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Engineering

Chemical Modification of Matrix Resin Networks with Engineering Thermoplastics

1. Phenolic Hydroxyl Terminated Poly(Aryl Ether Sulfone)-Epoxy Systems

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Summary

Functionally terminated bisphenol-A polysulfone oligomers were used in the modification of Epon Resin 828/4,4'-diaminodiphenylsulfone (DDS) network system. Phenolic hydroxyl terminated PSF oligomers were first capped with a large excess of bisphenol-A diglycidyl ether or Epon Resin 828 at both ends and then the resulting system was cured with DDS, in a two-step process. During these studies molecular weight and the amount of PSF oligomers incorporated into the network were varied and their effect on the overall properties of the resulting systems were investigated. The capping and curing reactions were followed by using FT-IR and NMR spectroscopy, GPC, HPLC and DSC techniques. As a function of the oligomer molecular weight, SEM studies showed the formation of two-phase structures with ductile PSF particles dispersed in the continuous epoxy matrix. Mechanical characterization and fracture toughness measurements showed a remarkable increase in K_{IC} or G_{IC} values of the modified networks over that of control, without significant loss in the modulus. This work would appear to be one of the first studies where well bonded ductile glassy modifiers have significantly improved the fracture toughness of highly crosslinked networks.

Introduction

Epoxy resins are one of the most important classes of thermosetting polymers and find extensive use as coatings, matrix resins for composite materials and high performance adhesives. They have various desirable properties such as high tensile strength and modulus, good thermal and chemical resistance and dimensional stability. However, in many applications they have one major drawback. They are very brittle and therefore have poor thermal cycling behavior and fairly low impact and fracture strengths. They also show high moisture absorption, which detracts from their performance.

In the last decade numerous studies have been conducted on the toughening of epoxy networks using reactive butadiene-acrylonitrile oligomers having both carboxyl and amine end groups (1-3). In some other systems acrylate elastomers (4) or amine terminated propyleneoxide oligomers (5) have also been utilized. For the last several years in our group we have been

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using functionally terminated siloxane oligomers in the modification of epoxy networks (6,7). Our aim in using siloxanes was three fold, first to improve the fracture toughness of the matrix (8), second to reduce the water sorption of the network due to highly hydrophobic nature of the siloxanes and finally to modify the surface properties and provide a low-friction surface to the resulting system (9). The improvement in the fracture toughness by the incorporation of rubber modifiers has usually been at the expense of the bulk properties and especially the modulus. In case of CTBN or ATBN modification thermal and chemical resistance of the final systems have also been reduced due to the nature of the modifier.

Recently another approach has been taken to modify the epoxy resins which seems to provide better improvement in the overall properties of the resulting networks without any significant loss in the modulus. In this method tough, ductile, chemically and thermally stable engineering thermoplastics such as polyethersulfones (10) and polyether-imides (11) have been utilized. These materials have no reactive functional groups so they were simply physically blended into the resin and cured. It has been reported that some improvement in the fracture toughness is obtained provided that a phase separation with good interfacial adhesion is achieved.

We have taken a somewhat similar approach in the modification of epoxy resins, except that we have used reactive functionally terminated Bisphenol-A Polysulfone (PSF) oligomers. By using reactive oligomers we are able to chemically bond the modifier into the network. Since these modifiers are synthesized in our laboratories we are also able to control the molecular weight and the solubility parameters of the oligomers by changing the stoichiometry and chemical composition during the reactions, as desired. These important variations enabled us to obtain good interfacial adhesion and yet also the desired phase separation in the modified networks.

In this communication we will report our preliminary investigations on the commercially available Epon Resin 828/ 4,4'-diaminodiphenylsulfone (DDS) system modified with phenolic hydroxyl terminated polysulfone oligomers. We will discuss the critical features that must occur during the curing process and also summarize the thermal and mechanical properties thus far investigated with the modified networks.

Experimental

Materials:

Epon Resin 828 was kindly supplied by Shell Development Company. The titrated equivalent weight of the resin was 190 g/equiv.

The curing agent, 4,4'-diaminodiphenylsulfone (DDS) was obtained from Aldrich Chemical Company and used without further purification.

Phenolic hydroxyl terminated polysulfone oligomers (PSF) were synthesized by the reaction of Bisphenol-A and 4,4'-dichloro-diphenylsulfone in NMP using K_2CO_3 as the base. Detailed procedure of the synthetic routes have been developed in our laboratory and are given elsewhere (12).

Modification and Curing Procedure:

As shown in the Reaction Scheme, modified networks were prepared in two steps. In the first step, hydroxyl terminated PSF oligomers were capped with a large excess of Epon Resin 828 in bulk at 110°C under the catalytic action of tetramethylammonium hydroxide. Then the catalyst was decomposed by heating it to 150°C for 3 hours and removing the volatile by-products from the system. In the second step the curing agent, DDS, was added into the above mixture and the system was kept at 150°C, under vacuum until it was homogeneous and clear. This temperature is necessary to melt the DDS. The reaction mixture was then cooled to approximately 80°C, poured into a silicone mold, cured for 2 hours at 140°C and post cured 2 hours at 190°C.

Characterization Techniques:

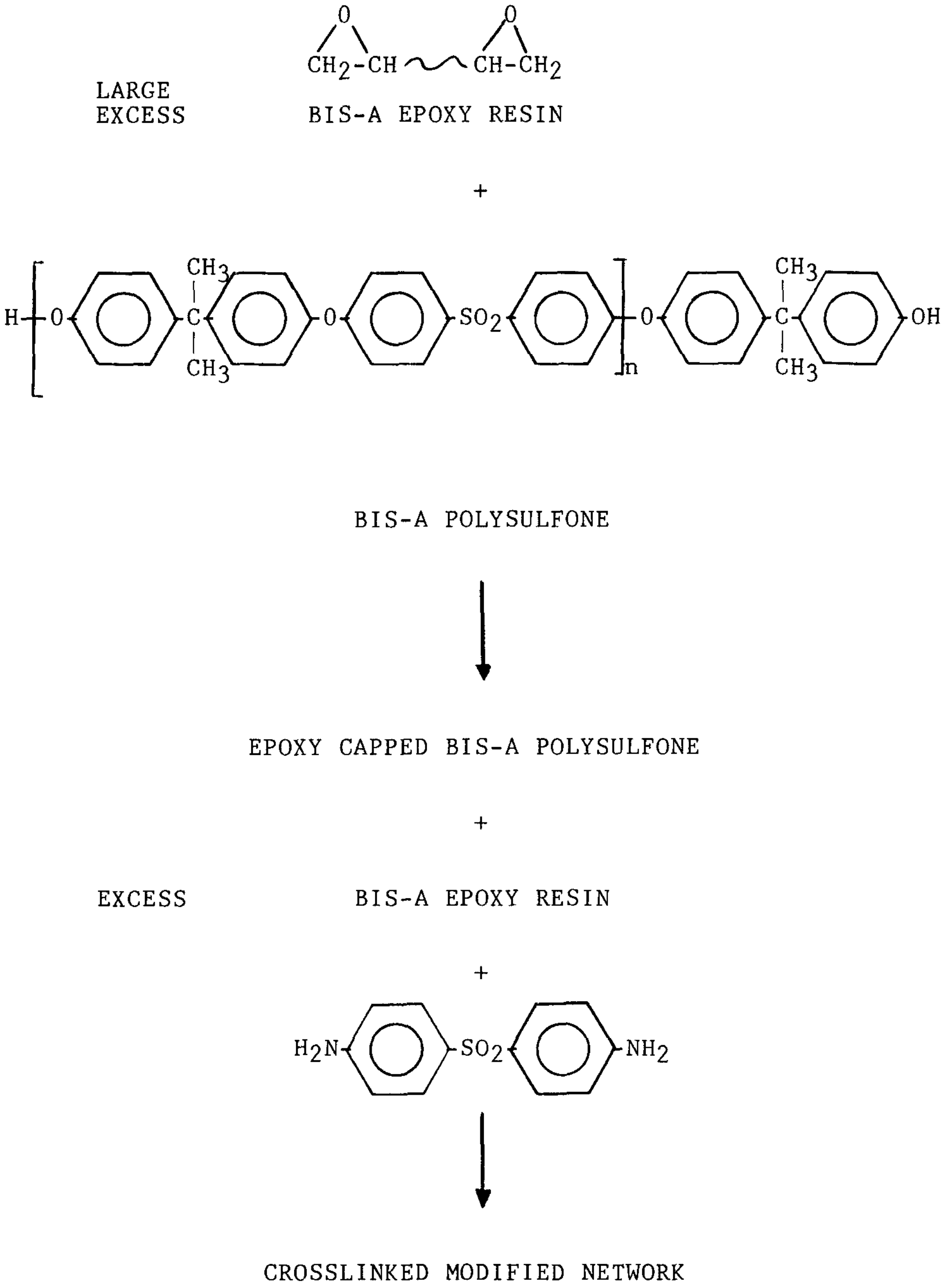
PSF oligomers were characterized by FT-IR and NMR spectroscopy, GPC, DSC and titration of their end groups (13). The first step of the curing reaction, capping of PSF oligomers, was followed by HPLC and GPC. Cured networks were characterized by DSC, DMTA and Scanning Electron Microscopy. Fracture toughness measurements were done according to ASTM Standard E399.

Results and Discussion

Phenolic hydroxyl terminated Bisphenol-A Polysulfone oligomers were used in the toughening of Epon Resin 828/ 4,4'-diaminodiphenylsulfone network systems. During these studies PSF oligomers of different molecular weights were incorporated into the networks at various levels and the properties of resulting materials were investigated. PSF oligomers were chosen as modifiers because of their known toughess (at high MW), high modulus, high Tg, thermal and chemical resistance and their stability against moisture.

The reactions were carried out in two steps, similar to the approaches taken in rubber modification of epoxy networks. The first step is the capping of PSF with epoxy resin, and is followed by second curing at high temperatures, after the addition of the hardener. We have used DDS as the curing agent throughout the reactions without any additional catalyst. This was so designed in order to have a slow curing reaction which would provide enough time for a good phase separation between the epoxy matrix and the PSF modifier. We suggest this is a critical point in achieving the optimum improvement in the fracture toughness. This approach no doubt also produces a more uniform crosslinked network than when mixed mode, e.g. diamine plus Lewis acid, cures are conducted.

SYNTHESIS SCHEME FOR MODIFIED NETWORKS



In this study PSF oligomers with molecular weights of 5300 and 8200 g/mole were utilized as the modifiers at the levels of 10 and 15 percent by weight. Table I summarizes the data on the compositions and the results on the DSC analysis of the networks produced. As can be seen from this Table in both control and the modified networks it is possible to obtain high Tg's which are in 195-200°C range. In DSC scans no exotherms are observed after the Tg which clearly indicates that the curing was complete in each case.

TABLE I

Thermal Characteristics of Polysulfone Oligomers and the Cured Networks

	PSF		PSF	Network
No.	Mn, (g/mole)	Tg (°C)	(wt. %)	Tg (°C)
1	Cured Epon Resin 828/DDS Control			195
2	5300	180	10	196
3	5300	180	15	196
4	8200	183	10	198
5	8200	183	15	200

Table II shows the results on fracture toughness (K_{IC}) and flexural modulus. The control network has a typical glassy flexual modulus around 2.5×10^9 N/M^2. When modified with PSF oligomers there is a slight drop in this value, however this is insignificant when compared with rubber modified networks (8). In fact, we have obtained even better results with higher

TABLE II

Mechanical Properties of Modified Epoxy Networks

	PSF		Flex. Mod.	Fract. Tough.
No.	Mn (g/mole)	(wt. %)	(N/M^2)	K_{IC} ($N/M^{3/2}$)
1	Epon Resin 828/DDS Control		2.5×10^9	0.6×10^6
2	5300	10	2.0×10^9	0.9×10^6
3	5300	15	2.0×10^9	0.9×10^6
4	8200	10	---	1.0×10^6
5	8200	15	2.2×10^9	1.3×10^6
6	UDEL P-1700 Polysulfone Control		---	2.4×10^6

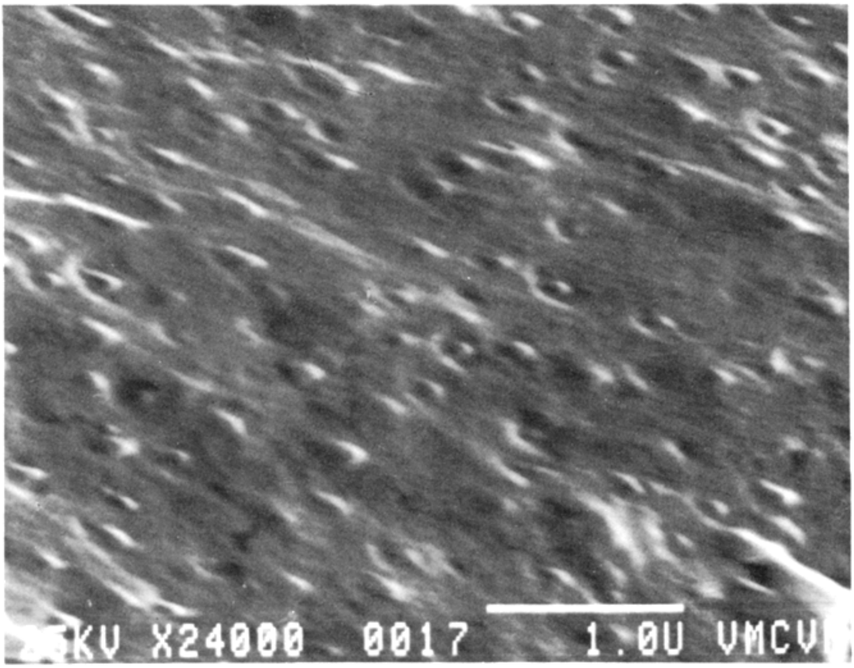


Fig. 1.a. SEM photomicrograph of the fractured surface of an Epon Resin 828/DDS Network modified with 15% by weight of 5300 Mn PSF oligomer.

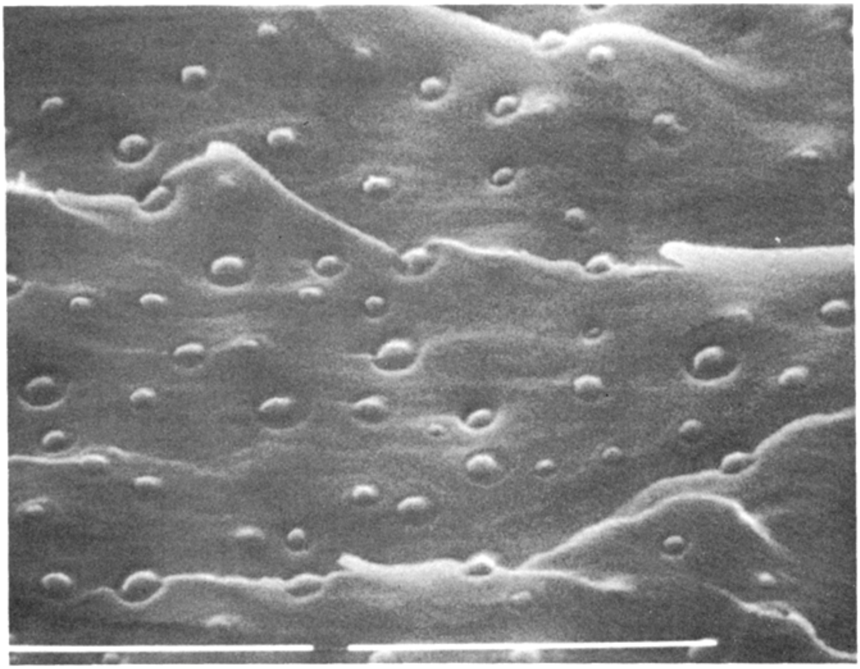


Fig. 1.b. SEM photomicrograph of the fractured surface of an Epon Resin 828/DDS Network modified with 15% by weight of 8200 Mn PSF oligomer.

molecular weight PSF modifiers which we will discuss in our future publications. On the other hand the improvement in the fracture toughness is remarkable and seems to be directly proportional to the molecular weight and the amount of the modifier in the range studied. This is an interesting behavior since it may indicate that chain extension and perhaps subsequently developed chain entanglements in the modifier may play an important role in the toughening of the network. When compared with the control, we observe a 50 percent increase in the K_{IC} value of Sample 3 and more than 100 percent in Sample 5. As expected, the amount of modifier incorporated into the system also increases the toughness.

Figure 1 shows the SEM micrographs of the fractured surfaces for several modified systems. Well-defined, two-phase morphology can clearly be seen with a relatively homogeneous distribution of PSF particles in the epoxy matrix. It is also important to note that the size of the particles increase as the molecular weight of the modifier increases. When closely examined, SEM pictures also suggest the ductile deformation (tearing) of PSF particles and the plastic deformation of the epoxy matrix around these particles. Further analysis and interpretation of the SEM results is in progress in order to better understand the toughening mechanisms in these systems.

As a conclusion of our preliminary investigation we can say that reactive, functionally terminated polysulfone oligomers are very useful modifiers for epoxy networks. A two-phase morphology is obtained with a homogeneous distribution of PSF particles in the epoxy matrix. Considerable improvements in the fracture toughness of the network are obtained, while retaining the high modulus and modulus temperature profile.

Our investigations on various aspects of this novel system as well as other thermoset systems is continuing.

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