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Toughening of Epoxy Resins by Amine Terminated Poly(arylene ether ketone)s having Pendant Tertiary Butyl Groups

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The paper has been dedicated to Prof. Dr. Abdülkadir Kuyulu

Summary

The objective of this study was to investigate the effects of the amine terminated poly(arylene ether ketone) (PAEK) oligomers as epoxy tougheners on the mechanical and thermal properties of diglycidyl ether of bisphenol A based epoxy resin. The reactive oligomers including pendant tertiary butyl groups were synthesized by nucleophilic aromatic substitution reaction and molecular weight of the oligomers were controlled through end group functionalization and characterized by FTIR spectroscopy. The stoichiometrical amount of the reactive oligomers as toughener 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 reactive oligomers.

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, hyperbranched polyethers-polyesters,

fluoroelastomers and acrylates. To incorporate rubber particles into rigid materials, especially carboxyl-terminated butadien-acrylonitrile copolymers have been applied to enhance toughness without sacrificing other useful properties such as dimensional stability, stiffness and strength [1-4]. The major problem of this type of elastomeric tougheners is the poor oxidative stability due to high olefin content of the polymer backbone [5-6]. 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 and thermal stability. By these excellent features, PDMS is a good modifier, but due to its extreme incompatibility with epoxy resins, it can not be used by blending. 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].

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. At first, commercial poly (ether sulfone)s (PES) were used as modifiers in the modification of polyfunctional epoxies. It was found that terminally functionalized polysulfones are more effective modifiers than are commercial PES. Other engineering thermoplastics have also been examined as modifiers, such as polyetherimides poly(aryletherketone)s, poly(phenyleneoxide), and aromatic polyesters [9-15].

In this work, amine terminated PAEKs including tertiary butyl group pendantly were prepared and used in various amounts for toughening of diglycidyl bisphenol- A based epoxy resin. The end capped reactive oligomers were mixed homogenously with an epoxy resin and 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.

Experimental

Materials

Hydroquinone (Merck) was purified in acetone. 3-aminophenol (Merck) and 4,4'-(hexaflouroisopropylidene)diphenol (6F-Bisphenol A, Riedel de Haen) was purified by sublimation. 5-tert-butyl isophthalic acid (Amaco), thionyl chloride (Merck A.G), florobenzene (Mallinckrodt), aluminum chloride (Merck A.G.), sodium sulfate (Merck A.G.) and 4,4' Diaminodiphenyl sulfone (DDS, Fluka) were used as received. Diglycidylether of bisphenol A (Araldite GY 250, Ciba) was used as epoxy resin. N,N-dimethylacetamide (Aldrich) was dried over P_2O_5 and vacuum distilled. Toluene was treated with concentrated H_2SO_4, then washed with distilled water, following an aqueous solution of Na_2CO_3 (10 wt%) and finally distilled water again and was dried over Na_2SO_4 and distilled over metallic sodium. Anhydrous K_2CO_3 (Merck A.G.) was dried under vacuum at 140°C for 24 hours before used.

Characterization Methods

Infrared spectra were obtained by using Perkin-Elmer Nicolet 510P 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 DuPont 951 Thermogravimetric Analyzer (TGA) with a heating rate of 10°C/min in air. Glass transition temperatures were determined with a Perkin-Elmer DuPont 910 Differential Scanning Calorimeter (DSC). Scans were run at a heating rate of 10°C/min under nitrogen purge at a rate of 30ml/min. Reported values were obtained from a second heating after a quick cooling. For mechanical characterization, the 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 hrs before all measurements. 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.

Synthesis of Monomers

5-tert-butyl-1,3 bis(4-fluorobenzoyl)benzene (TBFBB): It was synthesized in high yield and high purity, according to the literature [16]. 1H NMR: δ=1.40 (9H, s, *tert*-butyl), 7.18 (4H, t, ortho F), 7.87 (4H, t, meta F), 7.86 (1H, s, para *tert*-butyl), 8.04 (2H, s, ortho *tert*-butyl).
FTIR: 3070-3047 cm^{-1} (arom. C-H strech.), 2964 cm^{-1} (aliph. C-H strech.), 1668 cm^{-1} (C=O strech.), 1251 cm^{-1} (C-F strech.).
MS (EI$^+$): m/z=378 (M$^+$).
$C_{24}H_{20}O_2F_2$: Calcd. C 76.17, H 5.32; Found C 76.10, H 5.30.

Synthesis of Amine Terminated Poly(arylene ether ketone)s

The amine terminated PAEK oligomer (theoretical molecular weight: 10 000 g/mol) was prepared by charging TBFBB (0.07 mol, 26.4891 g), hydroquinone (0.0669 mol, 7.3664 g) and 3-AP (0.0062 mol, 0.6765 g) into a 250 ml four necked flask equipped with a mechanical stirrer, a Dean-Stark trap with a reflux condenser, a nitrogen inlet, a thermometer and dissolved in 30 ml of toluene as an azeotropic solvent and 84 ml of dimethylacetamide. K_2CO_3 (0.175 mol, 24.18 g) was added to the reaction mixture. The reaction mixture was refluxed at 140°C for 8 hrs. and toluene was distilled off from the reaction mixture and the temperature was raised to 160°C for 8 hrs. After cooling to room temperature, the reaction mixture was precipitated in 1:1 (v/v) methanol:water mixture. The oligomer was filtered, washed with methanol and purified by dissolving in chloroform, filtered, and reprecipitated in methanol. The product was dried at 150°C for 48 hrs under vacuum. Yield is 94% [17]. The reaction mechanism of amine terminated PAEK was shown in Scheme 1.

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) in order to stripping of air bubbles trapped during the mixing of sample. The resulting clear homogenous mixture was poured into a silicon mold preheated at 120°C. The curing cycle was 120°C for 1 hour and then 180°C for 6 hours.

Results and Discussion

PAEKs, are high temperature resistant engineering thermoplastics with excellent chemical, mechanical and thermal stabilities. The necessity and importance of heat resistant materials in the aerospace and electronic industries has become driving force for researches on high performance, processible PAEK with target applications. Epoxy resins were modified with PAEKs as oligomeric tougheners by incorporation of PAEKs including reactive end groups which reacts with oxirane groups of epoxy resins. The end group functionalization of PAEKs was achieved by nucleophilic aromatic substitution reaction mechanism with bisphenol, dihalide and an endcapping reagent which has an unreactive group in the polymerization reaction [17]. m- or p-aminophenol are widely used endcapping agents for amine terminated PAEK oligomers.
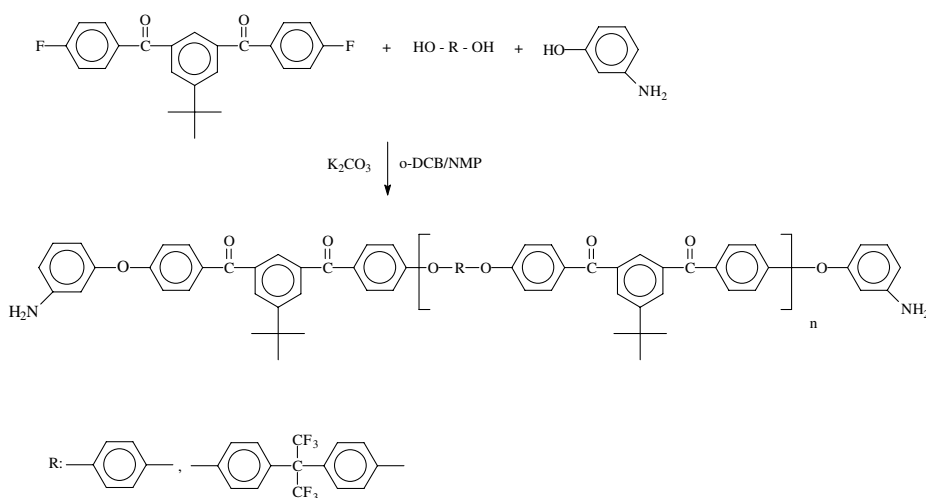
Scheme 1. Reaction mechanism of amine terminated PAEK oligomers

The number average molecular weights of amine terminated PAEK oligomers were determined by a non-aqueous potentiometric titration of the endgroups. The reactive oligomers were dissolved in a 1:1 (v/v) ratio of dry chloroform to glacial acetic acid and titrated with 0.1 N $HClO_4$ in glacial acetic acid [18-19]. The <Mn> values of Oligomer 1 and Oligomer 2 were calculated as 10400 g/mol and 10680 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 as 5, 10 and 20 mole %.

The structural characterizations of reactive oligomers were performed by FTIR spectroscopy technique. In the FTIR spectra of Oligomer 1 and 2, the peak at 3420 cm^{-1} N-H stretch. vibration, 1660 cm^{-1} C=O stretch. vibration, 1595 cm^{-1} aromatic C=C, 1220 cm^{-1} C-O-C stretch. vibrations indicated the formation of amine terminated PAEK oligomers. After the curing reaction, the cured resins were characterized by FTIR spectroscopy. 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. Figure 1 and Figure 2 shows the FTIR spectra of the oligomers and toughened epoxies by oligomers, respectively.
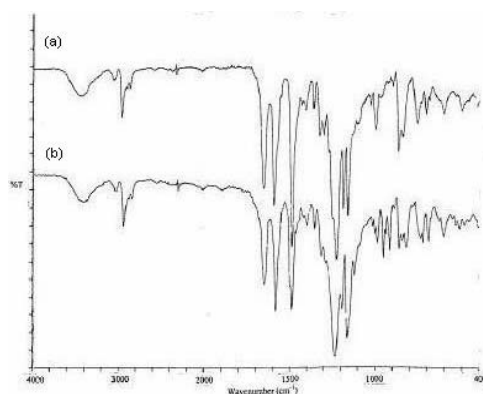

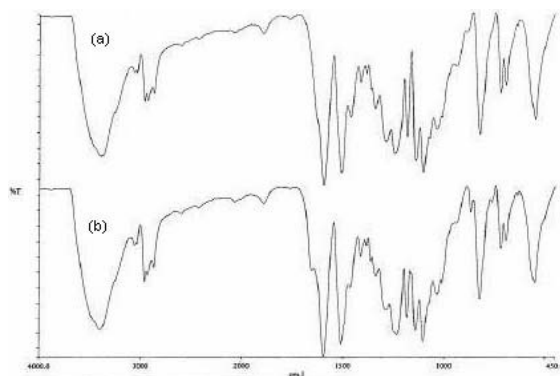Figure 1. FTIR spectra of (a) Oligomer 1 and (b) Oligomer 2

Figure 2. FTIR spectra of (a) toughened epoxy by Oligomer 2 (20 mol %) and (b) toughened epoxy by Oligomer 1 (20 mol %)

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 PAEK oligomers in different concentrations. The specimen edges

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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 hrs before all measurements. Figure 3 shows the tensile strength properties of the toughened resins with Oligomer 1 and 2 as a function of concentration of reactive oligomer.

Tensile strength of the cured resins significantly increased on addition of amine terminated PAEK oligomers but the concentrations more than 10%, the tensile strength properties of cured resins effected adversely. The spacer groups of the amine terminated PAEK oligomers effect on tensile strength properties of the cured resins. The tensile strength differences of the cured resins used same amount of tougeners can be attributed the chemical structure of spacer groups on the oligomer backbones.
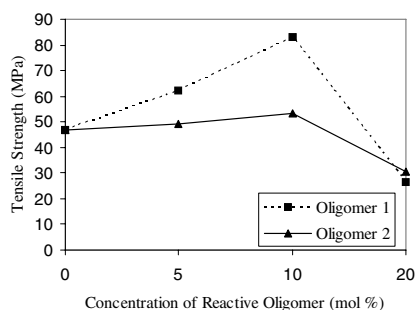

Figure 3. Tensile strength of toughened resins as a function of stoichiometry of Araldite GY/250/DDS/Toughener
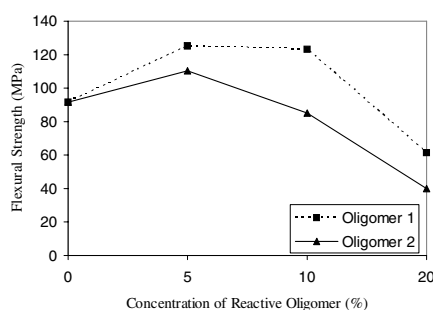
Figure 4. The flexural strength of toughened resins as a function of stoichiometry of Araldite GY 250/DDS/Toughener

Figure 4 shows the flexural strength of cured resins as a function of the amount of tougheners. The flexural strength values of cured resin toughened with Oligomer 1 and 2 has increased by the addition of equivalent weight of oligomers based on 5 mole % of amine hydrogen of DDS but there is no additional increase between 5-20 mol %. For Oligomer 1, addition of more than 10 mol %, the flexural strength property drops sharply below to flexural strength of neat resin.

As seen in Figure 5, impact strength value of cured resins toughened with Oligomer 1 reaches a maximum value by using 5 mol % for Oligomer 1 but 10 mol % for Oligomer 2. Further addition of oligomers decreased the impact strength values of toughened resins but the values are still higher that parent epoxy by addition of 20 mol %. It is also possible to establish a correlation between the chemical structure of the spacer groups on the reactive oligomer backbones and mechanical properties of toughened epoxy resins.

The cured resins toughened with Oligomer 2 bearing non-polar 6F-isopropylidene groups as spacer seems to increase the impact strength more that Oligomer 1 for 10 mol %. But it effects adversely the mechanical properties of epoxy networks. This can be attributed to the known behaviour of the fluorine groups which reduce the surface tension of cured resins. On the basis of mechanical properties tested, it can be said that Oligomer 1 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 [20-22].
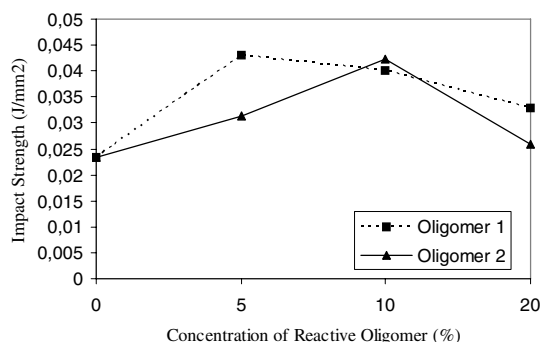
Figure 5. Impact strength of toughened resins as a function of stoichiometry of Araldite GY 250/DDS/Toughener

Amine terminated PAEK oligomer including hydroquinone as spacer unit seemed to have a good potential for epoxy toughening mechanism as a toughener.

Thermal Properties of the Toughened Epoxy Resins

In order to investigate the effect of amine terminated PAEK oligomers on the thermooxidative stabilities and glass transition temperatures of toughened epoxy networks, the parent and toughened epoxy networks were subjected to TGA and DSC, respectively. Thermooxidative stabilities of the cured epoxy resins were determined by TGA in air and are reported in Table 1. The thermooxidative decomposition temperatures of toughened resins by Oligomer 1 and 2 are higher than neat epoxy network and the concentrations and chemical structures of tougheners does not effect 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 the DSC cell at a heating rate of 10°C/min from ambient temperature to 300°C in N_2 atmosphere, then immediately cooled to 25°C and heated up to 300°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.

Table 1. 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)
Neat	350	380	580	1.5	224
5% Oligomer 1	360	420	635	1	224
10% Oligomer 1	360	420	635	1	215
20% Oligomer 1	365	425	635	1	200
5% Oligomer 2	360	420	630	1	222
10% Oligomer 2	360	420	635	1	220
20% Oligomer 2	365	425	635	1	215

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As seen in Table 1, in addition of 5 mol % amine terminated PAEK oligomers into the epoxy network as a toughener doesn't effect on the glass transition temperatures of the cured resins. But, the T_g values of toughened resins slightly decreased as the increasing amount of reactive oligomers. It is well known that the glass transition temperature of a polymer is closely correlated by the rigidity of the polymer backbone.

During the curing reaction of stoichiometrically epoxy/amine system, the crosslink density of the epoxy resin increases by the reaction of oxirane ring of epoxy with amine group of hardener and reaches a maximum at full conversion.

By the full conversion of epoxy-amine system, a stiffer network is formed by the increasing the crosslinked density of the cured resin and a corresponding increase in T_g is observed. 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 [21-23].

Conclusion

In order to investigate the incorporating of high temperature resistant engineering thermoplastics into the epoxy networks, two amine terminated PAEK oligomers including pendant tertiary butyl groups were synthesized and used as toughener into the epoxy/amine systems. The mechanical properties as tensile, flexural, impact strength and 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 thermoplastic oligomers as toughener. The concentration of reactive oligomer was the key factor for the mechanical properties of toughened resins. There was also a correlation between the chemical structure of the spacer groups on the reactive oligomer backbones and mechanical properties of toughened epoxy resins. The cured resins toughened with Oligomer 2 bearing non-polar 6F-isopropylidene groups as spacer seems to increase the impact strength more that Oligomer 1 for 10 mol %. But it effects adversely the mechanical properties of epoxy networks. Amine terminated PAEK oligomer including hydroquinone as spacer unit seemed to have a good potential for epoxy toughening mechanism as a toughener. The most suitable composition to improve the impact strength of the epoxy matrix was obtained at 5 mol % for Oligomer 1 and 10 mol % for Oligomer 2.

The thermooxidative decomposition temperatures of toughened resins by Oligomer 1 and 2 are higher than neat epoxy network and the concentrations and chemical structures of tougheners does not effect the thermooxidative stabilities of networks. The T_g values of toughened resins slightly decrease as the increasing amount of reactive oligomers.

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