



Modification of the epoxy resin with epoxide and ester group containing oligomers and compounds

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Abstract. Epoxy toluene oligomers (ETO) are very important substances due to effective functional groups in their structure and they are especially used as polymer additives that have been synthesized from toluene and epichlorhydrin. Flame-retardant properties of the neat epoxy resin (ER), ETO, and ETO/ER blend thermoset were evaluated by UL94 vertical flammability test. The chlorine atoms in ETO increase the stability of the polymer material against burning. For the synthesis other polymers, first the waste product of the industrial vegetable oil refinement acid oil was transformed into the glycidyl ester (FAGE). Unsaturated oligo(ether-ester) (OEE) was prepared by ring-opening polymerization of the propylene oxide (PO) with FAGE in the presence of cationic catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. Its chemical structure was characterized with FTIR spectroscopy. These polymers, isoamyl methacrylate (AMA) and 1,2-epoxy-hexane-5-en (EH) were used as modifiers in the DGEBA-type epoxy resin. The effects of the modifier structure and amount on the mechanical properties of epoxy were investigated. Tensile strength and Young's modulus of the modified samples were found higher than those of the neat epoxy resin.

Key words: epoxy resin, oligomer, modification.

1. INTRODUCTION

Thermosets, such as epoxy and novolac resins, is a class of important polymeric materials; they have widely been used as high performance materials such as adhesives, matrices of composites, and electronic encapsulating materials [1,2]. However, these thermosets are inherently of low impact resistance due to their high crosslinking density, which greatly restricts their application. A large number of studies has been conducted to improve the impact resistance of highly cross-linked epoxy resins by modification. Jin and Park [3] have studied the effects of bio-based epoxy materials on the impact strength of the DGEBA epoxy system and found that the impact strength value of the blends is 21.9 J/m^2 at 60 wt% of the epoxidized soybean oil, whereas DGEBA is very brittle, exhibiting an impact strength value of 13.9 J/m^2 . Similar results have been

reported in [4] using bio-based neat epoxy materials containing epoxidized linseed oil. Chen et al. [5] have used n-butyl glycidyl ether (BGE) to modify diglycidyl ether of bisphenol-F (DGEBF) epoxy system and observed that the impact strength is appreciably enhanced by the introduction of BGE in the epoxy resin. The impact strength increases by 77.6% with the addition of 40 phr BGE compared to that of the uncured epoxy. Yang et al. [6] have selected two flexible polyoxypropylene diamines (D-230 and D-400) to modify DETD cured DGEBA epoxy resins and found that the impact strength of epoxy resins increases from 19.2 to 53.56 kJ/m^2 with the increasing diamine content. The polybutadiene particles have been carried out to adhere to epoxy matrix and all modified epoxy networks exhibit higher impact resistance with respect to unmodified epoxy resin [7]. In our previous study, epoxy resin has been modified with the bio-based and styrene-based polymers. The results indicate that modification process enhances some properties of the

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epoxy resin such as surface hardness, tensile strength, percentage elongation, and stress at maximum load of the composites [8]. In this context, recent studies have shown that the addition of some modifying agents and additives into polymer matrices significantly affects their mechanical properties. Therefore, we report herein the modification process of the epoxy resin with compounds having epoxide, ester and alkene groups and how the modification process affects mechanical properties of the epoxy resin.

2. EXPERIMENT

2.1. Materials

The waste of the sunflower oil as fatty acid (FA) was supplied by Zade Chemical Industry, Konya, Turkey. The thermosetting matrix used in this study was a commercially available bisphenol A-type epoxy resin (DER 321, Dow Chemical Co.) modified with aromatic diluent and cured at high temperature with 30 wt% Polypox Hardener 043. The curing agent was a cycloaliphatic polyamine. The synthesized two polymers: epoxy toluene oligomer (ETO) and oligo(ether-ester) (OEE) based on fatty acid waste were used as modifiers in epoxy resin composites. Other modifiers, isoamyl methacrylate (AMA) and 1,2-epoxy-hexane-5-en (EH), were supplied by Chemistry Department of Selcuk University. Propylene oxide (PO), epichlorohydrin (ECH), toluene, and cationic catalyst $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ were purchased from Merck (Darmstadt, Germany).

2.2. Synthesis

2.2.1. Synthesis of glycidyl ester of fatty acid (FAGE)

FAGE was obtained by the esterification reaction of potassium salt of fatty acid with epichlorohydrin in the alkaline medium. The 10 g FA waste and 10 mL benzene were taken to the flask for the reaction and 4 mL 40% KOH solution was added to this mixture; 3 g epichlorohydrin was supplemented to the mixed solution drop-by-drop at 40 °C within 20–30 min. After this, the temperature was increased to 70–80 °C and the mixture was boiled for 5 h. The ester, that is obtained, was distilled under the vacuum [9,10].

2.2.2. Synthesis of unsaturated oligo(ether-ester)s (OEE)

A 150 mL flask, equipped with a magnetic stirrer and thermometer, was charged with PO and FAGE in mole ratio 1:1. The mixture was cooled to 0 °C with stirring, and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (1 wt%) was added to the mixture.

After completion of the reaction, methanol (1 mL) was added to the mixture in order to deactivate the catalyst. The starting materials and methanol were removed under reduced pressure (2 mmHg, 53 °C). Yield was calculated from the final weight.

2.2.3. Synthesis of epoxy toluene oligomer (ETO)

The 1 mol of toluene in a flask was reacted with 3 mole of ECH in the presence of 2% of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ by stirring and heating at 40 °C for 2 h. Then the temperature was increased to 60 °C and 1.2 mole NaOH (40% solution) was added to the reaction mixture and the mixture was heated for 6–8 h. At the end of the reaction, obtained mixture was cooled to the room temperature, the excess of toluene was removed under low pressure, washed and dried. Finally, a viscous product with yellow colour was obtained [11].

2.3. Formation of the modified epoxy samples

The modifier was mixed with an epoxy matrix in different weight ratios by using a Heidolph RZR1 stirrer (stirring rate of 1200 rpm) for 3 h and ultrasounded for 60 min at 60 °C to obtain a good dispersion. Later, 30 wt% Epamine PC17 hardener and 1 wt% epoxy accelerator were added and then transferred into the stainless-steel molds, in which the composite specimens were prepared according to the ASTM D 638 standard. Finally, the mixture was degassed for 60 min at room temperature, and the curing procedure was carried out in an oven within 24 h by increasing the temperature from 40 to 120 °C.

2.4. Analysis and testing

The FTIR spectra of the synthesized compounds were recorded with Bruker-Platinum ATR-vertex 70.

The morphology of neat ER and modified ER samples was examined with a Solver P47H atomic force microscope (NT-MTD) (Moscow, Russia) operating in tapping mode in air at room temperature. Diamond-like carbon (DLC) coated NSG01 DLC silicon cantilevers (from NT-MTD) with a 2-nm tip apex curvature were used at the resonance frequency of 150 kHz. The Nova 914 software package was used to control the SPM system and for the analysis of the AFM images.

Scanning electron microscopy (SEM) was performed with a Philips XL30 SFEG instrument. The resistance to stretch properties was determined by Stretch and Pressing Equipment TST-Mares/TS-mxe. The flammability of ER and ETO was determined using the vertical test according to the UL-94 standard (sample size of 130 mm × 13 mm × 3 mm).

3. RESULTS AND DISCUSSION

3.1. Characterization of samples

Synthesis reactions of ETO and OEE are shown in Figs 1 and 2, respectively. The chemical structure of polymers was determined via FTIR spectrum (Figs 3 and 4).

In the FTIR spectrum of ETO (Fig. 3), characteristic bands appeared in the regions of 2875, 1580, 1429, and 1344 cm^{-1} for aliphatic C-H, aromatic C=C, C-H bond of aliphatic CH_2 and C-H bond of aliphatic CH_3 , respectively. The most intense bands have been observed at 744 cm^{-1} for C-Cl and at 1094 cm^{-1} for the C-O-C ether bonds. Also, there were observed bands at 1256 and 908 cm^{-1} , which confirmed the presence of epoxide group in the oligomer. These results show that the reaction between toluene and ECH had taken place. As shown in Fig. 4, synthesized OEE contains double bond on the side chain. The characteristic bands appeared in the regions of 1661 cm^{-1} for C=C, 1740–

1746 cm^{-1} for C=O of the ester, and 722–724 cm^{-1} for the fatty acid $(\text{CH}_2)_4$ units (Fig. 4).

The fracture surface images of ER, ETO, and OEE are shown in Fig. 5. AFM is one of the most important microscopic techniques, which are used in the surface analysis of polymers on a nanometer scale. The additional advantage of using AFM is that it can give distinguished surface topography and surface heterogeneity. The representative 3-D surface morphologies of neat ER and modified ER with AMA and EH are shown in Fig. 6.

As it was expected, the surface morphologies of different modifications are quite different because the modifying agents have different chemical structure. As can be easily seen in AFM images, the heights on the surface of neat ER are not intense, but modification process increases the surface porosity. Generally, existence of modifiers with various chemical structures makes the polymer surface rougher.

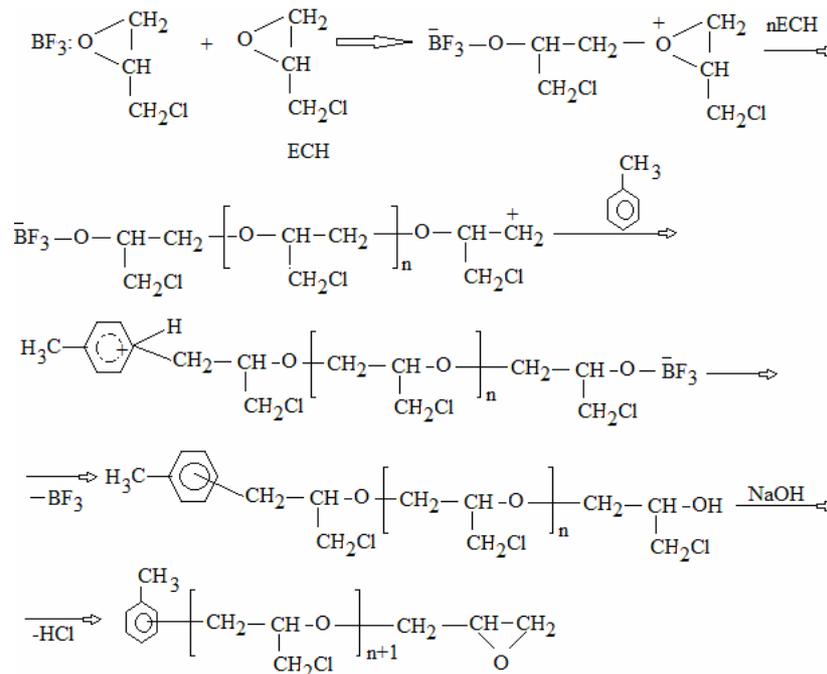


Fig. 1. Synthesis reaction of ETO.

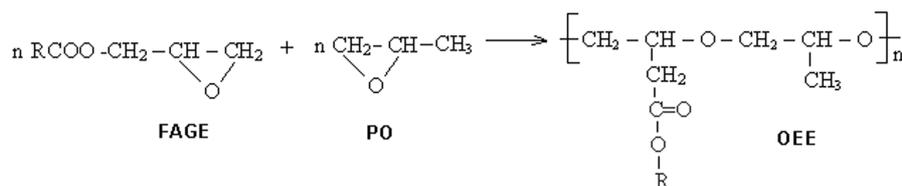


Fig. 2. Synthesis reaction of OEE.

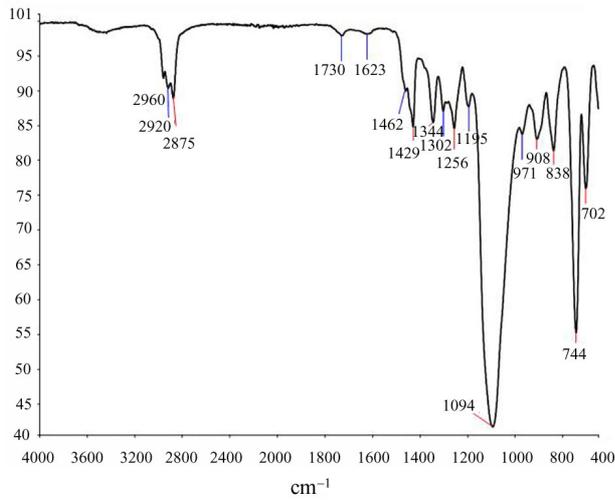


Fig. 3. FTIR spectrum of ETO.

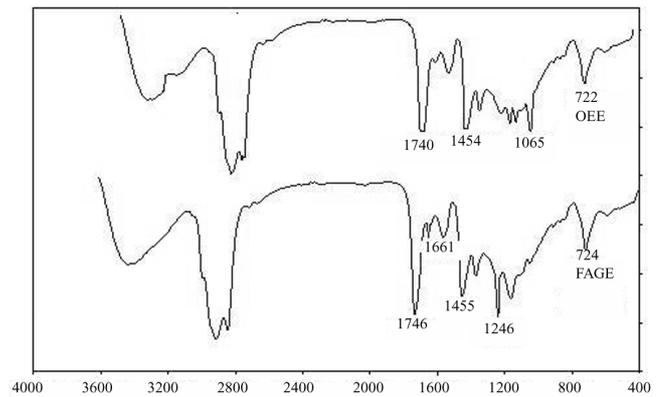


Fig. 4. FTIR spectrum of FAGE and OEE.

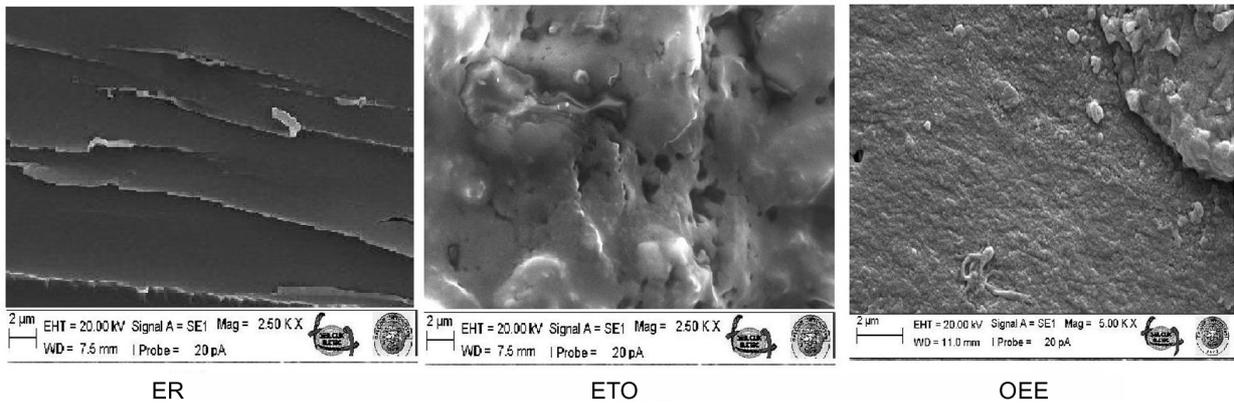


Fig. 5. SEM images of neat ER, ETO and OEE.

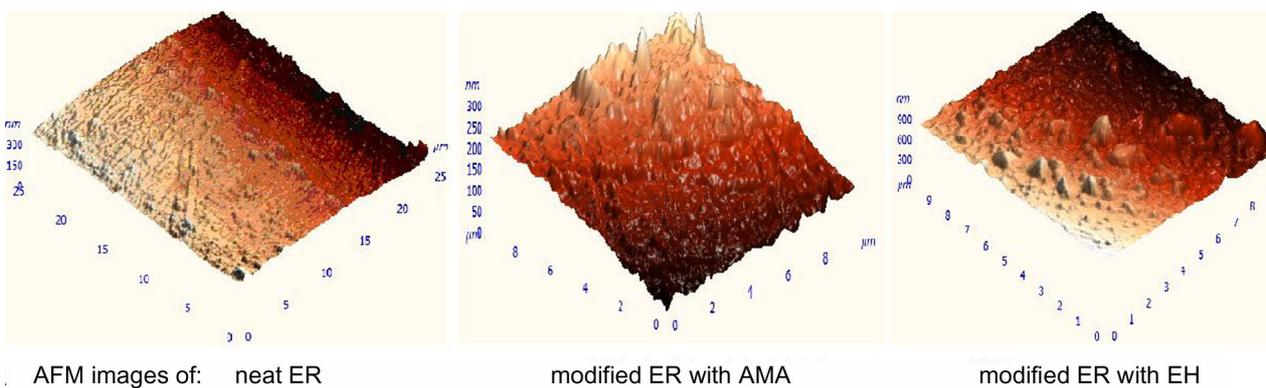


Fig. 6. AFM images of neat and modified ER.

3.2. Mechanical properties

The mechanical properties of polymers are influenced by molecular weight, crosslinking, branching, segmental

motion, morphology, and external conditions such as temperature, pressure, loading rate, environmental condition, extent of compound, etc. [12,13]. The structure of the side-chain substituents on the polymer backbone

is a major compositional factor, impacting polymer functionality. Important aspects of substitution are the chemical structure of the substituents, the extent of backbone substitution, and the uniformity of substitution. The nature of the side chain substituent type also significantly impacts mechanical properties. Increasing the amount of highly polar, ionic side-chains tends to result in an increased tensile strength [14]. The effect of side group structure on the compressive strength of novel biodegradable polyphosphazene based polymers was investigated by Sethuraman et al. [15]. Results of mechanical testing studies demonstrated that the nature and the ratio of the pendent groups attached to the polymer backbone play a significant role in determining the mechanical properties of the resulting polymer. The compressive strength of the polymer with aliphatic alanine side group was significantly higher than polymers with aromatic alanine groups.

Tensile test results are given in Table 1. Increasing the amount of highly polar, ionic side-chains in polymer tends to result in an increased tensile strength. Polarity order of functional groups is given as follows: amide > carboxylic acid > hydroxyl > ketone ~ aldehyde > amine > ester > ether > alkene > alkane [14]. Breaking strain ratio and tensile strength for neat ER are found as 0.48% and 41 MPa, respectively. Tensile strengths of modified ERs with OEE, AMA and EH are found to be higher than that of ER. The highest tensile strength is achieved with 20% of AMA content having ester group.

Table 1. Effect of the amount of modifiers on mechanical properties of ER

Modifier, wt%	Elongation at break, %	Tensile strength, MPa	Young's modulus, GPa
For pure ER			
–	0.48	41	5.6
For ETO/ER			
10	5.96	25	8.8
25	7.53	28	7.1
For OEE/ER			
10	0.71	67	2.0
15	0.72	75	1.9
20	0.72	76	1.8
25	0.74	62	1.6
For OEE/ER-ETO in 3 : 1 wt%			
10	7.34	49	6.7
20	5.46	50	6.0
For AMA/ER			
10	0.55	136	6.2
20	1.45	649	5.1
For EH/ER			
10	0.20	98	5.2
20	0.25	160	8.3

The order of tensile strengths of modified ERs with 20% of modifier content is given as follows: with AMA (649 MPa) > with EH (160 MPa) > with OEE (76 MPa) > with ETO (28 MPa).

Brittle materials, such as ceramic, do not undergo plastic deformation and break under low tension [16]. Therefore, Young's modules of hard and brittle polymers are high while breaking strain is low [17]. Similarly, Young's modules for soft polymers are low while breaking strain is high [18]. In the present study, the optimum modifier ratio is determined as 10% in terms of Young's modules.

3.3. Flame retardancy

One of the main drawbacks in using epoxy thermosetting resins for the production of composites is their poor fire resistance. The main fields where flame retardancy of epoxy resins is required are in electronics and transportation for composite structural and furnishing elements. Epoxy resins, cured with amines, tend to produce more char, and they apparently are less flammable than acid or anhydride cured resins at comparable cross-linking density. The char yield can be increased by using special epoxy monomers, containing aromatic rings or double bonds. The combustion behaviour of similar epoxy resins depends on the ratio of oxygen atoms to carbon atoms in the polymer structure [19].

As reported in literature, the chlorine atoms in the oligomeric compound increase the stability of the polymer materials against burning and heat [20]. Consequently, ETO will provide the fire endurance to the composites. Flame-retardant properties of the neat ER, ETO, and ETO/ER blend thermoset were evaluated by UL94 vertical flammability test, and the results are listed in Table 2. The UL94 value, obtained for ETO and ETO/ER, was V-0. The char yield can be used as criteria for evaluating limiting oxygen index (*LOI*) of the cured resin in accordance with Van-Krevelen and Hoftzyer equation [21], which has been suggested for the cured resins:

$$LOI = 17.5 + 0.4 Ch.Y,$$

where *Ch.Y* is char yield [22].

It can be seen from these results that ETO is effective flame retardant additive to the ER.

Table 2. Flammability data

Samples	Dripping	UL94 rating	Calculated <i>LOI</i>
Neat ER	Yes	No rating	22.3
Neat ETO	No	V-0	24.7
ETO/ER (1 : 1 wt% ratio)	No	V-0	23.9

REFERENCES

1. May, C. A. and Tanaka, G. Y. *Epoxy Resin Chemistry and Technology*. Marcel Dekker, New York, 1973.
2. Bauer, R. S. *Epoxy Resin Chemistry*. Adv. Chem. Ser. 114, American Chemical Society, Washington, DC, 1979.
3. Jin, F.-L. and Park, S.-J. Impact-strength improvement of epoxy resins reinforced with a biodegradable polymer. *Mat. Sci. Eng. A-Struct.*, 2008, **478**, 402–405.
4. Miyagawa, H., Mohanty, A. K., Misra, M., and Drzal, L. T. Thermo-physical and impact properties of epoxy containing epoxidized linseed oil. *Macromol. Mater. Eng.*, 2004, **289**, 636–641.
5. Chen, Z.-K., Yang, G., Yang, J.-P., Fu, Sh.-Y., Ye, L., and Huang, Y.-G. Simultaneously increasing cryogenic strength, ductility and impact resistance of epoxy resins modified by *n*-butyl glycidyl ether. *Polymer*, 2009, **50**, 1316–1323.
6. Yang, G., Fu, Sh.-Y., and Yang, J.-P. Preparation and mechanical properties of modified epoxy resins with flexible diamines. *Polymer*, 2007, **48**, 302–310.
7. Barcia, F. L., Amaral, T. P., and Soares, B. G. Synthesis and properties of epoxy resin modified with epoxy-terminated liquid polybutadiene. *Polymer*, 2003, **44**, 5811–5819.
8. Ahmetli, G., Deveci, H., Soydal, U., Pistil Gurler, S., and Altun, A. Epoxy resin/polymer blends: improvement of thermal and mechanical properties. *J. Appl. Polym. Sci.*, 2012, **125**, 38–45.
9. Yazicigil, Z. and Ahmetli, G. Synthesis of the fatty acid compounds obtained from sunflower oil refining products. *J. Appl. Polym. Sci.*, 2008, **108**, 541–547.
10. Yazicigil, Z., Ahmetli, G., Kara, H., and Kocak, A. Investigation of synthesis of copolymers from the waste products of industrial oil refinement having adhesion properties and strength to the thermal destruction. *J. Polym. Environ.*, 2006, **14**, 353–357.
11. Ahmetli, G., Deveci, H., Soydal, U., Seker, A., and Kurbanli, R. Corrosion and thermal characterization of styrene based copolymers. *Progr. Org. Coat.*, 2012, **75**, 97–105.
12. Krause, A., Lange, A., and Ezrin, M. *Plastics Analysis Guide, Chemical and Instrumental Methods*. Harver, New York, 1983.
13. Brown, R. P. *Physical Testing of Rubbers*. Applied Science, London, 1979.
14. Brady, J. E., Dürig, T., and Shang, S. *In Theories and Techniques in the Characterization of Drug Substances and Excipients* (Qui, Y., ed.). Chapter 9. Academic Press, New York, 2008.
15. Sethuraman, S., Nair, L. S., El-Amin, S., Nguyen, M.-T., Singh, A., Krogman, N. et al. Mechanical properties and osteocompatibility of novel biodegradable alamine based polyphosphazenes: side group effects. *Acta Biomater.*, 2010, **6**, 1931–1937.
16. Beer, F. P., Johnston, E. R., DeWolf, J. T., and Mazurek, D. *Mechanics of Materials*, 5th edn. McGraw Hill, New York, 2009.
17. Billmeyer, F. W. *Textbook of Polymer Science*, 3rd edn. Wiley-Interscience, New York, 1984.
18. Maiti, S., Banerjee, P., Purakayastha, S., and Ghosh, B. Silicon-doped carbon semiconductor from rice husk char. *Mater. Chem. Phys.*, 2008, **109**, 169–173.
19. Troitzsch, T. *Plastics Flammability Handbook*. Hanser Publications, Germany, 2004.
20. Kurbanova, R. A., Ragimov, A. V., and Bektasi, N. R. *Patent USSR*, G84044, 1979.
21. Van-Krevelen, D. W. and Hoftyzer, P. J. *Properties of Polymers, Their Estimation and Correlation with Chemical Structure* (2nd edn). Elsevier, New York, 1976.
22. Ghaemy, M., Rahpaima, G., and Behmadi, H. Effect of triphenylphosphine on the cure reaction and thermal stability of diglycidyl ether of bisphenol A-based epoxy resin. *Iran. Polym. J.*, 2008, **17**, 875–885.

Epoksüvaigu modifitseerimine oligomeere ja nende ühendeid sisaldavate epoksiidide ja estrite rühmadega

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Epoksütolueeni oligomeere (ETO) sünteesitakse toluleenist ja epikloorhüdrinist ning nende struktuuris olevate efektiivsete funktsionaalsete rühmade tõttu on neil polümeeri lisaainetena suur tähtsus. Uuriti puhta epoksüvaigu (ER), ETO ja termoreaktiivse ETO/ER-i sulandi tuletökeomadusi, hinnates neid UL94 vertikaalse süttivuse testi abil. Kloori aatomid ETO-s suurendavad polümeerse materjali vastupidavust põlemise suhtes. Teise polümeeri sünteesiks saadi tööstusliku taimeõli puhastamise jääkproduktist (rasvhappeõlist) esmalt glütsidüülester (FAGE). Küllastumata oligoeter-ester (OEE) saadi tsükliavamispolümerisatsiooni teel propüleenoksiidist (PO) ja FAGE-st katioonse katalüsaatori $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ juuresolekul. Selle keemilist ehitust iseloomustati FTIR-i spektroskoopia abil. Mõlemat polümeeri, isoamüülmetakrülaati (AMA) ja 1,2-epoksüheksaan-5-eeni (EH) kasutati DGEBA-tüüpi epoksüvaigu modifitseerimiseks. Uuriti modifitseerija struktuuri ja koguse mõju epoksüvaigu mehaanilistele omadustele. Modifitseeritud materjalist katsekehade tõmbetugevus ja Youngi moodul osutusid suuremateks kui puhta epoksüvaigu puhul.