# Reinforcement, Impact Modification and Nucleation of Polymers

*RETEC/SPE*

*FEBRUARY 1990*

*HOUSTON, TEXAS*

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# REINFORCEMENT, IMPACT MODIFICATION AND NUCLEATION OF POLYMERS

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# THERMAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF AMINE-TERMINATED POLY(ARYLETHERKETONE)/EPOXY-AMINE RESIN SYSTEMS

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## INTRODUCTION

The motivation to develop high performance lightweight composite materials is well documented[1]. Historically, manufacturers have used thermosetting matrix materials commonly based on epoxide technology[2]. These materials have the advantageous properties of high modulus, high glass transition temperature, good adhesion to fibrous reinforcement, and excellent processing properties. These materials, however, are inherently brittle and solvent sensitive, and as a result their uses are limited[3,4].

Recently, investigators have begun to examine the use of aromatic chain thermoplastics for high performance composite applications[5]. These thermoplastic materials are much tougher than the analogous thermosetting matrix materials and exhibit much better solvent resistance properties. These thermoplastic materials have the drawback of being difficult to process requiring, solvents and/or extreme temperatures.

The desirable properties of toughness and solvent resistance associated with thermoplastic-based matrix resins can be directly related to the molecular structure. The properties of materials such as poly(etheretherketone), PEEK, are a direct result of crystallinity and chain packing[6]. In contrast to highly crosslinked thermosetting resins, the amount of molecular motion thermoplastics can undergo in response to an applied load is much greater and hence their fracture energy is quite high.

Several researchers have improved the toughness of epoxy networks using reactive elastomers such as carboxyl-terminated butadiene-acrylonitrile liquid rubber oligomers[7]. Elastomer modification of the epoxy network leads to a two phase system consisting of rubber particles embedded in the epoxy network. The most widely accepted theory holds that the rubber-modified epoxy networks exhibit increased toughness as a result of energy-dissipating deformations near the vicinity of the crack tip[8]. The deformation processes, for well bonded systems, are interactive and consist of localized cavitation of the rubber or rubber/matrix interface. and localized plastic shear yielding of the epoxy network at areas of stress concentration near the included particle's equator, ahead of the crack tip, where stresses are large enough to induce these mechanisms. The incorporation of elastomeric modifiers to toughen epoxy networks leads to the detrimental effect of lowering the system's modulus and glass transition temperature, properties essential for high performance applications.

Recently, researchers have investigated the possibility of toughening epoxy networks with ductile engineering thermoplastics[9]. The use of these materials alleviates the large mismatch between the modulus and glass transition temperature of the matrix and the modifier, thereby maintaining the essential bulk properties of the network. The incorporation and phase separation of polyethersulfone, PES, from miscible melts of trifunctional and tetrafunctional epoxy resin systems on curing has shown that a two phase structure results, but only a slight improvement in the toughness properties was observed[9]. The lack of good interfacial adhesion between the two phases can be attributed to the absence of improved toughness properties. Good interfacial adhesion between the inclusion and the matrix has been achieved by functionally terminating bis phenol A based poly(arylethersulfone), and bis phenol A based poly(aryletherketone) oligomers before incorporation into the epoxy network[10]. These systems exhibit improved toughness at lower loading levels but macrophase separate, and require solvent processing techniques at higher loading levels.

The deficiencies associated with the above systems are the motivation for this research. The goal of this work is to produce through a solventless process a tough, solvent resistant thermoplastic-like high performance matrix material that is easily processable with conventional thermosetting technology and possess thermoset-like room temperature tack and drape. The technique to achieve this involves the incorporation of various amine-terminated poly(aryletherketone) oligomers with different desirable properties into a commercial epoxy resin at a temperature adequate to induce complete dissolution. A diamino crosslinking agent is then dissolved into the mixture and the miscible low viscosity ternary melt is then cast and cured. During the curing process the initially miscible melt phase separates into two phases; a lightly-crosslinked thermoplastic-rich phase, and a highly-crosslinked epoxy/amine-rich phase. The bulk properties of the resin are dependent on which phase is continuous[11]. The morphology of the system can be controlled by the loading level of the amine-terminated oligomer.

## EXPERIMENTAL

Materials: N-methyl pyrrolidinone, NMP, 99%, obtained from Aldrich was vacuum distilled in the presence of phosphorus pentoxide. Toluene obtained from Fisher was dried over calcium hydride and distilled before use. The following materials were obtained from Aldrich and purified by sublimation; 4,4'-diflourobenzophenone, 99%, m.p. 103-104°C, methylhydroquinone, 99%, m.p. 128-129°C, tertiary-butylhydroquinone, 97%, m.p. 127-129°C, 3-aminophenol, 98%, m.p. 125-126°C. The following materials were used as received; phenylhydroquinone, 97%, from Aldrich, m.p. 102-103°C, 4,4'-diaminodiphenylsulphone, DDS, from Lancaster Synthesis Ltd., m.p. 175-177°C, Epon 828 epoxy resin, courtesy of Shell Chemical Co., the diglycidyl-ether of bisphenol A. Anhydrous potassium carbonate obtained from Fisher was dried under vacuum before use.

Methods:

A) Synthesis: The amine-terminated poly(aryletherketone) oligomers were synthesized utilizing a one-step reaction technique[12]. The oligomers were based on three different hydroquinone derivatives; methylhydroquinone, tertiary-butylhydroquinone, and phenylhydroquinone, and are shown in Figure 1.

A one liter four neck reaction vessel equipped with a nitrogen inlet, mechanical stirrer, thermometer, and a Dean-Stark trap fitted with a condenser was charged with the 4,4'diflourobenzophenone, desired hydroquinone, potassium carbonate, and the endcapping agent 3-aminophenol. The NMP and toluene were then added.

The reaction mixture was then heated to reflux under a constant nitrogen purge until all of the water had been removed via azeotropic distillation. The temperature was then raised to 155°C and maintained for 8 hours. Toluene was then removed by quickly heating the reaction mixture to 180°C. The reaction mixture was then cooled and precipitated into rapidly stirring methanol. The polymer was filtered, washed in boiling methanol, filtered, washed with methanol and water, washed in boiling water, filtered, washed with hot water and methanol and vacuum dried.

The resins were produced by dissolving the amine-terminated oligomers into the epoxy at 140-170°C. A loading level of 0-50% w/w of oligomer to epoxy was studied. The curing agent, DDS, was then added in a 1:1 epoxy/amine stoichiometric ratio. The melt was then degassed. The resins were cast into a 3 mm thick teflon-coated sheet mold. The resins were cured for two hours at 175°C followed by two hours under vacuum at 235°C.

B) Characterization: The thermal properties of the amine-terminated oligomers and the poly(aryletherketone)/Epon 828-DDS materials were characterized by differential scanning calorimetry using a Perkin-Elmer Series 4 DSC using a heating rate of 20°C/minute.

The dynamic mechanical properties were evaluated with an IMASS Dynastat dynamic mechanical spectrometer using sinusoidal deformations in a 3-point bend mode. Measurements were made in the load control mode. The materials were tested at a heating rate of 2.5°C/minute. All reported data is at 1 Hz.

The flexural moduli were measured in a three-point bend configuration, following the operational procedures in ASTM D790M, at a crosshead rate of 0.05 cm/minute using a model 1115 Instron universal testing machine.

The critical stress intensity factor and fracture energy determinations were made following a modified ASTM E399 technique[13]. These samples were tested using a model 1115 Instron universal testing machine at a crosshead rate of 0.10 cm/minute.

The phase separated morphology of the materials was studied using transmission electron microscopy, TEM, utilizing a 100 kV JEOL electron microscope.

The end group analysis was performed using elemental analysis. This evaluation was provided by the Analytical Service Department of the University of Massachusetts.

## RESULTS AND DISCUSSION

The thermal and mechanical properties of three low molecular weight amine-terminated poly(arylether-ketone)/epoxy-amine systems are shown in Table 1. The results show that the fracture energy of the materials increases with the loading level of the amine-terminated oligomer, the modulus remains nearly constant, and the glass transition temperature decreases slightly.

The toughness and glass transition temperature values appear to undergo a discontinuous change near the 30% oligomer loading level. This abrupt change as well as the bulk properties of the resins can be attributed to the morphological changes that occur as a function of oligomer loading level. Representative TEM micrographs are shown in Figure 2.

The micrographs show the phase separated behavior associated with this type of system. Figure 2.a, 10% oligomer incorporation, is indicative of the traditional expected morphology consisting of thermoplastic inclusions embedded within the epoxy matrix. Figure 2.b, 30% oligomer loading level, shows continuous areas of each phase having inclusions of the other. Figure 2.c shows the morphology associated with the 50% loading level material where the lightly-crosslinked thermoplastic-rich phase is continuous and the highly-crosslinked epoxy-rich phase is the included phase.

Each morphology exhibits characteristic mechanical properties. The lower loading level materials are essentially toughened epoxy networks. The thermoplastic oligomeric modifier acts as a toughening agent most likely increasing the fracture toughness of the network by inducing local shear yielding, and by absorbing propagating crack energy through ductile tearing. The thermal properties of the low loading level resins indicate that neither phase is pure as would be expected for chemically bound systems. The glass transition temperatures of the modified low loading level resins are similar to the unmodified resin.

The high loading level systems show a lower glass transition temperature consistent with the fact that the thermoplastic-rich phase is now continuous, directly opposite of the previous case. The fracture toughness of this system is much greater, and is directly attributed to the mechanical properties associated with thermoplastic resins. These matrix resins represent an opportunity to produce engineering thermoplastic-like materials with epoxy-like processing properties. The thermal and mechanical properties of these systems are expected to increase as higher molecular weight oligomeric derivatives are studied.

The process that leads to the specific morphological state is quite complex. The situation is governed by both thermodynamic and kinetic factors. The ternary system of amine-terminated oligomer, epoxy, and amine curing agent, must first be heated above the upper critical solution temperature, U.C.S.T., of the system where a miscible mixture is attained. The system is kinetically influenced by the rate of reaction. As the crosslinking reaction proceeds the viscosity of the mixture greatly increases and the diffusional abilities of each species decreases. As the molecular weight of the epoxy-rich phase increases the conformational entropy effect that initially favored miscibility decreases and drives the system toward incompatibility. Also as the reaction proceeds the specific interactions, which helped lead to the initial miscibility, are changed and the enthalpic effects are no longer as favorable and the lower critical solution temperature, L.C.S.T., of the system decreases sufficiently to induce the observed two phase morphology before diffusional factors sufficiently bind the molecular transport. Complete phase separation into pure components is not observed because the thermoplastic oligomers are chemically bound to epoxide groups, a factor that favors miscibility.

## CONCLUSIONS

The thermal, mechanical, and morphological properties of three different low molecular weight amine-terminated poly(aryletherketone)/epoxy-amine systems have been discussed. These materials are shown to be unique by their solventless processing characteristics and by yielding three separate characteristic materials after curing; a thermoplastic-like resin with epoxy-like processing properties, a thermoplastic toughened epoxy network, and a mixed phase material with both thermoplastic and thermoset continuous phase regions embedded with regions of the opposite phase. The morphologies have been shown to determine the bulk properties of the resin, and the morphology can be governed by the thermoplastic loading level. Future work will involve the studying of higher molecular weight oligomeric derivatives.

## ACKNOWLEDGEMENT

The authors wish to thank the Center for UMass-Industry Research on Polymers (CUMIRP) for financial support.

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Greggory S. Bennett, a native of Hudson, WI., received his B.S. degree in Chemical Engineering from the University of Wisconsin-Madison in 1987. He entered the Polymer Science and Engineering doctoral program at the University of Massachusetts the same year. Under the advisement of Dr. Richard J. Farris his research has primarily focused on the engineering of properties in high performance polymeric systems.

## TABLE 1
## THERMAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES

3100 Mn ATtBPK/Epon 828-DDS Resins

| Loading (%) | Tg (DSC) (°C) | Tg (DMA) (°C)[a] | $G_{IC}$ ($J/m^2$) | $K_{IC}$ ($MN/m^{3/2}$) | Modulus (GPa) |
|---|---|---|---|---|---|
| 0[d] | 218.7 | 213 | 260 | 0.79 | 2.41 |
| 10[d] | 162.1<br>197.0 | 194 | 248 | 0.76 | 2.33 |
| 20[d] | 164.9<br>204.6 | 167[c]<br>207 | 309 | 0.82 | 2.17 |
| 30[e] | 156.3<br>202.3 | 163[c]<br>202 | 623 | 1.16 | 2.16 |
| 40[f] | 170.7<br>200.2 | 173 | 826 | 1.32 | 2.11 |
| 50[f] | 171.7<br>197.8 | 175 | 1191 | 1.57 | 2.07 |

3100 Mn ATMePK/Epon 828-DDS Resins

| Loading (%) | Tg (DSC) (°C) | Tg (DMA) (°C)[a] | $G_{IC}$ ($J/m^2$) | $K_{IC}$ ($MN/m^{3/2}$) | Modulus (GPa) |
|---|---|---|---|---|---|
| 0[d] | 218.7 | 213 | 260 | 0.79 | 2.41 |
| 10 | 141.2<br>206.2 | 210 | 303 | 0.87 | 2.52 |
| 20 | 135[b]<br>197.4 | 196 | 322 | 0.91 | 2.56 |
| 30 | 135[b]<br>187.3 | 180 | 662 | 1.26 | 2.39 |
| 40 | 135[b]<br>181.2 | 175 | 751 | 1.38 | 2.57 |

2600 Mn ATPhPK/Epon 828-DDS Resins

| Loading (%) | Tg (DSC) (°C) | Tg (DMA) (°C)[a] | $G_{IC}$ ($J/m^2$) | $K_{IC}$ ($MN/m^{3/2}$) | Modulus (GPa) |
|---|---|---|---|---|---|
| 0[d] | 218.7 | 213 | 260 | 0.79 | 2.41 |
| 10 | 172.2<br>204.8 | | 307 | 0.84 | 2.29 |
| 20 | 135[b]<br>189.8 | | 322 | 0.89 | 2.47 |
| 30 | 135[b]<br>173.3 | | 580 | 1.17 | 2.36 |
| 40 | 166.2<br>181.8 | | 299 | 0.85 | 2.40 |
| 50 | 135[b]<br>165.7 | | 447 | 1.07 | 2.56 |

[a] Loss modulus peak at 1 Hz

[b] Broad transition

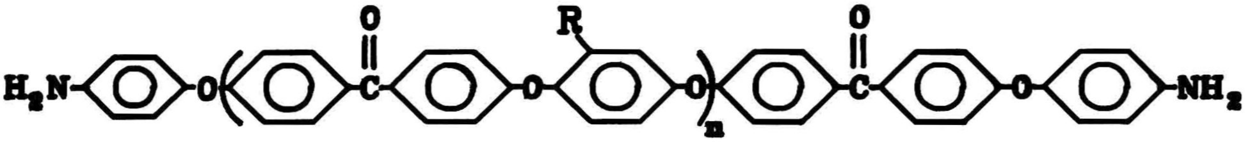
[c] Loss modulus peak corresponding to largest decrease in the storage modulus

[d] Epoxy phase continuous

[e] Mixed continuous phases

[f] PEEK derivative continuous phase

# FIGURE 1



**Amine–terminated poly(aryletherketone) oligomer**

**R = methyl, t–butyl, or phenyl**

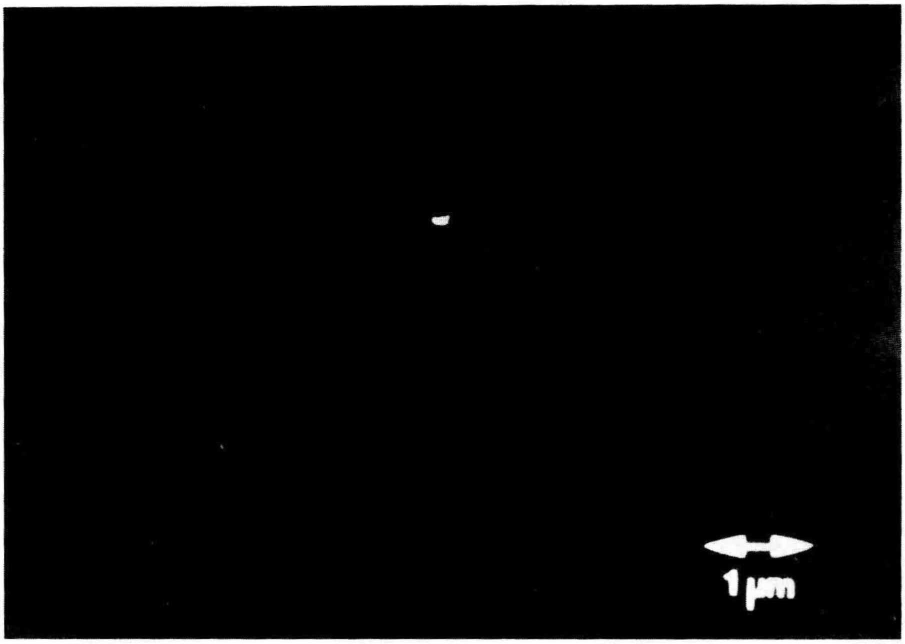


FIGURE 2.A 10% AMINE-TERMINATED OLIGOMER INCORPORATION WITH AN EPOXY-RICH CONTINUOUS PHASE (LIGHT IS THE EPOXY-RICH PHASE, DARK IS THE OLIGOMER-RICH PHASE)

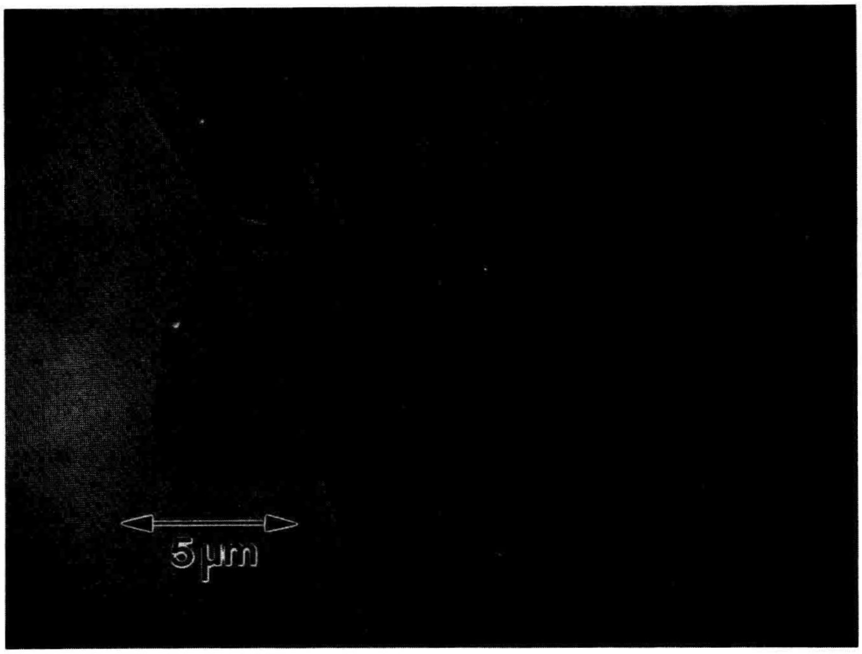


FIGURE 2.B 30% AMINE-TERMINATED OLIGOMER INCORPORATION WITH MIXED CONTINUOUS PHASES (LIGHT IS THE EPOXY-RICH PHASE, DARK IS THE OLIGOMER-RICH PHASE)

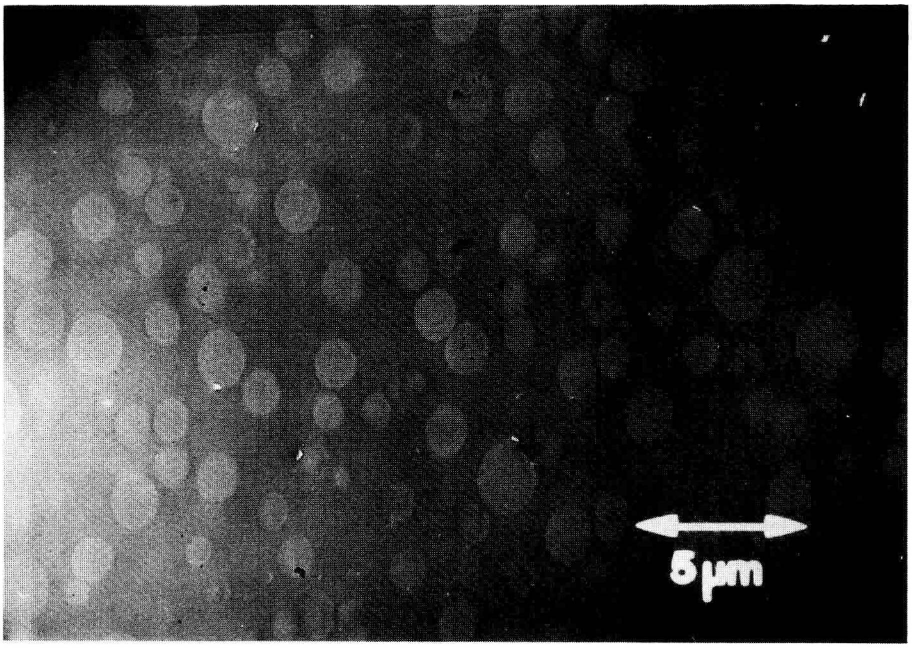


FIGURE 2.C 50% AMINE-TERMINATED OLIGOMER INCORPORATION WITH AN OLIGOMER-RICH CONTINUOUS PHASE (LIGHT IS THE EPOXY-RICH PHASE, DARK IS THE OLIGOMER-RICH PHASE)

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# IMPACT MODIFICATION OF POLYAMIDE

DEXTER PLASTICS

KHEM NANGRANI

DAVID YU