World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:10, No:4, 2016

UV-Cured Coatings Based on Acrylated Epoxidized Soybean Oil and Epoxy Carboxylate

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Open Science Index, Materials and Metallurgical Engineering Vol:10, No:4, 2016 publications.waset.org/10004382/pdf

***Abstract*—**During the past two decades, photoinitiated polymerization has been attracting a great interest in terms of scientific and industrial activity. The wide recognition of UV treatment in the polymer industry results not only from its many practical applications but also from its advantage for low-cost processes. Unlike most thermal curing systems, radiation-curable systems can polymerize at room temperature without additional heat, and the curing is completed in a very short time. The advantage of cationic UV technology is that post-cure can continue in the 'dark' after radiation. In this study, bio-based acrylated epoxidized soybean oil (AESO) was cured with UV radiation using radicalic photoinitiator Irgacure 184. Triarylsulphonium hexafluoroantimonate was used as cationic photoinitiator for curing of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. The effect of curing time and the amount of initiators on the curing degree and thermal properties were investigated. The thermal properties of the coating were analyzed after crosslinking UV irradiation. The level of crosslinking in the coating was evaluated by FTIR analysis. Cationic UV-cured coatings demonstrated excellent adhesion and corrosion resistance properties. Therefore, our study holds a great potential with its simple and low-cost applications.

***Keywords*—**Acrylated epoxidized soybean oil, epoxy carboxylate, thermal properties, UV-curing.

I. Introduction

UV-RADIATION curing has become a well-accepted technology, because of its extraordinary properties and multiple industrial applications such as fast-drying protective coatings, printing inks and adhesives. A liquid resin can be transformed almost instantly into a solid polymer material by simple exposure to UV light at ambient temperature, without emission of volatile organic compounds [1]. The presence of unsaturation at the end of the polymer backbone as a result of the reaction with acid functional acrylic monomers has shaped epoxy resins for the radiation curing industry. Cured epoxy resins display excellent adhesion to a variety of substances, good chemical and corrosion resistance, extraordinary electrical insulation, high tensile, flexural and compressive strength and thermal stability. The curing process is faster and depends on the radiation dose and the time of radiation [2]. Mechanical and thermal properties of cured epoxy resins are very sensitive to the chemical and structural nature of the epoxy resins and crosslinker, the type and concentration of cure initiators, crosslinking reaction conditions in the UV chamber, epoxy conversion, and crosslinker to epoxy acrylate ratio [3]-[5].

In the present study, biobased AESO and 3,4-epoxycyclohexylmethyl-3,4-epoxy-cyclohexane-carboxylate were cured by UV radiation using radical and cationic photoinitiators.

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II. Experimental

A. Materials

AESO and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate were obtained from Sigma-Aldrich, as illustrated in Fig. 1. Radicalic photoinitiator Irgacure 184 and cationic photoinitiator triarylsulphonium hexafluoroantimonate from Sigma-Aldrich were used in this study, as illustrated in Fig. 2.

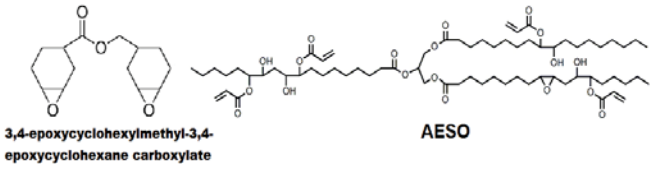


Fig. 1 Chemical formula of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate and AESO

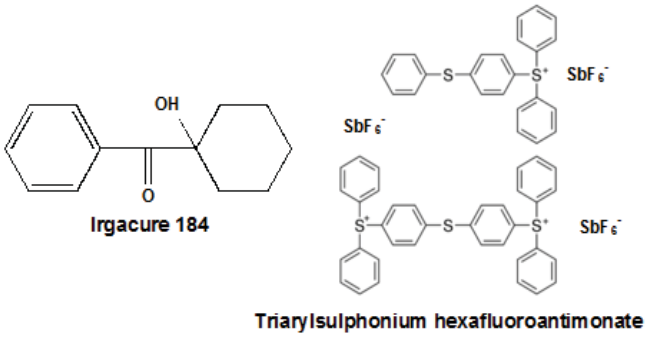


Fig. 2 Chemical formula of photoinitiors

B. UV-Cure

1 g of resin and 20 mg of photoinitiator were mixed with different percentages, 2% and 4%, respectively. The liquid formulations were coated onto a glass substrate of approximately 0.2 mm thickness with the help of an applicator and exposed to UV radiation, then post-cured at 100 °C. All samples were irradiated for 3 and 6 min by UV lamp, which was the emission wavelength of 246-365 nm. The irradiation

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power of the lamp was 80 W/cm^2 and the distance between sample and lamp was 2.54 cm.

C. Analysis and Testing

1) FTIR Analysis

The FTIR spectra were recorded with Bruker-Platinum ATR- vertex 70 between 500 and 4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} using an attenuated total reflectance (ATR) accessory.

2) Calculation of the Curing Degree

According to the Beer–Lambert law, the absorption peak at 1600-1616 cm^{-1} of a benzene ring can be regarded as an internal standard; thus, the degree of curing can be determined from the FTIR spectra of uncured and cured epoxy [6].

3) Thermal Analysis

The thermal analyses were performed with aMettler Toledo Thermo Gravimetric Analyser. Samples were heated under a nitrogen atmosphere from 50 °C to 600 °C at a heating rate of 20 °C min^{-1} during the analyses.

III. Results and Discussion

A. Curing Degree

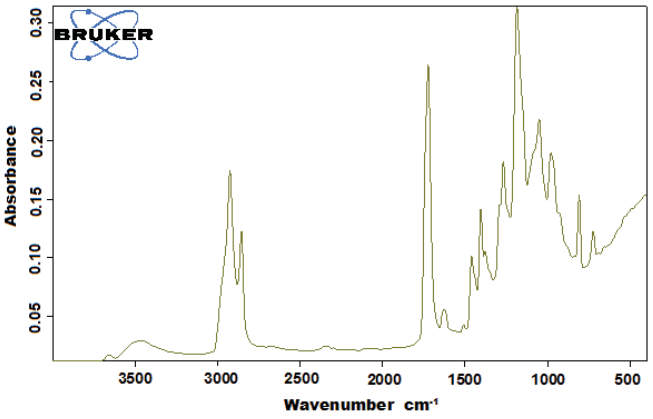
The chemical structures of uncured and cured epoxides are confirmed by FTIR spectra (see Fig. 3). Table I summarizes the calculated curing degree values.

Characteristic bands belonging to C-H vibrations are observed in the regions of 2830-3000, 1600, 1400-1450, and 1375 cm^{-1} for aliphatic C-H stretching, aromatic C=C stretching, aliphatic C-H bending, and C-H rocking, respectively. Additionally, the presence of epoxide groups is characterized by the appearance of typical bands at 1250, 913, and 830 cm^{-1} corresponding to stretching C-O-C of ethers, stretching C-O of oxirane group, and stretching C-O-C of oxirane group. As reported by [7], the absorption assigned to C–O stretching of the epoxide at 906 cm^{-1} almost disappeared after curing in the neat epoxy resin. The band in the range of 912 cm^{-1} is not observed in the FTIR spectra of most of the cured M-ERs, which indicates that these modified epoxy samples are cured very well as shown in Figs. 3 (a)-(h).

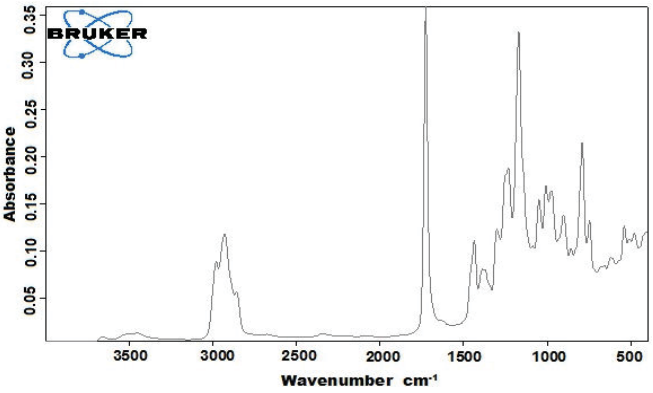
Table I shows that 2% of photoinitiator curing degrees of cured AESO were higher than cured 3,4-epoxy-cyclo-hexyl-methyl-3,4-epoxy-cyclohexane carboxylate. 100% curing degree for 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate was obtained with 4% of photoinitiator.

TABLE I
Curing Degrees

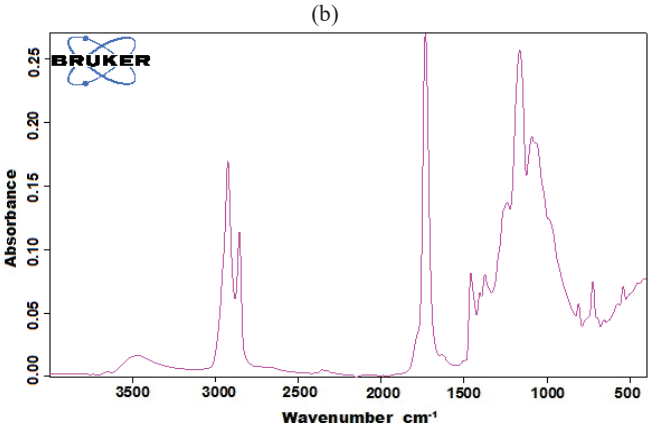
Time (min.)	AESO (UV-cured with Irgacure 184)	3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (UV-cured with triarylsulphoniumhexafluoroantimonate)
For 2% photoinitiator		
3	100	97
6	100	98
For 4% photoinitiator		
3	-	100
6	-	100



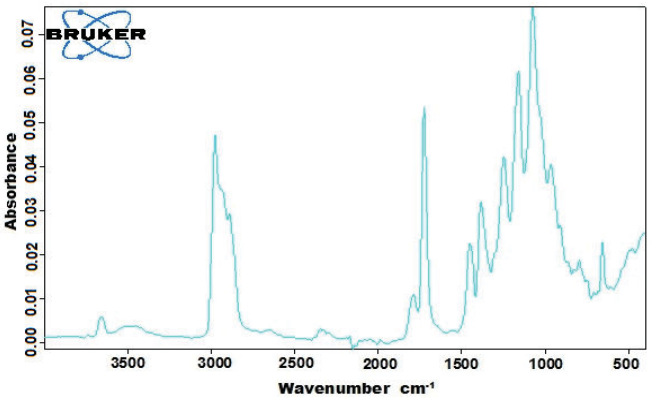
(a)



(b)

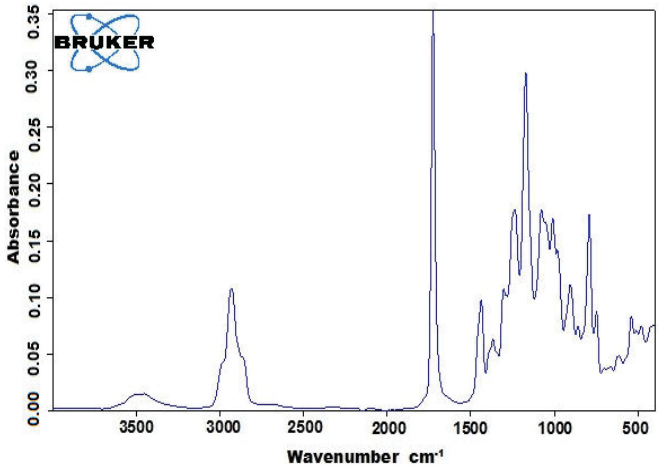


(c)

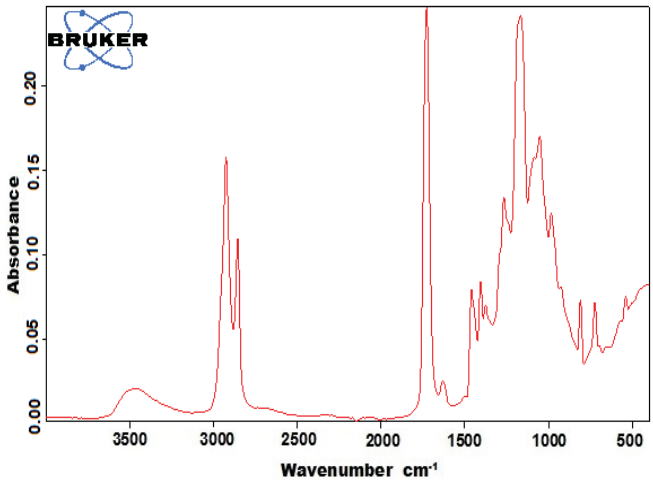


(d)

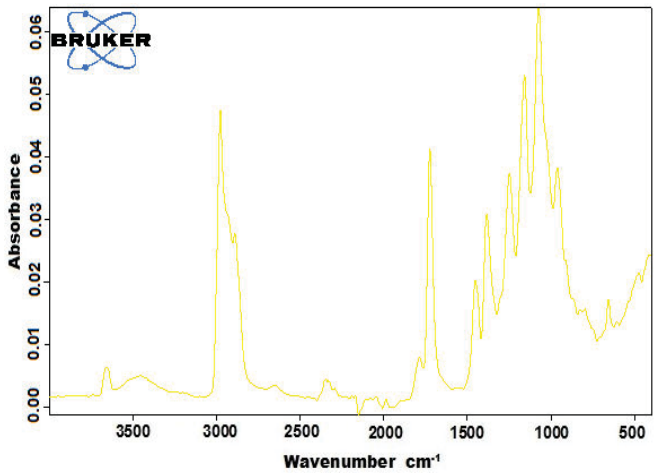
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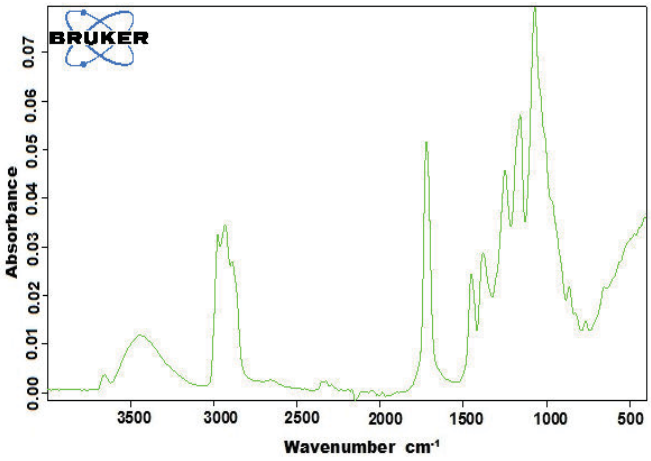
(e)



(f)



(g)



(h)

Fig. 3 FTIR spectra of UV-cured samples: (a) uncured AESO; (b) uncured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; (c) cured AESO (3 min., 2% photoinitiator); (d) cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (3 min., 2% photoinitiator); (e) cured AESO (6 min., 2% photoinitiator); (f) cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (6 min., 2% photoinitiator); (g) cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (3 min., 4% photoinitiator); (h) cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (6 min., 4% photoinitiator)

The thermal stabilities of the uncured and cured epoxies were determined from degradation behavior in nitrogen atmosphere and were assessed using thermo gravimetric analyses (TGA) (see Figs. 4-9). Table II summarizes the test results.

TABLE II
THERMAL PROPERTIES OF UNCURED AND UV-CURED EPOXIES

t, min	IDT	Loss of weight (%) at 1. SD	T_{50}	SDT	Loss of weight (%) at 2. SD	T_{50}	RW (%)
For uncured AESO							
-	220	97.4	315	-	-	-	2.9
For uncured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate							
-	168	99	311	-	-	-	1.3
For cured AESO (2% photoinitiator)							
3	226	95.3	404	-	-	-	4.2
6	164	32.4	289	357	60.5	415	7.4
For cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (2% photoinitiator)							
3	272	95.2	408	-	-	-	5.4
6	258	70.6	412	-	-	-	30.8
For cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (4% photoinitiator)							
3	262	95.44	414	-	-	-	7.1
6	276	77.9	416	-	-	-	23.7

*IDT-initial decomposition temperature
**SDT-second decomposition temperature
***T_{50}-temperature at 50 wt% loss weight
****RW-residual weight

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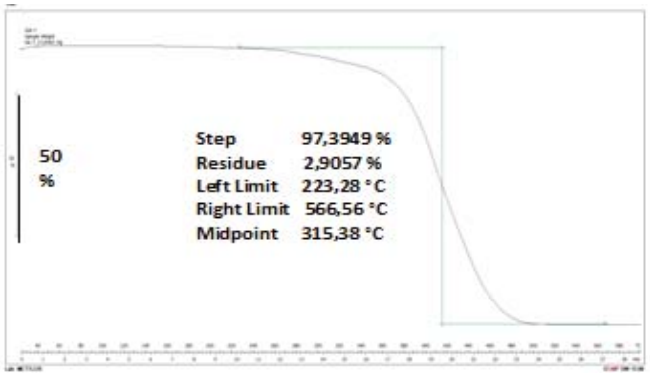


Fig. 4 TGA curve of uncured AESO

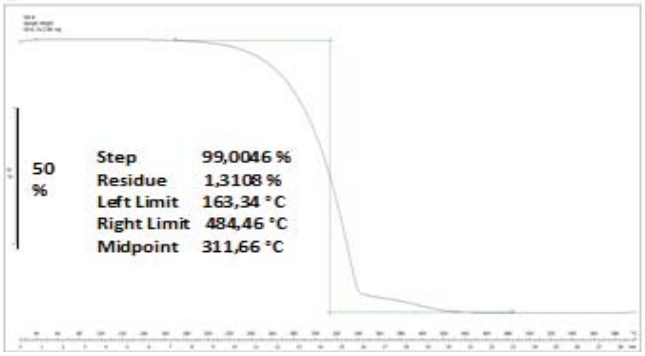


Fig. 5 TGA curve of uncured 3, 4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate

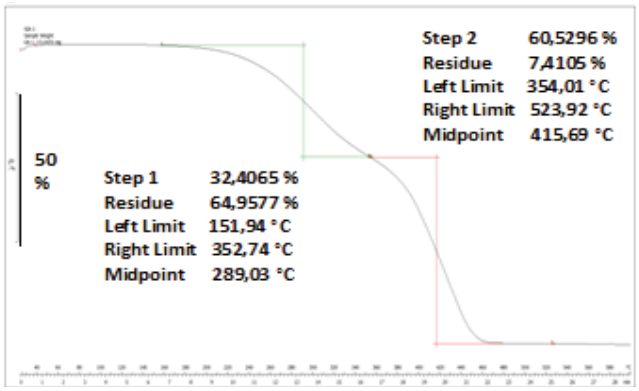


Fig. 6 TGA curve of cured AESO (6 min., 2% photoinitiator)

Table II summarizes that comparing the cured systems at 2% photoinitiators, the thermal stability increased with curing time for both systems. Increasing photoinitiator amount up to 4% did not have a significant effect on the T_{50} value and residual %.

IV. Conclusion

The curing degrees of both epoxy compounds were determined higher than 97%. However, cured 3,4-epoxy-cyclo-hexylmethyl-3,4-epoxy-cyclo-hexane carboxylate was found more thermally stable than cured AESO.

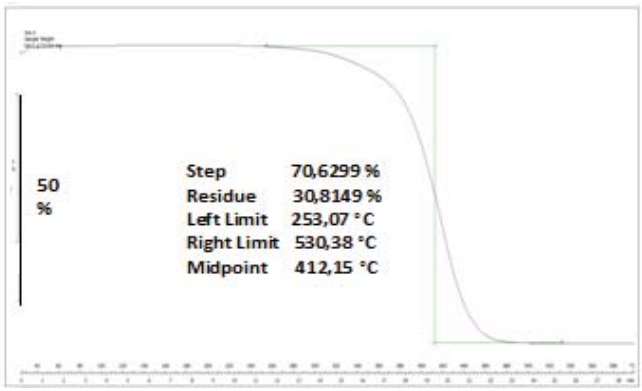


Fig. 7 TGA curve of cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (6 min., 2% photoinitiator)

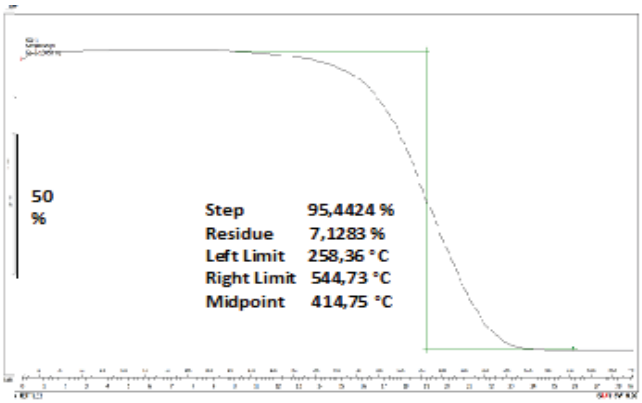


Fig. 8 TGA curve of cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (3 min., 4% photoinitiator)

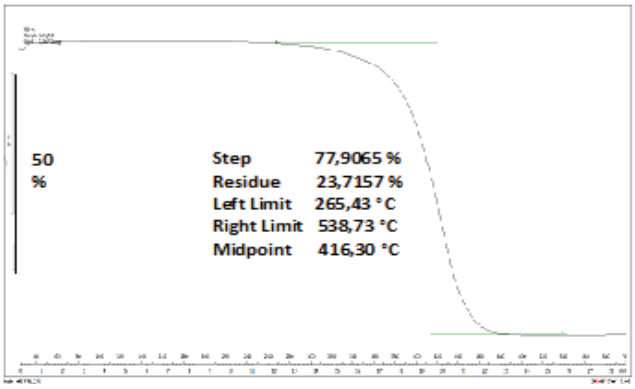


Fig. 9 TGA curve of cured 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (6 min., 4% photoinitiator)

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