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Development of sustainable bio-based photocurable coatings on aluminum alloy surfaces

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Abstract The aim of this study is the development of photocurable phosphorus-containing coatings based on soybean oil as a promising green alternative with higher bio-content to conventional heat and VOC-based metal coatings. Considering this aim, acrylic acid (AA) and a reactive monomer containing phosphorus (Sipomer PAM-200) reacted with the epoxide groups of epoxidized soybean oil (ESBO). The synthesized AA modified ESBO (A-ESBO) and Sipomer PAM-200 modified ESBO (S-ESBO) oligomers were then chemically characterized using Fourier transform infrared and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. Photocured free films of these oligomers were evaluated by means of hardness, mechanical, and thermal properties. Coatings were formulated by using the synthesized oligomers, photoinitiator, and reactive diluents with various functionalities, then applied on iron–silicon–aluminum (Al) alloy surfaces, and cured by UV-light. The coating quality was evaluated by contact angle, water resistance, gloss, hardness, and abrasion resistance tests. The overall findings demonstrated that adding more phosphorus-containing oligomer (S-ESBO) to the coating formulation improved the thermal stability, tensile, modulus, and hardness values. This can be attributed to a number of factors, including the presence of polar hydroxyl groups in phosphate ester, the penta polypropylene glycol groups of the phosphorus-containing oligomer, and an increase in the crosslinking density of the polymeric network.

Keywords Photocuring, Metal coating, Phosphorus, Soybean oil, Aluminum layer

Introduction

Surface coatings on various types of substrates, such as metal, wood, glass, and fabric, must show the required protective properties against water, air, chemicals, corrosive media, bacteria, and scratching, based on the usage area.[1] Among all coatings, metal coatings are extensively being used in various applications, such as aerospace, automotive, marine, and oil/gas industries, due to their excellent mechanical properties, corrosion resistance, and esthetic appeal.[2] However, the conventional metal coatings require the usage of petrochemicals, thermal energy, and toxic/hazardous volatile organic compounds (VOCs), which pose serious health and environmental risks. Therefore, there is an urgent need to develop environmentally friendly, solventless, low-temperature curable, bio-based metal coatings having the required coating properties in order to be used as a sustainable alternative to the conventional metal coatings.[3–5]

In this context, photocurable coatings have emerged as a promising alternative to the traditional coatings due to their eco-friendliness, ease of application, and

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fast curing properties. The photocurable coatings can be cured using UV radiation, which eliminates the need for organic solvents and reduces the curing time. Furthermore, the incorporation of phosphorus-containing materials into the photocurable coatings can enhance the thermal, anticorrosive, and mechanical degradation properties due to the inorganic nature of phosphorus groups and their action as an adhesion promoter.[6,7] In a previous study, self-photocurable polyurethane acrylate oligomer was synthesized by Michael addition reaction and then included in metal coating formulations for home appliances. The results showed that the best physical properties, including adhesion, bending, and hardness, were recorded when the reactive diluent (ethoxylated trimethylolpropane triacrylate) ratio was lower than 10%.[8] In another study, maleic acid capped trianiline was synthesized and included in photocurable formulations together with an aromatic hexafunctional acrylate and photoinitiator. Formulations were applied on carbon steel surfaces to obtain an electroactive corrosion resist property. After electroactive oligoaniline was added to coating formulations, a corrosion protection efficacy of over 99% was found.[9] In order to protect the hull of the ship from corrosion by seawater media, photocurable coating formulations were prepared by using siloxane epoxy resin, bisphenol-A epoxy resin, and photoinitiator. By changing the amount of siloxane epoxy resin, coating formulations were applied on galvanized steel surfaces, and the best corrosion resistance result of 28 days in 3 M NaCl solution was recorded with 15% siloxane epoxy inclusion.[10] The use of petrochemicals is necessary for all of the above photocurable metal coating investigations, which is a serious disadvantage in terms of environmental concerns.

After various chemical modifications, vegetable oils can be used as a resource alternative to the petrochemical compounds. The popularity of soybean oil among vegetable oils is a result of its affordability, abundance, and low toxicity. It also has five unsaturated groups on its chemical structure, which allow it to interact with various substances to form polymers with the appropriate functionality.[11,12] Epoxidation, which is carried out by hydrogen peroxide initiated by a catalyst, is the most often used reaction in the modification of soybean oil. The generated oxirane ring can then be used in other chemical reactions to give the desired functionality to the polymer.[13] In the literature, the epoxide group of epoxidized soybean oil (ESBO) has been chemically modified by some chemical compounds such as acrylic acid, vinyl phosphonic acid, and methacrylic acid, in order to be used for various purposes including textile finishing agent, wood coating, oligomer branching, and flame resist coatings.[14]

In this study, soybean oil-based sustainable photocurable oligomers were synthesized and used in coatings in the presence of different types of reactive diluents for Al alloy surfaces. The effects of the phosphorus-containing oligomer amount in the formulation on the quality of the metal coatings including hardness, gloss, surface wettability, abrasion resistance, and rust formation in water were all reported. The results demonstrate that the soybean oil-based photocurable phosphorus-containing coatings exhibit acceptable coating performances with enhanced gloss, hardness, water, and abrasion resistance properties, which make them a promising green alternative with higher bio-contents to the traditional heat and VOC-based metal coatings.

Experimental

Materials

Iron–silicon–aluminum alloy plates with 0.8 mm thickness, 150 mm length, and 75 mm width were supplied from Guray Aluminum Marketing Industry Trade Ltd., Co., Kocaeli, Turkey. 1-Vinyl-2-pyrrolidone (NVP, reactive diluent), trimethylolpropane triacrylate (TMPTA, reactive diluent), acrylic acid (AA), 1,6-hexanediol diacrylate (HDDA, reactive diluent), ESBO (MW = 952 g/mole, EEW = 232 g/equiv.), triphenylphosphine (TPP, catalyst), phenolphthalein (indicator), hydroquinone (HQ, inhibitor), potassium hydroxide (KOH), and ethanol were all purchased from Merck and used as received. 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184®, photoinitiator) was procured from Ciba. A specially designed phosphorus-containing methacrylate functional chemical, namely, penta polypropylene glycol (PPG) monomethacrylate phosphate (Sipomer PAM-200) was procured from Solvay.

Synthesis of the oligomer

In this study, two different oligomers were synthesized with the reaction of ESBO and AA (A-ESBO) and ESBO and Sipomer PAM-200 (S-ESBO), respectively. The A-ESBO oligomer was synthesized according to the following procedure. First, ESBO and AA were mixed, and then 30% HDDA, 300 ppm HQ, and 1000 ppm TPP were added to the mixture according to total weight of ESBO and AA. The reaction mixture was mixed with the magnetic stirrer at 800 rpm under nitrogen environment at room temperature during 30 min first and then 2 h at 100°C and another 2 h at 120°C. The completion of the reaction was determined by following the depletion of AA via acid titration according to ASTM standard.[15] The S-ESBO oligomer was synthesized for the first time by the author in a previous study and applied on cotton fabrics.[16] Here, by using these oligomers, sustainable photocurable metal coatings with high bio-contents were searched. For the synthesis of S-ESBO oligomer, at first, certain amount of ESBO and Sipomer PAM-200 were mixed,

and then 30% HDDA and 1000 ppm TPP were added to the glass flask according to total weight of ESBO and Sipomer PAM-200. The reaction mixture was mixed with the magnetic stirrer at 800 rpm in the three-necked flask for 30 min under nitrogen environment at room temperature. Then, all the components in the reaction were heated for 1.5 h at 50°C. The reaction was followed by periodically measuring the epoxy equivalent weight (EEW) value according to ASTM standard[4] and ended when the highest EEW value was obtained. The reaction schemes of the oligomers are given in Fig. 1.

Preparation and application of the coatings

The compositions of the coating formulations are given in Table 1. Formulations were prepared by using the synthesized A-ESBO and S-ESBO oligomers, reactive diluents with various functionalities, and 4% photoinitiator. The percentages of the reactive diluents were determined after a number of coating trials until achieving the optimum gloss and tackiness properties. After blending all the components, the formulation was heated to 40°C in order to lower the viscosity resulting a better leveling property on the metal surface. Then, 2 g of formulation was poured onto the metal surface and covered by a transparent polyethylene film to prevent the loss of formulation during spreading, to dissipate the air bubbles on the surface, and to prevent the oxygen inhibition. A squeezing roller was employed to spread the formulation on the metal surface. The distance between UV light source and the Al alloy plate was set as 30 cm during photocuring process. Each plate was exposed to UV light (300 W, OSRAM Ultra-Vitalux) for 3 min. Additionally, UV-cured free films were also prepared for further characterization by using a polytetrafluoroethylene mold.

Characterization

The synthesized A-ESBO and S-ESBO oligomers were characterized by Fourier transform infrared (FTIR) (PerkinElmer Spectrum-100 ATR FTIR) and proton nuclear magnetic resonance (^{1}H NMR) (Bruker AMX 500 MHz NMR instrument, in $CDCl_3$ solvent, tetramethylsilane internal reference) spectroscopies, respectively. In order to perform the mechanical evaluation of the oligomers, coating formulations were casted on PTFE molds and cured by UV-light. The obtained UV-cured free films were tested by means of thermal, physicochemical, tensile, elongation, and hardness properties. Thermal properties of UV-cured free films of each oligomer were analyzed by using thermogravimetric analysis (TGA) (TA TGA Q50, from room temperature to 600°C, with a heating rate of 10°C/min, with nitrogen flow) and differential scanning calorimetry (DSC) (TA DSC Q200, from − 80 to 400°C, with a heating rate of 10°C/min, with nitrogen flow), respectively. The gel fraction (GF) test was performed by immersing the UV-cured free films in THF for 1 week. Then the films were dried at room temperature for 48 h and then weighted. The GF (%) value was measured according to the following equation where w_2 and w_1 refer to the weight of the sample after and before the immersion in THF.[17]

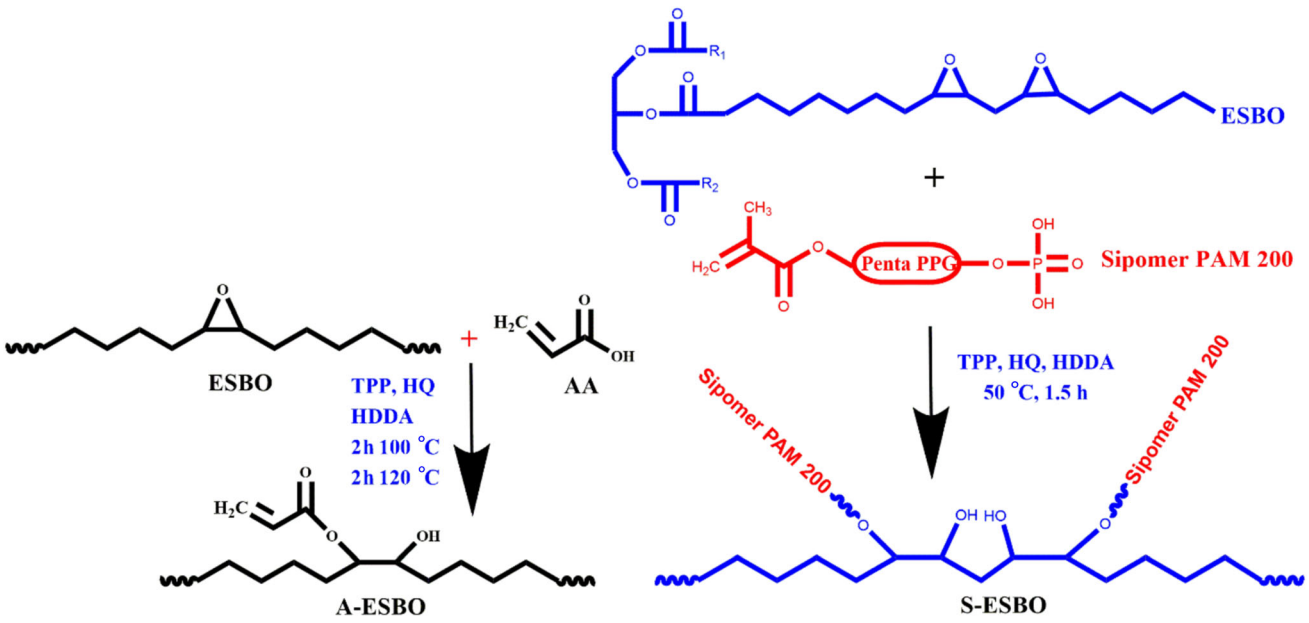

Fig. 1: The synthesis scheme of the A-ESBO (left) and S-ESBO (right) oligomers

Table 1: The composition of the coating formulations with the sample codes

Sample Codes	A-ESBO Oligomer (wt%)	S-ESBO Oligomer (wt%)	NVP (%)	HDDA (%)	TMPTA (%)
S1	50	0	15	20	15
S2	40	10			
S3	30	20			
S4	20	30			
S5	10	40			
S6	0	50			

$$\mathrm{GF}(\%) = \left[\frac{w_2}{w_1}\right] x100$$

The degree of swelling (DS) was measured by dipping the UV-cured free films of the formulations into the 10 mL aliphatic (ethanol), aromatic (toluene), and neutral (distilled water) solvent for one week at room temperature. Then the DS (%) was calculated according to the following equation where w_2 and w_1 are the weight of samples after and before swelling.[17]

$$DS(\%) = \left[\frac{w_2 - w_1}{w_1}\right] x100$$

The resistance against chemicals was evaluated by dipping the UV-cured free films into 10% hydrochloric acid (HCl) and 10% sodium hydroxide (NaOH) solutions for 1 week at room temperature according to the ASTM standard. Then, films were washed by distilled water, dried at 55°C, and finally weighed. The following equation was employed to observe the weight loss with chemical exposure, where w_2 and w_1 refer to the weights of samples after and before immersion.[18]

$$\text{Weight Loss}(\%) = \left[\frac{w_1 - w_2}{w_1}\right] x100$$

The tensile properties of UV-cured free films were recorded by using Instron 4411 tensile testing device according to the ASTM D638-22 standard in terms of tensile strength, elongation at break, and Young's modulus.[15] ASTM D2240 standard was employed to achieve Shore D hardness test (Zwick Shore D Durometer) of the free films under a 5 kg loading.[19]

The water immersion test was applied on Al alloy plates after coating and UV-curing stages according to ASTM D870-15 standard.[20] The water immersion test was performed by dipping only the one side of the coated UV-cured Al alloy plates parallel to the flow of distilled water in a beaker equipped with a magnetic stirrer and heated to 38°C for 24 h. After the test, the visual evaluation was made according to the ASTM D610–08 standard[21] through looking at the shape of rusted areas by means of pinpoint (P), general (G), and spot (S). The rating of the rusted area is determined in the range of 0–10, by giving 10 for the best one (less than 0.01% rusted area) and 0 for the worst one (greater than 50% rusted area). For instance, the water immersion test result of 6S means that 0.3–1% rusted area in spot shaped was recorded.[21]

The specular gloss test was applied on Al alloy plates after coating and UV-curing processes at 20° and 60° by using BYK micro-TRI-gloss meter according to the ASTM D523-14 standard.[22] The gloss test at 20° geometry is needed when the gloss value at 60° is greater than 70 GU. The ASTM D3363-05 standard was employed to perform the pencil hardness test of UV-cured coatings on Al alloy plates.[23] The pencil hardness of the coated surface was measured by the movement of the pencils having the hardness values in the range of 6H–6B from harder to softer by using an apparatus with a 45° angle. The scratch hardness rating shows which pencil is the strongest without causing any scratches or rupturing the coating layer. The abrasion resistance property of the coated UV-cured Al alloy plates was evaluated by Taber Type Abrasion Tester GT-7012-T (Gotech Testing Machine) according to the ASTM D4060-19 standard.[24] The Taber test was performed by measuring the weight loss of samples in mg after 100 cycles abrading at 72 rpm with CS10 wheels under 250 g/wheel loading. A total of 500 cycles were applied for each sample.

Results and discussion

Properties of A-ESBO and S-ESBO oligomers

Chemical structure analysis

During the reaction, for the A-ESBO oligomer AV and for the S-ESBO oligomer, EEW values were checked periodically to observe the depletion of acid and epoxide groups. Accordingly, in A-ESBO oligomer, the synthesis reaction was ended when the least and constant AV of 26.18 mgKOH/g was obtained, whereas in S-ESBO oligomer, the reaction completed when the highest and constant EEW value of 380.04 g/Eq. was recorded. EEW refers to the amount of the S-ESBO oligomer (g) that has a 1 g equivalent of an

epoxy group. Figure 2a illustrates the FTIR spectra of the ESBO, A-ESBO, and S-ESBO oligomers, respectively. The triglyceride ester peak of soybean oil was observed at 1740 cm^{-1} in all spectra. The existence of the epoxide group in the ESBO spectra was followed by the peaks at 825 and 905 cm^{-1} attributing to the C–O–C asymmetric vibration peaks. After the reaction with AA and Sipomer PAM-200, the epoxide peaks disappeared. Instead, newly formed stretching peak of acrylate group (C=C) and absorption peak of carbonyl group (C=O) were recorded at 1626 and 1643 cm^{-1}, in both A-ESBO and S-ESBO spectra, respectively. Considering the S-ESBO spectra, the inclusion of phosphate ester group to the soybean oil structure can be observed by the newly formed peaks of P–O at 998 cm^{-1}, P=O at 1248 cm^{-1}, P–O–C at 1072 cm^{-1}, and ester vibration peak at 1100 cm^{-1}.[14,25–28]

Figure 2b and c shows the ^{1}H NMR spectra of the synthesized A-ESBO and S-ESBO oligomers in $CDCl_3$. According to the ^{1}H NMR spectra of A-ESBO

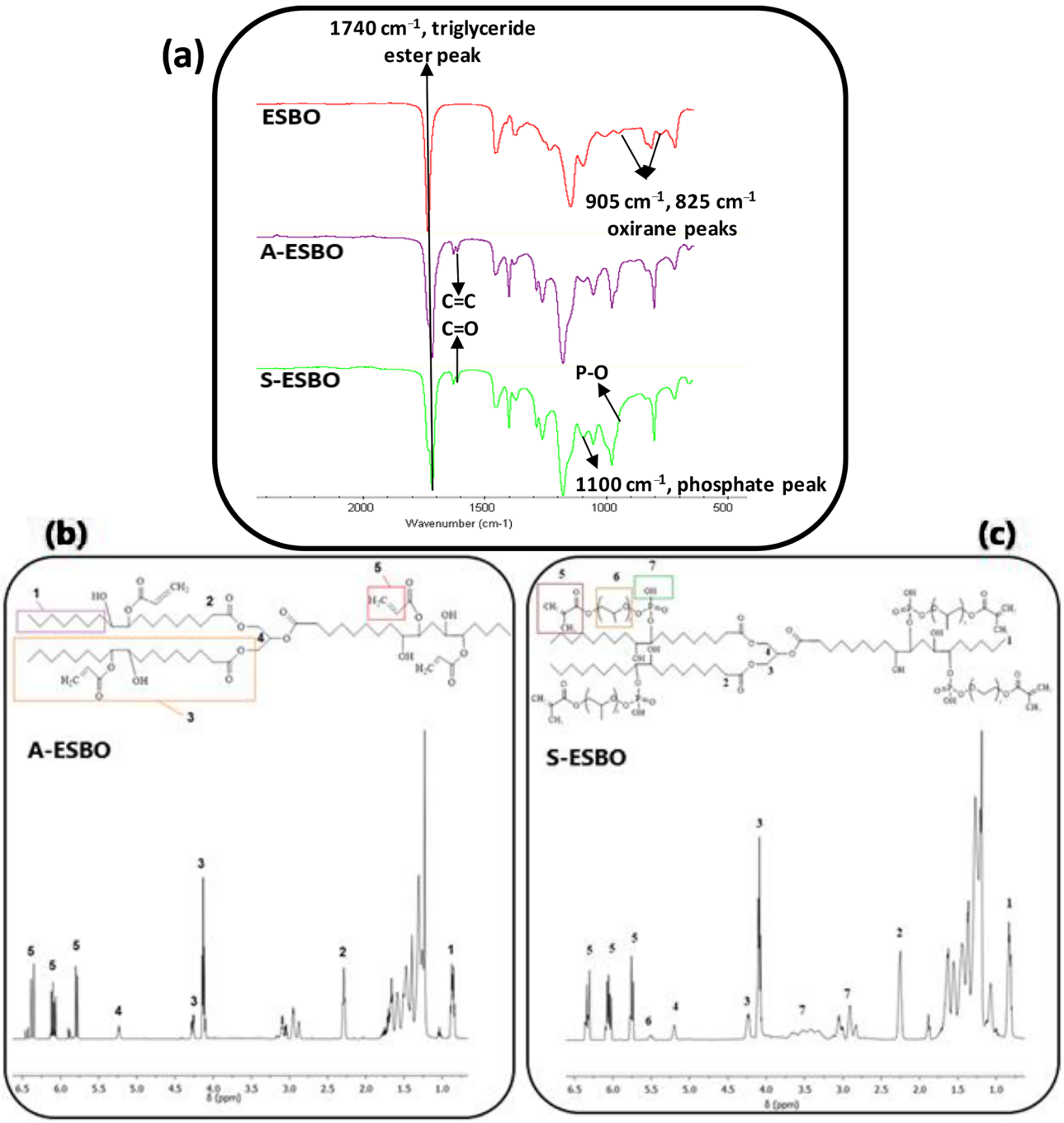

Fig. 2: (a) FTIR spectra, (b) and (c) ^{1}H NMR spectra of the synthesized A-ESBO and S-ESBO oligomers

oligomer (Fig. 2b), the acrylate functionality proton peaks were recorded at 5.6–6.5 ppm region. The methyl proton peaks of saturated triglyceride backbone were observed at 0.82–1.45 ppm region. The methylene protons of adjacent epoxy groups were observed at 1.4–1.7 ppm region. The protons of the carbonyl group in triglyceride molecule at 2.2–2.3 ppm, $-CH_2$ protons of the glycerol unit at 4.1–4.4 ppm, and –CH proton of the glycerol unit at 5.25 ppm were all recorded.[29,30] In the ^1H NMR spectra of S-ESBO oligomer (Fig. 2c), the methine group proton peaks at 4.35 ppm and hydroxyl group proton peaks at 3.3–3.6 ppm region confirm ring opening reaction of the epoxide groups. The peaks at 5.59–5.60 ppm and 6.10–6.18 ppm regions refer to the methacrylate functional group of Sipomer PAM-200 oligomer that is $C(CH_3) = CH_2$ in trans and cis positions, respectively. The hydroxyl aliphatic protons of phosphorus group were recorded at 2.8–3.2 ppm region. The peaks at 0.82–1.45 ppm region show the methyl protons of the penta PPG, methacrylate functionality, and saturated triglyceride group. The $-CH_2$ protons of the glycerol unit at 4.0–4.4 ppm, –CH– proton of the glycerol unit at 5.22 ppm, –OH proton of the glycol unit at 5.5 ppm, and the $-CH = CH_2$ protons of the methacrylate functionality at 5.7–6 and 6.35 ppm were all observed.[29–32]

Thermal properties

Thermal properties of UV-cured free films were investigated by TGA. Figure 3 shows the TGA results of the UV-cured free films by means of each formulation. The analysis was carried out under oxygen atmosphere in order to observe the oxidative stability of the samples. The main decomposition started at around 350°C for all the UV-cured free films. The most remarkable decomposition was recorded in 420–431°C temperature range. According to a previous study, the weight loss of phosphorus-containing polymers is lower than that of nonphosphorus-containing polymers at higher temperatures.[33] Thus, above 500°C, the least weight loss through decomposition was observed in the sample of S6 due to having the highest amount of phosphorus-containing oligomer. Table 2 shows the thermogravimetric data of UV-cured free films. Considering the char yield values, it can be seen that, with increasing amount of S-ESBO oligomer in the coating formulation, the char formation also increases. In some studies, it was argued that a phosphorus group containing chemical decreases the energy of the flame in the gas phase and increases the combustion resistance of the flammable particles such as –H or –OH in the formulation.[34,35] Additionally, it was reported that the phosphorus group in the formulation decomposes first and acts as an acid catalyst, then it interacts to methylene bonds and ester groups. This situation leads to char formation from degraded products.[36,37] Furthermore, the existence of phosphorus-containing S-ESBO oligomer in the formulation contributes to a low rate of decomposition and a decreased production of combustible gas by preventing the transfer of heat through the UV-cured free film.[38] Therefore, the increasing amount of phosphorus-containing oligomer in the formulation enhances the thermal stability by increasing the char amount due to phosphorus group on the S-ESBO oligomer structure.

The DSC thermograms of UV-cured free films of S1 and S6 oligomers are given in Fig. 4. Each oligomer showed two distinct thermal transitions: first glass transition temperature (T_{g1}) and second glass transition temperature (T_{g2}). Accordingly, two different glass transition temperatures were recorded for the

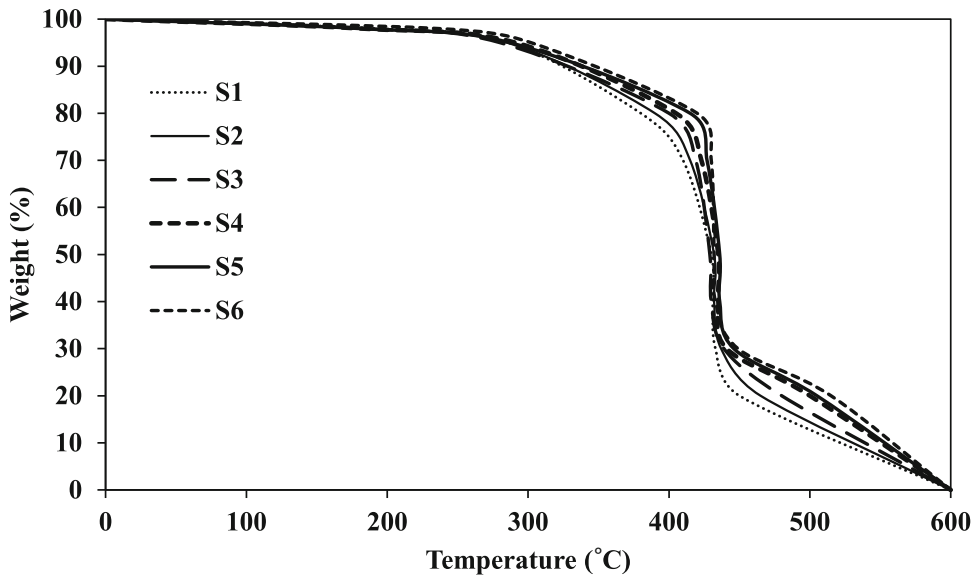

Fig. 3: TGA results of the UV-cured free films for each formulation

Table 2: TGA data of the UV-cured free films

Sample codes	Weight loss (%), Temperature (°C)			Char yield (%)
	2%	5%	50%	
S1	190.53	286.17	430.42	0.268
S2	182.45	285.17	432.32	0.274
S3	183.35	279.48	429.43	0.285
S4	181.43	290.66	435.03	0.302
S5	180.32	287.44	435.88	0.372
S6	236.17	301.68	432.45	0.513

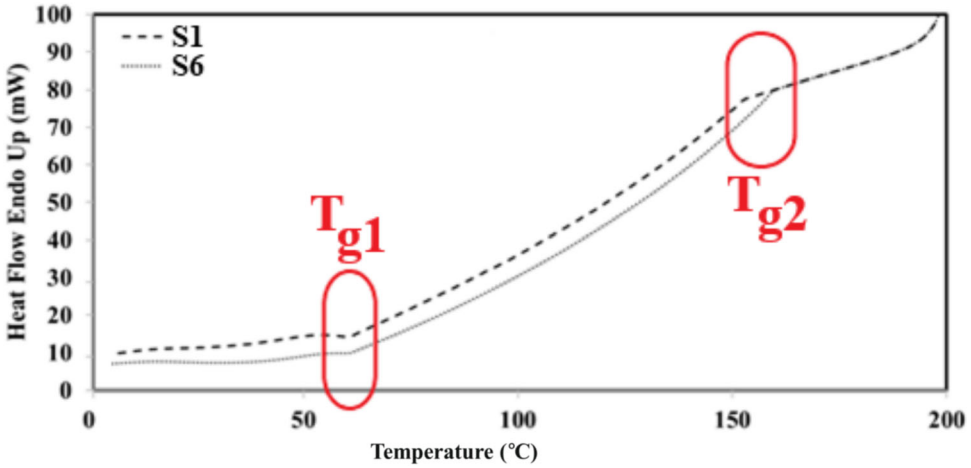

Fig. 4: DSC results of UV-cured free films of each oligomer

UV-cured free films due to the presence of the synthesized oligomer (A-ESBO and S-ESBO) along with reactive diluents (NVP, HDDA, and TMPTA). The first glass transition temperature was observed at around 59°C for the sample of S1, whereas in the sample of S6, the T_{g1} point shifted to a higher temperature, 62°C. The T_{g2} peaks were observed at 152°C and 160°C for the samples of S1 and S6, respectively. This result can be explained by the incorporation of the S-ESBO oligomer into the polymer network, which is responsible for the increase in crosslinking density, leading to restriction in chain mobility. In other words, after the chemical modification of ESBO with methacrylate-phosphate-containing species, the obtained S-ESBO oligomer causes a slight increase in glass transition temperature. The –OH groups of S-ESBO oligomer cause intermolecular interactions resulting in an increase in crosslinking density and a decrease in free volume.[35]

Physicochemical properties

Table 3 illustrates the physicochemical properties of UV-cured free films of each formulation by means of GF, swelling degree, and chemical resistance in solvents. The increasing crosslinking density leads to increase in GF value and decrease in swelling degree and weight loss values with chemical exposure. The hydrophilic functional groups on the polymer chain are responsible for the increase in crosslinking density.[36] According to Table 3, the GF values increased, whereas the swelling degrees decreased with increasing amount of S-ESBO oligomer in the formulation. This result stems from the presence of –OH groups in S-ESBO oligomer which are responsible for the crosslinking density increment. When comparing the level of swelling by means of the environment of the substrate, due to the neutral characteristic of distilled water, the least swelling degrees were recorded in water, whereas the UV-cured free films showed lower swelling degrees in the aromatic solvent (toluene) than in the aliphatic solvent (ethanol) that can be explained by the polarity differences of ethanol and toluene. The polarity of ethanol is higher than toluene thus ethanol is more capable of forming interaction with the polymer chains of free films. Considering the solvent resistance test results, the UV-cured free films are significantly degraded in 10% NaOH, which means that the proposed formulations are not resistant to such strong base environment. The ester groups of soybean oil are broken due to the alkaline hydrolysis that is

Table 3: Physicochemical properties of UV-cured free films

Sample codes	GF (%) in THF	Degree of Swelling			Solvent Resistance	
		In Ethanol	In Toluene	In Distilled Water	In 10% NaOH	In 10% HCl
S1	73.85	26.38	27.50	0.86	30.03	2.35
S2	75.42	25.19	23.50	0.60	23.47	2.28
S3	77.47	20.12	21.90	0.28	23.43	2.23
S4	79.68	19.80	19.03	0.21	24.37	0.73
S5	81.66	18.42	17.34	0.13	29.90	1.22
S6	82.83	15.84	14.82	0.11	29.93	1.89

Table 4: Mechanical testing results of UV-cured free films

Sample Codes	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Shore D Hardness
S1	103	1.27	637	52
S2	117	1.57	690	53
S3	127	1.84	720	55
S4	132	2.07	728	56
S5	152	2.11	745	57
S6	161	2.41	793	59

initiated by the free Na^+ and OH^- ions in NaOH solution. Then, sodium turns into sodium carboxylate and degradation takes place. On the contrary, a slight degradation was recorded in acidic media that can be inferred as the obtained formulations are more resistant to the acids than alkaline media.[17,37]

Mechanical properties

The crosslinking density and functionality of a polymer network are the main deterministic factors on ductility and brittleness property of the structure. Higher functionality, such as higher crosslinking density, leads to an enhanced tensile and hardness character of the substrate.[39] Table 4 illustrates the mechanical testing results of UV-cured free films of each formulation. Accordingly, the increasing amount of S-ESBO oligomer in the formulation improves the tensile, modulus, and hardness values due to the increase of crosslinking density of the polymer network. Besides, the structural flexibility of the polymer chain added by the aliphatic penta PPG groups of S-ESBO oligomer leads to an increase in elongation under tension. On the contrary, the increasing amount of A-ESBO oligomer in the formulation leads to decrease in the elongation and hardness values due to the poor mechanical properties of A-ESBO oligomer with a brittle and fragile nature.[31,33,40]

Properties of coated UV-cured Al alloy plates

Surface wettability

The surface functionality and the surface ability to interact with water molecules are both the key factors to determine the surface wettability nature of the coated substrates. Functional groups of the coating formulation cause decline in contact angle values by increasing the surface energy along with the crosslinking density.[41] Figure 5 shows the results of contact angle measurement test along with the images of water droplets on the coated UV-cured Al alloy surfaces. The Al alloy plate without any coating layer showed a contact angle value of 74°. After the application of the coating formulations, the contact angle values were all gradually decreased due to the increased surface energy and functionality. Considering the composition of the coating formulation, the contact angle values gradually decreased through increasing amount of phosphorus-containing oligomer (S-ESBO) in the formulation. This result stems from the polar hydroxyl groups of phosphate ester and penta PPG groups in S-ESBO oligomer which cause intermolecular interaction, resulting in a decrease in free volume and increase of crosslinking density and surface energy.[42] Thus, the smallest contact angle value of 65° was recorded in the sample of S6 coated UV-cured Al alloy plate due to the highest S-ESBO oligomer amount.

Figure 6 shows the water immersion test results of coated UV-cured Al alloy plates based on the visual

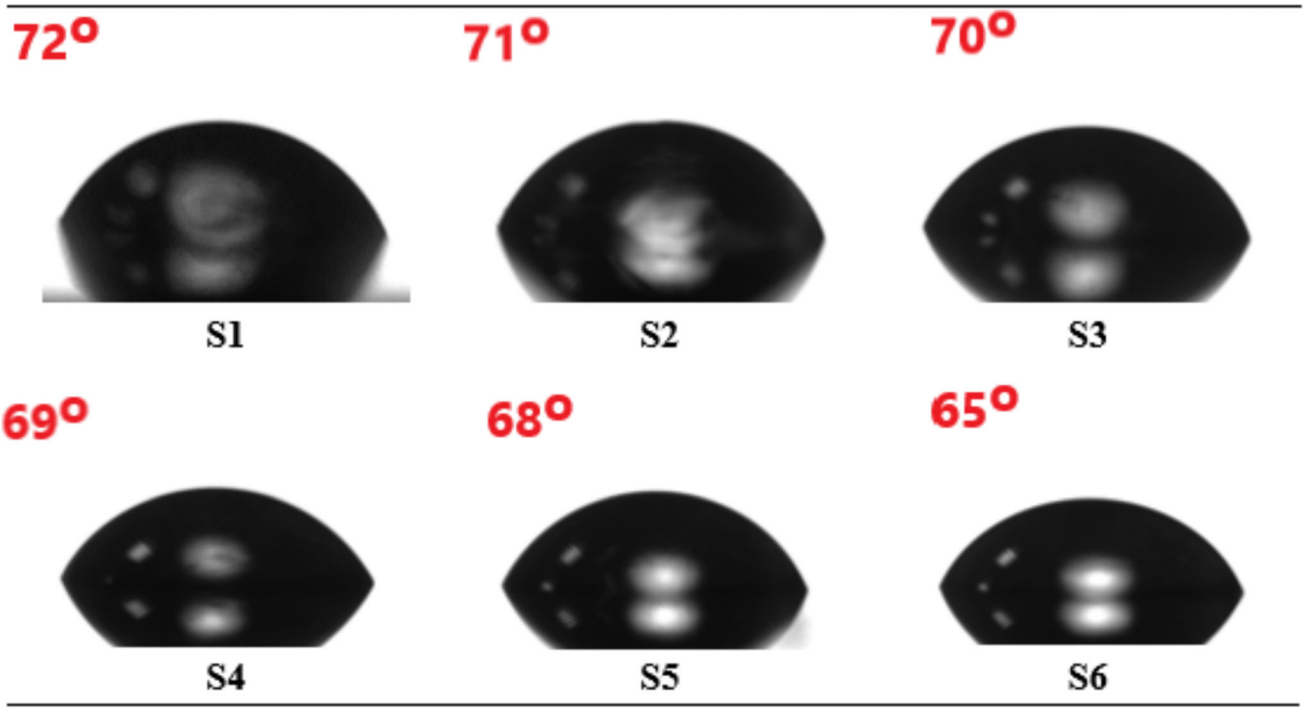

Fig. 5: Contact angle values with water droplet images on coated UV-cured Al alloy plates

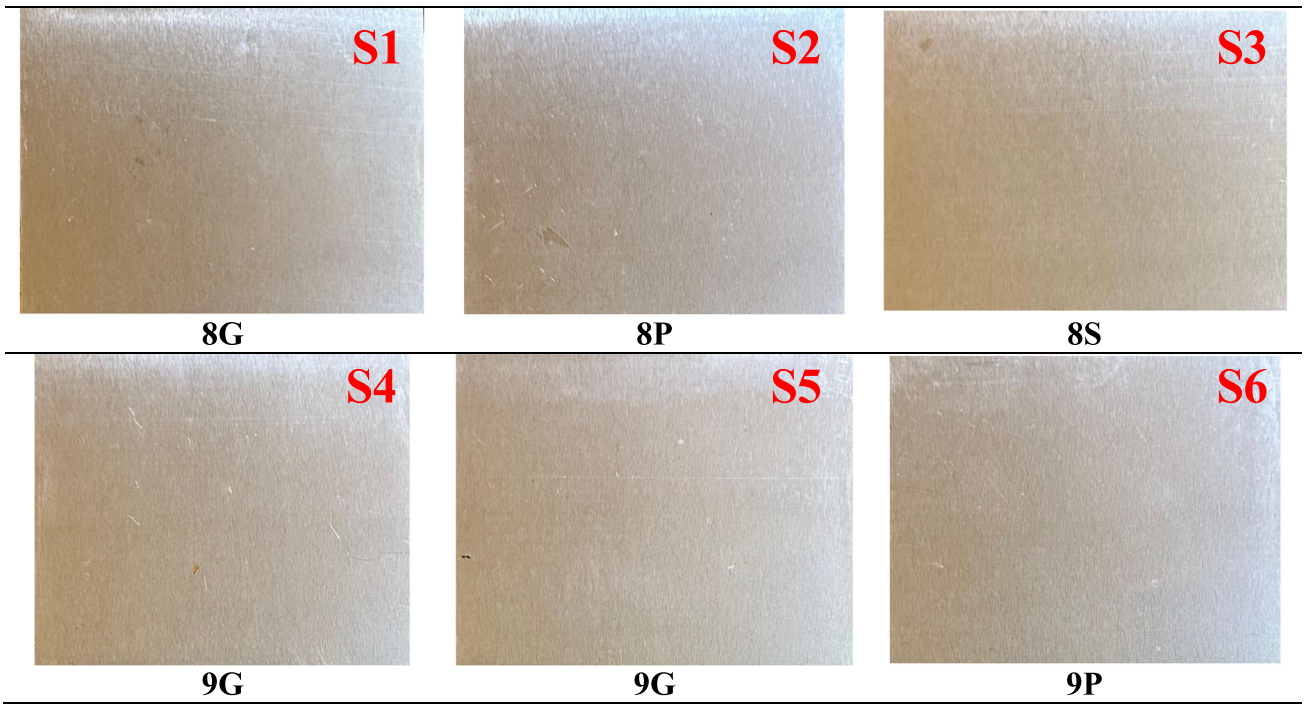

Fig. 6: The water immersion test results and images of Al alloy plates after the testing. (G: General rusting, P: Pinpoint rusting, S: Spot rusting)

evaluation along with the images of the plates after 24 h immersion in water. A video of the water immersion test is also provided as a supplementary file. Considering the shape of rusted areas, the P-shaped rusting is the best one and refers to very small individual rusts, whereas S-shaped rusting means that rusting is concentrated in a few areas. The G-shaped rusting is the worst one among all shapes and illustrates

Table 5: Visual evaluation of surface characteristics of coated UV-cured Al alloy plates

Sample codes	The gloss test results (GU)		The pencil hardness test results (6B to 6H)
	20°	60°	
S1	157	228	4B
S2	162	257	3B
S3	192	299	3B
S4	187	291	3B
S5	185	291	3B
S6	187	250	3B

that rusts in various sizes randomly occurred on the surface.[21] According to Fig. 6, all Al alloy plates showed similar and acceptable water immersion test result of 8 and 9, which means that the amount of the rusted areas are only limited in the range of 0.01–0.1%. The highest amount of rust formation was recorded as 8G in the sample of S1 coated Al alloy plates, without the inclusion of phosphorus-containing oligomer (S-ESBO) to the formulation, by showing 0.03–0.1% general shaped rusted areas. The best coating performance by means of rust occurrence was recorded in the sample of S6 coated Al alloy plates with the result of 9P, which means that the amount of rusted areas is in the range of 0.01–0.03% with a pinpoint shaped. The increasing amount of phosphorus-containing oligomer (S-ESBO) in the coating formulation protects the coated UV-cured Al alloy surfaces against rusting by improving the water resistance. This result can be explained by the enhanced interfacial adhesion between the coating layer and Al alloy plate with the help of phosphorus groups.

Visual evaluation and hardness

The visual coating quality of the coated UV-cured Al alloy plates was also evaluated by means of gloss and pencil hardness tests, respectively. Table 5 summarizes the gloss and pencil hardness test results for each coating formulation. The gloss evaluation at 20° is made according to the following classification; the gloss unit (GU) values of greater than 80 GU are called high glossy, the GU values of 65–80 are called glossy, and the GU values of 55–65 are called semiglossy, respectively. The gloss property of a surface demonstrates the ability of the surface to reflect more light that is highly correlated to the surface shininess of the sample.[43] Due to the smoothness and inherent shininess of the Al alloy plates, the GU values were all recorded as high glossy. When the S-ESBO oligomer was added to the coatings, the gloss values increased for all samples. Considering the hardness properties, the least pencil hardness value of 4B was recorded in S1 coated UV-cured sample due to the absence of S-ESBO oligomer

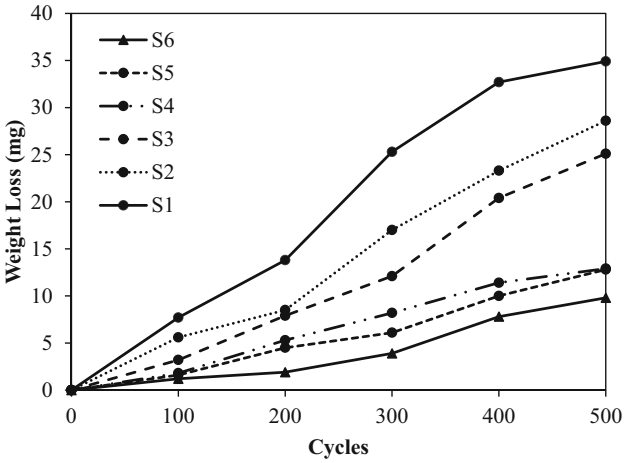

Fig. 7: Taber abrasion resistance test results of coated UV-cured Al alloy plates

in the coating formulation. After the inclusion of S-ESBO oligomer to the coating formulation, the pencil hardness value was slightly increased and reached to 3B value from the sample of S2 through the S6. This result can be explained by the existence of hydroxyl groups of phosphate ester and penta PPG groups in S-ESBO oligomer which leads to the increased crosslinking density thus increased hardness. In other words, AA by itself has a linear and less functional structure compared to S-ESBO oligomer, thus a lower pencil hardness value was recorded in S1 coated UV-cured sample.[4]

Abrasion resistance

The abrasion resistance property was evaluated by means of Taber Type abrasion test. Figure 7 shows the Taber abrasion test results of coated UV-cured Al alloy plates based on the weight loss values of samples after 500 cycles at 72 rpm. Accordingly, as the ratio of S-ESBO oligomer in the coating formulation increases, the weight loss due to the wearing of coating layer decreases. In other words, the phosphorus groups of S-ESBO oligomer enhance the adhesion between the coating layer and Al alloy plate.[44] Thus, the weight loss values with abrasion decrease from S1 through S6 coated UV-cured Al alloy samples.

Conclusions

In this study, due to being an environmentally friendly and solventless/waterless process, and requiring less energy and time, photocuring technology was proposed as a sustainable alternative to the conventional heat- and solvent-based metal coating techniques. For this purpose, ESBO was reacted with AA and a monomethacrylate phosphate functional reactive

monomer (Sipomer PAM 200) in order to obtain the photocurable soybean oil-based oligomers. Then, FTIR and ^{1}H NMR spectroscopies were employed to characterize these oligomers. Coatings were formulated by using the synthesized oligomers, photoinitiator, and reactive diluents with various functionalities, then coated on Al alloy plates, and cured by UV-light. The coated photocured Al alloy surfaces were evaluated by means of wettability, water resistance, gloss, hardness, and abrasion resistance properties, respectively. The effects of the oligomer composition on the coating performance characteristics were all searched. The overall results of the photocured free films illustrate that the increasing amount of phosphorus-containing oligomer in the formulation improves the thermal stability and enhances the tensile, modulus, and hardness values by increasing the crosslinking density of the polymer network. Considering the coated photocured Al alloy plates, surface wettability, hardness, and gloss were all improved with increasing amount of phosphorus-containing oligomer in the formulation due to the polar hydroxyl groups of phosphate ester and penta polypropylene glycol groups. The interfacial adhesion between the coating layer and Al alloy plate was also improved with the help of phosphorus groups in the formulation, resulting inwater resistance with less rust formation. As a promising green alternative with higher bio-contents to the conventional heat- and VOC-based metal coatings, the results show that the soybean oil-based photocurable phosphorus-containing coatings exhibit acceptable coating performances with enhanced gloss, hardness, water, and abrasion resistance properties.

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Conflict of interest The authors declare that they have no conflict of interest.

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References

1. Randis, R, Darmadi, DB, Gapsari, F, Sonief, AAA, Akpan, ED, Ebenso, EE, ''The Potential of Nanocomposite-Based Coatings for Corrosion Protection of Metals: A Review.'' *J. Mol. Liq.*, **390** 123067 (2023)
2. Aljibori, H, Alamiery, A, Kadhum, A, ''Advances in Corrosion Protection Coatings: A Comprehensive Review.'' *Int. J. Corros. Scale Inhib.*, **12** (4) 1476–1520 (2023)
3. Wang, X, Zhang, J, Liu, J, Liu, R, Luo, J, ''Synthesis of Acrylated Tannic Acid as Bio-Based Adhesion Promoter in UV-Curable Coating with Improved Corrosion Resistance.'' *Colloids Surf. A: Physicochem. Eng. Asp.*, **644** 128834 (2022)
4. Choi, J-S, Seo, J, Khan, SB, Jang, ES, Han, H, ''Effect of Acrylic Acid on the Physical Properties of UV-Cured Poly (Urethane Acrylate-Co-Acrylic Acid) Films for Metal Coating.'' *Prog. Org. Coat.*, **71** (1) 110–116 (2011)
5. Yoon, S, Kim, B, ''UV-Curable Water-Borne Polyurethane Primers for Aluminum and Polycarbonate Interfaces.'' *Polym. Bull.*, **68** 529–539 (2012)
6. Yıldız, Z, ''Green Photocurable Phosphorus Containing Coatings on Cotton Fabrics.'' *Uludağ Üniversitesi Mühendislik Fakültesi Dergisi*, **28** (2) 645–664 (2023)
7. Kraśkiewicz, A, Kowalczyk, A, Kowalczyk, K, Markowska-Szczupak, A, Idzik, TJ, Sośnicki, JG, ''Anticorrosive and Antimicrobial Efficiency of Photopolymerizable Phosphorus (Meth)Acrylate Oligomers-Based Coating Materials.'' *Prog. Org. Coat.*, **187** 108141 (2024)
8. Park, S-Y, Cheon, J, Jeong, BY, Lee, DH, Huh, P, Chun, JH, ''Preparation and Properties of Photo-Curable Coatings Based on Synthesis of Self-Photocuring Polyurethane Acrylate Oligomer for Pre-Coated Metal.'' *Mol. Cryst. Liq. Cryst.*, **706** (1) 129–135 (2020)
9. Chen, B, Ma, J, Gu, L, Liu, S, Zhao, H, Yu, H, Chen, J, ''Anticorrosive Properties of Oligoaniline Containing Photocured Coatings.'' *Int. J. Electrochem. Sci.*, **10** 9154–9166 (2015)
10. Liao, F-Q, Chen, Y-C, ''Siloxane-Based Epoxy Coatings Through Cationic Photopolymerization for Corrosion Protection.'' *Prog. Org. Coat.*, **174** 107235 (2023)
11. Liu, R, Luo, J, Ariyasivam, S, Liu, X, Chen, Z, ''High Biocontent Natural Plant Oil Based UV-Curable Branched Oligomers.'' *Prog. Org. Coat.*, **105** 143–148 (2017)
12. Yildiz, Z, Onen, H, Gungor, A, ''Soybean Oil Based UV-Curable Coating Formulations for Improvement of Washing Fastness of Waterproof Cotton Fabrics.'' In: *Proc. 3rd International Congress of Innovative Textiles ICONTEX 2022*, 18–19 May 2022
13. Li, X, Wang, D, Zhao, L, Hou, X, Liu, L, Feng, B, Li, M, Zheng, P, Zhao, X, Wei, S, ''UV LED Curable Epoxy Soybean-Oil-Based Waterborne PUA Resin for Wood Coatings.'' *Prog. Org. Coat.*, **151** 105942 (2021)
14. Baştürk, E, İnan, T, Güngör, A, ''Flame Retardant UV-Curable Acrylated Epoxidized Soybean Oil Based Organic–Inorganic Hybrid Coating.'' *Prog. Org. Coat.*, **76** (6) 985–992 (2013)

15. ASTM D638-22 Standard Test Method for Tensile Properties of Plastics (2022)
16. Yildiz, Z, ''Photocurable Soybean Oil Based Phosphorus Containing Coatings for Cotton Fabrics: The Influence of Reactive Diluents.'' *Prog. Org. Coat.*, **174** 107255 (2023)
17. Bhusari, GS, Umare, SS, Chandure, AS, ''Effects of NCO: OH Ratio and HEMA on the Physicochemical Properties of Photocurable Poly(Ester-Urethane) Methacrylates.'' *J. Coat. Technol. Res.*, **12** (3) 571–585 (2015)
18. ASTM D543-21 Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents (2021)
19. ASTM D2240-15(2021) Standard Test Method for Rubber Property—Durometer Hardness (2021)
20. ASTM D870-15(2020), Standard Practice for Testing Water Resistance of Coatings Using Water Immersion (2020)
21. ASTM D610-08(2019) Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces (2019)
22. ASTM D523-14(2018) Standard Test Method for Specular Gloss (2018)
23. ASTM D3363-22 Standard Test Method for Film Hardness by Pencil Test (2022)
24. ASTM D4060-19 Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (2019)
25. Wu, Y, Liu, A, Li, W, Li, Z, ''Synthesis of Carborane Acrylate and Flame Retardant Modification on Silk Fabric via Graft Copolymerization with Phosphate-Containing Acrylate.'' *Fire Mater.*, **43** (7) 880–891 (2019)
26. Ugur, M, Kılıç, H, Berkem, M, Güngör, A, ''Synthesis by UV-Curing and Characterisation of Polyurethane Acrylate-Lithium Salts-Based Polymer Electrolytes in Lithium Batteries.'' *Chem. Papers*, **68** (11) 1561–1572 (2014)
27. Shi, L-S, Wang, L-Y, Wang, Y-N, ''The Investigation of Argon Plasma Surface Modification to Polyethylene: Quantitative ATR-FTIR Spectroscopic Analysis.'' *Eur. Polym. J.*, **42** (7) 1625–1633 (2006)
28. Liu, H, Xu, K, Cai, H, Su, J, Liu, X, Fu, Z, Chen, M, ''Thermal Properties and Flame Retardancy of Novel Epoxy Based on Phosphorus-Modified SCHIFF-Base.'' *Polym. Adv. Technol.*, **23** (1) 114–121 (2012)
29. Wu, Q, Hu, Y, Tang, J, Zhang, J, Wang, C, Shang, Q, Feng, G, Liu, C, Zhou, Y, Lei, W, ''High-Performance Soybean-Oil-Based Epoxy Acrylate Resins:'Green' Synthesis and Application in UV-Curable Coatings.'' *ACS Sustain. Chem. Eng.*, **6** (7) 8340–8349 (2018)
30. Uysal, N, Acik, G, Tasdelen, MA, ''Soybean Oil Based Thermoset Networks via Photoinduced CuAAC Click Chemistry.'' *Polym. Int.*, **66** (7) 999–1004 (2017)
31. Liu, Z, Wang, L, Bao, C, Li, X, Cao, L, Dai, K, Zhu, L, ''Cross-Linked PEG via Degradable Phosphate Ester Bond: Synthesis, Water-Swelling, and Application as Drug Carrier.'' *Biomacromolecules*, **12** (6) 2389–2395 (2011)
32. Colak, S, Küsefoğlu, SH, ''Synthesis and Interfacial Properties of Aminosilane Derivative of Acrylated Epoxidized Soybean Oil.'' *J. Appl. Polym. Sci.*, **104** (4) 2244–2253 (2007)
33. Jeng, R-J, Shau, S-M, Lin, J-J, Su, W-C, Chiu, Y-S, ''Flame Retardant Epoxy Polymers Based on All Phosphorus-Containing Components.'' *Eur. Polym. J.*, **38** (4) 683–693 (2002)
34. De Almeida, NR, Beatriz, A, de Arruda, EJ, de Lima, DP, de Oliveira, LCS, Micheletti, AC, ''Ozonized Vegetable Oils: Production, Chemical Characterization and Therapeutic Potential.'' In: *Vegetable Oil: Properties, Uses and Benefits*, pp. 129–160. (2016)
35. Abdelkhalik, A, Elsayed, H, Hassan, M, Nour, M, Shehata, A, Helmy, M, ''Using Thermal Analysis Techniques for Identifying the Flash Point Temperatures of Some Lubricant and Base Oils.'' *Egypt. J. Pet.*, **27** (1) 131–136 (2018)
36. Mestry, S, Mhaske, S, ''Synthesis of Epoxy Resins Using Phosphorus-Based Precursors for Flame-Retardant Coating.'' *J. Coat. Technol. Res.*, **16** 807–818 (2019)
37. Al-Shamary, MN, Al-Lohedan, HA, Rafiquee, M, El-Ablack, F, Issa, ZA, ''Micellar Effect Upon the Rate of Alkaline Hydrolysis of Carboxylic and Carbonate Esters.'' *J. Saudi Chem. Soc.*, **21** S193–S201 (2017)
38. Xu, L, Wang, W, Yu, D, ''Preparation of a Reactive Flame Retardant and Its Finishing on Cotton Fabrics Based on Click Chemistry.'' *RSC Adv.*, **7** (4) 2044–2050 (2017)
39. Mudri, NH, Abdullah, LC, Aung, MM, Salleh, MZ, Awang Biak, DR, Rayung, M, ''Comparative Study of Aromatic and Cycloaliphatic Isocyanate Effects on Physico-Chemical Properties of Bio-Based Polyurethane Acrylate Coatings.'' *Polymers*, **12** (7) 1494 (2020)
40. Dai, J, Jiang, Y, Liu, X, Wang, J, Zhu, J, ''Synthesis of Eugenol-Based Multifunctional Monomers via a Thiol–Ene Reaction and Preparation of UV Curable Resins Together with Soybean Oil Derivatives.'' *RSC Adv.*, **6** (22) 17857–17866 (2016)
41. Yu, Y, Liao, B, Jiang, S, Li, G, Sun, F, ''Synthesis and Characterization of Photosensitive-Fluorosilicone–Urethane Acrylate Prepolymers.'' *Des. Monomers Polym.*, **18** (3) 199–209 (2015)
42. Bouvet, G, Dang, N, Cohendoz, S, Feaugas, X, Mallarino, S, Touzain, S, ''Impact of Polar Groups Concentration and Free Volume on Water Sorption in Model Epoxy Free Films and Coatings.'' *Prog. Org. Coat.*, **96** 32–41 (2016)
43. Farzad, H, Najafi, F, Bengisu, M, Yilmaz, E, Hadavand, BS, ''Synthesis and Characterization of Aliphatic Tri-Functional Oligomeric Urethane Methacrylate Used for UV-Curable Aluminum Pigmented Coatings.'' *J. Macromol. Sci. Part A*, **50** (5) 504–512 (2013)
44. Hu, Y, Jia, P, Shang, Q, Zhang, M, Feng, G, Liu, C, Zhou, Y, ''Synthesis and Application of UV-Curable Phosphorous-Containing Acrylated Epoxidized Soybean Oil-Based Resins.'' *J. Bioresour. Bioprod.*, **4** (3) 183–191 (2019)

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