

Synthesis and performance of a thermosetting resin: acrylated epoxidized soybean oil curing with rosin based acrylamide

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Abstract: A synthesized rosin based polymeric monomer (N-dehydroabiatic acrylamide) was introduced into an AESO/DHA-AM (acrylated epoxidized soybean oil/N-dehydroabiatic acrylamide) system to afford thermosetting resin by thermocuring. Different molar ratios of thermosetting AESO/DHA-AM samples were obtained through curing in the presence of the initiator and the curing processes of the AESO/DHA-AM systems were evaluated by Differential scanning calorimetry (DSC). The structure and performance of the resulting thermosets were characterized by Fourier transform infrared (FT-IR), Dynamic mechanical analysis (DMA), Elemental analysis, Thermogravimetric analysis (TGA) and Contact angle analysis. The analyses manifested that: with increasing the content of DHA-AM introduced in the copolymer, the storage modulus, the glass transition temperature (T_g), the thermal stability and

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the contact angle of the cured samples all increased. Moreover, the copolymers changed from hydrophilic material to hydrophobic material. The results also demonstrated that rosin acid derivatives showed comparable properties to the reported petroleum-based rigid compounds for preparing soybean oil-based thermosets. The presence of DHA-AM moieties in the composite structures could expand the utilization of AESO to make its development toward heat-resisting and hydrophobic materials.

INTRODUCTION

With the lack of conventional fossil fuels and the aggravation of environmental pollution, biomass sources such as rosin, cellulose, starch and vegetable oil are getting growing attraction.¹ As one of the most abundant renewable vegetable oils, soybean oil contains double bonds which can be used in many reactions.² More significantly, epoxidized soybean oil, the primary modified product of natural soybean oil, is obtained through the epoxidation reaction with soybean oil.³ With the characteristic of small irritation and low viscosity, epoxidized soybean oil is widely used in the area of plasticizers, food packaging materials, pharmaceutical products, etc.^{4,5} The further derivative acrylated epoxidized soybean oil (AESO, shown in Fig.1), containing reactive vinyl groups, was applied in the area of coatings, packaging material, paint and adhesive.⁶⁻¹⁰ Although there being other advantages like low toxicity and inherent biodegradability, the inferior glass transition temperature, mechanical properties and weak rigidity of AESO limited its application prospects in structural applications due to its aliphatic structure.¹¹

For the sake of improving the relatively poor properties, rigid polymeric monomer performing as a copolymer was introduced into the polymerization system to enhance its glass transition temperature, rigidity and mechanical properties. For example, reactive diluents were blended with AESO to improve the unfavorable properties.^{12,13} Coincidentally, vinyl ester resin which contains stiff aromatic unit was copolymerized with AESO to form a possible interpenetrating network structure.¹⁴ Furthermore, acting as the rigid components, petroleum-based products such as styrene^{15, 16}, divinylbenzene¹⁷⁻²⁰, dicyclopentadiene, norbornadiene²¹ and acrylated epoxidized fatty methyl ester²² were introduced into the AESO.

Rosin, an important nature resource which contains a three phenanthrene ring skeleton, is obtained by heating fresh resins to eliminate volatile terpene components from pines and other plants (such as conifers).²³ The modified product of rosin is manifold and they have been used in paper sizing, printing inks and adhesives.²⁴ On the other hand, polymerized rosin derivatives are important parts of modified rosin products. Rosin based polymers including epoxy resin²⁵, polyester, polyamide, polyimide are mainly investigated by researchers.²⁶ Vinyl, acrylate and allyl ester based rosin polymeric monomers acting as free radical chain polymeric monomer are the main modified rosin products which are widely utilized in paint, curing agent and resin.²⁷ Rosin based polymeric monomers contain polyimide²⁸ or polyamide unit make the polymers put up good mechanical properties, wear resistance and heat resistance, hence it is widely concerned by the researchers.^{29,30} Ma and coworkers prepared a full bio-based thermosetting resin from soybean oil

and rosin derivatives.³¹ The rosin derivatives showed great potential to replace the petroleum-based rigid compounds for the synthesis of bio-based thermosets with satisfactory properties. In order to achieve the necessary rigidity and improve the strength of bio-based thermosetting resin for some end applications³², we designed and synthesized a rosin based polymeric monomer N-dehydroabietic acrylamide, with polymeric double bond structure and amide unit in the monomer. The homopolymer of synthesized monomer appears good thermal stability and high glass transition temperature.³³

In this paper, synthesized N-dehydroabietic acrylamide was blended with AESO to prepare thermosetting resin by thermocuring. The FT-IR, DSC, TGA, DMA and contact angle test were used to characterize the structure and properties of polymers. With increasing the content of DHA-AM introduced in the copolymer, the storage modulus, the glass transition temperature (T_g) and the thermal stability of the cured samples all increased. As reported in our study, the breaking elongation of AESO/DHA-AM40 (AESO: DHA-AM=60:40 in molar) increased to 36.1%, which was higher than the breaking elongation of AESO/rosin derivates copolymers (13.9%) reported in the literature.³¹ The hydrogen bond in our synthesized N-dehydroabietic acrylamide has played a necessary role on the breaking elongation in the copolymer.

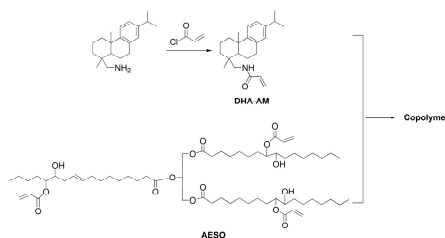


Fig.1 The scheme for copolymerization of AESO/DHA-AM system

EXPERIMENTAL MATERIALS AND METHODS**Materials**

Dehydroabietylamine was provided by Hangzhou Wanjing New Materials Co. Ltd., China. Acryloyl chloride (AC, with 200 ppm MEHQ as stabilizer, 96%) and *tert*-butyl peroxybenzoate (TBPT, 96%) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Dichloromethane (CH₂Cl₂, 99.5%), hydrochloric acid (HCl, 37%), potassium carbonate (K₂CO₃, 99%) and sodium chloride (NaCl, 99.5%) were all offered by Chinese Medicine Group Chemical Reagent Co., Ltd., China.

Preparation of rosin-based monomer (DHA-AM)

DHA-AM was prepared according to the procedure described by our previously published paper and the characterization was provided in the supplementary information.³³ Acryloyl chloride (8.145 g, 0.09 mol) dissolved in 50 mL dried CH₂Cl₂. Then the mixture was added into a 250 mL three-necked flask with a magnetic stirrer, a thermometer and a reflux condenser. The solution was cooled to -5°C and stable for a while at this temperature. Subsequently, a solution of dehydroabietylamine (17.128 g, 0.06 mol) in dried CH₂Cl₂ (50 mL) was added dropwise into the cooled acryloyl chloride solution within 30 min. After that, the temperature was elevated to 23°C and reacting for 30 min. The resulting mixture was washed successively with diluted hydrochloric acid, saturated potassium carbonate solution and distilled water. Final white solid was obtained as the product after removing the residual solvent by vacuum distillation.

Curing process of acrylated epoxidized soybean oil (AESO) and N-dehydroabiatic acrylamide monomer (DHA-AM)

Acrylated epoxidized soybean oil (AESO) and dehydroabiatic acrylamide (DHA-AM) were added into a three-necked flask with different molar ratios (in table 1). After the dissolution of DHA-AM in AESO, 2% initiator benzoyl peroxide tert butyl was added to the flask. Upon finishing the addition, the mixture was stirred vigorously until a homogeneous system was obtained. Until all the preparation finished, the reaction media was then poured into a mold and reacted at the curing temperature (the temperature was listed in Table 1 according to the DSC exothermic curves) for 4 h, followed by 170°C for 5 h. In order to prevent cracking, the cured samples were cooled to the room temperature slowly after the curing reaction.

Table 1 Composition and curing temperature of different samples

Samples	molar ratio(%)		Exothermic peak temperature (T _{max})	Curing temperature (°C)	Post-curing temperature (°C)
	AESO	DHA-AM			
AESO/DHA-AM0	100	0	135	110	170
AESO/DHA-AM10	90	10	144	120	170
AESO/DHA-AM20	80	20	151	130	170
AESO/DHA-AM30	70	30	153	130	170
AESO/DHA-AM40	60	40	156	130	170

The purification of cured sample

CH₂Cl₂ (500 ml) was added into a 1000 ml round-bottomed flask equipped with Soxhlet extractor which was put into 1 g cured sample. After 40 h reflux, the resultant samples were removed and dried for 8 hours in the vacuum oven before further characterization.

Characterization

Fourier transform infrared (FT-IR) spectra were obtained using the IS10 FT-IR (Nicolet, USA) for attenuation total reflection (ATR) test. Differential scanning calorimetry (DSC) was recorded with DSC 8000 (Perkin-Elmer, USA) using 3~4 mg sample, nitrogen flow rate of 50 mL/min and a temperature of 10°C/min ranging from 60 to 250°C. Dynamic mechanical analysis (DMA) was performed on a Q800 dynamic mechanical analyzer (TA, USA) using three point bending mode. The temperature of the sample with the size of 20 mm×15 mm×2 mm was ramped from -10 to 120°C at a heating rate of 2°C/min and a frequency of 1 Hz. The mechanical properties of cured resins were evaluated on a universal testing machine CMT 6503 (Shenzhen SANS Test Machine Co. Ltd., China) with a crosshead speed of 10 mm/min and an average value of at least five replicates for each sample was taken. All the testing samples were processed with a support span of 50 mm following ASTM D638-03. All the samples were tested in the condition of 25°C. Thermogravimetric analysis (TGA) was tested using a 409PC thermogravimetric analyzer. Each of samples was conducted from 35 to 700°C using a heating rate of 15°C/min under nitrogen atmosphere. The hydrophobic characters of cured samples were carried on a Kruss tensiometer (Easy Drop DSA-2). The sessile drop method was utilized to testing contact angles (θ), in which drops were created by using a syringe. The contact angle of each sample was determined with 3~5 μ L distilled water dropping on the surface of samples. After three times testing, the average was taken.

RESULTS AND DISCUSSION

Thermal curing behavior of the different proportion of AESO/DHA-AM

In order to investigate the curing behavior of the different proportion of AESO/DHA-AM, scanning curing exotherms of these cured samples were obtained from DSC measurements. The image of scanning curing exotherms was shown in Fig.2 and the results were summarized in Table.1. The results suggested that only a large exothermic peak appeared in all proportions of AESO/DHA-AM curves. The curing exothermic starting temperature and the exothermic peak temperature were all growing followed by the adding of rosin-based monomer. The more DHA-AM was added, the higher curing exothermic starting temperature and the exothermic peak temperature it had. To our knowledge, the curing exothermic starting temperature and the exothermic peak temperature had direct relation with the reactivity of the component.^{31, 34} The higher the curing exothermic starting temperature and the exothermic peak temperature of the curing process are, the lower reactivity of the component it has. Obviously, the curing exothermic starting temperature of AESO/DHA-AM0 was about 110°C and the exothermic peak temperature was about 135°C, which were lower than other proportion of AESO/DHA-AM systems during the polymerization. With the increase of the DHA-AM content, the curing exothermic starting temperature and the exothermic peak temperature were elevated. This result showed that with the adding of DHA-AM, the reactivity of the component was lower than the single AESO system, which was due to the lower reactive vinyl electron density in AESO/DHA-AM systems than in the single AESO system.

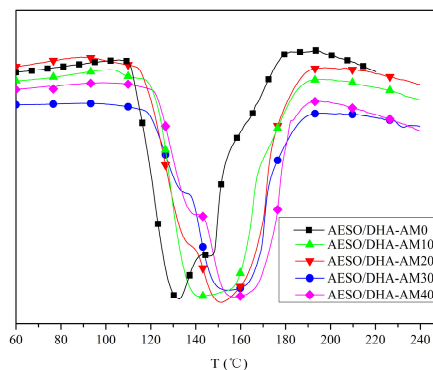
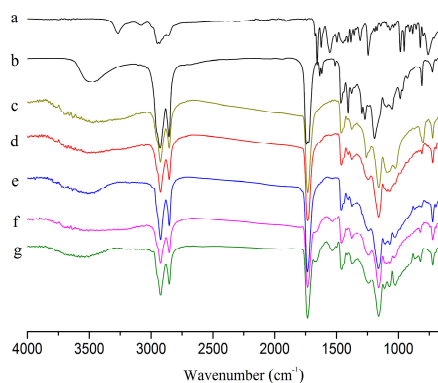


Fig.2. DSC thermogram of the curing procedure with different AESO/DHA-AM contents

FT-IR spectrum of the AESO and cured samples

Fig. 3 shows FT-IR spectrum of the monomers and cured samples, in which the C=O bond in AESO and cured samples could be confirmed by the characteristic peak shown at 1735 cm^{-1} . The C=O bond at 1656 cm^{-1} could be found in DHA-AM due to its conjugation with N-H. The characteristic absorptions for C=C were detected at 1623 cm^{-1} and 1638 cm^{-1} in AESO, respectively. The peak at 1623 cm^{-1} was formed owing to the conjugation between C=C and C=O in AESO. However, in the cured samples, the characteristic absorption for C=C stretching vibrations peak could not be observed. Moreover, the characteristic absorption bands for aromatic ring skeleton at approximately 1667 cm^{-1} and 1534 cm^{-1} gradually enhanced in intensity due to the increase of the content of DHA-AM. These results implied that the reactants have been completely copolymerized.



a. DHA-AM monomer b. AESO monomer c. AESO/DHA-AM0
d. AESO/DHA-AM10 e. AESO/DHA-AM20 f. AESO/DHA-AM30
g. AESO/DHA-AM40

Fig.3. FT-IR spectrum of the monomers and cured samples

Dynamic mechanical properties of the cured samples

The dynamic mechanical properties of different molar ratio cured samples were shown in Fig.4 and the data were summarized in Table 2. Concerning the curves in Fig.4, similar DMA behaviors were found in this study. The peak of the loss tangent ($\tan \delta$) was single, which indicated that the cured samples were compatible and homogenous.³⁵ Glass transition temperature (T_g) of each cured sample was measured from the peak temperature of $\tan \delta$. As is known to all, T_g of a cured resin would rest with the structure of the monomers and the cross-linked density of cured samples. As the DHA-AM content increased, T_g s of the cured samples became higher, which suggested that the adding of DHA-AM rendered the copolymer possess stronger rigid molecular structure than single AESO polymer. These results were likely attributed to the large phenanthrene ring structure in DHA-AM rather than long aliphatic chains,

which seemed to have more restriction on the chain segment movement. On the other hand, the cross-linked density, which would be discussed below, should be another reason to interpret the improved T_g s. The formation of AESO-rich and DHA-AM-rich regions with variable compositions in the polymer was a possible effect which results in broad glass transition behavior and spanning the range of the different phase transitions. As reported, interpenetrating polymer networks was commonly explained for this behavior on the micro level.³⁶ Obviously, the storage modulus (E'), which was also related to the chemical structure and cross-linked state, was strengthened signally with the increasing DHA-AM content. Clearly, the endsville E' could be obtained from the AESO/DHA-AM40 sample. Nevertheless, the cross-linked density was conversely influenced by E' , which can be considered to be equivalent to the elastic modulus (E) in the rubber plateau region. The experimental crosslinking density (ν_e) of the cured resins can be calculated in the formula as follows:^{31,37}

$$E=3\nu_eRT$$

where E is the elastic modulus of the cross-linked polymer, which can be considered to be equivalent to E' in the rubber plateau region ; R is the gas constant and T is the temperature in Kelvin. To make sure the cured resins were in the rubber state, the value of E' at $T_g+40^\circ\text{C}$ was used to replace that of E . The data of the crosslink density of the cured systems were shown in Table 2.

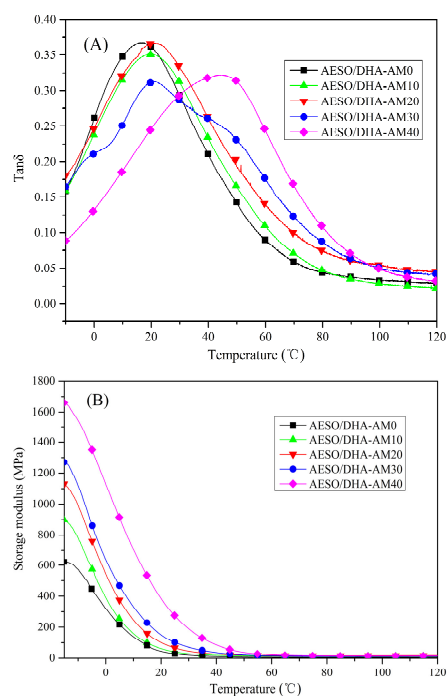


Fig.4. (A) $\tan \delta$ and (B) storage modulus curves of cured samples

Table 2 Mechanical and thermal properties analysis of the cured samples

Samples	T_g (°C)	Storage	Breaking	tensile	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	crosslink density (mol/m ³)
		modulus (MPa)	elongation (%)	strength (MPa)				
AESO/DHA-AM0	16	28	24.7±0.3	1.1±0.2	329.8	404.4	402.1	751
AESO/DHA-AM10	19	41	27.0±0.1	1.6±0.1	332.6	403.5	407.2	1531
AESO/DHA-AM20	20	67	27.4±0.1	2.0±0.1	331.5	406.0	409.5	1987
AESO/DHA-AM30	22	102	32.0±0.3	4.3±0.1	333.3	407.1	410.4	1616
AESO/DHA-AM40	45	273	36.1±0.3	5.7±0.2	335.6	408.8	411.6	1606

Mechanical properties of the cured samples

The mechanical properties of cured samples were investigated. The compared results including crosslink density were listed in Table 2 and the tensile stress-strain curves of AESO/DHA-AM samples with different molar ratios were shown in Fig.5. It

could be seen that the breaking elongation of copolymers ranged from 24.7% to 36.1% and tensile strength changed from 1.1 to 5.7 MPa. The cured AESO/DHA-AM40 sample exhibited the highest tensile strength and breaking elongation, while the cured pure AESO showed the lowest tensile strength and breaking elongation. The result was indicative of the improvement on tensile strength and breaking elongation by the adding of DHA-AM.

With different molar ratios of monomers, the chemical structures and cross-linked states in the cured resins varied accordingly and significantly.³⁷ The residual monomers in the copolymers served as plasticizer, meanwhile the DHA-AM was the hardening agent for the cured resins.³⁸ When lower content of DHA-AM was added, the components in the cured system were mostly homopolymerized rather than copolymerized. Therefore, AESO/DHA-AM10 and AESO/DHA-AM20 had the similar properties with the cured AESO/DHA-AM0. Moreover, AESO/DHA-AM30 and AESO/DHA-AM40 with higher DHA-AM contents, exerted significant improvement on both tensile strength and breaking elongation. The stronger tensile strength may be explained by the fact that hydrogen bond of N-H and main crosslink densities in the copolymer were enhanced with the increasing DHA-AM. Moreover, higher crosslink density also bestowed higher breaking elongation. More narrowly, AESO/DHA-AM30 and AESO/DHA-AM40 improved in tensile strength visibly could be explained by the synergistic effect of hydrogen bond and crosslink density.

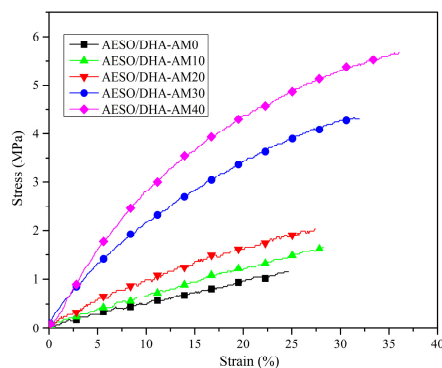


Fig.5. Tensile stress-strain curves of cured samples

Thermogravimetric analysis of the cured samples

Fig.6 showed different TGA curves of the samples. The 5%, 50% and the maximum weight loss temperatures ($T_{5\%}$, $T_{50\%}$ and T_{max}) are summarized in Table 2. As we know, initial weight loss temperatures ($T_{5\%}$) is related to the decomposition of soluble or unreacted components. Obviously, we could find $T_{5\%}$ s of all cured samples were higher than 329°C, which revealed the cured samples all had high thermal stabilities. In addition, the $T_{50\%}$ which represents the main chain degradation was above 404°C, indicating the rigid structure in the polymer. Furthermore, T_{max} , which is the corresponding temperature at the maximum rate of weight loss, was also improved from 402.1°C to 411.6°C. These results demonstrated that $T_{5\%}$, $T_{50\%}$ and T_{max} in AESO/DHA-AM40 were all highest than those of other samples. The decomposition of unreacted components and the main chain degradation were all improved slightly with DHA-AM due to the rigid confined phenanthrene ring structure and the higher cross-linking density.³⁹ These results were indicative of improvements which related to the high thermostability.

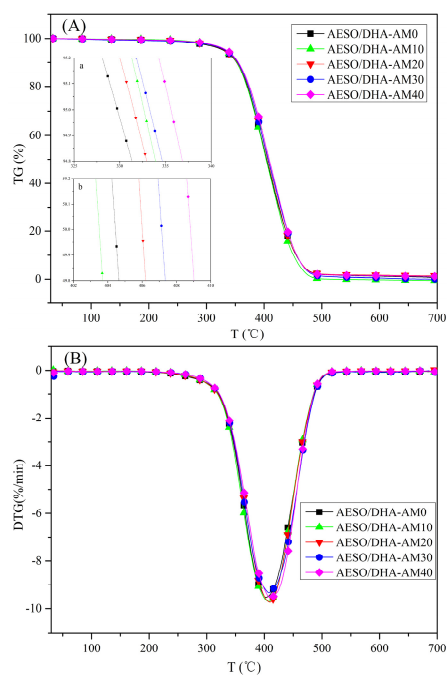


Fig.6. (A) TG and (B) DTG curves for the different cured samples

Elemental analysis of the cured samples

In order to verify AESO and DHA-AM were combined by the chemical linking, the purification process was prepared for AESO/DHA-AM samples before elemental analysis. The elemental analyses of the purified AESO/DHA-AM samples were performed and the calculated results were listed in Table 3. Mass fraction of N and C element can be represented by the formula (1) and (2) respectively. The C_1 and C_2 in the formulas are the molar quantity of DHA-AM and AESO in W g copolymer units, respectively. According to formula (1) and formula (2), the mole fraction of the DHA-AM monomer in the purified AESO/DHA-AM can be derived in formula (3). With increasing the DHA-AM content, the percentages of nitrogen content in the polymers

increased. The phenomenon could be explained by fact that nitrogen element only existed in the DHA-AM monomer. Additionally, the changes of calculated element content were basically in accord with the theoretical values. The results indicated DHA-AM was copolymerized with AESO in the system.⁴⁰

$$N\% = \frac{14C_1}{W} \quad (1)$$

$$C\% = \frac{12(23C_1 + 62C_2)}{W} \quad (2)$$

$$\frac{C_1}{C_1 + C_2} = \frac{372N\%}{234N\% + 7C\%} \quad (3)$$

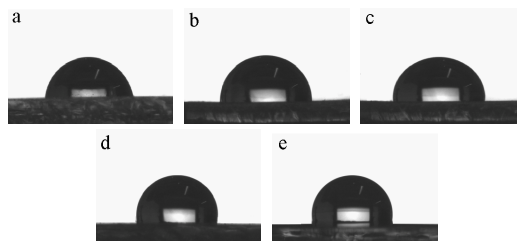
Table 3 Elemental analysis of purified AESO/DHA-AM samples

Samples	C (wt%)		H (wt%)		N (wt%)		DHA-AM (mol%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
AESO/DHA-AM0	68.2	67.5	9.72	9.64	0	0	0	0
AESO/DHA-AM10	68.6	68.0	9.72	9.71	0.138	0.0629	10	4.77
AESO/DHA-AM20	69.2	68.3	9.72	9.71	0.297	0.214	20	15.1
AESO/DHA-AM30	69.8	68.6	9.72	9.35	0.485	0.291	30	19.7
AESO/DHA-AM40	70.5	69.3	9.72	9.65	0.709	0.538	40	32.8

Contact angle analysis of cured samples

The contact angle diagrams of the cured samples were shown in Fig.7. The pure cured sample without DHA-AM was tested to be hydrophilic material with a contact angle of 81°. For AESO/DHA-AM10, AESO/DHA-AM20, AESO/DHA-AM30 and AESO/DHA-AM40, the contact angles were measured at 91°, 95°, 102° and 105°, respectively. All the copolymers exhibited hydrophobic characters and the AESO/DHA-AM40 sample showed the highest contact angle value owing to the largest molar proportion of DHA-AM was added. The large phenanthrene ring structure of DHA-AM would be responsible for their hydrophobicities. Moreover,

water resistance was enhanced due to the adding of DHA-AM which changed the interface energy of cured resin.



a. AESO/DHA-AM0: 81° b. AESO/DHA-AM10: 91° c. AESO/DHA-AM20:95°
d. AESO/DHA-AM: 102° e. AESO/DHA-AM: 105°

Fig.7 Contact angles of the cured samples

CONCLUSION

N-Dehydroabiatic acrylamide (DHA-AM), a rosin based polymeric monomer, was synthesized and introduced into an AESO/DHA-AM system to afford thermosetting resin by thermocuring. The large phenanthrene ring structure in DHA-AM contributed more restriction on the chain segment movement than long aliphatic chains. With the content of DHA-AM in the copolymer increased from 0 to 40% (molar ratio), the cured samples exhibited the increasing storage modulus, glass transition temperature (T_g) and thermal stability. The hydrogen bond of N-H and main crosslink densities in the copolymer enhanced the tensile strength with the increasing DHA-AM molar ratio. The large phenanthrene ring structure with hydrophobic characters makes the copolymers changed from hydrophilic material to hydrophobic material. In conclusion, DHA-AM monomer, with a large phenanthrene ring structure and hydrogen bond interaction, copolymerized with AESO will make its

development toward heat-resisting and hydrophobic materials.

ACKNOWLEDGEMENTS

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