Novel Amine Terminated Elastomeric Oligomers and Their Effects on Properties of Epoxy Resins as a Toughener

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ABSTRACT: The objective of this study was to investigate the effects of amine terminated elastomeric epoxy tougheners on the mechanical and thermal properties of diglycidyl ether of bisphenol A based epoxy resin. The amine terminated polycaprolactone (PCL) (1) and PCL-PDMS-PCL (2) based oligomers were synthesized and characterized by FTIR spectroscopy. The stoichiometrical amount of the reactive oligomers as toughener, reactive epoxy resin and the curing agent, 4,4′-diaminodiphenyl sulfone (DDS) were mixed and degassed. The homogenous mixtures were cured at 120°C into the preheated molds. The mechanical and thermal characterizations of toughened epoxy resin system were evaluated. It has been shown that the mechanical and thermal properties of toughened epoxy system vary as a function of the chemical structure and the concentration of rective oligomers. Higher mechanical properties were obtained for epoxy resin toughened by PCL-PDMS-PCL (2) based oligomer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 37–45, 2010

Key words: oligomers; toughness; curing of polymers; thermosets; mechanical properties

INTRODUCTION

Epoxy resins are known for their high performance, especially with respect to thermal and dimensional stabilities. They also show resistance to many solvents. But, as a consequence of their highly cross-linked structure, these materials tend to suffer from brittleness, poor crack resistance, and low fracture toughness. A well-known method to toughen such brittle polymers is to use reactive elastomeric oligomers, such as butadiene-acrylonitrile rubber, polysiloxanes, fluoroelastomers, and acrylates.[1–4] To incorporate rubber particles into rigid particles, especially carboxyl-terminated butadien-acrylonitrile copolymers have been applied to enhance toughness without sacrificing other useful properties such as dimensional stability, stiffness, and strength. The major problem of this type of elastomeric tougheners is the poor oxidative stability because of high olefin content of the polymer backbone. Engineering thermoplastics are interesting materials as modifiers for epoxy resins. Modification of epoxy resins with various types of ductile thermoplastics has been studied as alternatives to reactive rubber.[5–11]

Also, silicon rubber, especially poly(dimethylsiloxane) PDMS, exhibit a number of attractive properties, high chain flexibility, low surface tension and surface energy, low solubility parameters and hydrophobic behavior as well as UV insensitivity, oxygen resistance, and thermal stability.[12,13] By these excellent features, PDMS is a good modifier, but it can not be used by blending because of its extreme incompatibility with epoxy resins. So, this incompatibility problem may be overcome either by the use of it as a copolymer like in the case of PCL-PDMS-PCL block copolymer or as a functionally ended reactive modifier.[6–8]

In this work, amine terminated polycaprolactone (PCL) (1) and amine terminated PCL-PDMS-PCL block copolymer (2) were prepared and used in various amounts for toughening diglycidyl ether bisphenol-A based epoxy resin. The amine functionalized oligomers were mixed homogenously with an epoxy resin and diaminodiphenyl sulfone (DDS) as hardener. The effect of molecular structure and concentrations of reactive oligomers on the mechanical and thermal properties of cured epoxy networks were discussed.

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†Deceased.
The article has been dedicated to Prof. Dr. Abdülkadir Kuyulu.
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EXPERIMENTAL

Materials

3-nitrobenzoyl chloride (Merck) and 4,4′ DDS (Fluka) were used as received. PCL (Tone 0230, Union Carbide) and PCL-PDMS-PCL block copolymer

(Tegomer 6440, Goldschmidt) were dried under high vacuum. Diglycidylether of bisphenol A (Araldite GY 250, Ciba) was used as epoxy resin. Other reagents were used as received.

Characterization methods

Infrared spectra were obtained by using Perkin–Elmer Spectrum One FTIR Spectrophotometer. [1]NMR and ^{13}C-NMR spectra were recorded with a Bruker AC 200L FT-NMR Spectrophotometer. Mass spectra studies were performed at 70 eV with a Fission instruments VG ZabSpec Mass Spectrometer. Thermal stability of polymers was measured by Perkin–Elmer Pyris1 thermogravimetric analyzer (TGA) with a heating rate of $10°C$ min^{-1} in air. Glass transition temperatures were determined with a Perkin–Elmer Pyris1 differential scanning calorimeter (DSC). Scans were run at a heating rate of $10°C$ min^{-1} under nitrogen purge at a rate of 30 mL min^{-1}. Reported values were obtained from a second heating after a quick cooling. Stress–strain measurements of toughened samples were performed using an Instron 4505 tensile testing machine according to ASTM D 638-02. Flexural tests were carried out according to ASTM D 790-02. Impact strength measurements of samples were performed according to ASTM D 256-02. Toughened samples were conditioned at 65% relative humidity before all measurements.

Morphological investigations of parent and toughened epoxy resins were performed by JEOL/JSM-6335F scanning electron microscope (SEM).

Synthesis of amine terminated elastomeric reactive oligomers

In a three necked 250 mL flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet, 50 g vacuum dried polyol (PCL) was dissolved in 50 mL dry THF; 3 mL of triethylamine was added as catalyst; 0.18 mol of excess 3-nitrobenzoylchloride was added as portions. Reaction was completed at $90°C$ in 6 h. 150 mL of distilled water was added at room temperature and viscous yellow organic phase was separated and washed several times with 100 mL of ethanol carefully in order for the elimination of unreacted 3-nitrobenzoylchlodride and its hydrolysis derivatives. Residual viscous product was dried at $60°C$ in a vacuum oven. Yield: 90%. And then, 40 g of synthesized dinitro functionalized oligomer in 250 mL of THF was reduced to amine form in a Parr reactor. Reduction was performed at 100 psi hydrogen atmosphere at $50°C$ in 16 h; 0.1 g Pd/C was used as catalyst. After the workup procedure, light yellow waxy product was obtained with 85–90% yield (Scheme 1). Similar procedure was
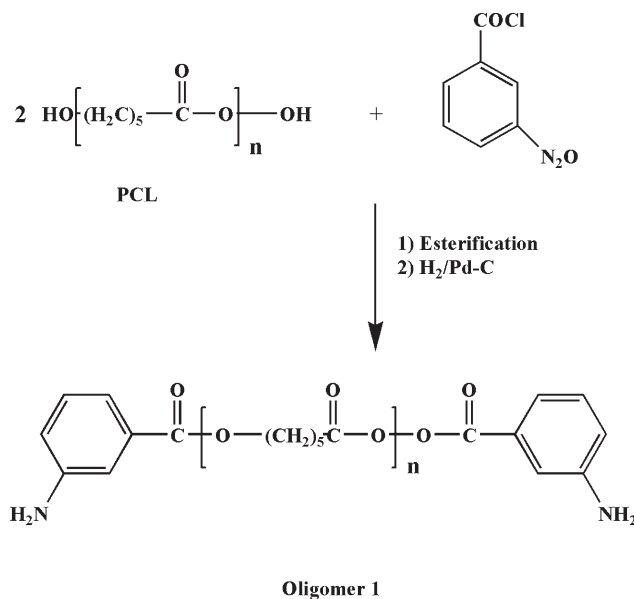
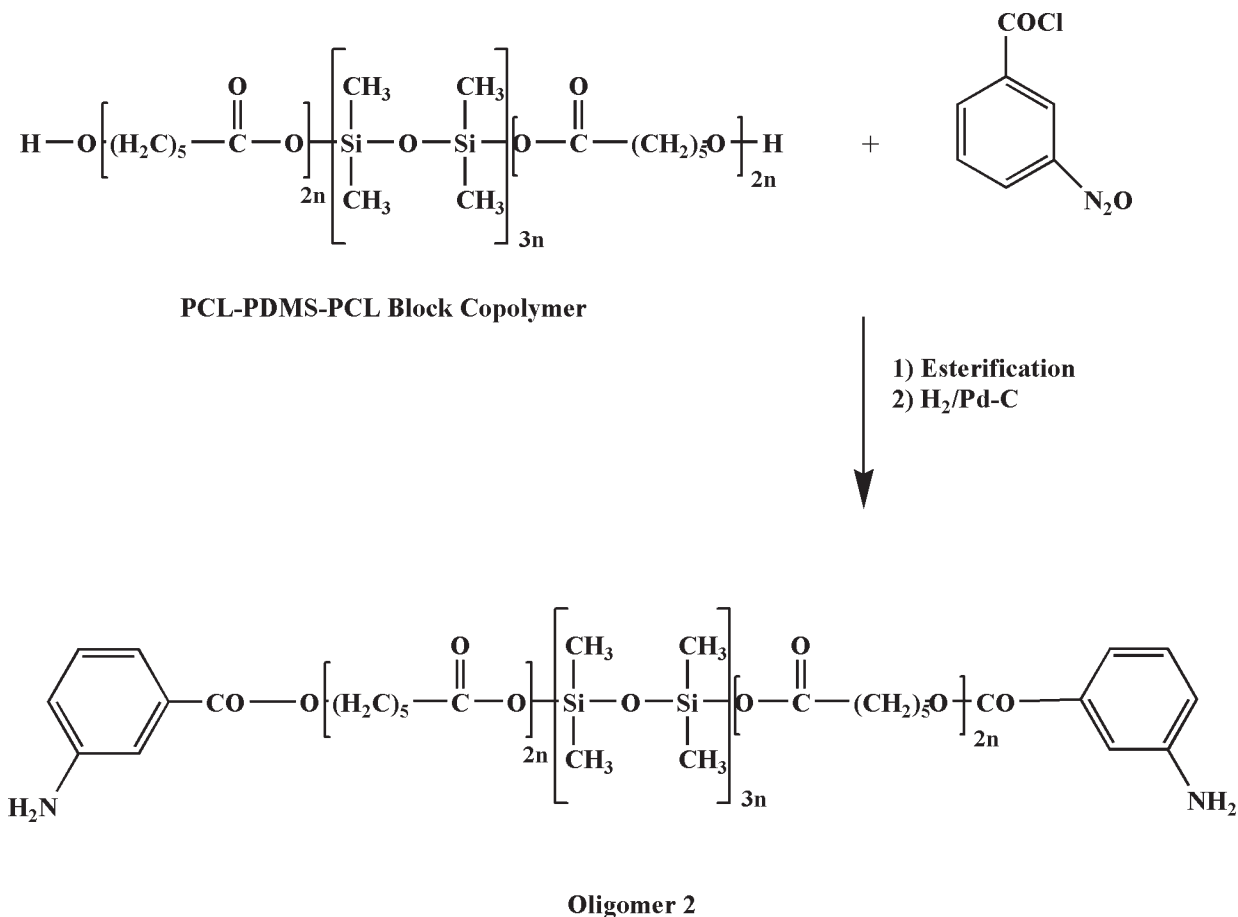**Scheme 1** The synthetic route of amine terminated, PCL based reactive oligomer.

applied for the synthesis of amine terminated PCL-PDMS-PCL reactive oligomer and yellow waxy product was obtained with 80% yield (Scheme 2).

Curing procedure

The epoxy resin used in this work is Araldite GY 250, a bifunctional epoxy resin formulated from the reaction of epichlorohydrin and bisphenol A. The epoxy equivalent weight of the resin is 186.52 and calculated stoichiometry of epoxy resin/hardener (DDS) is 100/30.1 w/w. Epoxy resin, hardener (DDS), and reactive oligomer were mixed at room temperature ($25°C$) and degassed at $120°C$ under vacuum (200 Torr) until bubble free mixtures were obtained. The resulting clear homogenous mixture was poured into a silicon mold preheated at $120°C$. The curing cycle was $120°C$ for 1 h and then $180°C$ for 6 h.

RESULTS AND DISCUSSION

The synthetic routes of amine terminated elastomeric reactive oligomers are shown in Scheme 1 and Scheme 2. The aliphatic elastomeric reactive oligomers were prepared in two steps. The first step is the esterification reaction of hydroxy-terminated PCL or hydroxy-terminated PCL PDMS-PCL block copolymer by 3-nitrobenzoylchloride. The second step is the catalytic reduction of nitro groups of reactive oligomers to amines. Typical oligomers were yellow to orange in color, softened in the range of 49–59°C and soluble in common solvents. The number average molecular weights of Oligomer (1) and Oligomer

PCL-PDMS-PCL Block Copolymer

1) Esterification
2) H$_2$/Pd-C

Oligomer 2

Scheme 2 The synthetic route of amine terminated, PCL-PDMS-PCL based reactive oligomer.

(2) were determined by a nonaqueous potentiometric titration of the end groups. The reactive oligomers were dissolved in a 1 : 1 (v/v) ratio of dry chloroform to glacial acetic acid and titrated with 0.1N HClO4 in glacial acetic acid.[14,15] The <Mn> values of Oligomer 1 and Oligomer 2 were calculated as 1505.8 g/mol and 7663 g/mol, respectively.

The resin system used in this work is a thermally cured epoxy consisting of Araldite GY 250 epoxy resin and DDS amine curing agent. The stoichiometric ratio of 30.1 parts of curing agent per 100 parts epoxy resin yields one oxirane group for every amine hydrogen of DDS. The amount of amine terminated reactive oligomer used in the formulations was calculated as the mole based on amine hydrogen of hardener (DDS). For Oligomer (1) 5, 10, and 20 mol % amine hydrogens of DDS were replaced by equivalent amount of amine hydrogen of Oligomer (1) calculated by molecular weight. The calculated amount of Oligomer (2) in the system (1, 3, and 5 mol % amine hydrogen of DDS) are less then Oligomer (1) because of the compatibility and mixing problems when Oligomer (2) was added more than 5 mol % to epoxy resin system.

FTIR spectroscopic characterizations of reactive oligomers and toughened epoxy networks

The structural characterizations of reactive oligomers based on PCL and PCL-PDMS-PCL were performed by FTIR spectroscopy technique. In the FTIR spectra of PCL based toughener, the peak at 3420 cm^{-1} N—H stretching vibration, 1720 cm^{-1} C=O stretching vibration, 1600 cm^{-1} aromatic C=C, 1240 cm^{-1} ester and 1190 cm^{-1} ether stretching vibrations indicated the formation of amine terminated PCL based reactive Oligomer (1). In the FTIR spectra of PCL-PDMS-PCL based toughener, the peak at 3420 cm^{-1} N—H stretching vibration, 1720 cm^{-1} C=O stretching vibration, 1600 cm^{-1} aromatic C=C, 1260 cm^{-1} ester and 1190 cm^{-1} ether stretching vibrations, 1100–1000 cm^{-1} Si—O—Si stretching vibrations indicated the formation of amine terminated PCL-PDMS-PCL based reactive Oligomer (2). FTIR spectrum of Oligomer (1) and Oligomer (2) are shown in Figure 1(a,b), respectively.

After the curing reaction of epoxy resin with reactive oligomers and DDS, the crosslinked structures were characterized by FTIR spectroscopy. The FTIR
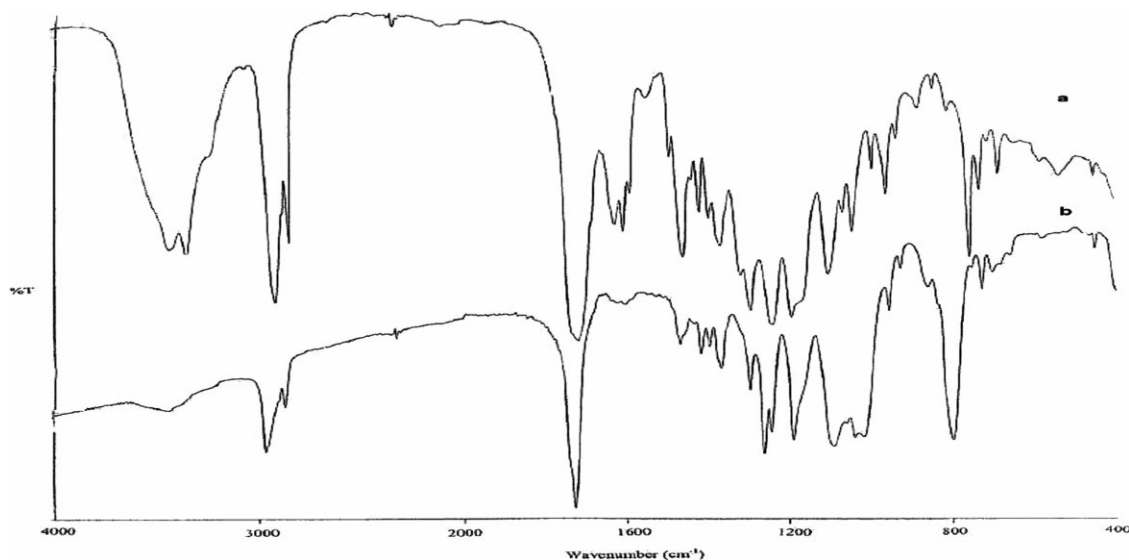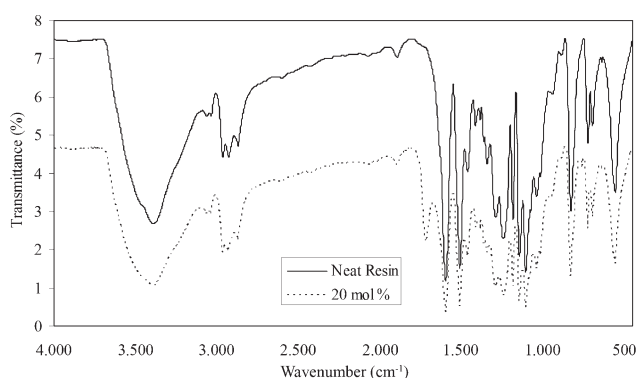
Figure 1 FTIR Spectrum of (a) Oligomer (1) and (b) Oligomer (2).

spectra of epoxy resins toughened by Oligomer (1) and Oligomer (2) as compared with the cured parent epoxy resin are shown in Figure 2 and 3, respectively. The characteristic peak of oxirane group at 940 cm^{-1} diminished and the absorption of carbonyl of the ester groups at 1720 cm^{-1} appeared as proportional by amount of reactive oligomers. The absence of the characteristic peaks of the —NH$_2$ and oxirane groups indicated the oxirane ring opening reaction by —NH$_2$ groups of reactive oligomers and curing agent were completed.

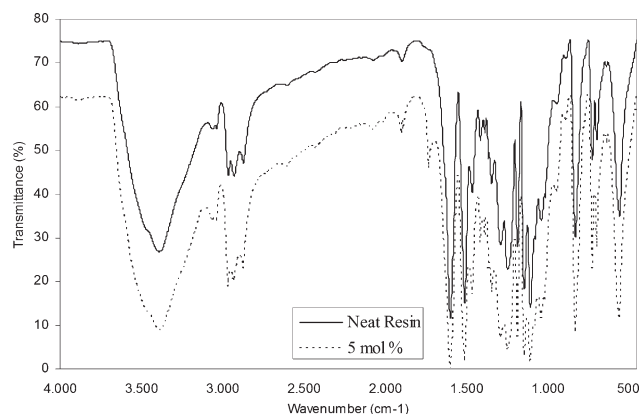## Mechanical properties of the toughened epoxy resins

To determine the effect of toughening mechanism on the mechanical properties of epoxy resin system, various formulations were performed by the incorporation of amine terminated elastomeric oligomers in different concentrations. Test specimens were prepared by casting the resin onto silicon molds having

precise size and shape according to ASTM D 790-02. The specimen edges were smoothed after curing to remove burrs and notches cause by bubbles in the surface. They were conditioned at 25°C and 65% relative humidity for 24 h before all measurements. Flexural tests were performed on unmodified and modified test samples according to ASTM D 790-02.

Table I shows the mechanical properties of toughened resins with the comparison of unmodified one. From the mechanical properties of toughened samples, the critical concentrations of Oligomer (1) and (2) to obtain optimum toughening without any adverse effect on overall mechanical properties were 5 mol % and 3 mol %, respectively. The highest flexural strength value (126.70 MPa) was obtained by incorporation of 5 mol % Oligomer (1) although the critical concentration of Oligomer (2) to achieve same level flexural strength value (128.70 MPa) was 1 mol %. The flexural strength properties of toughened samples by Oligomer (1) was effected

Figure 2 FTIR spectrum of epoxy resins toughened by 20 mol % Oligomer (1) as compared with the neat resin.

Figure 3 FTIR spectrum of epoxy resins toughened by 5 mol % Oligomer (2) as compared with the neat resin.

TABLE I
Mechanical Properties of Unmodified and Modified Epoxy Resin with Different Amounts of Reactive Oligomers

| Oligomer	Amount of toughener (mol %)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (J mm^{-2})
Unmodified	–	91.50	47.00	0.02326
1	5	126.70	48.70	0.02847
	10	120.50	58.75	0.03454
	20	119.20	77.60	0.03318
2	1	128.70	125.35	0.07517
	3	157.20	127.30	0.10520
	5	105.40	131.75	0.03442

adversely when the amount of reactive oligomer was increased more than 5 mol % but it increased with increasing Oligomer (2) concentration between 1 and 3 mol %. The flexural strength value for the toughened resin increased 70%, compared with that for the unmodified resin by using 3 mol % Oligomer (2) as toughener. For the highest flexural strength value, Oligomer (2) was more effective than was Oligomer (1).

The reason of the concentration differences of the reactive oligomers on the mechanical properties of

cured resins can be explained by the molecular weights and chemical structures of oligomers. The PCL-PDMS-PCL based reactive oligomer (2) has higher mechanical properties even in lower concentrations because of the molecular weight of unmodified oligomer, 7000 g/mol.

The stress–strain measurements were performed according to ASTM D 638-02 and the results were given in Table I. The tensile strength properties of toughened samples increased with the increasing amount of reactive oligomers. For the highest tensile strength properties for toughening even in lower concentrations as like 1 to 5 mol %, the incorporating of Oligomer[2] in epoxy formulation as toughener was more effective than Oligomer (1). The tensile strength value for the toughened resin by 5 mol % Oligomer (2) increased 180%, compared with that for the unmodified resin.

To investigate the effect of reactive elastomeric oligomers on the impact strength of the epoxy networks, a series formulations were prepared by the incorporation of various amounts of reactive oligomers as toughener. Impact strength measurements performed according to ASTM D256 were given in Table I. An improvement on impact strength
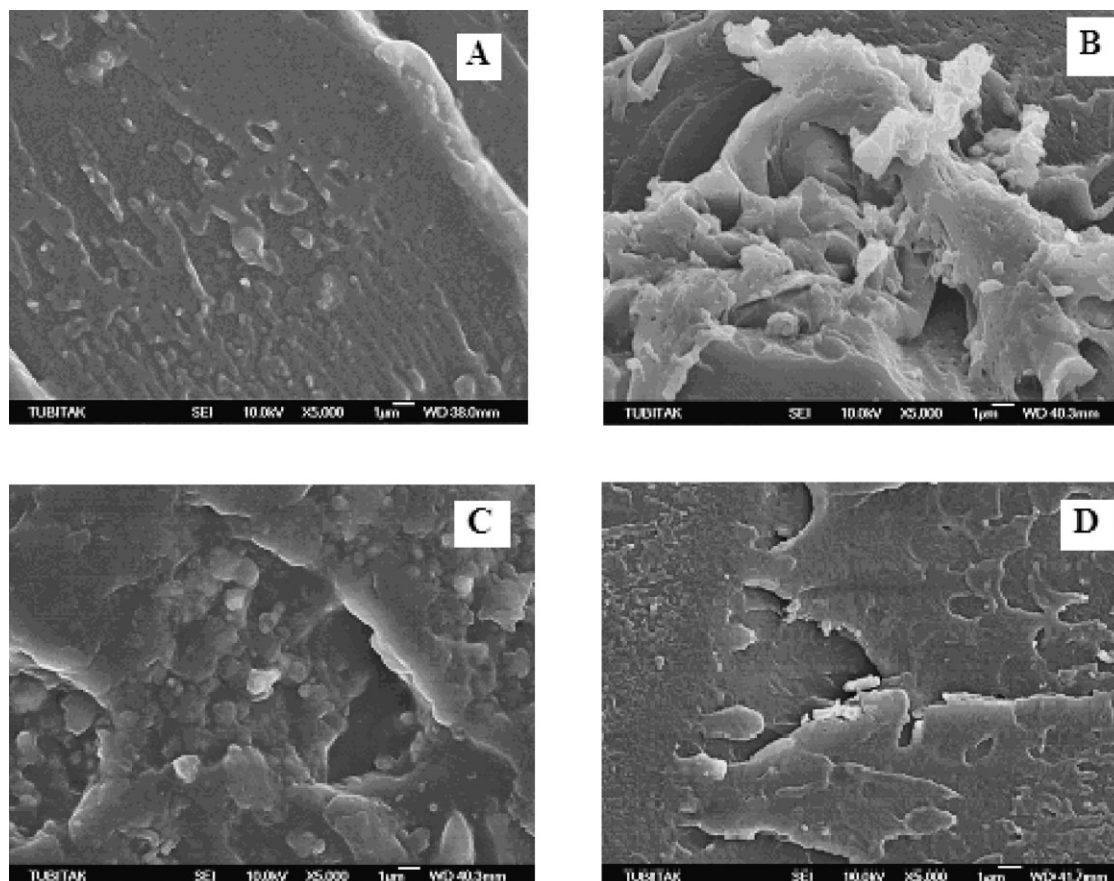
Figure 4 The scanning electron micrographs of fracture surfaces for tepoxy resins toughened by Oligomer (1). (A) The parent epoxy resin; (B) 5 mol %; (C) 10 mol %; (D) 20 mol %.

properties of cured epoxy resins was achieved by the corp. of PCl and PCl-PDMS-PCl based, amine functionalized elastomeric oligomers into the epoxy matrix. The increase in the impact strength values depended on the concentration of the tougheners. The maximum impact strength value was obtained at 10 mol % Oligomer (1) and 3 mol % Oligomer (2), compared with the cured parent epoxy resin. An increase of about more than four fold in impact strength was achieved by incorporating of 3 mol % Oligomer (2) in epoxy formulation as toughener, but the impact strength property has drastically decreased in the toughening with more than 3 mol % of Oligomer (2). The incorporation of 5 mol % Oligomer (2) into the epoxy formulation has created similar effect by 10–20 mol % of Oligomer (1) on the impact strength properties of toughened epoxy resin system because of the Mn value of OH functionalized, PCl-PDMS-PCl based, neat oligomer is higher than OH functionalized, PCl based Oligomer.

According to the mechanical properties, Oligomer (2) is the better one as a toughener and the structure and concentration of the reactive oligomer in the epoxy resin formulations is the key factor to determine the efficiency of functionalized oligomer as the toughener. PCL-PDMS-PCL block copolymer based reactive oligomer including amine group seemed to have a good potential for epoxy toughening mechanism as a toughener. It has been well known that elastomeric oligomers including functional groups as like amine, ─COOH, phenolic ─OH compatible with epoxy resins can react with oxirane rings and create flexible linkages to increase the fracture toughness by different mechanisms.[16]

Morphologies of the toughened epoxy resins

The morphologies of the parent epoxy resin and toughened epoxy resins were investigated by the SEM. The fracture morphologies of epoxy resins modified by Oligomer (1) and Oligomer (2) as compared with the cured parent epoxy resin are shown in Figure 4 and 5, respectively. The fracture surface of the parent epoxy resin is homogenous and had only one phase but heterogenous morphological structures of the toughened epoxy resins can be recognized by micrographs at same magnification. The dark colored space in the micrographs represents the parent epoxy resin. The heterogenity of fracture surface of toughened samples increased with the
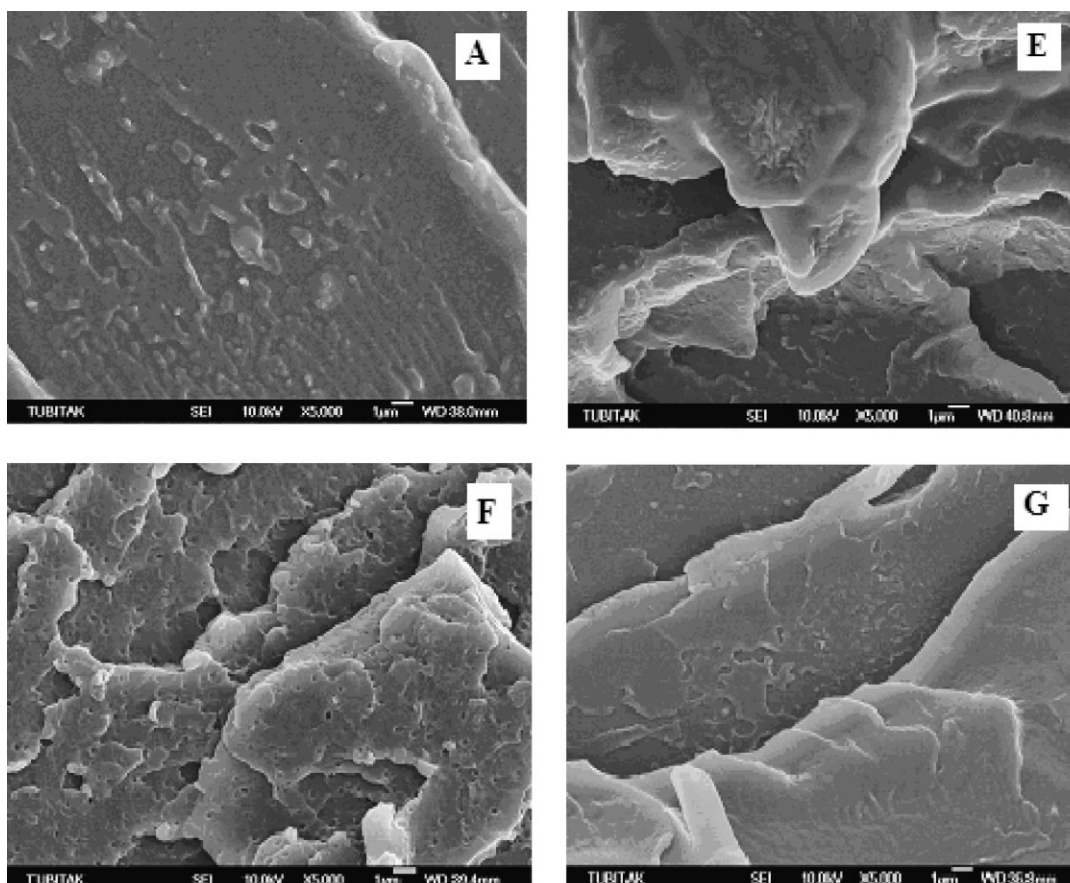
Figure 5 The scanning electron micrographs of fracture surfaces for tepoxy resins toughened by Oligomer (2). (A) The parent epoxy resin; (E) 1 mol %; (F) 3 mol %; (G) 5 mol %.

TABLE II
Thermal Properties of Toughened and Neat Epoxy Resins

| Sample	5% Weight loss (°C)	50% Weight loss (°C)	95% Weight loss (°C)	Residue (%)	T_g (°C)
Unmodified	350	380	580	1.5	148.2
5% Oligomer 1	360	390	610	5	138.4
10% Oligomer 1	360	390	610	5	132.5
20% Oligomer 1	350	390	600	5	117.5
1% Oligomer 2	355	415	600	1	145.2
3% Oligomer 2	355	420	610	3	145.8
5% Oligomer 2	355	420	610	3	145.9

increasing amount of reactive oligomers. As seen on the mechanical properties of toughened samples, there is a significant decrease in the flexural and impact strength values by incorporating more than 3 mol % of Oligomer (2). The reason of reduction on the flexural and impact strength values of modified epoxy resins can be revealed by the decreasing compatibility of the system, as seen by micrographs of toughened samples including 10–20 mol % of Oligomer (1) and 3–5 mol % Oligomer (2) in Figure 4 and 5, respectively.

Thermal properties of the toughened epoxy resins

To investigate the effect of the amine terminated elastomeric oligomers on the thermal properties of toughened epoxy network, thermooxidative stability and glass transition temperature measurements were performed by TGA and DSC techniques, respectively. Thermooxidative stabilities of the cured epoxy resins were determined by TGA in air and reported in Table II. The thermooxidative stability of the samples are directly related with the concentra-

tion of the toughener used in the formulations. The thermooxidative decomposition temperatures of the resins toughened by Oligomer (1) and (2) are higher than neat epoxy resin network and the concentrations and chemical structures of tougheners does not effect dramatically the thermooxidative stabilities of networks. The effect of concentrations and structures of amine terminated oligomers on the glass transition temperatures of networks were investigated using dynamic DSC experiments. The formulated samples including epoxy resin, hardener, and toughener were cured in DSC cell at a heating rate of 10°C min⁻¹ from ambient temperature up to 230°C in N_2 atmosphere, then immediately cooled to −100°C and heated up to 230°C again. The glass transition temperatures were obtained from second heating after quick cooling and taken from the second scan as midpoint of the change in slope of the baseline. All the cured epoxy resins are transparent and showed one glass transition. DSC thermograms of toughened samples are shown in Figure 6 and 7.

As seen in Table I, the T_g values of the samples toughened by Oligomer (1) slightly decreased as the
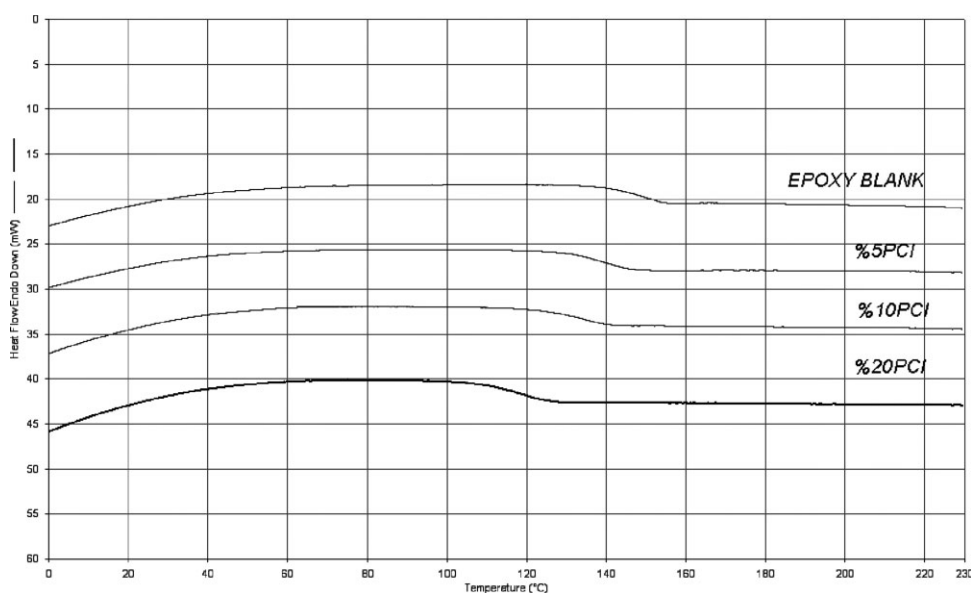
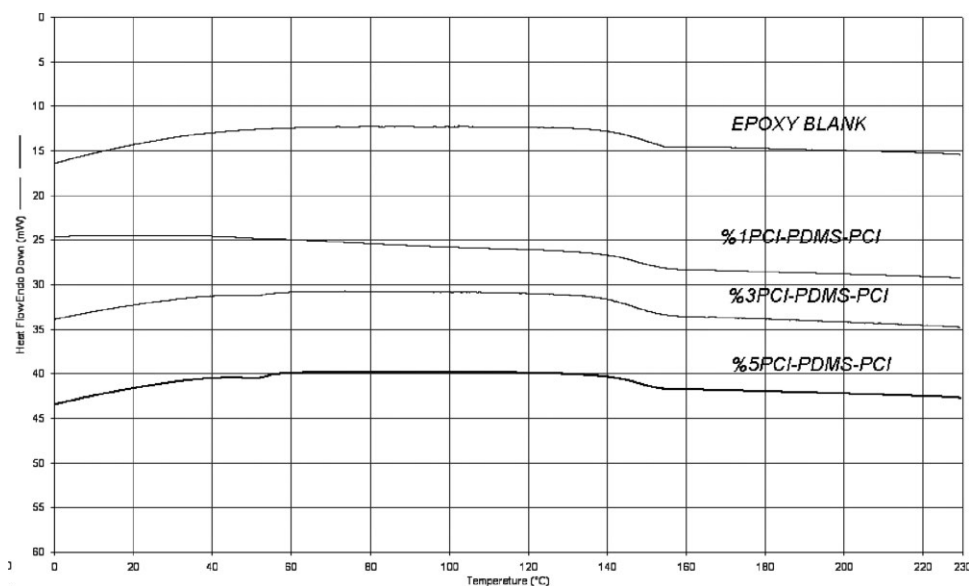**Figure 6** DSC Thermograms of epoxy resins toughened by Oligomer 1.

Figure 7   DSC Thermograms of epoxy resins toughened by Oligomer 2.

increasing amount of reactive oligomers. But for Oligomer (2) case, there is no significant effect on T_g values because of the amount of Oligomer (2) in the matrix was less than Oligomer (1). It is well known that the glass transition temperature of a polymer is closely correlated by the rigidity of the polymer backbone. Introducing of oligomeric structure including functional group react with oxirane ring of epoxy resin, into the epoxy network decrease the crosslinked density. The excess free volume of epoxy networks and flexible linkages into the oligomer structure can ease the molecular motion and this can also decrease the T_g values of epoxy networks.[17–21]

CONCLUSION

To investigate the incorporating of reactive elastomeric oligomers into the epoxy networks, two PCL and PCL-PDMS-PCL based amine terminated oligomers were synthesized by end capping reaction of hydroxyl terminated PCL and PCL-PDMS-PCL based oligomers via 3-nitrobenzoyl chloride in first step and hydrogenation of nitro groups in second step. The amine terminated elastomeric oligomers were used as toughener into the epoxy/amine systems to improve the impact strength of the networks. The mechanical properties as tensile, flexural, and impact strength, thermal properties as thermooxidative stability and glass transition temperatures of Araldite GY 250/DDS/toughener system were measured as a function of concentration and structure of reactive elastomeric oligomers as toughener. Modification of epoxy resins with synthesized elastomeric oligomers led to an increase on the impact strength and shows no adverse effect on mechanical and thermal properties of the cured resin.

The improvement on the impact strength values was achieved by the incorporation of the reactive oligomers into the epoxy resin/hardener systems. The increase on the mechanical properties of the cured resins depends on the structure and concentration of the toughener. The most suitable composition to improve the impact strength of the epoxy matrix was obtained at 10 wt % Oligomer (1) and 3 wt % Oligomer (2). The thermooxidative decomposition temperatures of toughened resins by Oligomer (1) and (2) are slight higher than neat epoxy network. However, the concentrations and chemical structures of tougheners were not effective on the thermooxidative stabilities of networks. But the amounts of % residue are relatively higher because of polymeric moiety in reactive oligomers. It is acceptable that the T_g values of toughened resins slightly decrease as the increasing amount of reactive oligomers. The morphological investigations of toughened epoxy resins revealed the heterogenity of the system. But there is no two-phase morphology in the toughened systems because of the oligomers has chemically attached to the resin system.

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