

Influence of Epoxidized Sunflower Oil on the Properties of the Polymer Composite Materials Based on Epoxy Resin GELR 128 Cured by Diethylenetriamine

Bach Trong Phuc¹, Vu Huu Hung², Nguyen Thanh Liem¹

¹ Polymer Centre, Hanoi University of Science and Technology, Hanoi, Vietnam

² Ministry of Public Security

Abstract: Epoxidized sunflower oil (ESO) has been used to toughen epoxy resin GELR 128 cured with an ambient temperature hardener (diethylenetriamine – DETA). The ESO was mixed with epoxy resin to obtain modified networks having various concentrations of ESO by one-stage and two-stage process. All the modified networks were characterized for their morphological structure, mechanical and thermal properties, and compared to the parent epoxy network. The two-stage process was considered to be more advantageous than the one-stage process. The optimum properties were obtained at 15 parts per hundred grams of epoxy resin (phr) of ESO. The best tensile strength, flexural strength and decomposition temperature are 44.81 MPa, 22.189kJ/m², 375.05°C respectively.

Keywords: epoxidized sunflower oil, epoxy resin GELR 128, diethylenetriamine, ambient temperature, toughness.

I. INTRODUCTION

Epoxy resins are one of the thermoplastic resins widely used such as adhesives, surface coatings, engineering composites, insulating materials and auto technique. The major disadvantage of cured epoxy resins is crispy so epoxy resins is low impact resistance in composite application and low tensile strength tear strength for the glueapplication [1].

Therefore, the epoxy resin toughening method is necessary to improve their disadvantage which has been studied by researches[2, 3]. Elongation is the absorption capacity abilities of the material and the plastic deformation without cracks is achieved by reducing the cross-linking density or using plasticizers to increase plastic deformation [4]. However, this method may affect to the modulus and thermal properties of the material so the toughness is only slightly increased. The most achieved effective method is added another component to phase separation, such as adding an active liquid rubber [5, 6], thermoplastic [7, 8] core- shellstructure material [9, 10]. The epoxy resins synthesis from epoxidized vegetable oils for incorporating into cured epoxide resins which is a promising method to increase the mechanical strength and mechanical properties of the original epoxy resin. There are environmental

advantages over petroleum based plastics. This paper discusses the thermal, mechanical properties and morphology of ESO modified epoxy resin GELR 128 cured with an ambient temperature hardener (DETA).

II. EXPERIMENT

2.1 Materials

- Epoxyresinused in this study was DGEBA supplied by Epoxy Base Electronic Material Corporation Limited of China (GELR 128) which had an epoxide equivalent weight (EEW) of 184-190g eq⁻¹ and a viscosity at 25°C: 11-15 Pa.s;

- Epoxidized sunflower oil (ESO) was synthesized by using ion exchange method. The content of epoxy group is 16.45% with oxiran value 6.12.

- Diethylenetriamine(C₄H₁₃N₃) DETA was purchased from Dow Chemicals (USA) (density 0.95 g/cm³ at 25°C, boiling point 207°C and molecular weight 103g/mol)

2.2 Modified epoxy resins

Modified epoxy resins were prepared by mixing DGEBA GELR 128 and epoxidized sunflower oil in two processes:

One-stage process: the various amount of ESO (0 – 30phr)was added into 100 g of GELR 128 epoxy resin in 250 ml glass beakers, stirring for 45 minutes. Then DETA was added with a pre-calculated ratio and stirred for 5 minutes. The all components werepoured into a mold for curing at room temperature.

Two-stage process: Mixing ESO and DETA in a 3-necked 250-ml flask were stirred for 20 hours, adding epoxy resin GELR 128 and continued stirring for 5 minutes and then poured the mixture into the mold to cure at room temperature.

2.3 Research Methods

- The morphologies at the fracture surfaces of the epoxy samples were evaluated from Scanning Electron Microscopy

(SEM) on Hitachi (Japan) S4800 at the main laboratory, Institute of Materials Science - Vietnam Academy of Science and Technology

- Thermal stability was studied by simultaneous thermo gravimetric analyzer (TGA) by SETARAM TG under a heating rate of $10^{\circ}\text{C}/\text{min}$. within a temperature range of ambient room temperature to 800°C at Hanoi University of Sciences, Hanoi National University.

- The tensile strength was determined according to ISO 527-2012 on the INSTRON 5582-100kN (USA) with the crosshead speed of 2 mm / min at the Polymer Centre, Hanoi University of Science and Technology.

- The flexural strength was determined according to ISO 178 on the INSTRON 5528-100kN (USA) with the crosshead speed of 2mm / min at the Polymer Centre, Hanoi University of Science and Technology.

- Izod impact strength was determined according to ISO 180 on the Tinius Olsen Model 92T (USA) at the Polymer Centre, Hanoi University of Science and Technology.

- The critical stress intensity factor, K_{IC} value was determined according to ASTM D5045-99 by three point sided on a Lloyd 500N (UK) with the crosshead speed of 10mm / min at the Polymer Centre, Hanoi University of Science and Technology.

III. RESULTS AND DISCUSSION

3.1 Morphological structure

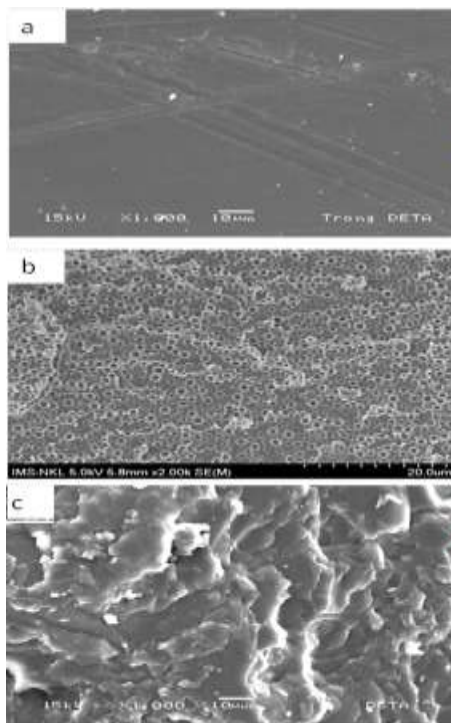


Fig.1 SEM image of modified epoxy resin GELR 128 a) without ESO b) 1 stage process with 15phr ESO b) 2 stage process with 15phr ESO

SEM of modified epoxy resin GELR-128 without ESO and with 15phr ESO was shown in Figure 1. From Figure 1 (a), the unmodified epoxy resin GELR 128 is smooth surfaces as a mirrors with cracks in different surfaces characterize which is the lower impact strengths of thermoplastic resins. The fractured surface of the modified ESO epoxy resin GELR-128 consists of two distinct phases: spherical resins dispersed in a continuous epoxy network. The seeds are about $1-2\mu\text{m}$ in diameter. DETA is an aliphatic amine that interacts with epoxy resin GELR-128 higher than ESO's epoxy group so that it forms a durable grid while epoxidized sunflower oil decomposes into second phase as small liquid droplets (Figure 1b). The surface of epoxy resin GELR-128 with added ESO has an uneven roughness profile as unmolded epoxy resin GELR-128, which shows the durability of the material.

3.2 Mechanical properties

The results of tensile and flexural properties of epoxy resin GELR 128 were denominated in two processes with and without epoxidized sunflower oil as shown in Table 1. The tensile strength of epoxy resin GELR-128 without ESO is 63.92 MPa with high flexural strength (104.9 MPa) and low modulus (1.84 GPa) which showed the hardness and brilliance of epoxy resin. When ESO is added, tensile strength and flexural strength decrease in proportion to the increase in the amount of ESO in the 1-stage process. Phase separation also does not affect the reduction of tensile strength and flexural strength in the two-stage processes due to the presence of low modulus phases in the epoxy network. This suggests that epoxy resins with ESO are more resilient than epoxy resins without the addition of a modified substance. In both process, tensile strength decreases gradually as increase the amount of ESO from 5-20 phr. The tensile strength suddenly decreases while the amount of ESO is higher than 30 phr. This trend is similar to the flexural strength value, but this significant decline occurs when ESO content is higher than 15 phr. Comparing with the one-stage process, the mechanical values of the epoxy resin GELR 128 after the denaturation by two-stage process are always lower, proving the superiority of the two-stage process, the material after the modify is more toughness with less amount of denaturation.

TABLE 1

THE EFFECT OF ESO TO THE TENSILE AND FLEXURAL PROPERTIES OF EPOXY RESIN GELR 128

	ESO (phr)	Tensile strength (MPa)	Elastic modular (GPa)	Flexural strength (MPa)	Flexural modular (GPa)
	0	63.92	1.84	104.9	3.43
One - stage process	5	58.01	1.76	91.9	2.98
	10	53.22	1.72	86.9	2.86
	15	52.84	1.58	67.1	2.34

	20	50.72	1.36	65.5	2.21
	30	35.23	1.26	50.2	1.35
Two - stage process	5	57.85	1.74	83.5	2.76
	10	50.09	1.67	81.7	2.64
	15	44.81	1.47	57.3	2.27
	20	42.38	1.31	50.7	2.08
	30	22.12	1.16	46.9	1.32

The relationship between the amount of ESO content and impact strength is shown in Figure 2. The impact strength of the epoxy resin GELR 128 after denaturation with ESO was significantly higher than without ESO. However, the impact strength of the epoxy resin GELR 128 was made by one-stage process which is only moderately increased due to single-phase morphology (as SEM image results). In the two-stage process, the energy of the shock increases significantly. The maximum impact strength of material was achieved at ESO content of 15 phr and decreases as ESO content increases.

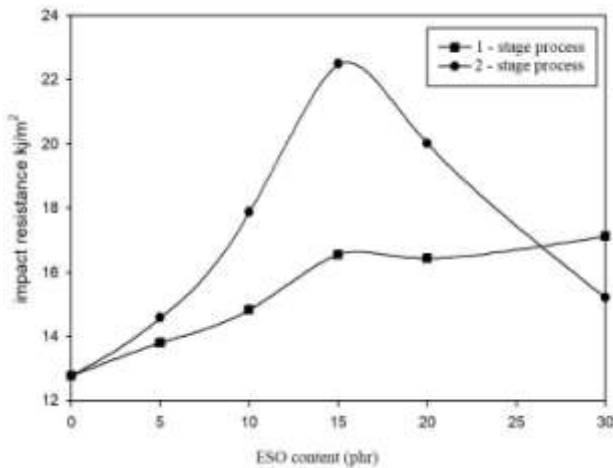


Fig. 2 Impact strength of epoxy resins after denaturation at different concentrations of ESO

The change in the durability deterioration was characteristic by the K_{IC} -concentrated stress ratio by ESO content is shown in Figure 3. It can be seen that the addition of ESO to the epoxy resin GELR 128 which is increased the stress concentrate coefficient. From Figure 3, in the two-stage process, the stress ratio was higher than this in the one-stage process in all five samples and reached the highest value of $1.68 \text{ MPa}\cdot\text{m}^{1/2}$ at the ESO level of 15 phr. Then this is tending to decrease to 1.61 and $1.41 \text{ MPa}\cdot\text{m}^{1/2}$ in samples with higher ESO content of 20 and 30phr respectively. This is explained by the fact that the amount of epoxidised sunflower oil increases, the agglomeration of the oil particles occurs and this causes the material to lose its elongation.

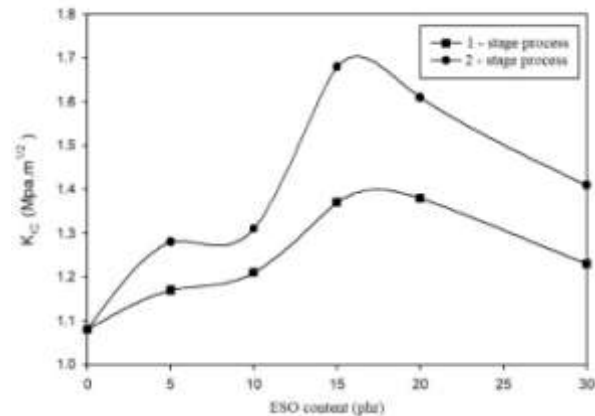
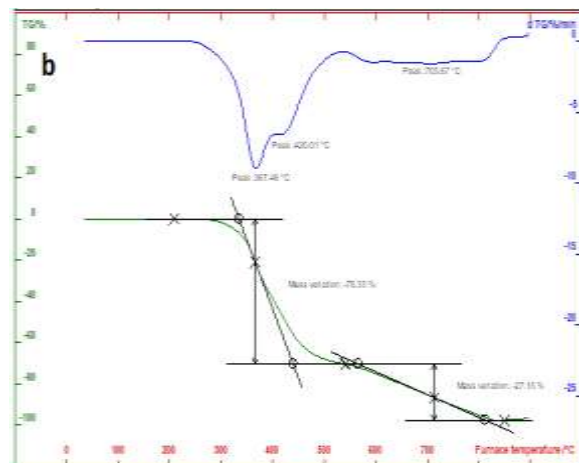
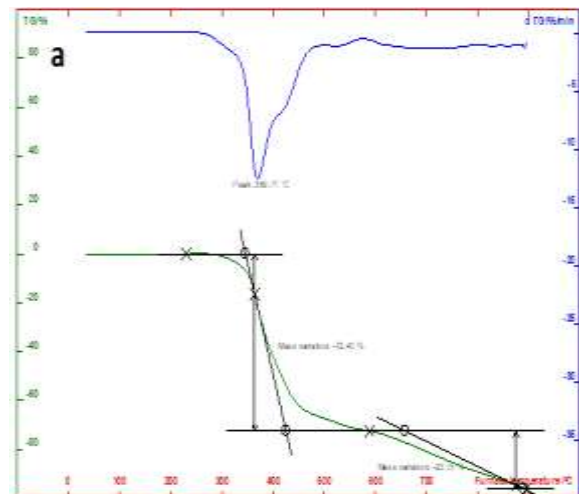


Fig. 3 Stress concentrate coefficient K_{IC} of epoxy resin after modification at various ESO content

From the above results, the epoxy resin GELR 128 with high content of ESO 15phr was chosen as the suitable ratio to improve the mechanical properties of epoxy resin GELR 128.

3.3. Thermal properties



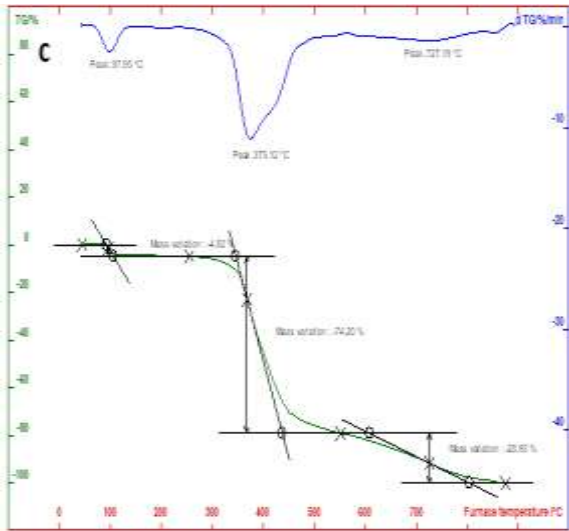


Fig. 4 The TGA of a) epoxy resin, epoxy resin modified with ESO by b) one-stage process, c) two-stage process.

From Table 2 and Figure 4 show the TGA results of epoxy resin GELR 128 (Fig 4a), epoxy resin GELR 128 mixture with ESO by one-stage process (Fig 4b), and by two-stage process (Fig 4c), it can be seen that when ESO adds into the denaturation of the epoxy resin GELR 128, the maximum decomposition temperature of the epoxy resin increased in the two-stage process and decreased in the one-stage process which is demonstrating that in the two-stage process the reaction is more complete.

Table 2

EFFECT OF ESO CONTENT ON THE MAXIMUM DECOMPOSITION TEMPERATURE(MDT) OF EPOXY RESIN GELR 128

Number	ESO content (phr)	MDT, °C
1	0	369.71
2	15 (one-stage process)	367.46
3	15 (two-stage process)	375.12

IV. CONCLUSION

Blends of epoxy resin GELR 128 with the epoxidized sunflower oil was carried out in a one-stage process (by direct mixing) to compare the properties with those made by the

two-stage process (by prepolymerization). The epoxidized sunflower oil acts as a plasticizer, does not phase separate when mixed directly ESO with epoxy resin GELR 128 and cured by DETA at ambient temperature. Phase separation was achieved when ESO mixed with epoxy resin GELR 128 by the two-stage process. The polymer composite materials based on epoxy resin mixing with the ESO by the two-stage process show higher impact strength than those made by one-stage process. The modified epoxy resin GELR 128 network (by two-stage process) with 15 phr ESO shows the best impact and thermal performance.

ACKNOWLEDGMENT

The authors gratefully acknowledge National Key Laboratory of Polymer and Composite Materials, Hanoi University of Science and Technology and Polymer Centre (HUST) for financial and equipment support.

REFERENCES

- [1]. D. Ratna and Ajit K.Banthia, (2000). Polymer International: Toughened epoxy adhesive modified with acrylate based liquid rubber.
- [2]. LêXuânHiền, Nguyễn ThịViệtTriều, PhạmThịHồng, Nguyễn Thiên Vương, (2000). Tạp chí Khoa học và Công nghệ: Nghiên cứu ảnh hưởng của hàm lượng dầu thầu đến tính chất của lớp phủ trên cơ sở nhựa epoxy biến tính.
- [3]. D. Ratna, A.K. Banthia, P.C. Deb, (2004). Journal of Applied Polymer Science: Processing and chemorheology of epoxy resins and their blends with dendritic hyperbranched polymers.
- [4]. D. Ratna, (2001). Polymer International: Mechanism properties and morphology of epoxidizedsoyabean-oil-modified epoxy resin.
- [5]. Sultan J.N., McGarry F.J., (1973). Polymer Engineering and Science: Effect of rubber particle size on deformation mechanisms in glassy epoxy.
- [6]. Reiw C.K., (1985). Rubber Chemistry and Technology: Elastomer modification of structural adhesives.
- [7]. Pasquale G.D., Motta O. and Recca A., Carter J.T.,McGrail P.T., Acierno D., (1997). Polymer: New high-performance thermoplastic toughened epoxy thermosets.
- [8]. Hodgkin J.H., Simon G.P. and Varley R.J.,(1998). Polymer Advanced Technology: Thermoplastic toughening of epoxy resin: acritical review.
- [9]. QianJ.Y., Pearson R.A., DimonicV.L.&E.I. AasserM.S.,(1995).Journal of Applied Polymer Science: Synthesis and application of core-shellparticles as toughening agents for epoxies.
- [10]. King Fu L., Yow Der,(1998). Applied Polymer Science: Core-shell particles designed for toughening the epoxy resins.II.Core-shell-particle-toughned epoxy resins.