

Effect of the Structure of Curing Agents Modified by Epoxidized Oleic Esters on the Toughness of Cured Epoxy Resins

Xu Cheng, Yan-Xiong Chen, Zong-Liang Du, Pu-Xin Zhu, Da-Cheng Wu

Textile Institute, Sichuan University, Sichuan Province, Chengdu 610065, China

Received 23 December 2009; accepted 25 June 2010

DOI 10.1002/app.32998

Published online 29 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The aim of this study was to determine the effect of the ester carbon chain length of curing agents modified by epoxidized oleic esters on the toughness of cured epoxy resins. An amine-terminated prepolymer (i.e., curing agent G) was synthesized from a bisphenol A type liquid epoxy resin and triethylene tetramine. The toughening curing agents (G1 and G2) were prepared by reactions of epoxidized oleic methyl ester and epoxidized oleic capryl ester, respectively, with curing agent G. Fourier transform infrared spectrometry was used to characterize the chemical structure of the curing agents. The effects of the carbon chain length of the oleic ester group in the curing agents on the toughness and other performances of the curing epoxy resins were investigated by analysis of the

Izod impact strength, tensile strength, elongation at break, thermal properties, and morphology of the fracture surfaces of the samples. The results denote that the toughness of the cured epoxy resins increased with the introduction of oleic esters into the curing agents without a loss of mechanical properties and that the toughness and thermal stability of the materials increased with increasing ester carbon chain length. The toughness enhancement was attributed to the flexibility of the end carbon chains and ester carbon chains of the oleic esters in the toughening curing agents. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3504–3510, 2011

Key words: curing of polymers; thermosets; toughness

INTRODUCTION

Epoxy resins are widely used in many fields, such as composite materials, coatings, adhesives, and electric encapsulating materials, because of their good performances in adhesiveness, mechanical capacity, electric properties, chemical resistance, and corrosion protection, especially at elevated temperatures. However, the brittleness and low impact resistance of the resins restrict their wide application. In the late 1960s, epoxy resins toughened by the incorporation of liquid rubber were first introduced by McGarry.¹ Since then, studies of epoxy toughening with elastomers that have reactive end-group liquid rubber have developed rapidly. Several reactive liquid rubbers, including carboxyl-terminated butadiene–acrylonitrile rubber, hydroxyl-terminated polybutadiene, hydroxyl-terminated butadiene–acrylonitrile rubber, amine-terminated butadiene–acrylonitrile,^{1–7} carboxyl-terminated (or randomized) polyacrylate,^{8,9} and silicone elastomer,^{10,11} have been used to toughen epoxy resins. In the curing process, phase

separation occurs at a certain stage and leads to the formation of a two-phase microstructure. Such rubber particles dispersed and bonded to the epoxy matrix have unique crack resistance and play an important role in toughening effects.^{3,8,12,13} The use of the rubbers, however, leads to decreases in the thermal stability and modulus values of the toughening materials. To improve the properties of epoxy resins toughened by rubbers, high-modulus and heat-resistant thermoplastics, for example, poly(ether sulfone),^{14–16} poly(ether ether ketone),¹⁷ poly(ether imide),^{18,19} and polyimide,²⁰ have been used as toughening agents. However, their low solubility and fluidity deteriorate the curing and adhesive performances of the epoxy resins. Liquid-crystalline polymers have also been used recently as fillers to improve the toughness of epoxy resins.^{21,22} Compared with other materials, a relatively smaller amount of the liquid-crystalline polymers can not only improve the toughness of the epoxy resins but also increase their modulus and heat resistance. In addition, rigid nanoparticles and nanotubes, hyperbranched polymers, and block copolymers that can form nanospherical/wormlike micelles in a solvent selective for a block have also been used to toughen epoxies.^{23–34}

Epoxidized vegetable oils, with numerous advantages, such as low toxicity, inherent biodegradability, low cost, and ecofriendliness, are renewable resources for industrial applications in the replacement of

Correspondence to: Z.-L. Du (dzl407@163.com).

Contract grant sponsor: National High-Tech R&D Program of China; contract grant number: 2007AA03Z344.

petroleum-based products through innovative design.^{35–37} In recent years, many researchers have attempted to develop epoxidized triglycerides [e.g., epoxidized soybean oil (ESO)] or epoxidized fatty acid esters to partially replace commercial epoxy resins. The addition of a certain quantified amount of epoxidized triglycerides or epoxidized soya fatty acid esters (EFAEs; obtained by the process of transesterification and the epoxidation of soybean oil) into epoxy systems can form a two-phase structure and, thus, enormously improve the toughness of the cured epoxy resins.^{38–44} Because of the low reactivity of internal epoxy groups, especially sluggish reactivity with nucleophilic curing agents, ESO or EFAE normally has a low crosslinking density.⁴⁵ Therefore, part of the ESO or EFAE plays only a plasticizer role in curing systems, and therefore, the thermal and mechanical properties of curing resins are decreased.⁴¹ In attempts to enhance these properties, epoxidized soybean liquid rubber, a prepolymer of ESO with an amine hardener, has been used as a toughening and curing agent by a few researchers.^{38,39,41}

In this study, toughening curing agents for epoxy resins were prepared from epoxidized oleic ester with amine-terminated epoxy-triethylene tetramine (TETA) prepolymer. The aim of this study was to determine the effect of the ester carbon number of the epoxidized oleic ester on the toughness of an epoxy resin. The toughening effect was evaluated by impact experiments. The mechanical properties were investigated by tensile testing. The morphology of the fracture surfaces of all of the specimens was examined by scanning electron microscopy (SEM). The thermal stability was studied with a thermogravimetric analyzer.

EXPERIMENTAL

Materials

The epoxy resin was diglycidyl ether of bisphenol A (trade name Epon828, epoxy value = 0.51 mol/100 g, Nanxin Wuxi Resin Corp., Wuxi, China, no further purification). Glycol, ethylene glycol monomethylether (EGMME), and TETA were supplied by Chengdu Kelong Chemical Reagent Co. (Chengdu, China) and were used as received. Epoxidized capryl oleic ester (epoxy value = 0.25 mol/100 g) and epoxidized methyl oleic ester (epoxy value = 0.17 mol/100 g) were obtained from Zhangjiakou Guangshen Chemical Reagent Co. (Zhangjiakou, China) and were used as received.

Synthesis of the toughening curing agents

The reaction was carried out in a glass reactor equipped with a reflux condenser, an agitator, a thermocouple, and a feed stream. The brief synthesis procedure that was applied in this study and the

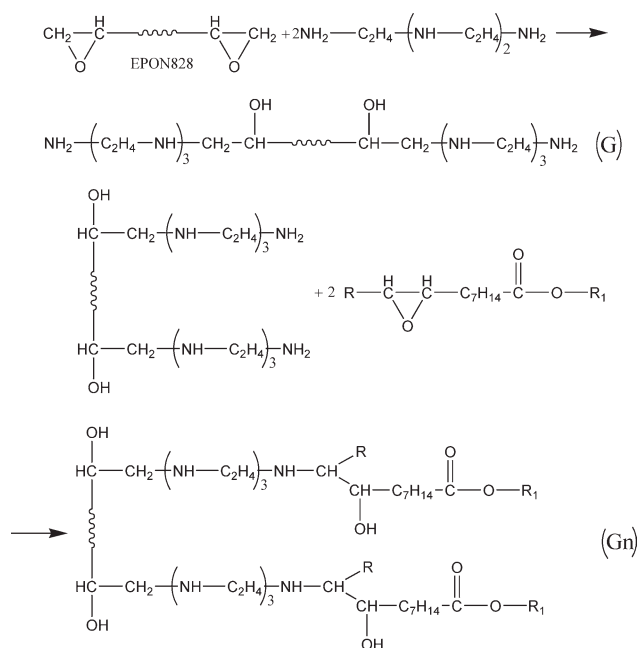


Figure 1 Schematic diagram of the synthesis procedure for the curing agents and their chemical structure ($-R_1$ with carbon number 1, Gn-G1; $-R_1$ with carbon number 8, Gn-G2).

chemical structure schematics of the resulting G1 and G2 are presented in Figure 1. In a typical synthesis experiment for the amine-terminated prepolymer (curing agent G), TETA was added to the reactor and heated to 65°C; then, the Epon828 solution (dissolved in EGMME, molar ratio of TETA to Epon828 = 2.2) was fed into the stream, and the condensation polymerization was conducted for 5 h under stirring. After the completion of the reaction, the unreacted TETA was removed by distillation under reduced pressure. Curing agents G1 and G2 were prepared by an end-capping reaction of the curing agent G in EGMME solvent with epoxidized methyl oleic ester and epoxidized capryl oleic ester, respectively, at 60–65°C for approximately 5 h. Then, EGMME was removed by distillation under reduced pressure. The resulting products were yellow viscous liquids and were soluble in Epon828.

Fourier transform infrared (FTIR) spectral analysis of the curing agents

The chemical structures of the curing agents were characterized by FTIR spectroscopy. The EGMME solutions of curing agents G, G1, and G2 were coated on KBr pellets and dried at room temperature. FTIR spectra were obtained with a Digilab FTS-3000 FTIR spectrometer (Varian, Inc., Palo Alto, California). The scanning scope was 650–4000 cm^{-1} with a resolution of 4 cm^{-1} .

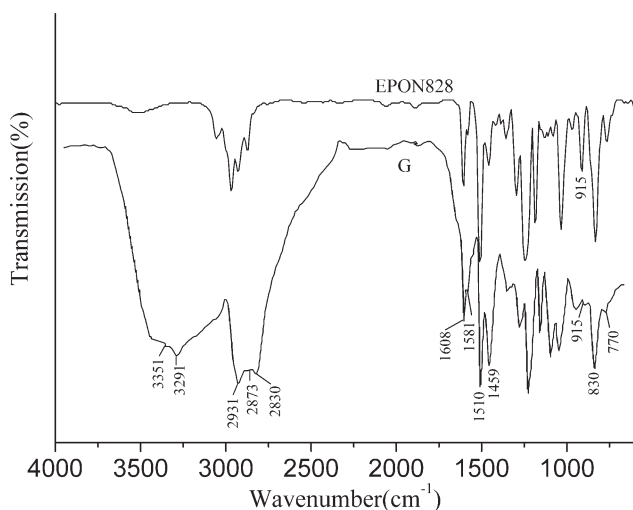


Figure 2 FTIR spectra of Epon828 and curing agent G.

Tensile and Izod impact strength of the cured epoxy resins

Each of the curing agents (G, G1, and G2) was mixed with epoxy resin Epon828 at a calculated stoichiometric ratio, and then, the mixture was poured into a Teflon mold and cured at room temperature for 24 h; it was then cured for 8 h at 50°C and postcured at 130°C for 4 h. The films were cut into strip samples 100 mm long, 10 mm wide, and 0.1 mm thick. According to National Standard GB/13022-91 of China, tensile testing was conducted on a model YG061-1500 tensile strength tester (Laizhou Electronic Instrument, Ltd., Laizhou, China) at a stretching rate of 5 mm/min. The quoted result is the average of the determination for five samples. The Izod impact strength of notched samples was carried out with an XJ-40A Izod impact strength apparatus (Wuzhong Material Tester Limited Co., Wuzhong, China) according to National Standard GB/T 1843-1996 of China. The dimensions of the samples were $60 \times 10 \times 4 \text{ mm}^3$. The quoted result is the average of five tested samples.

Morphology of the fracture surfaces of the cured epoxy resins

The morphology of the fracture surfaces was observed under a JEOL JSM-5900LV scanning electron microscope (JEOL Ltd, Tokyo, Japan). Before SEM observation, the fracture surfaces were sputter-coated with a thin layer of gold to make the surfaces conductive.

Thermal degradation properties of the cured epoxy resins

Thermogravimetric analysis (TGA) was used to study the thermal degradation properties of the cured ep-

oxy resins on a Q600 thermogravimetric analyzer (TA Instruments, Delaware, New Castle) with a nonisothermal process. A temperature program from 50 to 550°C at a heating rate of 10°C/min was used. The test was carried out under a nitrogen atmosphere. The polymer generally showed a three-stage weight loss. The initial decomposition temperature (T_i) was defined by the point of intersection of the tangent drawn at the points of greatest slope on the initial and second weight-loss stages of the TGA curves.

RESULTS AND DISCUSSION

FTIR spectra

The FTIR spectra of curing agent G is shown in Figure 2. As shown in Figure 2, the peaks at 1608, 1581, 1510, and 1459 cm^{-1} corresponded to the characteristic absorption bands of the phenyl in the epoxy resin. The peaks at 830 and 770 cm^{-1} further confirmed that the phenyl was a *p*-substituted compound. The peaks near 3300 cm^{-1} represented the symmetric and asymmetric stretching vibration bands of the primary amine. The peaks at 3351 and 3291 cm^{-1} corresponded to the primary amine-terminated TETA-Epon828 prepolymer (curing agent G). The peak at 915 cm^{-1} represented oxirane groups in the epoxy resin. No oxirane group absorption peak was found in the prepolymer sample because of the disappearance of the oxirane after polymerization. All of these results indicate that the TETA-Epon828 prepolymer appeared to have the structural characteristic of a block polymer with amine termination.

The FTIR spectra of the curing agents G1 and G2 are shown in Figure 3. The characteristic absorption double bands of primary amine groups disappeared,

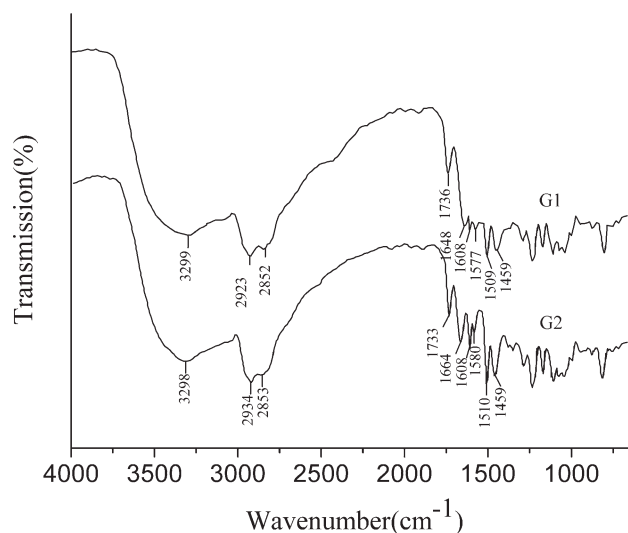


Figure 3 FTIR spectra of curing agents G1 and G2.

TABLE I
Mechanical Properties of the Curing Samples

Curing sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Izod impact strength (kJ/cm ²)
Epon828/G	186 ± 3.8	37.2 ± 1.8	2.05 ± 0.28	3.18 ± 0.22
Epon828/G1	183 ± 3.2	35.1 ± 2.7	2.25 ± 0.21	5.05 ± 0.12
Epon828/G2	189 ± 2.0	34.3 ± 0.9	2.21 ± 0.30	5.98 ± 0.08

and only single peaks appeared at 3299 and 3298 cm⁻¹, which corresponded to the characteristic absorption bands of the secondary amine in G1 and G2, respectively. New peaks at 1736 and 1733 cm⁻¹ appeared concurrently in the IR spectrogram, which represented the absorption bands of carbonyl from the epoxidized oleic ester. Moreover, no oxirane group absorption peak was found in the IR spectrogram of sample G1 or G2. These results illustrate that the reaction occurred completely between the epoxy in the epoxidized oleic ester and the terminated amine in curing agent G.

Mechanical properties and toughness

The mechanical properties and toughness of the Epon828/curing agent systems were measured by a tensile strength tester and an Izod impact strength apparatus, respectively. The results are listed comprehensively in Table I. The Young's moduli of the three samples were almost similar. For the three cured samples, in contrast with Epon828/G, the Epon828/G1 and Epon828/G2 curing systems demonstrated a slightly decreased mean tensile strength and an increased mean elongation at break. After reaction with the epoxy groups, the primary amine groups in curing agent G had a higher reactivity than the *para*-amine on curing agents G1 and G2. When the active hydrogen atom numbers in the three curing agent molecules were the same, the Epon828/G curing system demonstrated relatively high crosslinking density and breaking tensile strength values. With regard to the standard deviations of the data listed in Table I, the results indicate that the mechanical properties of the epoxy curing systems were not practically decreased by curing agent G modified by epoxidized oleic esters but were better than the epoxy curing systems blended with ESO for the toughening epoxy resin.³⁹

It is well known that epoxies are brittle because of their high degree of chemical crosslinking.³³ The Epon828/G1 and Epon828/G2 curing systems demonstrated 59 and 88% Izod impact strength improvements, respectively, compared to the Epon828/G cured sample because of the flexibility of the carbon chain in the curing agents. This confirmed that the

toughening epoxy was effective as a curing agent modified by epoxidized oleic esters. The differences in the Izod impact strength values between the Epon828/G1 and Epon828/G2 curing systems are shown in Table I. The Epon828/G2 cured sample demonstrated an increased value because the ester carbon chain (R1) in curing agent G2 was longer than that (methyl) in G1. This result indicates that the enhancement in the Izod impact strength was due to the flexibility of the fatty carbon chain R and R1 in the toughening curing agents. This conclusion may be useful for the development of higher performance epoxy toughening curing agents by use of epoxidized fatty acid esters.

Morphology of the fracture surfaces

The fracture surfaces of the three cured samples were investigated by SEM, as shown in Figure 4. With a high crosslinking density, the fracture surfaces of the cured epoxy resins usually appeared to have a smooth surface, which indicated a brittle structure.⁴² For the Epon828/G cured sample shown in Figure 4(a), the fracture surfaces appeared to have parallel and smooth cracks, which indicated brittle fracture surfaces,⁴⁰ whereas the Epon828/G1 showed a considerably different fracture morphology, as shown in Figure 4(b), where relative roughness appeared with numerous ridges and irregularly shaped microvoids. This indicated increased plastic deformation. The microvoids or ridges acted as obstacles, forcing the crack to bow and causing deflection of the crack propagation. The arrest of cracks is also shown in Figure 4(c); this is represented by the arrest lines and regions of striations around the microvoids and ridges.⁴⁶ This could have been one of the main toughening mechanisms for the toughening curing system. Figure 4(d) shows the morphology of the fracture surfaces of the Epon828/G2 curing system, in which the curing agent G2 was modified by epoxidized oleic capryl ester. From the morphology, the crack bifurcation was quite evident. The disordered sand ridgelike or furrows and more and smaller microvoids appeared, together with shorter cracks and a rougher fracture surface. These indicated that the toughness of this curing sample

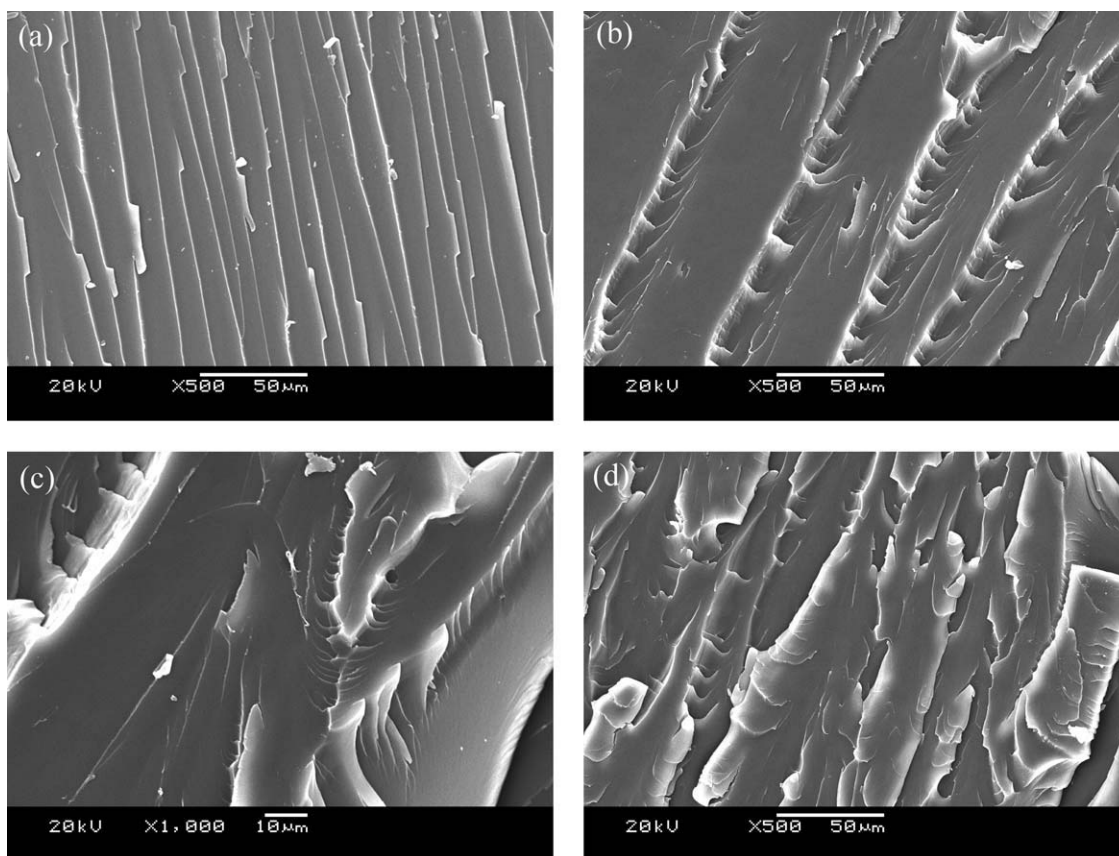


Figure 4 SEM micrographs of the impact fracture surfaces of curing samples: (a) Epon828/G, (b) Epon828/G1 (50- μ scale), (c) Epon828/G1 (10- μ scale), and (d) Epon828/G2.

was better than that of the Epon828/G1 curing system. They also confirmed that with increasing carbon chain length of the ester group R1 in the curing agents, the toughness of the curing system increased. The results, thus, suggest that the toughness enhancement of these novel epoxy curing systems was attributed to the flexibility of the carbon chains R and R1 in the toughening curing agents. A distinct phase separation in the novel matrix was not observed from the SEM micrographs, as shown in Figure 4(b–d). This morphology of the fracture surfaces was observed in an epoxy resin cured with flexible curing agents.⁴⁷

Thermal properties

We expected that the epoxy network was toughened without any defects to the final thermal properties.⁵ The replacement of commercial epoxies with partially epoxidized triglycerides can improve the toughness of cured materials remarkably, but their thermal properties decrease observably.^{39,43} The TGA curves of the three Epon828/G, Epon828/G1, and Epon828/G2 curing system samples are shown in Figure 5.

All three specimens showed a three-stage weight loss. The initial losses and their differences, beginning around 100–335°C, were attributed to the evaporation and decomposition of the unreacted, unseparated reactants (mainly epoxidized capryl oleic ester

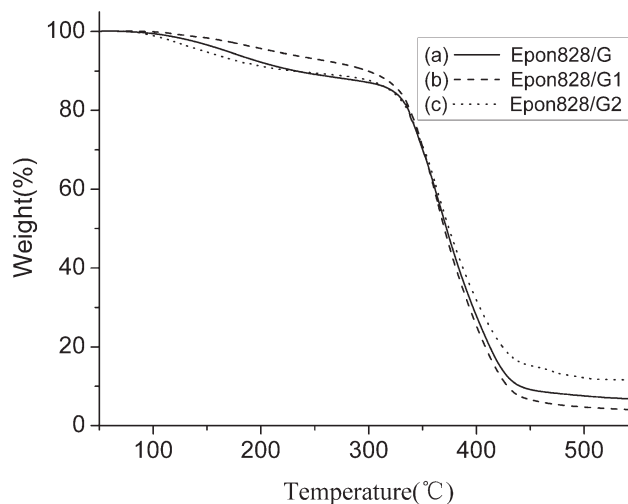


Figure 5 TGA curves of the curing samples at a heating rate of 10°C/min: (a) Epon828/G, (b) Epon828/G1, and (c) Epon828/G2.

TABLE II
Thermal Data for the Curing Samples

Curing sample	T_i (°C)	T_{50} (°C)	T_t (°C)	W_{544} (wt %)
Epon828/G	335	372	418	6.8
Epon828/G1	333	370	413	4.0
Epon828/G2	334	375	416	11.6

and epoxidized methyl oleic ester and their reactants) and remnant solvents in the bulk materials. The second losses around 330°C were considered to be caused by the pyrolysis of the crosslinked epoxy resin networks.⁴⁸ The final losses at about 415°C were indicative of the complete decomposition of the smaller fragments. The values of T_i , the termination decomposition temperature (T_t), the temperature corresponding to 50% weight loss (T_{50}), and the residues at 544°C (W_{544}) of the three samples are summarized in Table II. The T_i values of the three systems were similar. The T_{50} value of Epon828/G was higher than that of Epon828/G1 and was lower than that of Epon828/G2. However, the differences in the T_{50} values of the three samples were very small. This indicated that the weight loss rate, that is, the degradation rate, of the three samples showed slight differences from 335 to 413°C. Because the flexible carbon chains R and R1 in the toughening curing agents were cured into the networks of the cured resins and no obvious phase separation was observed from the SEM, the thermal stabilities of the three cured resins were considered to be similar. The W_{544} value of the Epon828/G2 curing system was higher than that of Epon828/G1; this indicated that the thermal stability of the ester carbon chain R1 in G2 may have been higher than that of the methyl in G1.

CONCLUSIONS

The toughening curing agents G1 and G2 were prepared via the reaction between epoxidized oleic methyl ester and epoxidized oleic capryl ester, respectively, with the amine-terminated epoxy-TETA prepolymer (G), which was synthesized from Epon828 and TETA (molar ratio of TETA to Epon828 = 2.2). FTIR was used to follow the reactions. The TETA-Epon828 prepolymer (G) appeared to have the structural characteristic of a block polymer with amine termination. The toughening curing agents G1 and G2 appeared to have the structural characteristic of block polymers with oleate termination because the reactions only occurred between the end amine groups of G and the oxirane groups of the epoxidized oleic esters. Compared to the Epon828/G curing system, the Epon828/G1 and Epon828/G2 curing systems showed obviously

increased Izod impact strengths and elongations at break, slightly decreased tensile strengths, and almost similar Young's modulus values. The toughness enhancement of these novel epoxy curing systems was attributed to the flexibility of carbon chains R and R1 of the toughening curing agents. As the carbon chain length of the ester group R1 of the curing agents increased, the toughness of the curing system increased. The results of TGA illustrate that the initial thermal stability of the Epon828/G1 curing sample was better than those of the Epon828/G and Epon828/G2 samples and that for the thermal stability from 335 to 554°C, the Epon828/G sample was better than the Epon828/G1 sample and inferior to the Epon828/G2 sample. In this article, we presented an innovative method with epoxidized fatty acid esters derived from renewable plant oils to develop toughening curing agents for epoxy resins with enhanced impact strength and thermal stability values.

References

- Sultan, J. N.; McGarry, F. J. *Polym Eng Sci* 1973, 13, 29.
- Treverton, J. A.; Paul, A. J. A. *Int J Adhes Adhes* 1995, 15, 237.
- Frigione, M. E.; Mascia, L.; Acierno, D. *Eur Polym J* 1995, 31, 1021.
- Dzturk, A.; Kaynak, C.; Tincer, T. *Eur Polym J* 2001, 37, 2353.
- Chikhi, N.; Fellahi, S.; Bakar, M. *Eur Polym J* 2002, 38, 251.
- Arias, M. L.; Frontini, P. M.; Williams, R. J. J. *Polymer* 2003, 44, 1537.
- Thomas, R.; Ding, Y. M.; He, Y. L.; Yang, L.; Moldenaers, P.; Yang, W. M.; Czigan, T.; Thomas, S. *Polymer* 2008, 49, 278.
- Ratna, D. *Polymer* 2001, 42, 4209.
- Ratna, D.; Simon, G. P. *Polymer* 2001, 42, 7739.
- Yilgör, E.; Yilgör, İ. *Polymer* 1998, 39, 1691.
- Liu, P. G.; Song, J. X.; He, L. H.; Liang, X. Q.; Ding, H. Y.; Li, Q. F. *Eur Polym J* 2008, 44, 940.
- Bagheri, R.; Pearson, R. A. *Polymer* 1996, 37, 4529.
- Bagheri, R.; Pearson, R. A. *Polymer* 2000, 41, 269.
- Mimura, K.; Ito, H.; Fujioka, H. *Polymer* 2000, 41, 4451.
- Varley, R. J.; Hodgkin, J. H.; Simon, G. P. *Polymer* 2001, 42, 3847.
- Agius, S. L.; Magniez, K. J. C.; Fox, B. L. *Compos Struct* 2010, 92, 2119.
- Francis, B.; Thomas, S.; Jose, J.; Ramaswamy, R.; Rao, V. L. *Polymer* 2005, 46, 12372.
- Chen, M. C.; Hourston, D. J.; Schafer, F. U.; Huckerby, T. N. *Polymer* 1995, 36, 3287.
- Wang, M. H.; Yu, Y. F.; Wu, X. G.; Li, S. J. *Polymer* 2004, 45, 1253.
- Agag, T.; Takeichi, T. *Polymer* 1999, 40, 6557.
- Punchaipetch, P.; Ambrogi, V.; Giamberini, M.; Brostow, W.; Carfagna, C.; D'Souza, N. A. *Polymer* 2001, 42, 2067.
- Punchaipetch, P.; Ambrogi, V.; Giamberini, M.; Brostow, W.; Carfagna, C.; D'Souza, N. A. *Polymer* 2002, 43, 839.
- Wetzel, B.; Rosso, P.; Hauptert, F.; Friedrich, K. *Eng Fracture Mech* 2006, 73, 2375.
- Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D.; Taylor, A. C.; Sprenger, S. *Polymer* 2007, 48, 530.
- Ma, J.; Mo, M. S.; Du, X. S.; Rosso, P.; Friedrich, K.; Kuan, H. C. *Polymer* 2008, 49, 3510.
- Liang, Y. L.; Pearson, R. A. *Polymer* 2009, 50, 4895.

27. Liu, W. P.; Hoa, S. V.; Pugh, M. *Compos Sci Technol* 2005, 65, 307.
28. Brunner, A. J.; Necola, A.; Rees, M.; Gasser, P.; Kornmann, X.; Thomann, R.; Barbezat, M. *Eng Fracture Mech.* 2006, 73, 2336.
29. Lakshmi, M. S.; Narmadha, B.; Reddy, B. S. R. *Polym Degrad Stab* 2008, 93, 201.
30. Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Compos Sci Technol* 2005, 65, 2300.
31. Yu, N.; Zhang, Z. H.; He, S. Y. *Mater Sci Eng A* 2008, 494, 380.
32. Mezzenga, R.; Boogh, L.; Manson, J. A. E. *Compos Sci Technol* 2001, 61, 787.
33. Deng, S. Q.; Zhang, J. N.; Ye, L.; Wu, J. S. *Polymer* 2008, 49, 5119.
34. Lorena, R. P.; Royston, G. J.; Fairclough, J. P. A.; Ryan, A. J. *Polymer* 2008, 49, 4475.
35. Khot, S. N.; Lascala, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, G. R.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 82, 703.
36. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem Soc Rev* 2007, 36, 1788.
37. Sharma, V.; Kundu, P. P. *Prog Polym Sci* 2008, 33, 1199.
38. Ratna, D.; Banthia, A. K. *J Adhes Sci Technol* 2000, 14, 15.
39. Zhu, J.; Chandrashekhara, K.; Flanigan, V.; Kapila, S. *J Appl Polym Sci* 2004, 91, 3513.
40. Park, S. J.; Jin, F. L.; Lee, J. R. *Mater Sci Eng A* 2004, 374, 109.
41. Kar, S.; Banthia, A. K. *Mater Manuf Process* 2004, 19, 459.
42. Miyagawa, H.; Misra, M.; Drzal, L. T.; Mohanty, A. K. *Polym Eng Sci* 2005, 45, 487.
43. Shabeer, A.; Sundararaman, S.; Chandrashekhara, K.; Dharani, L. R. *J Appl Polym Sci* 2007, 105, 656.
44. Liu, Z. S.; Erhan, S. Z.; Calvert, P. D. *Compos A* 2007, 38, 87.
45. Earls, J. D.; White, J. E.; López, L. C.; Lysenko, Z.; Dettloff, M. L.; Null, M. J. *Polymer* 2007, 48, 712.
46. Lu, J.; Wool, R. P. *Compos Sci Technol* 2008, 68, 1025.
47. He, S. J.; Shi, K. Y.; Bai, J.; Zhang, Z. K.; Li, L.; Du, Z. J.; Zhang, B. L. *Polymer* 2001, 42, 9641.
48. Liu, P. G.; Song, J. X.; He, L. H.; Liang, X. Q.; Ding, H. Y.; Li, Q. F. *Eur Polym J* 2008, 44, 940.