor resin was obtained as a clearviscousliquid.

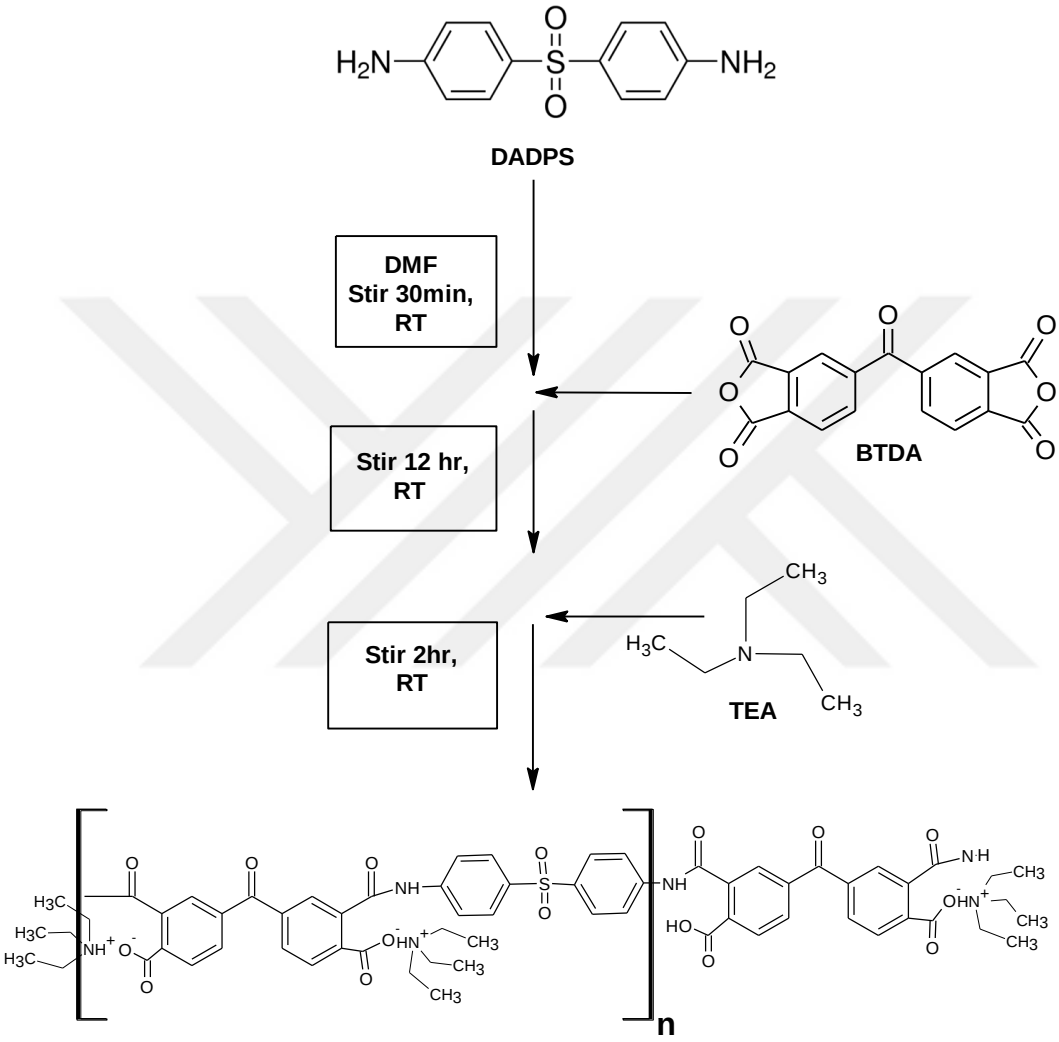


Figure 3.2.1. The synthesis scheme of PAAS-T precursor resin

3.2.3.2.2. Preparation of NA-terminated PAA precursor resin for advanced thermoset composite

First, DADPS and DMF were fed into a flask. The DADPS and some of the DMF were stirred for 30 min at RT. Then, the BTDA and the remaining amount of the DMF were gradually added to the contents in the flask and stirred for 2 h at RT. After stirring BTDA and DADPS, NA was added into the flask and stirred for 12 h at RT. A clear viscous

solution was obtained. The advanced thermosetting composite which was obtained from this precursor resin solution was termed as PAA-TS. The molar ratio of the monomers was adjusted according to the stoichiometry of 2NA/(n + 1)DADPS /nBTDA. This ratio belonged to the PMR-15 polyimide resin that had a molecular weight of 1500 [178]. NA was used for the termination and crosslinking of the polymer chains. This precursor resin solution was prepared as a 50 wt % solid. Information about the synthesized PI precursor resins for the thermoplastic and thermoset composite laminates is given in Table 3.2.1.

Table 3.2.1. Information about the manufactured PI advanced composite laminates

Advanced Composite Faces	Synthesis Method	Composite Type
PAAS-T	Poly amic acid ammonium salt precursor resin	Thermoplastic
PAA-TS	NA terminated poly amic acid precursor resin	Thermoset

3.2.3.3. Prepreg Fabrication with Two-step Impregnation in Vacuum Oven

The prepreg fabrication process involved two-step impregnation by a glass cylindrical bar followed by solvent evaporation in a vacuum oven at mild temperatures and below atmospheric pressure. The CF fabric was cut into six equal parts so that the dimensions of each one would be 15 cm x 15 cm before the impregnation process. Each CF fabric was laid down on the polypropylene (PP) film. The prepared precursor resins were then poured in lines, brushed and spread on the fabrics by the glass cylindrical bar. The resin was impregnated into the fabrics homogeneously with the reciprocating action of the glass resin roller in line. After the first impregnation step, the excess solvent from the wet fabrics on the PP film was evaporated at a mild temperature in the vacuum oven. The excess solvent of the precursor resin was evaporated at 60 °C under a 0.5-bar vacuum for 1 h. After the removal of the excess solvent in the wet CF fabrics, the second impregnation step was carried out by turning the backside of the CF fabrics on the PP film. The resin was then poured, brushed and spread with the reciprocating action of the glass cylindrical bar again. Vacuum evaporation was carried out again under the same conditions in the vacuum oven as before. Finally, the CF fabric was taken out of the vacuum oven, wrapped with the PP film and held for 30 min. The prepregs gained adequate tackiness for composite manufacturing.

3.2.3.4. Composite Manufacturing

Figure 3.2.2 presents the detailed process scheme of composite manufacturing. Composite manufacturing included two stages. The first stage was the vacuum bagging process. The second stage was the compression molding process involving high-temperature curing and high pressure.

3.2.3.4.1. Vacuum Bagging and Compression Molding Processes

All prepreg laminates were separated from the PP release films and overlapped with each other on the Teflon surface of a vacuum infusion heating platform. All prepregs were overlapped with each other by applying hand force by a Teflon roller. All overlapped prepregs were placed between thin Teflon films. The prepregs were vacuum bagged and heated on a vacuum infusion heating platform to minimize the quantity of the solvent and consolidate the prepregs by partial imidization. Regarding the process parameters, the prepregs were firstly exposed to full vacuum and held at 60 °C for 30 min. Then, a 0.2-bar pressure load was applied to the prepregs and followed by holding at 140 °C and 150 °C for 1 h in near-full vacuum condition. When process was completed, heater was turned off, and the prepregs were allowed to cool slowly for 2 h under near-full vacuum.

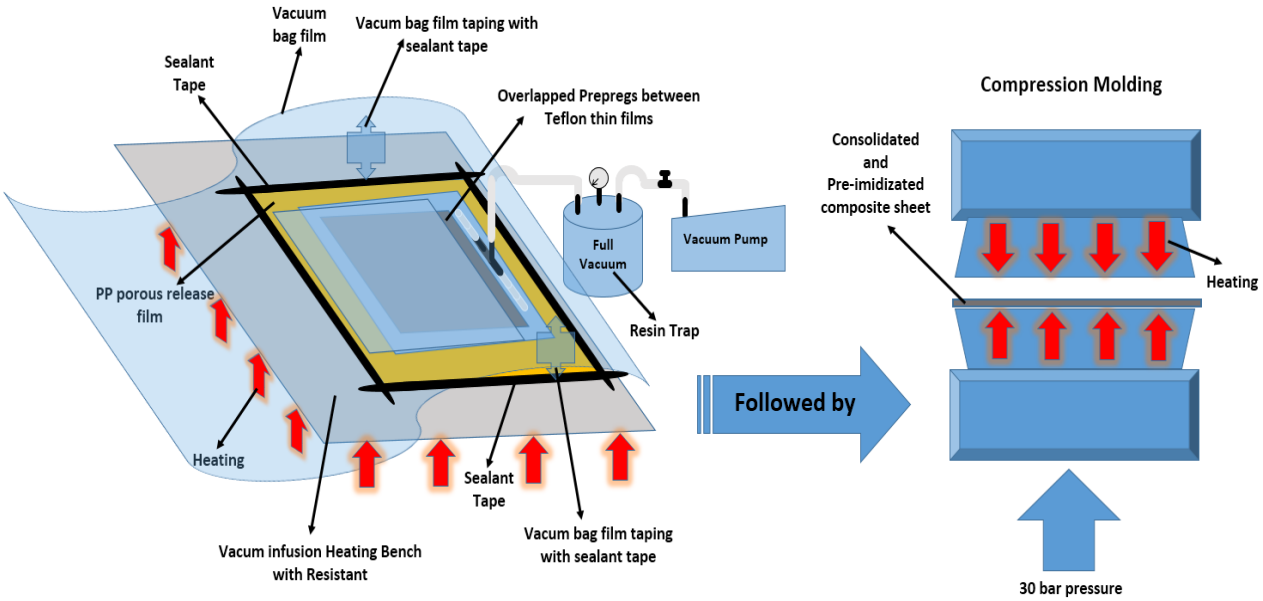


Figure 3.2.2. The detail process scheme of composite manufacturing

After the cooling period of vacuum bagging process, the prepregs were removed from the vacuum bag on the vacuum infusion heating platform, and the Teflon films were easily taken from the upside and downside of the consolidated prepregs. These intermediate

products were put between aluminum foil-covered steel plates. These steel plates were taken and placed on the lower mold half at 175 °C, and the upper mold half was closed at a pressure value of 30 bar. When the molds were closed, the process temperature was immediately reduced to 160 °C. As soon as the temperature decreased to 160 °C, the furnace temperature was adjusted to 330 °C. The temperature was increased from 160 °C to 330 °C in 1 h and held at 330 °C for 30 min. After the completion of the process, the heater of the compression molding machine was turned off, and the products were cooled under pressure. Finally, the composite laminates were post-cured at 330 °C for 4 h in an air-circulation furnace. The detailed process scheme of the composite manufacturing process is shown in Figure 3.2.2.

3.2.3.5. Preparation of Isocyanate-based PI Foams

First, 10 g PMDA was added into 8 gr DMF solvent in a flask at RT. The suspension was stirred and heated to 60 °C until the PMDA was completely dissolved. To esterify the PMDA completely, the solution was cooled to RT, and then, methanol (stoichiometrically) was dripped into the solution and stirred magnetically at 60 °C for 1 h. After this esterification reaction, the solution was cooled to RT, and the additives (surfactant, water and/or TEA) were added into the flask. After stirring for 10 min, the A component in the flask was obtained. The amount of the B component (PMDI) was adjusted to react with the A component stoichiometrically. The B component was added to the A component solution, stirred at 2000 rpm and poured immediately into an open mold. After foaming in the open mold, the pre-product was held in a furnace to be cured. Figure 3.2.3 shows the preparation of the isocyanate-based PI foams. Two kinds of PI foams were obtained. While one of them displayed a density of 15 kg/m^3, the other displayed a density of 50 kg/m^3 as shown in Table 3.2.2. The one with the lower density was termed as the LDPI foam, while the other was termed as the HDPI foam. The additive amount and curing process parameters exhibited some variations for the HDPI and LDPI foams.

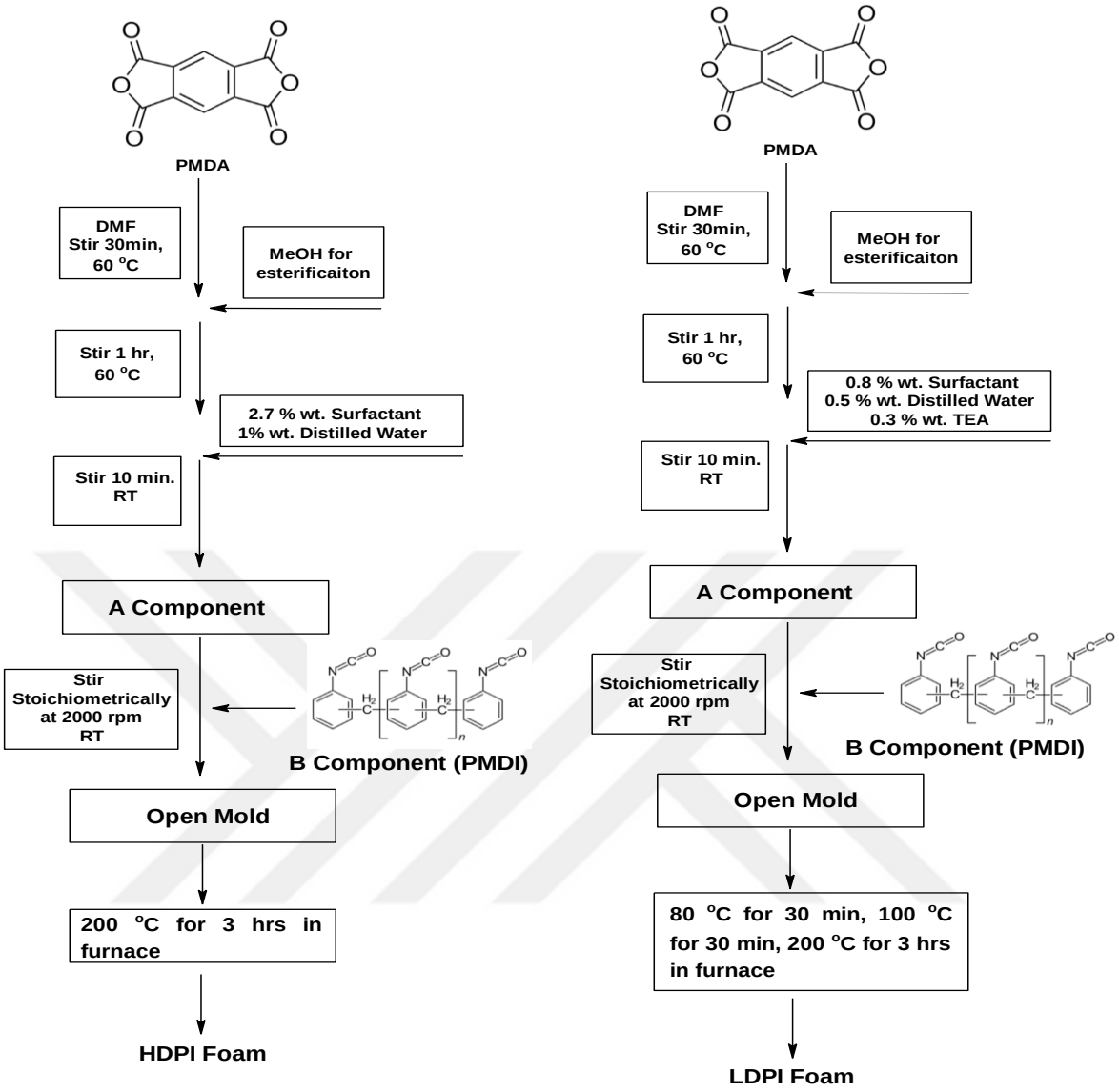


Figure 3.2.3. The synthesis scheme of isocyanate-based polyimide foam

3.2.3.6. Synthesis of PMR-type Polyimide Adhesive Resin

BTDA and NA were added into the methanol solvent in a flask at RT and stirred for 10 min. Afterward, the suspension was stirred and heated to 70 °C for 2 h until the BTDA and NA were completely dissolved and esterified. After the esterification of the anhydrides, the solution was cooled down to RT, and then, DADPS was slowly dripped into the solution. The solution was mixed magnetically in ambient conditions for 12 h. Finally, a clear viscous PMR-type resin was obtained. This adhesive resin solution was prepared as a 50 wt % solid.

Table 3.2.2. Physical properties of isocyanate-based PI foams

Foam Samples	Density (kg/m^3)
LDPI Foam	15
HDPI Foam	50

The molar ratio of the monomers was adjusted according to the stoichiometry of 2NA/(n + 1)DADPS /nBTDA. The "n" value was adjusted to 2.087. This ratio belonged to the PMR-15 polyimide resin that had a molecular weight of 1500. NA was used for the termination and crosslinking of the polymer chains [178].

3.2.3.7. Preparation of Heat-resistant Advanced Composite Sandwich Panels

After the preparation of the advanced composite laminates and the PI foams, these components were bonded with each other by using the synthesized PMR-type PI adhesive resin. The composite laminates and the PI foams were cut according to the dimensions of the test specimen. The adhesive resin that was prepared was spread by using a 75-µm wire wound applicator on the laminate surfaces. Net the cut PI foams were placed between the laminates by applying little hand pressure. These sandwich specimens were firstly held at 40 °C by applying vacuum for 24 h to evaporate excess solvent. After this process, the sandwich specimens were taken into an air circulation furnace and cured at 80 °C for 30 min, 150 °C for 30 min, 240 °C for 1 h, 300 °C for 30 min and 330 °C for 30 min. Post-curing was also applied at 300 °C for 4 h.

3.2.3.8. Measurements

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the PIs were recorded with a Shimadzu 8303 FTIR Spectrometer. The FT-IR curves of the isocyanate-based PI Foams and the PI matrix of the advanced composite laminates are given in Figure 3.2.4. DMA is used to observe thermo-mechanical properties of a material in different frequencies. Heating rate was applied as 5 °C / min starting from -150 °C up to 400°C. Composite specimens were run at a frequency of 1 Hz with the dual cantilever bending mode.

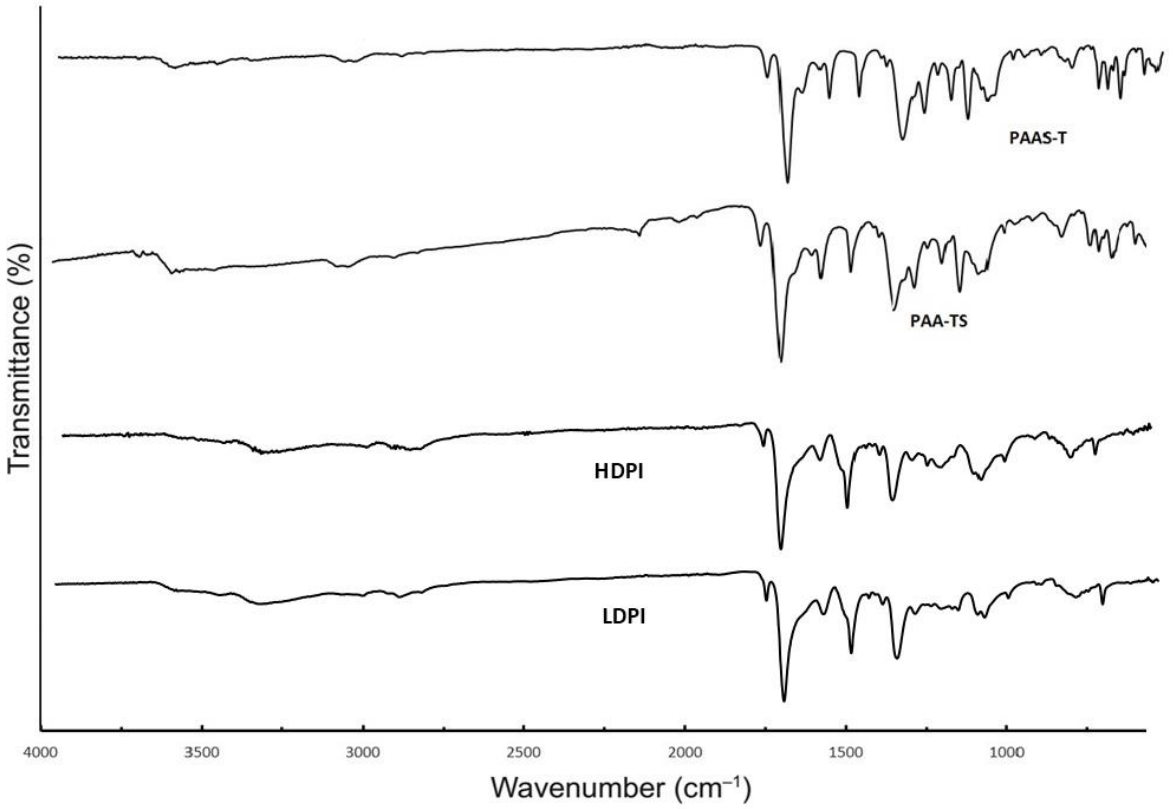


Figure 3.2.4. The FT-IR results

The three-point flexural test was used to calculate flexural strength, flexural modulus for the HRACSs and the advanced composite laminates according to the ASTM D790 method. These formulations are given in Equations 1 and 2, where σ (Mpa) is termed as the stress, P is termed as applied load (N), L is termed as support span, b is termed as the width of the specimen, d is termed as the depth of the specimen, E is termed as flexural modulus and m is the slope of the tangent of load and load-deflection (mm). Flexural tests were applied with an Instron model 4505 frame and the Series IX acquisition software. Table 3.2.2 exhibits the flexural properties of the two kinds of the advanced composite laminates that were prepared.

$$\sigma=3PL/2bd^2 \quad (3.2.1)$$

$$E=L^3m/4bd^3 \quad (3.2.2)$$

According to the ASTM C393 method, some properties of heat-resistant sandwich composite panels such as core shear ultimate strength (CSUS) and facing bending stress (FBS) were calculated by using Equations 3 and 4, where T is the CSUS value (MPa), P is termed as load, L is the support span (mm), b is the sandwich width (mm), d is the

sandwich thickness (mm), c is the core thickness (mm), σ_F is the FBS value (MPa), and t is the facing thickness (mm).

$$T = P/(d+c)b \quad (3.2.3)$$

$$\sigma_F = PL/2t(d+c)b \quad (3.2.4)$$

Table 3.2.3. Flexural properties of advanced composite laminates

Composite Laminate Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)	Force (N)	d (thickness, mm)	b (width, mm)	Density (gr/cm^3)
PAAS-T	940	97000	197	1.1	13	1.44
PAA-TS	921	73300	255	1.26	13.1	1.50

According to ASTM C365, the flatwise compressive properties of the sandwich cores such as flatwise compressive strength and flatwise compressive modulus were calculated by using Equations 5 and 6, where σ^c_{10} is the flatwise compressive strength (MPa) at a 10% relative deformation, P is the ultimate load (N), E is the flatwise compressive modulus, S is the ($\Delta P/\Delta u$) slope of the initial linear portion of the load deflection curve (N/mm), u is the displacement of the loading block (mm), and c is the core thickness (mm).

$$\sigma^c_{10} = P/A \quad (3.2.5)$$

$$E = Sc/A \quad (3.2.6)$$

The compressive properties of the PI foams which were used as the core materials were also characterized according to the ISO 844 method. Furthermore, the compressive strength and modulus were also calculated with Equations 5 and 6. The flatwise compressive force for the sandwich cores and the compressive force for the PI foams were evaluated at a 10% relative deformation. Scanning electron microscopy (SEM) analysis was performed using a JOEL JSM-5910LV scanning electron microscope to investigate the fracture surfaces of the composites, core shear, compressive and tensile effects after the flexural tests.

3.2.4. Results and discussion

FT-IR results were observed for both the isocyanate-based PI foams and the diamine-based PI matrices of the advanced composite laminates. The C=O bond of imide ring

stretching frequency appeared at around 1780 cm $^{-1}$ and 1720 cm $^{-1}$. The peak at 1370 cm $^{-1}$ represented the C-N stretching vibration of the imide rings. The out-of-phase bending of imide ring vibration could be observed at around 720 cm $^{-1}$. For the isocyanate-based PI foams, NCO group vibrations were not observed at around 2275 cm $^{-1}$ [172,202].

In this study, HRACSs consisting of two kinds of core materials and outer faces were prepared. The outer faces and the core materials were all polyimide-based materials. The thicknesses of the core materials varied as 1 mm, 2 mm, 4 mm, 7 mm and 12 mm. Accordingly, the sandwich panels up to the thickness of 4 mm were termed as thin HRACSs, and those with higher thickness values were termed as thick HRACSs. The isocyanate-based PI foams were termed as the LDPI and HDPI foams according to their densities. The outer faces were obtained from CF-reinforced PI matrix thermoplastic and thermoset advanced composite laminates, and they were termed as PAAS-T and PAA-TS as mentioned in the previous sections. Therefore, the HRACSs were identified by using these definitions according to the thicknesses of the core materials. For instance, in the definition of "PAAS-T-LD1C", "PAAS-T" indicates the CF-reinforced PI matrix thermoplastic advanced composite obtained from the PAAS-T precursor resin, and "LD1C" indicates the LDPI foam and the core thickness of 1 mm.

The mechanical properties of the HRACSs were observed with the three-point flexural test. The flexural strength and flexural modulus and flexural force values of all HRACSs are given in Tables 3.2.3 and 3.2.4. Additionally, the stress-strain curves and the comparison schemes of the thin HRACSs are given in Figures 3.2.5 and 3.2.6. There were various flexural samples prepared for both thin HRACSs and thick HRACSs. The HRACSs with a core thickness higher than 4 mm did not exhibit shear failure at the core materials. Therefore, in this study, CSUS (Core Shear Ultimate Strength) was calculated only for the thin HRACSs. According to ASTM C393, the width should not be less than twice the total thickness and not less than three times the thickness of a core cell. The width dimensions of the thick HRACS samples did not correspond to this recommendation due to the high core thickness compared to the width of the specimens.

Table 3.2.4. The flexural properties of thin heat-resistant advanced composite sandwich panels

Sandwich Panel Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)	Force (N)	CSUS (MPa)	FBS (MPa)
PAAS-T-LD1C	210	8630	443	7.44	155
PAAS-T-HD1C	244	14700	518	8.70	181
PAAS-T-LD2C	131	152	515	5.55	115
PAAS-T-HD2C	145	210	535	6.0	125
PAAS-T-LD4C	51	131	370	2.73	57
PAAS-T-HD4C	59	210	380	2.95	67
PAA-TS-LD2C	109	157	422	4.75	93
PAA-TS-HD2C	101	609	390	4.34	85
PAA-TS-LD4C	49	59	420	2.87	56
PAA-TS-HD4C	49	206	362	2.61	51

The flexural strength, flexural modulus, CSUS and FBS values presented the decreasing trend with the increase in the core thickness. The HRACSs with the HDPI foams exhibited higher mechanical properties than the HRACSs with the LDPI foams. Moreover, the HRACSs with the PAAS-T composite laminates presented higher mechanical properties than the HRACSs with the PAA-TS composite laminates. PAAS-T-HD1C exhibited the highest mechanical properties with a flexural strength of 244 MPa, a flexural modulus of 14700 MPa, a CSUS value of 8.7 MPa and an FBS value of 181 MPa. According to the results of the comparison of PAAS-T-HD1C to PAAS-T-HD2C and PAAS-T-HD4C, the flexural strength of PAAS-T-HD1C was 68% higher than that of PAAS-T-HD2C and 309% higher than that of PAAS-T-HD4C. The CSUS value of PAAS-T-HD1C was 45% higher than that of PAAS-T-HD2C and 194% higher than that of PAAS-T-HD4C. The FBS value of PAAS-T-HD1C was 44% higher than that of PAAS-T-HD2C and 167% higher than that of PAAS-T-HD4C. According to the information in the literature, thin composite sandwich panels can be alternative materials for the outer bodies of various machines and appliances such as automobiles, refrigerators, washing machines, lathes, drill presses, cupboards and light furniture. For instance, Kumar et al. [200] prepared thin sandwich panels (thickness close to 3 mm) consisting of glass fiber-reinforced epoxy composite faces and glass fiber chopped strand mat-epoxy constructed polyester foam.

They prepared these thin sandwich panels to replace a mild steel sheet enclosure used in many appliances and machines including automobile bodies. While the 0.8-mm mild steel sheet presented a flexural strength of 120 MPa, the sandwich panels they developed presented flexural strength and force with 350 MPa and 450 N, respectively. In this study, PAAS-T-HD1C presented exhibited a flexural force of 515 N and a flexural strength of 244 MPa. Moreover, this thin sandwich panel can be used close to engines for the outer body of various machines and appliances such as those used in the automobile and aerospace industries due to the high thermal stability of polyimide.

Table 3.2.5. The average flexural properties of thick heat-resistant advanced composite sandwich panels

Sandwich Panel Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)	Force (N)
PAAS-T-LD7C	29.9	54.1	460
PAAS-T-HD7C	28.7	77.6	455
PAAS-T-LD12C	9.26	6.0	330
PAAS-T-HD12C	8.9	15.9	420
PAA-TS-LD7C	19	47.9	340
PAA-TS-HD7C	27.2	64.4	418
PAA-TS-LD12C	8.76	6.8	255
PAA-TS-HD12C	7.66	13.4	263

The examination of the mechanical properties of the thick HRACSs revealed a much steeper decreasing trend than the trend in the thin HRACSs along with the increase in the core thickness. PAA-TS-HD12C exhibited very low mechanical properties with a flexural strength of 8.9 MPa and a flexural modulus of 15.9 MPa. These thick HRACSs also did not exhibit core shear failure.

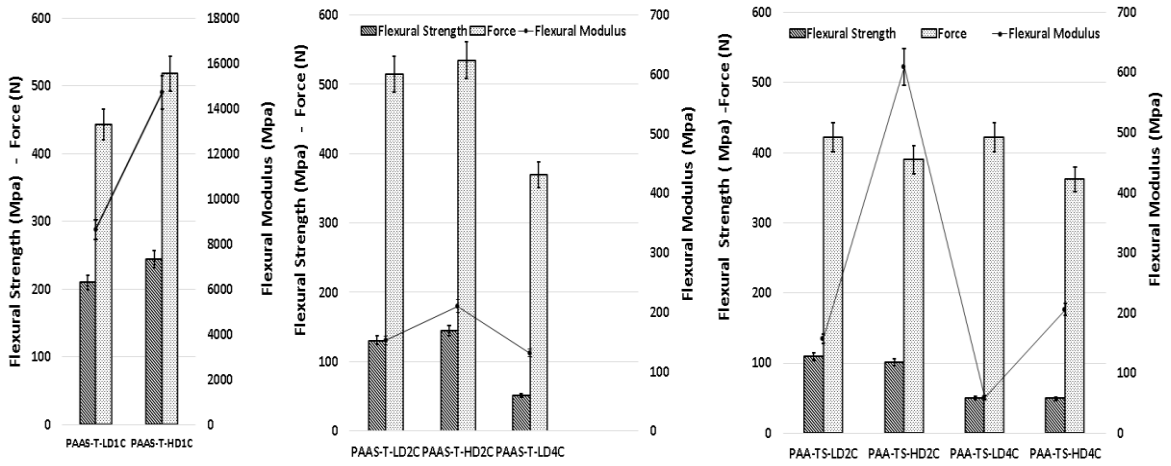


Figure 3.2.5. The comparison scheme of the flexural properties for thin HRACSs

This situation may be attributed to the explanation of the ASTM C393 method about the relationship between sandwich core thickness and specimen width. The flexural modulus values of the HRACSs with the thickness of 1 mm were found to be outstanding and out of the increasing trend. While PAAS-T-HD1C showed a flexural modulus of 14700 MPa, PAAS-T-LD1C showed a flexural modulus of 8630 MPa. These high flexural modulus values may be attributed to the filling of the adhesive PI resin into the PI foams due to the very thin core material at a thickness of 1 mm. They may be also be explained by loading transfer due to the very thin core material at a thickness of 1 mm. In the comparison between the HRACSs with the HDPI foam and the HRACSs with the LDPI foam, the HRACSs with the HDPI foam exhibited higher mechanical properties. For instance, while PAAS-T-HD2C represented flexural strength and modulus with 145 MPa and 210 MPa, PAAS-T-LD2C represented a flexural strength and modulus with 131 MPa and 152 MPa. In addition to this, PAAS-T-HD2C showed a CSUS value of 6 MPa and an FBS value of 125 MPa, whereas PAAS-T-LD2C showed a CSUS value of 5.55 MPa and an FBS value of 115 MPa.

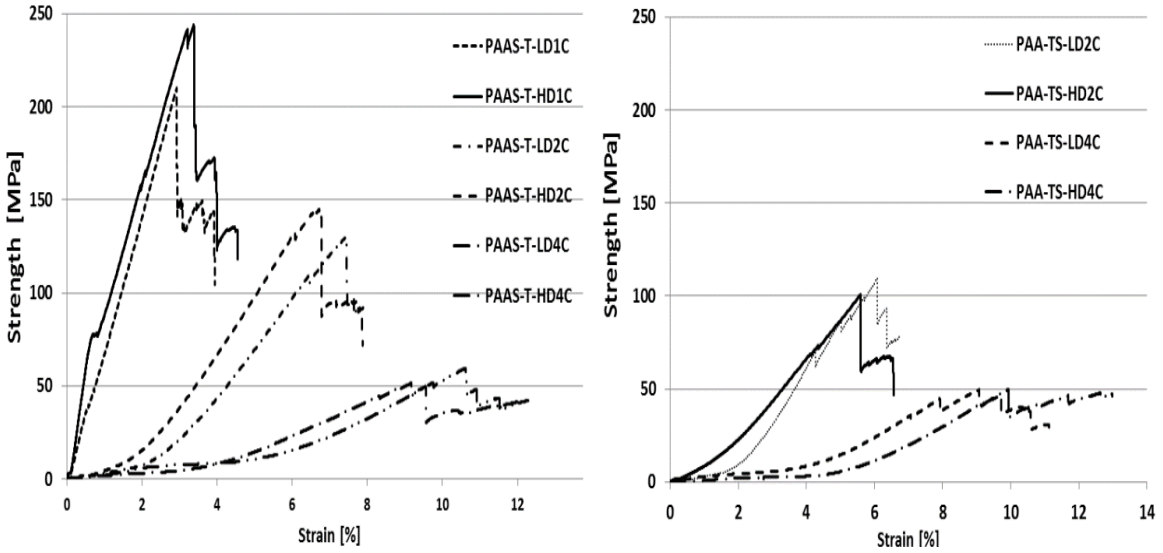


Figure 3.2.6. The average stress-strain curves of thin HRACSs

For the thick HRACSs, the same trend was available in terms of the flexural modulus, but the flexural strength values exhibited discontinuity. This situation may be attributed to the indentation failure mode on the sandwich panel during the three-point flexural test [201,204]. The flexural force of the HRACSs was observed to increase up to the core thickness of 2 mm. PAAS-T-HD2C and PAAS-T-LD2C provided the highest flexural forces values as 535 N and 515 N, respectively. They showed increases in flexural force by 3% and 16% in comparison to PAAS-T-HD1C and PAAS-T-LD1C, respectively. PAAS-T-HD4C and PAAS-T-LD4C showed slight decreases.

The flexural force values of the thick HRACSs generally decreased with the increase in the core thickness. These decreases may be explained by the indentation failure and compressive failure mode on the outer face of the sandwich panels [178, 204]. The fracture failure views of the sandwich panels are given in the scanning electron microscopy (SEM) images taken after the flexural test. In the comparison of the flexural forces of the composite laminates (PAAS-T and PAA-TS) that were prepared to the values of the HRACSs, the HRACSs exhibited outstanding flexural force values as shown in Figure 3.2.7.

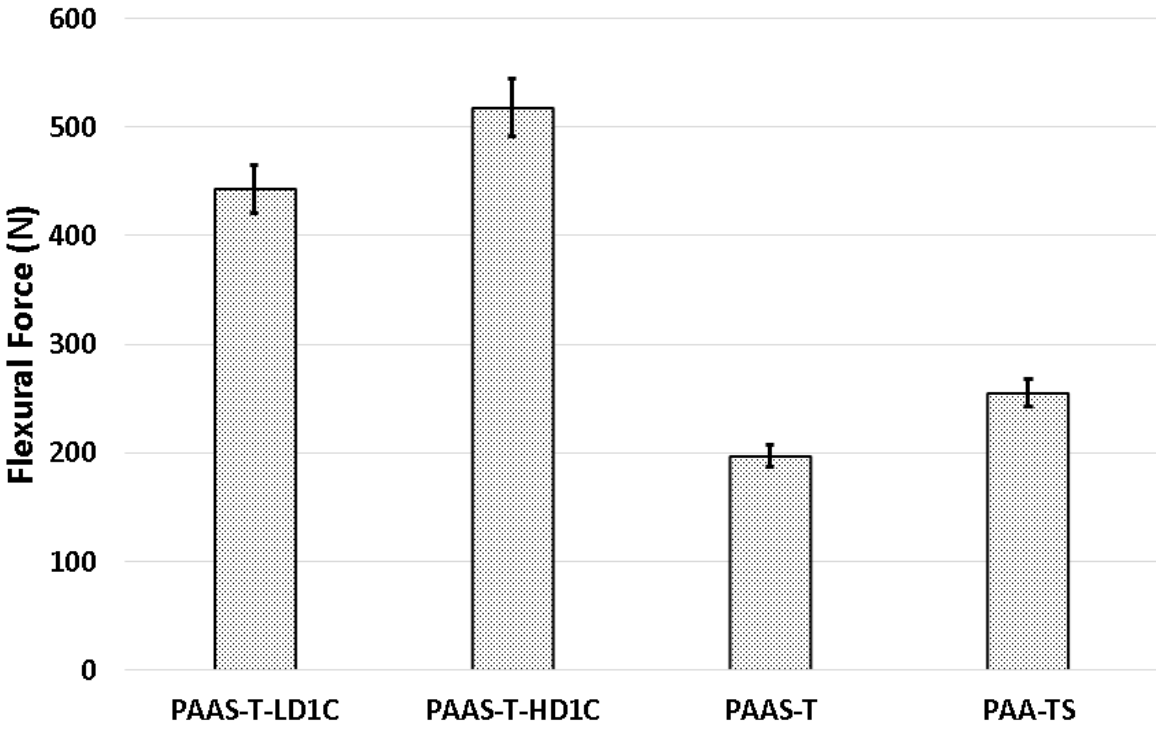


Figure 3.2.7. The flexural force values of the advanced composite laminates and HRACSs

As demonstrated in Table 3.2.2., the flexural force values of PAAS-T and PAA-TS were 195 N and 255 N, respectively. All HRACSs presented flexural force values in the range between 535 N and 362 N. In particular, PAAS-T-HD2C and PAAS-T-LD2C displayed the highest flexural force values as 535 N and 515 N, respectively. These values were much higher than the flexural force values of the advanced composite laminates. The densities of the HRACSs were also much lower than those of the advanced composite laminates because of the densities of the PI foams that were used as the core materials. While the density values of the HDPI foam and LDPI foam were found as 50 kg/m^3 and 10 kg/m^3, respectively, the PAAS-T and PAA-TS advanced composite laminates exhibited the respective density values of 1440 g/cm^3 and 1500 g/cm^3 as shown in Table 3.2.1.

Besides, the HRACSs consisting of the PAAS-T advanced composite laminate exhibited higher mechanical properties than the HRACSs consisting of the PAA-TS advanced composite laminate. As mentioned, two kinds of outer faces as the PAAS-T and PAA-TS advanced composite laminates were used in the HRACSs. Both types of composite laminates exhibited enhanced mechanical properties, where PAAS-T presented higher mechanical properties than PAA-TS. The PAA-TS precursor resin was synthesized from the reaction of DADPS and BTDA in the DMF solvent, and NA was used as the terminating agent and crosslinker. An NA-terminated PAA precursor resin in the DMF

solvent (PAA-TS precursor resin) was obtained. NA provided the crosslinking of the polyimide chains with the reverse Diels-Alder reaction at a high temperature (above 300 °C) and a high pressure during the manufacturing process. The molecular weight of the PAA-TS precursor resin was adjusted according to the PMR-15 polyimides. Therefore, it was expected that the molecular weight of the PAA-TS precursor resin would be lower than that of the PAAS-T precursor resin [200, 205]. A low molecular weight can increase the impregnation processability and the crosslinking density of composites. Thermoplastic PIs with crystalline and linear imide chain structures can be synthesized by using PAAS (poly amic alkyl salt) precursor resins. General Electric's thermoplastic PI (ULTEM) was synthesized by this method. In order to block COOH groups, General Electric used base molecules such as ammonium salts [130,188]. In addition to this, it has been known that PAAS precursor resins can be used as a fiber-matrix interface sizing agent. Therefore, a PAAS-T advanced thermoplastic composite was prepared by using the PAAS precursor resin in this study. The PAAS-T precursor resin was synthesized from DADPS and BTDA with the stoichiometry of an equal molar ratio in the DMF solvent. After the obtaining the PAA, TEA was added into the DADPS and BTDA solution to block the COOH groups completely. Finally, the PAAS-T precursor resin was prepared to impregnate the T300 CF fabric. During the prepreg preparation process, two-step impregnation was carried out by using a vacuum oven. This could be one of the reasons for the higher mechanical properties of the PAAS-T composite laminate than the PAA-TS composite laminate. Accordingly, a strong fiber-matrix interface could be obtained by the first impregnation of the PAAS-T precursor resin into the CF fabric. Another cause could be the possibility of the higher molecular weight of the PAAS-T precursor resin than the PAA-TS precursor resin due to the stoichiometric reaction of an equal molar ratio [188,206].

As mentioned above, the core materials were obtained from two kinds of isocyanate PI foams as the LDPI foam and the HDPI foam. In the synthesis and manufacturing of these PI foams, different process techniques were utilized. During the synthesis process of each PI foam, two components were prepared separately as component A and component B. These components were added into each other and stirred mechanically at 2000 rpm to facilitate polymerization and foaming reactions. Component A consisted of PMDA and the additives in the DMF solvent. Component B was the PMDI prepolymer. The isocyanate index was adjusted to 1. The additives consisted of a surfactant, distilled water and TEA. While the additives in the HDPI foam synthesis process consisted of the

surfactant by 2.7% and distilled water by 1%, the additives in the LDPI foam synthesis process consisted of the surfactant at 0.8%, and distilled water at 0.5% and TEA at 0.3%. The percentage ratios of the additives were calculated according to the weights of the resulting solution. The physical and compressive properties of the HDPI foam were higher than those of the LDPI foam. The process technique of the HDPI foam increased the density, compressive strength and modulus. The density of the HDPI foam was 50 kg/m^3, and the LDPI foam showed a density of 15 kg/m^3. While the HDPI foam (HDPI15) displayed a compressive strength of 43.4 KPa and a compressive modulus of 420 KPa, the LDPI foam (LDPI15) showed a compressive strength of 23.7 KPa and a compressive modulus of 140 KPa.

Farrissey et al. [207] revealed that distilled water facilitated imide formation in the synthesis of isocyanate-based PI foams. Water can cause the hydrolysis of isocyanate into urea, and ureas are known to react with anhydrides to form imides. The same researchers also reported that excellent PI yields were obtained with as little as 0.4 equivalents of water (based on isocyanate). On the other hand, water reacts with isocyanates and significantly promotes the foaming of the synthesized polymer due to the formation of CO_2 gas [202, 206]. The CO_2 forming with these reactions behaves as a blowing agent. However, when these reactions are completed, undesired by-products such as ureas can remain inside the final product. For these reasons, the isocyanate-based PI foams generally exhibited lower thermal properties than the diamine-based PI foams. Another parameter was the difference of the surfactant amount between the synthesis processes of the HDPI foam and the LDPI foam. A surfactant is chosen to achieve a uniform cell structure and provide cell opening at the proper time to vent the excess carbon dioxide [207]. The last parameter was the triethylamine basic catalyst that makes the reactions faster.

The compressive properties of the HRACSs such as the flatwise compressive strength and modulus were also examined in this study. As the outer faces, the PAAS-T samples were used for the compressive test samples of HRACSs, and the LDPI and HDPI foams were used as the core materials. The compressive stress – strain curves of the HRACSs and the PI foams are given in Figure 3.2.8.

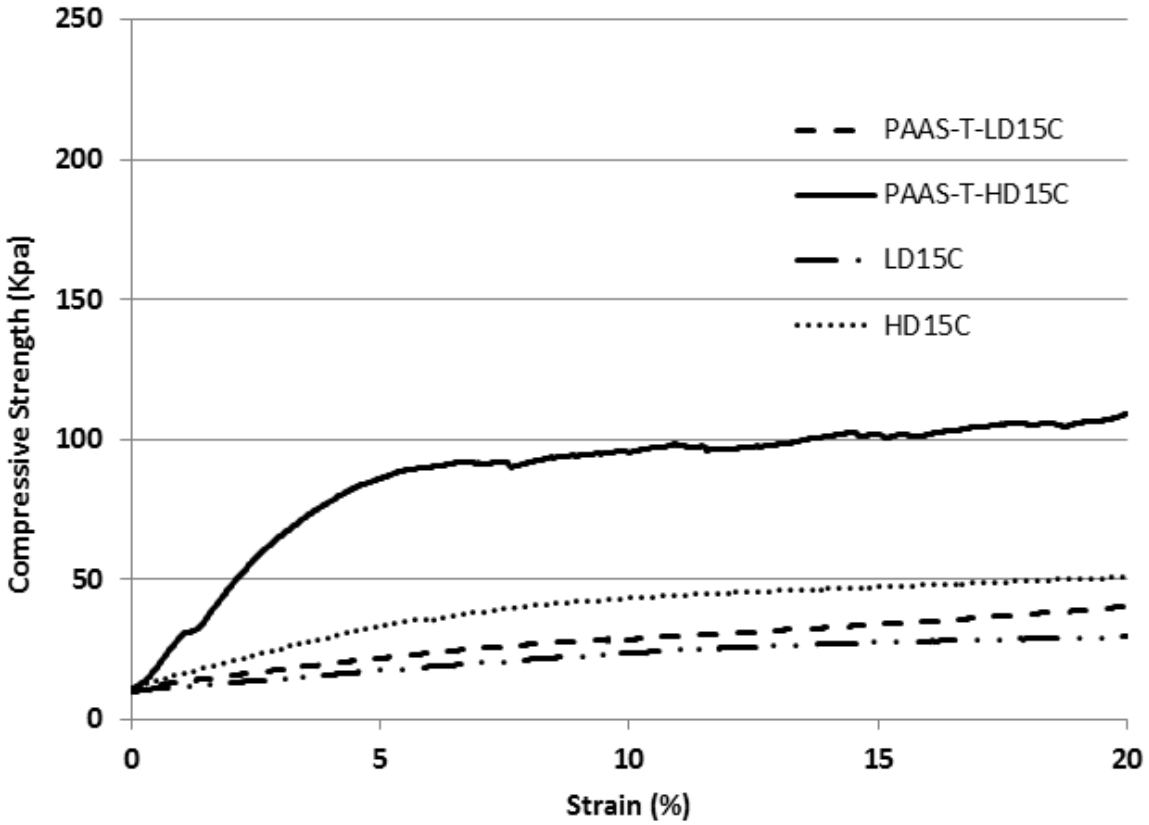


Figure 3.2.8. Compressive stress – strain curves of the HRACSs and the PI foams

The thickness of the core materials was adjusted to 15 mm. For this reason, these flatwise compressive sandwich panel specimens were termed as PAAS-T-HD15C and PAAS-T-LD15C.

Table 3.2.6. The flatwise compressive properties of the sandwich cores

Sandwich Panel Samples	Flatwise Compressive Strength (KPa)	Flatwise Compressive Modulus (KPa)
PAAS-T-LD15C	28.7	200
PAAS-T-HD15C	95.4	1760

Additionally, the PI foams (not as sandwich cores) were characterized by a compressive test. Two thickness values were determined for the PI foams as 15 mm and 25 mm. The effect of sample thickness on the compressive properties of the PI foams was also examined.

Table 3.2.7. The compressive properties of the PI foams

Foam Samples	Compressive Strength (KPa)	Compressive Modulus (KPa)
LD15C	23.7	140
HD15C	43.4	420
LD25C	25.5	190
HD25C	49.7	550

The compressive properties of the HRACSs and PI foams are given in Tables 3.2.5 and 3.2.6. It is well-known that higher densities can mean smaller cellular diameters and thicker cell edges and walls. PI foams with higher densities and smaller cellular diameters can present higher compressive properties than those with lower densities and larger average cellular diameters [202]. It was thought that the HDPI foam exhibited more enhanced compressive properties compared to the LDPI foam due to these reasons. Likewise, the compressive properties of the PI foams increased with the increase in the thickness of the PI foams. For instance, while HD15C exhibited a compressive strength of 43.4 KPa and a compressive modulus of 420 KPa, HD25C represented compressive strength and modulus with 49.7 KPa and 550 KPa. However, the flatwise compressive strength and modulus of PAAS-T-HD15C and PAAS-T-LD15C were enhanced more in comparison to the compressive properties of the PI foams. It was thought that these increases could have been caused mainly by the curing regime of the PI foams at high temperatures during the manufacturing process of the HRACSs as shown in Figure 3.2.9.

Liu et al. [205] investigated the thermal properties of PI foams prepared from aromatic dianhydride and isocyanate. They pyrolyzed the PI foams at 250 ˚C, 550 ˚C and 750 ˚C and observed the thermal degradation. They reported that there is no pyrolysis products available at 250 ˚C. This situation states that the polymer chains of that polyimide foam was thermostable. Farrissey et al. [207] reported an isocyanate-based PI foam which exhibited excellent thermal stability and fire resistance. It was exposed to air at 232 °C for 14 days, and it suffered weight losses of less than 2% with no loss in its compressive strength. Similarly, a 6% weight loss was measured in 10 min at 450 °C. In this study, the

curing process of sandwich composites were respectively applied as: at 80 ˚C for 30 min, 150 °C for 30 min, 240 °C for 1 h, 300 ˚C for 30 min and 330°C for 30 min in an air circulation furnace as shown in Figure 3.2.10. Finally, they were post-cured at 300 ˚C for 4 h in the air circulation furnace. After the curing process, the sandwich cores became slightly darker. Nevertheless, in the comparison of the compressive properties of the sandwich cores to those of the PI foams (HDPI and LDPI foams), the sandwich cores exhibited higher mechanical properties. Moreover, it was observed in the DMA of the PI foams that their storage modulus had increasing trends at higher temperatures than their onset temperatures.

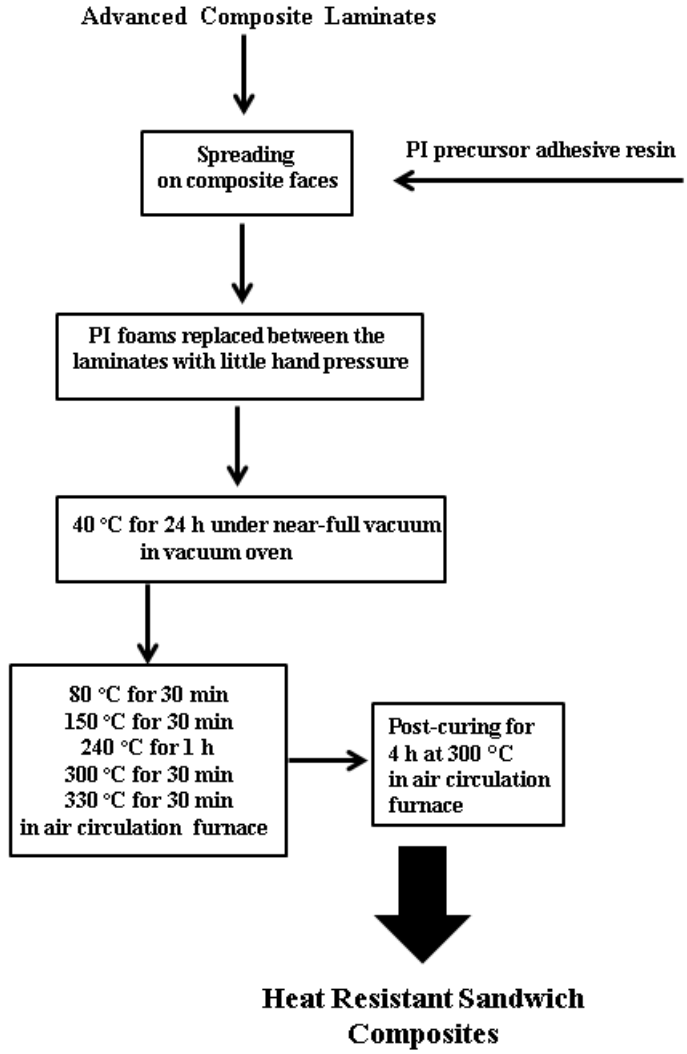


Figure 3.2.9. The manufacturing flow scheme of the HRACSs

The storage modulus curves of these PI foams and the advanced composite laminates are separately shown in Figure 3.2.10, and the analysis results are given in Table 3.2.7 and 3.2.8. It was thought that the remaining by-products such as ureas after the synthesis reactions of the PI foams could be crosslinked with the polymer chains, and the storage

modulus increased.

According to the DMA results of the advanced composite laminates, PAAS-T exhibited a higher storage modulus than PAA-TS up to the onset temperature of PAAS-T. However, PAAS-T showed a sharp decrease at higher temperatures, while PAA-TS exhibited a stable curve. The difference in the trends of the storage modulus curves could be attributed to the thermosetting and thermoplastic properties of the advanced composite laminates.

Table 3.2.8. DMA results of the PI foams and the advanced composite laminates

Samples	Storage Modulus at – 150 °C (Pa)	Storage Modulus at RT (Pa)	The Onset Temperature (°C)	Storage Modulus at Onset Temperature	Storage Modulus at 400 °C (Pa)
LDPI Foam	0.86 E^6	0.74 E^6	239	0.70 E^6	1.36 E^6
HDPI Foam	2.45 E^6	1.92 E^6	231	1.88 E^6	2.22 E^6
PAAS-T	4.75 E^{10}	4.62 E^{10}	288	4.33 E^{10}	1.27 E^{10}
PAA-TS	4.28 E^{10}	4.10 E^{10}	359	3.80 E^{10}	3.79 E^{10}

It is well-known that the crosslinking of polymer chains can provide higher thermo-mechanical properties. While the onset temperature of PAAS-T was 288 °C, the onset temperature of PAA-TS was 359 °C. Moreover, the Tan δ value of PAA-TS was very low. Hence, PAA-TS exhibited an improved storage modulus at higher temperatures than the onset temperatures, even at 400 °C.

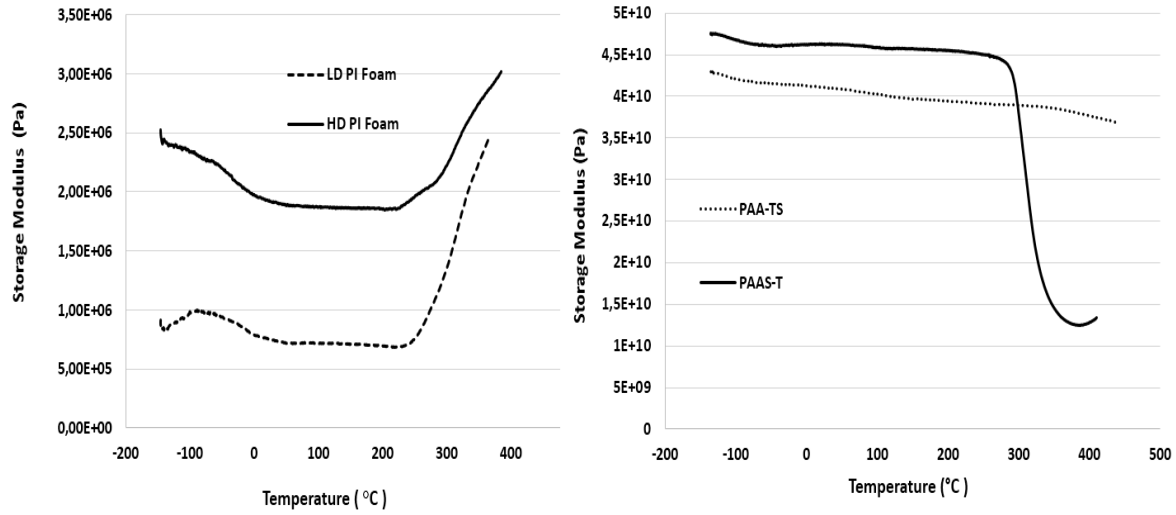


Figure 3.2.10. The storage modulus of the PI foams and the advanced composite laminates

The most important difference between the composite laminates and the PI foams was the opposite trend of the storage modulus curve at higher temperatures than the onset temperatures. As expected, polymers at temperatures close to the Tg (glass transition temperature) value or the Tm (melting temperature) value show a substantial increase in their molecular mobility, and their mechanical properties decrease significantly. This situation was observed in PAAS-T after its onset temperature. PAA-TS was much more stable after the onset temperature due to its crosslinking structure. While the decrease in the storage modulus of PAAS-T from the onset temperature to 400 °C was found as 70%, the decrease in PAA-TS was determined to be 0.26%. In addition to this, the LDPI foam exhibited a storage modulus increase of 94% from the onset temperature to 400 °C, while the LDPI foam exhibited an increase of 18%.

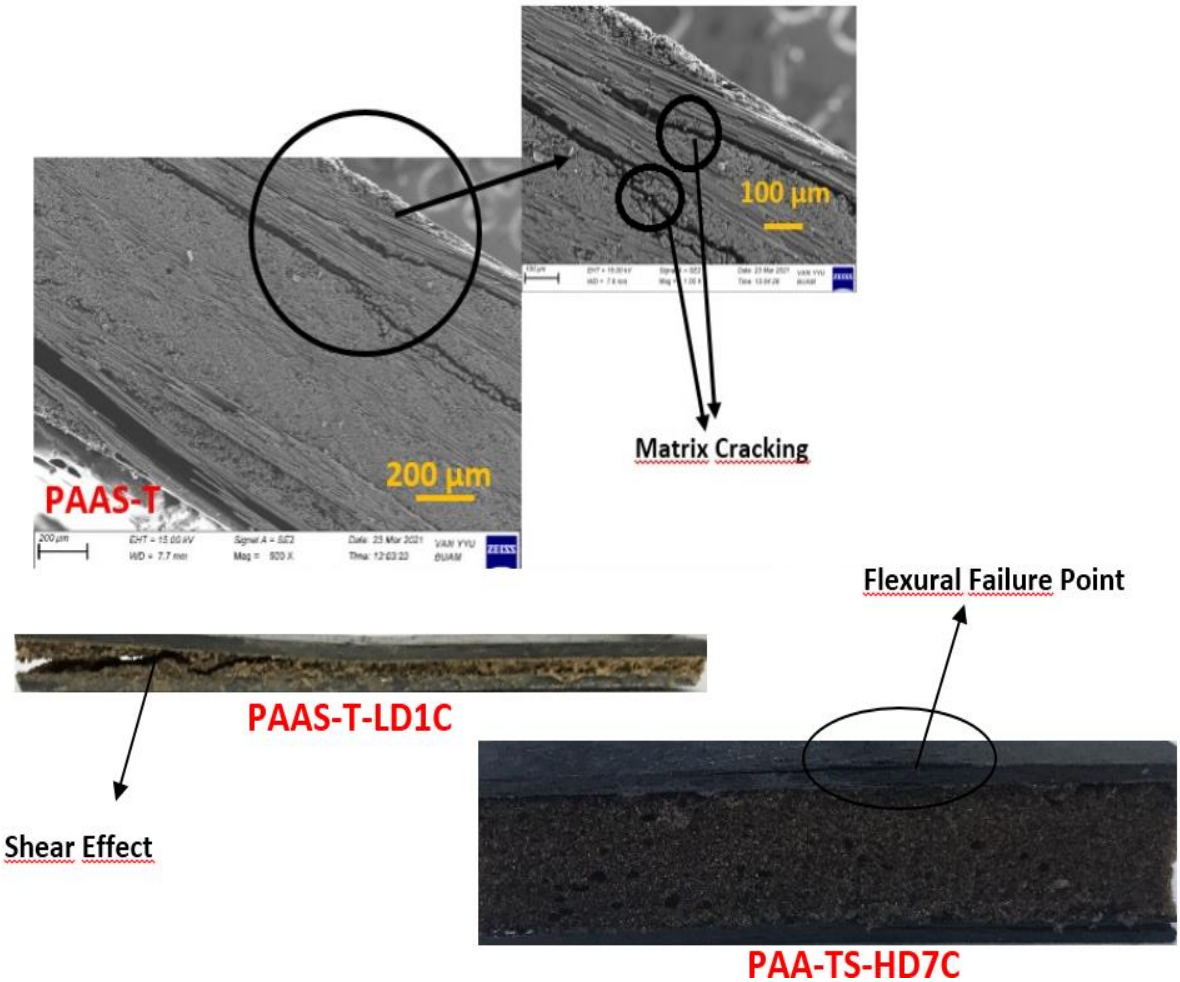


Figure 3.2.11. The SEM images of the PAAS-T advanced composite laminate and the images of some HRACSs

The cross-section of the PAAS-T advanced composite laminate after the flexural test was viewed in the thickness direction by using SEM as shown in Figure 3.2.11. Furthermore,

Figure 3.2.11 shows some photographs of the HRACSs such as PAAS-T-LD1C and PAA-TS-HD7C after the flexural test. The matrix of PAAS-T seemed to have a proper attachment to the fibers (coherence), and the formation of matrix cracking presented shear stress compatibility at the interface of the fiber and the matrix [205]. In the observation of the sandwich cores of the HRACSs, PAAS-T-LD1C exhibited a core shear failure mode, but PAA-TS-HD7C did not exhibit any core shear failure. The fracture failure of PAA-TS-HD7C was observed on the outer face, and the interlaminar cracks were seen.

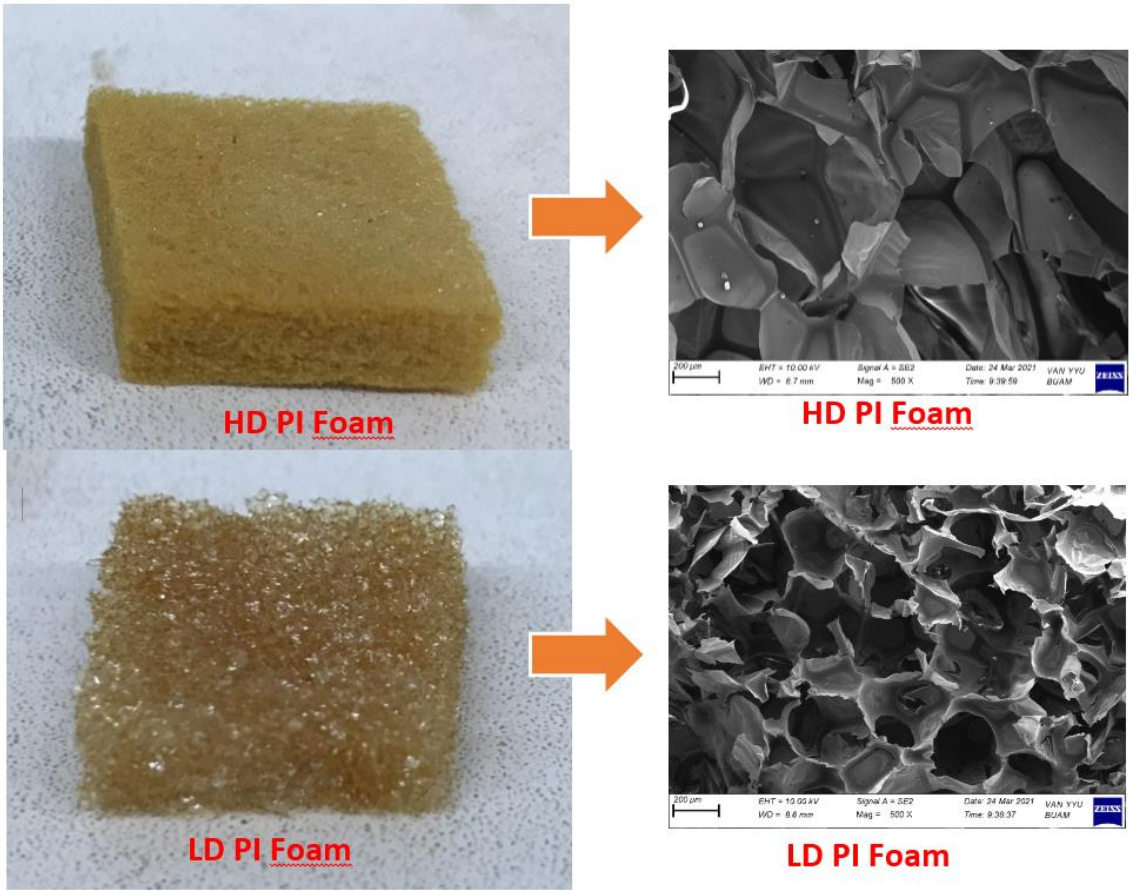


Figure 3.2.12. The pictures and SEM images of the PI foams

Figure 3.2.12 shows the pictures and SEM images of the PI foams. The SEM images indicated that the LDPI foam had more enlarged and destroyed cells than the HDPI foam. The low surfactant amount could have caused the expansion of the CO_2 gas in the cell and exerted pressure on the cell wall. Therefore, the pressure could have destroyed the cells, and in connection to this, the shape and size of the cells may have been changed. The TEA present in the reaction might also have contributed to this result by accelerating the reactions [202].

3.2.5. Conclusion

In this study, heat-resistant polyimide-based advanced composite sandwich panels (HRACS) with different core thickness were prepared. Outer faces were obtained from carbon fiber-reinforced thermoplastic and thermoset polyimide (PI) matrix composites. These PI composites were manufactured by using prepregs that were prepared from PAAS-T and PAA-TS precursor resins. The PAAS-T precursor resin was a poly (amic acid) ammonium salt solution (PAAS) that was prepared with the blocking of the COOH groups on the PAA backbone by using TEA for manufacturing thermoplastic advanced PI composites. The PAA-TS precursor resin was an NA-terminated poly amic acid (PAA) solution that was synthesized according to the molar ratio of PMR-15 for manufacturing advanced thermoset PI composites. Instead of using the MDA monomer in PMR-15, the DADPS monomer was used to synthesize the precursor resins of the advanced thermoplastic and thermoset PI composites. Besides, the thermo-mechanical properties of these advanced PI composite laminates were determined to be outstanding. The manufacturing of the advanced PI composite laminates were achieved with prepregs. These prepregs were prepared by two-step impregnation by applying vacuum at a mild temperature. At the stage of manufacturing, these composite prepregs were vacuum-bagged on a vacuum infusion heating platform at the determined temperatures and process times by applying near-full vacuum. After the vacuum-bagging process, the consolidated prepregs were cured with the compression molding method under a high pressure and at a high temperature. Both of these advanced PI composite laminates exhibited enhanced properties. PAAS-T interestingly showed higher mechanical properties despite its thermoplastic structure. It also exhibited a more enhanced and less decreasing trend of a storage modulus curve up to its onset temperature in comparison to PAA-TS. However, PAA-TS presented outstanding storage modulus values at temperatures higher than 300 °C. As the core materials, two kinds of isocyanate-based PI foams (HDPI and LDPI foam) were prepared by using different process techniques. These foams exhibited different compressive properties and densities. The HDPI foams displayed higher density values and compressive properties than the LDPI foams. In order to manufacture the HRACSs, these core materials and outer faces were bonded with each other by using a synthesized PMR-type adhesive PI resin. This resin was cured and crosslinked between the outer faces and the core materials at high temperatures. As a result of these processes, the HRACSs were characterized by flexural and compression tests. The flexural force values of the

HRACSs were much more enhanced than those of the advanced PI composite laminates. The thin HRACSs exhibited high CSUS and FBS values. On the other hand, the thick HRACSs did not exhibit core shear failure, and thus, their CSUS values could not be calculated. The HRACSs with the PAAS-T composite and HDPI foam exhibited higher mechanical properties. While the HRACSs with the core thickness of 1 mm produced the highest flexural strength and modulus values, those with the core thickness of 2 mm presented the highest flexural force. In compression, HRACSs with the core thickness of 15 mm were prepared, and the properties of the sandwich cores were compared to the properties of the PI foams. The flatwise compressive properties of sandwich cores were higher than these properties of the PI foams. It was thought that the curing regime, especially the high temperatures, could have improved the properties of the PI foams. This thought was brought about by the increasing trend of the storage modulus curves above the onset temperatures. The approach that is presented in this study may contribute to the literature on increasing the mechanical properties of PI foams by using the pyrolysis method, even in atmospheric conditions.

3.3. Thermal properties, Fire resistance and Thermal Insulation Properties of the Components Constituting Heat-resistant Polyimide-based Advanced Sandwich Composites (HRACSs)

3.3.1. Introduction

As mentioned, HRACSs were prepared from CF reinforced thermoset and thermoplastic PI matrix advanced composite faces and isocyanate based PI foams. Among these composite faces, PAA-TS as thermoset composite face and PAAS-T as thermoplastic composite face were became prominent in terms of their properties. Moreover, isocyanate based PI foams (LDPI and HDPI foams) present satisfactory mechanical properties besides low densities. As mentioned in the previous sections, DADPS was used to enhance the thermal properties of the PI composites and the synthesized PI adhesive resin. The polymer backbones of these PI precursors contained the BTDA and DADPS monomers. Huo et al. [169] prepared a thermoplastic adhesive PI film, and they used DADPS to improve the thermal properties of the adhesive PI film. In this section, thermal properties, flame reterdancy and thermal insulation properties of these components (PAA-TS and PAAS-T composite faces; LDPI and HDPI foam cores) constituting the HRACSs were

investigated in detail. DMA of the PI foams and composite faces at certain frequencies was carried out to observe the alteration of the modulus with an increase in the temperature. DSC and TGA were carried out for measuring thermal stability and transition temperature peaks. Thermal conductivity analysis was carried out to evaluate thermal insulation. LOI (Limiting Oxygen Index) and UL94 tests were carried out for measuring fire resistance and flame retardancy. These components of the HRACSs exhibited outstanding and attractive thermal properties.

3.3.2. Measurements

DMA is used to observe thermo-mechanical properties of a material in different frequencies. Heating rate was 5 ˚C / min starting from -150 ˚C up to 400 ˚C. The composite samples were run at a frequency of 1 Hz in the dual cantilever bending mode. The values and curves of Tan δ and storage modulus were observed. The thermal conductivity coefficient and effusivity of the advanced composite laminates (PAAS-T and PAA-TS) and the PI foams (HDPI foam and LDPI foam) that formed the HRACSs were separately measured by a C-Therm TCI 2A conductivity analyzer. These measurements were carried out at ambient temperature. TGA of the PI foams and the PI matrix of the advanced composite laminates were performed using a TA Instruments Q50 model TGA device with differential thermal analysis (DTA). The samples were run from 30 °C to 800 °C. Heating rate was 10 °C / min in nitrogen atmosphere. The TGA samples of the PI matrix of the advanced composite laminates were prepared as film according to the process parameters of the vacuum bagging and compression molding processes such as time and temperature. On the other hand, the obtained PI foams (HDPI foam and LDPI foam) were crushed and obtained as powder. These powders were also used as the TGA samples for the PI foams. DSC characterization is a function of the absorption of heat change and temperature. This test was applied with a 10 °C/min heating rate up to 450 °C to determine the transitions of the PI foams and the PI matrix of the advanced composite laminates. Fire resistance and flame retardancy were determined by LOI and UL94 vertical burning tests for the PI foams and the advanced composite laminates.

3.3.3. Results and discussion

As mentioned, the prominent thermoplastic and thermoset composite face and the PI foam components of the HRACSs were thermally investigated in detail. This is very important

to use HRACSs in high temperature applications. Some datas in DMA analysis of PI matrices of the composite faces and the PI foams, the TGA datas of the PI matrices of the composite faces were also given in the previous studies in 3.1 and 3.2 sections.

The thermal properties of all components that were used in the HRACSs were investigated in detail. As mentioned, two kinds of CF-reinforced PI matrix advanced composite laminates were manufactured as thermoplastic and thermoset composites to be used as the outer faces. As also mentioned, two kinds of isocyanate-based PI foams were prepared as the core materials. These components were all characterized by DMA, TGA and DSC. The thermal conductivity coefficient and effusivity of the samples were also measured. Fire resistance and flammability were determined by LOI and UL94 vertical burning tests for the PI foams and the advanced PI composite laminates.

DMA is an important device in order to observe thermo-mechanical properties of materials. As mentioned, Tan δ value means the division of loss modulus (E″) to the storage modulus (E′). For this reason, when the E″ value decreases rapidly, the Tan δ value makes a peak simultaneously. The temperature value of this peak is termed as glass transiton temperature (Tg) region of the polymers. The Tan δ value indicates the dissipation of energy derived from the chains of polymer. The peak value of Tan δ also indicates the damping property of materials. The viscoelasticity of the PIs was observed with loss tangent (Tan δ) measurements. When Tan δ is bigger than 1, materials exhibit behavior like viscoelastic liquid. Moreover, when Tan δ is lower than 1, they can exhibit behavior like viscoelastic solids [170].

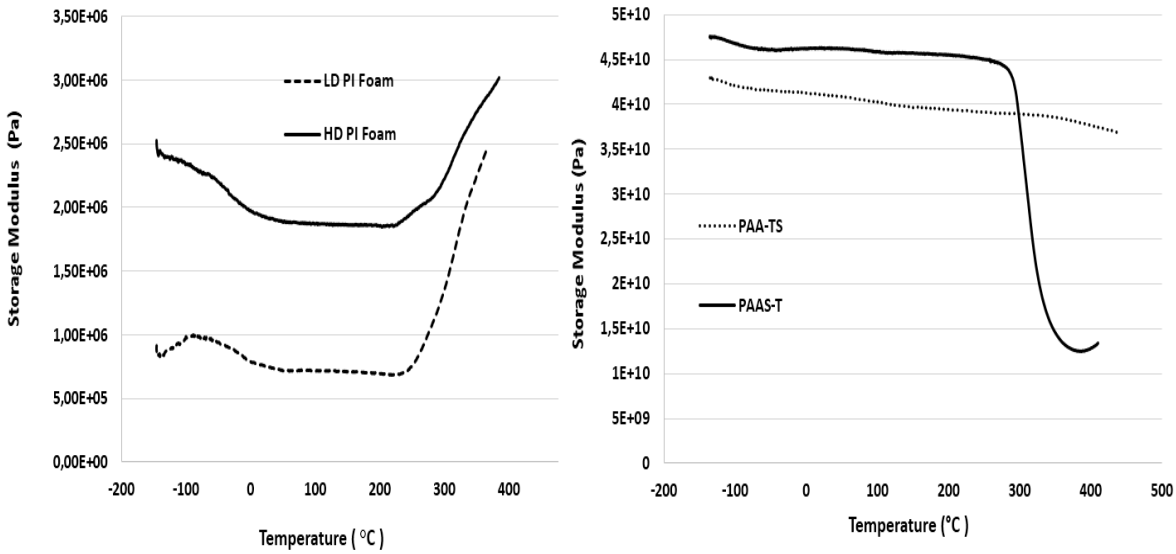


Figure 3.3.1. The storage modulus of the PI foams and the advanced composite laminates

It is known that PIs have high performance properties under high-temperature and cryogenic conditions. Fiber-reinforced composites, foams and sandwich panels have been exposed to dynamic loads at different frequencies and temperatures in their application areas. Because of these reasons, the advanced composite laminates and the PI foams were characterized by DMA to determine their thermal and mechanical stability values at a 1 Hz frequency from -150 °C to 400 °C. Storage modulus and Tan δ values were observed for this study. The onset temperature on the storage modulus curve for the thermoset advanced composite laminate (PAA-TS) was substantially higher than the thermoplastic advanced composite laminate (PAAS-T). While the storage modulus curve of PAAS-T exhibited a sharp decrease above 288 °C, the storage modulus curve of PAA-TS did not present a distinct sharp decrease as shown in Figure 3.3.1. The onset temperature values of the advanced composite laminates are given in Table 3.3.1. PAA-TS exhibited a very small Tan δ peak that was not distinct above 359 °C. The damping coefficient values of Tan δ (DCT) also confirmed this situation. This was because the DCT for PAA-TS exhibited very low values as 0.03 and 0.04, while the DCT values of PAAS-T were 0.20 as given in Table 3.3.2 and shown in Figure 3.3.2. It was thought that crosslinking could have restricted the movements of the molecular chains substantially. Therefore, segmental motion and relaxation could only occur at high temperatures, and the DCT value of PAA-TS was much lower. Hence, the sample's thermo-mechanical properties were more enhanced at high temperatures (above the onset temperature value of PAAS-T) [180,197]. PAA-TS was much more stable above the onset temperature value due to its crosslinking structure. While the decrease in the storage modulus of PAAS-T from the onset temperatures to 400 °C was found as 70%, the decrease for PAA-TS was determined as 0.26%. These results exhibited the usage possibility of PAA-TS at very high temperatures as 400 °C.

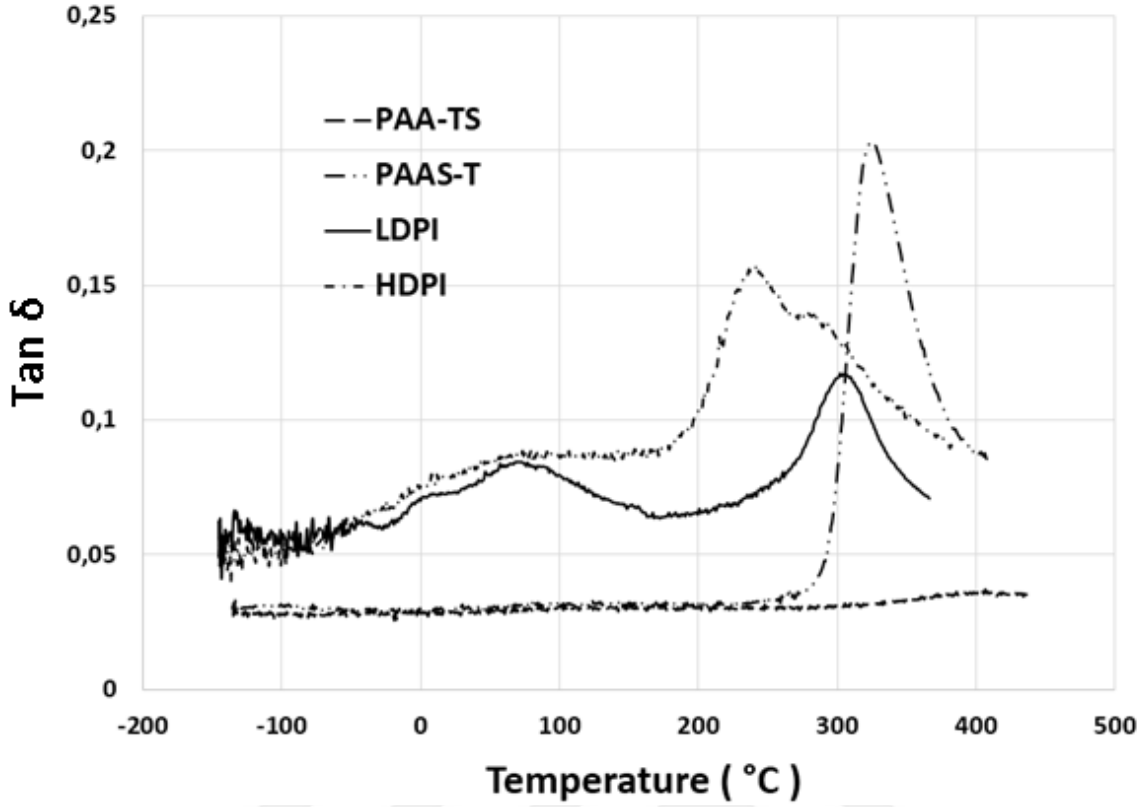


Figure 3.3.2. Tan δ curves of the advanced PI composite laminates and the PI foams

Moreover, the storage modulus value of PAAS-T from RT to the onset temperature showed a decrease of 6.2%, while that of PAA-TS showed a decrease of 7.3%. PAAS-T exhibited more improved thermo-mechanical properties than PAA-TS from RT to their respective onset temperatures. It is known that the modulus of elasticity of materials generally increases when their temperature decreases. Thus, the material generally displays brittleness in cryogenic conditions. In order to minimize these adverse conditions for a material, a little increase in the stability of the modulus for media with very low temperatures has importance. According to the results of the observation of the storage modulus of the advanced composite laminates from RT to -150 °C, both advanced PI composite laminates exhibited a little increase from RT to -150 °C. While the storage modulus of PAAS-T showed an increase of 2.8%, that of PAA-TS showed an increase of 4.3%. PAAS-T exhibited a more stable behavior than PAA-TS in the cryogenic medium.

Table 3.3.1. DMA results of the PI foams and the advanced composite laminates

Samples	Storage Modulus at – 150 °C (Pa)	Storage Modulus at RT (Pa)	The Onset Temperature (°C)	Storage Modulus at Onset Temperature (Pa)	Storage Modulus at 400 °C (Pa)
LDPI Foam	0.86 E^6	0.74 E^6	239	0.70 E^6	1.36 E^6
HDPI Foam	2.45 E^6	1.92 E^6	231	1.88 E^6	2.22 E^6
PAAS-T	4.75 E^{10}	4.62 E^{10}	288	4.33 E^{10}	1.27 E^{10}
PAA-TS	4.28 E^{10}	4.10 E^{10}	359	3.80 E^{10}	3.79 E^{10}

In the analysis on the PI foams, the storage moduli of the PI foams were much lower than those of the advanced composite laminates as expected. The most important differences of the PI foams from the advanced composite laminates were the increases in their storage moduli at higher temperatures than the onset temperatures contrary to what is commonly expected. As well known, polymers at close temperatures to Tg or Tm (melting temperature) show a substantial increase in their molecular mobility, and their mechanical properties decrease prominently. Hence, it was expected that the storage moduli of the PI foams would decrease. Nevertheless, the opposite behavior was observed.

While the HDPI foam exhibited an increase of 94% in its storage modulus from the onset temperatures to 400 °C, the LDPI foam exhibited an increase of 18%. It was thought that these increases could have been caused by the crosslinking of the isocyanate-based PIs at high temperatures. These PI foams could have been partially degraded. The curing temperatures of 300 °C and 330 °C could affect the properties of the PI foams. The TGA results also showed small decreases from the initial decomposition temperatures to the curing temperatures as 300 °C. It was thought that these decreases in TGA could have been derived from the vaporization of by-products, the low amount of remaining molecules and degraded small molecules.

Table 3.3.2. DSC, thermal conductivity and Tan δ values of the PI foams and the advanced composite laminates

Samples	DMA		DSC	Thermal Conductivity	
	Damping Coefficient Values (Tan δ)	Tan δ Tg (°C)	Peak Temperature (°C)	TCC k(W/m.K)	Effusivity (Ws½/m²K)
LDPI Foam	0.11	305	313-430	0.031	29
HDPI Foam	0.15	239-280	294-401	0.033	39
PAAS-T	0.20	324	428	0.552	923
PAA-TS	0.03	412	410-430	0.586	956

Degradation reactions or by-products such as ureas could cause the crosslinking of the PI foams at high temperatures. In the comparison of the compressive properties of the PI foams and the flatwise compressive properties of the HRACSs, the flatwise compressive strengths and moduli of the HRACSs increased in the previous section of 3.2. Hence, it was thought that the compressive properties of the PI foams could have been improved by the curing process parameters.

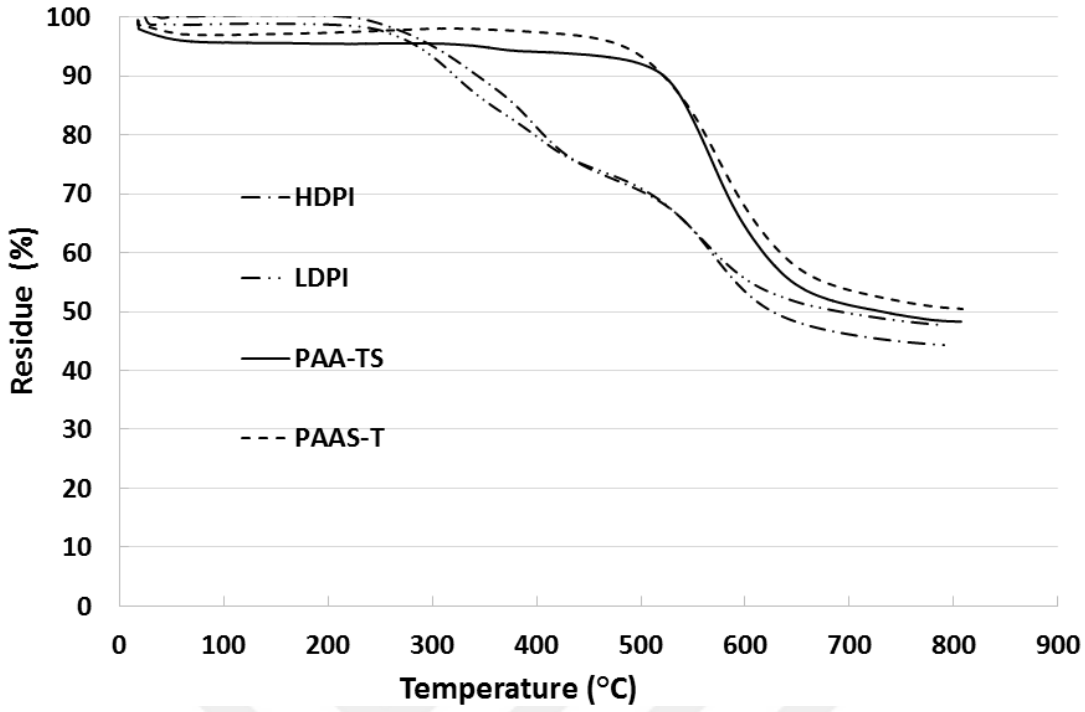


Figure 3.3.3. The TGA curves of all components

The PIs show high thermal stability due to their heterocyclic and rigid structures. TGA is an important analysis method for assessing thermal stability. The initial decomposition temperature (IDT), 5% and 10% weight decomposition temperature (T_{d5}, T_{d10}) and char yield at 800 °C were observed by TGA. The TGA curves are shown in Figure 3.3.3, and these values are given in Table 3.3.3. The PI matrix of the advanced PI composite laminates and the PI foams had high thermal stability. As expected, the PI matrix of the advanced composites displayed much more enhanced thermal stability values in comparison to the PI foams. This was because diamine-based PIs generally present much higher thermal properties than isocyanate-based PI foams.

Table 3.3.3. The TGA results of all components

Samples	Initial Decomposition Temperature (°C)	5% Weight Decomposition Temperature (T_{d5}, °C)	10% Weight Decomposition Temperature (T_{d10}, °C)	Char Yield at 800 °C (%)
PAAS-T	500	509	554	48
PAA-TS	512	500	538	46
LDPI	270	296	330	46
HDPI	262	303	344	44

The PI matrix of the composite laminates showed improved IDT results at temperatures higher than 500 °C. While PAA-TS had an IDT value of 512 °C, PAAS-T had an IDT value of 500 °C. Contrary to the IDT values, the T_{d10} and T_{d5} values of PAAS-T were slightly higher than those of PAAS-T. While PAAS-T had a T_{d10} value of 554 °C, PAA-TS had a T_{d10} value of 538 °C. The PI foams had much lower TGA values than the composite laminates. While the HDPI foam had an IDT value of 262 °C, the LDPI foam had an IDT value of 270 °C. The T_{d10} and T_{d5} values of the HDPI foam were 303 °C and 344 °C, and those of the LDPI foam were 296 °C and 330 °C, respectively. However, the char yields were different between the PI foams and the PI matrix of the composite laminates, as opposed to the case in the IDT, T_{d10} and T_{d5} values. The char yield values of all components were close to each other. Çakir et al. [208] produced graphene oxide-containing isocyanate-based PI foams with enhanced thermal stability and flame retardancy. In comparison to the PI foams in their study, the IDT values in the TGA in this study exhibited similar results to those of graphene oxide-containing isocyanate-based PI foams. On the other hand, the char yields and flame retardancy (according to LOI values) of the PI foams in Çakir et al.'s study were more enhanced than the PI foams in this study.

The DSC curves of all components are shown in Figure 3.3.4, and the approximate values of these are given in Table 3.3.2. While the PI matrix of the advanced composite laminates showed peaks above 400 °C, the PI foams exhibited various broad peaks around and below 300 °C. PAA-TS showed two distinct peaks at 410 °C and 430 °C, whereas PAAS-T showed one distinct peak at 428 °C. The peak at 410 °C belonging to PAA-TS was broad. Except for the HDPI foam, all samples exhibited a sharp and small peak above 400 °C and a similar curve trend. However, the HDPI foam showed a very broad peak above 400 °C and a substantial exotherm curve trend between 250 °C and 350 °C.

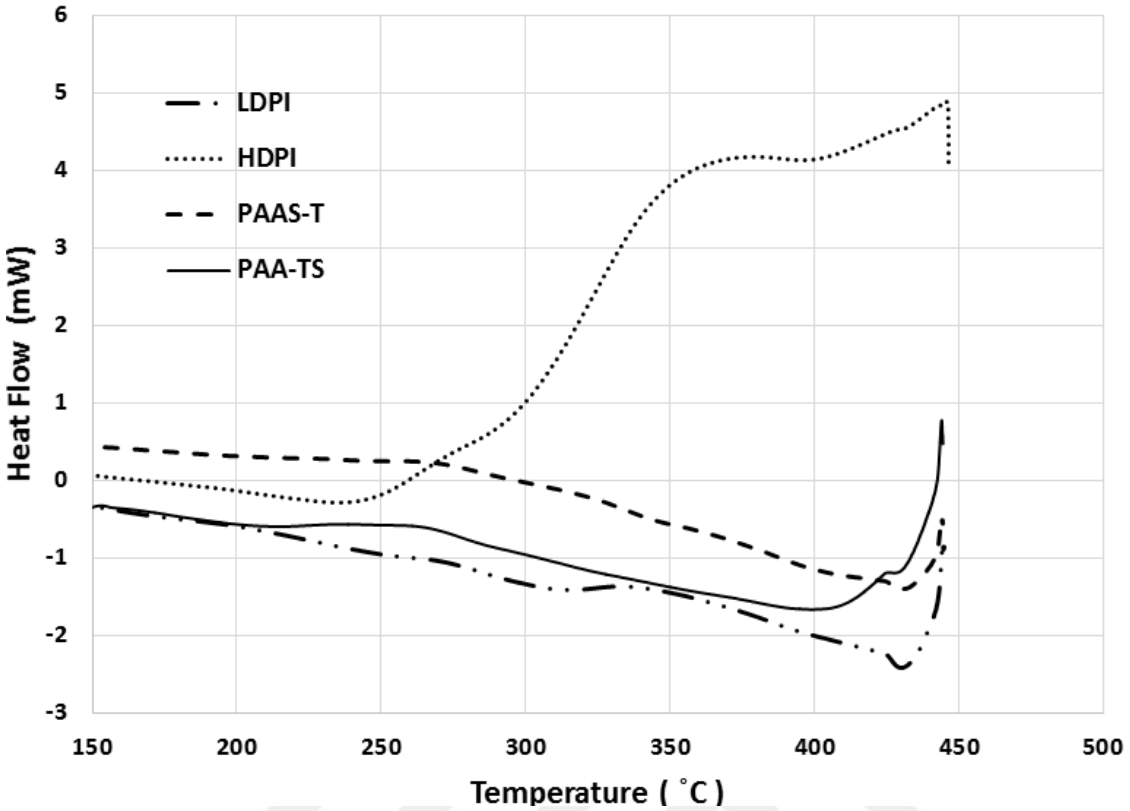


Figure 3.3.4. The DSC curves of all components

Thermal insulation is a very important property for sandwich panels, and preferable insulation materials should have the lowest thermal conductivity in order to decrease heat transmission coefficient. Thermal conductivity is the intrinsic property of a material. This property is affected by thermal conductivity coefficient of the material. In terms of achieving low thermal conductivity values, porous materials, such as foams, mineral wool and concrete, have become prominent. Nevertheless, materials such as mineral wool and concrete that can be used at high temperatures for thermal insulation have high densities compared to polymers. Accordingly, PI foams have substantial importance for high-temperature insulation up to 300 °C. As mentioned above, the sandwich panels manufactured in this study (HRACSs) consisted of two different outer faces (PAAS-T and PAA-TS composites) and two different core components (LDPI and HDPI foams). The thermal conductivity values of all components were measured and are given in Table 3.3.2. As expected, the PI foams exhibited a much smaller thermal conductivity coefficient compared to the advanced composite laminates. For foam materials, higher numbers of cells (which can provide stagnant gas) and smaller sizes indicate lower thermal conductivity values desirable in insulation materials [209, 210]. As seen in the thermal conductivity coefficient data in Table 3.3.2., the LDPI and HDPI foams had coefficients of

0.031 and 0.033 W/m.K, respectively. The thermal conductivity coefficients of PAAS-T and PAA-TS were respectively 0.552 and 0.586 W/m.K. The CF-reinforced PI matrix advanced composite laminates had results that were very close to each other. The PI foams also had very close results to each other. While the LDPI foam had a density of 15 kg/m^3, the HDPI foam had a density of 50 kg/m^3. However, the density difference between the PI foams did not significantly affect their thermal conductivity. It was thought that this situation could be attributed to the difference in the closed cell ratios of the PI foams, because unconnected closed microcells reduce thermal conductivity significantly [209, 210]. Figure 3.2.12 in the section of 3.2 shows the pictures and SEM morphologies of the LDPI and HDPI foams. The LDPI foam presented larger numbers of more interconnected open cells compared to the HDPI foam in their SEM morphologies. On the other hand, these measured thermal conductivity coefficients of the PI foams were highly enhanced values compared to other insulation materials that have been reported in the literature. For instance, Resewski and Buchgraber [211] developed diamine-based PI foams with high and low densities (7kg/m^3 to 300 kg/m^3). They produced diamine based PI foams by using diamines and dianhydrides and their esterified derivatives such as ODPA, BTDA, PMDA, ODA, PDA, DADPS. They reported outstanding thermal properties. The thermal conductivity coefficients of these synthesized diamine-based PIs were around 0.09 W/m.K. Another issue is effusivity, which is the rate at which a material can absorb heat. It was also measured in our study. It has also been known as the heat penetration coefficient. It determines the contact temperature of both bulk materials touching each other. While the LDPI foam and HDPI foam had effusivity coefficients of 29 and 39 Ws½/m²K, PAAS-T and PAA-TS had effusivity coefficients of 923 and 956 Ws½/m²K, respectively.

Table 3.3.4. The UL94 and LOI results

Samples	LOI (%)	UL94 Test	Total Burning Time (s)	Dripping
PAAS-T	>50	V0	-	None
PAA-TS	>50	V0	-	None
LDPI Foam	25-30	V0	-	None
HDPI Foam	25-30	V0	-	None

In order to measure flame retardancy and fire resistance, the UL94 vertical burning test and LOI analysis were carried out for the advanced composite laminates and the PI foams. The UL94 V rating method evaluates the self-removing time of polymer specimen. The polymer specimen is entegrated in the aparatus vertically. The bottom of the sample is burned and the behavior of the fire is observed such as dripping and burning time. There are three rating levels for the tested materials as V0, V1 and V2, and the explanations of these ratings are shown below. V0 is the best rating of all.

- V0: if fire blows out without dripping within 10 seconds
- V1: if fire blows out without dripping within 30 seconds
- V2: if fire blows out with dripping within 10 seconds

The vertical burning UL94 method of all samples presented a rating of V0. However, the LOI results were different between the advanced composite laminates and the PI foams. LOI is measured by finding the minimum oxygen concentration of oxygen and it is stated as percentage. It is well-know that oxygen affect positively the combustion of polymer. In this method, a mixture of nitrogen and oxygen gases are passed through in tunnel that polymer specimen was taken placed. And oxygen concentration of this mixture is adjusted and the minimum oxygen concentration is found to burn the polymer. While the LOI results of the PI foams were between 25% and 30%, the advanced PI composite laminates exhibited values higher than 50%. All samples showed outstanding results in terms of flame retardancy and fire resistance. These values are given in Table 3.3.4.

3.3.4 Conclusion

In this section, the thermal properties, fire resistance and fire reterdancy of some prominent components of the HRACSs were investigated in detail in addition to the results

in the sections of 3.1 and 3.2. As mentioned before, the prominent composite outer faces of the HRACSs were obtained from 2x2 twill CF fabric-reinforced thermoplastic and thermoset PI matrix composites. These matrix composites were diamine-based PIs that were synthesized from PAAS-T and PAA-TS precursor resins. The PAAS-T precursor resin was prepared with the blocking of the COOH groups on the PAA backbone by using TEA. The PAA-TS precursor resin was prepared as a NA-terminated PAA in DMF solvent according to the molar ratio of PMR-15. BTDA and DADPS were used for the PAA backbone, and NA was used as a crosslinking and end capper agent. The DADPS monomer was used to synthesize the PAAS-T and PAA-TS precursor resins instead of the MDA monomer used in PMR-15. It was thought that DADPS contributed to obtain high thermal properties. As the core materials, two types of isocyanate-based PI foams (HDPI and LDPI foams) were prepared by using different amounts of surfactant, water and TEA, as mentioned before. These foams had different densities as 50 kg/m^3 and 15 kg/m^3. In order to bond the outer faces and the core materials to each other, a PMR-type adhesive PI resin was synthesized. By means of curing and crosslinking this resin between the outer face and the core components, the HRACSs were obtained. For these reasons, the detail investigation on the thermal properties of these components was very important because of their uses in high temperature applications. Moreover, thermal characterization of PI matrices is also very important for the using PI adhesive resin. Thermo-mechanical properties were evaluated by DMA, and the results were outstanding. As expected, the DMA results of the advanced composite laminates were much more enhanced than those of the PI foams. The storage modulus of PAAS-T was higher values up to its onset temperature (288 °C) than that of PAA-TS. However, PAAS-T showed a sharp decrease at its onset temperature, and PAA-TS did not show a distinct decrease. PAA-TS showed a high storage modulus at even 400 °C due to its crosslinking structure. Its damping coefficient of 0.03 confirmed this situation. PAAS-T and PAA-TS presented outstanding Tg values as 324 °C and 412 °C, respectively. On the other hand, the PI foams exhibited lower Tg values between 240 °C and 300 °C in DMA. Their storage moduli were interestingly higher at temperatures higher than their onset temperatures. DSC properties were evaluated for the PI matrix of the advanced composite laminates and the PI foams. While the PI matrix of the composite laminates showed peaks above 400 °C, the PI foams exhibited various broad peaks around and below 300 °C. As expected, the diamine-based PI matrix of the composite laminates showed higher DSC peaks than the isocyanate-based

PI foams. The thermal stability values of the components were observed by TGA. While the IDT values of the composite laminates were higher than 500 °C, the PI foams provided values of 262 °C and 270 °C. Still, the char yields of all components were very close, ranging between 44% and 48%. In order to evaluate thermal insulation, TCC and effusivity values were observed. The PI foams provided outstanding TCC values as 0.031 W/m.K and 0.033 W/m.K. LOI and UL94 test were carried out to observe flame retardancy and fire resistance for both the composite laminates and the PI foams. The vertical burning UL94 test of all samples showed the best rating, i.e., V0. The LOI results were different between the advanced composite laminates and the PI foams. However, all LOI values were high (higher than 21% O_2). While the advanced composite laminates exhibited values higher than 50%, the PI foams had values between 25% and 30%.

4. CONCLUSION

This study presents heat-resistant polyimide based advanced composite sandwich panels (HRACSs) consisting of carbon fiber reinforced PI matrix thermoset and thermoplastic advanced composite laminates (outer faces) and PI foams (core materials). CF-reinforced thermoset and thermoplastic PI matrix advanced composite laminates were manufactured by synthesizing various PI precursors. These precursors were synthesized as poly (amic acid), poly (ester amine) salt and poly (amic acid) ammonium salt. By using these PI precursors, thermoplastic and thermoset advanced composite faces were obtained. The poly (amic acid) ammonium salt precursor resin was applied as a novel method for manufacturing these advanced composites. The thermoplastic composite obtained from the ammonium salt precursor exhibited superior mechanical properties and enhanced thermal properties in comparison to the other advanced composites in this study and those in the literature. On the other hand, the thermosetting composites exhibited highly enhanced storage modulus values up to 400 ˚C and outstanding thermal stability. The thermosetting composite that was obtained from the nadic anhydride terminated poly (amic acid) precursor exhibited high mechanical properties besides its thermal properties. These two advanced composites became prominent and were used for outer faces of the heat resistant sandwich composites. The heat resistant sandwich composites had also two kinds of core materials with low densities. Isocyanate-based PI foams were synthesized and used as core materials. These foams presented different and satisfactory compressive properties. Moreover, these foams exhibited outstanding thermal insulation values. In addition to this, thermosetting adhesive polyimide precursor resin was synthesized to bond these produced outer faces and cores. These heat-resistant sandwich composites exhibited high compressive and flexural properties. Table 4.1 presents a summary table giving prominent results of all components of heat-resistant sandwich composites and makes a comparison to prominent studies in literature.

Table 4.1. Summary of prominent experimental results for all components of heat-resistant sandwich advanced composite panels and comparison to prominent studies in literature

Products	Product Detail	Tan δ Tg (°C)	Tan δ Coefficient	Thermal Conductivity (k(W/m.K)	Compressive Strength (KPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Tensile Strength (MPa)	Density (g/cm^3)
Advanced Thermoplastic Composite Face	**This study (PAAS-T)**	324	0.2	0.552	-	940	97	-	1.44
Advanced Thermoset Composite Face	**This study (PAA-TS)**	413	0.03	0.586	-	921	73.3	-	1.5
Advanced Thermoset Composite	CF/RP46 (improved PMR) with VARTM [29]	355-368	0.9-0.12	-	-	-	-	314	-
Advanced Thermoset Composite	CF/DMBZ-15 for high Tg PMR [12]	425	0.1	-	-	1027	58	-	-
Advanced Thermoset Composite	CF/PMR-15 [11]	375	0.1	-	-	1080	58	-	-
Core Material	**This study (LDPI Foam)**	305	0.12	0.031	23.7	-	-	-	0.015
Core Material	**This study (HDPI Foam)**	239-280	0.16	0.033	43.4	-	-	-	0.050
Core Material	Polyimide Foam [155,203]	-	-	-	47.5-25	-	-	-	0.016-0.012
Core Material	Polyimide Foam [211]	-	-	0.09	-	-	-	-	0.012
Heat resistant Sandwich Composite	**This study (PAAS-T-HD1C and PAAS-T-HD15C)**	-	-	-	95.4 (15C)	244 (1C)	14.7 (1C)	-	-

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Articles Published in Journals That Entered SCI, SSCI and AHCI Indexes

- Çakır, M., Akın, E. (2022). Characterization of carbon fiber-reinforced thermoplastic and thermosetting polyimide matrix composites manufactured by using various synthesized PI precursor resins. Composites Part B: Engineering, 231, 109559.
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