Chapter 11

Modifications of Epoxy Resins with Functional Hyperbranched Poly(arylene ester)s

11.1 Introduction

Epoxy resins are widely used in industry as adhesives and matrix resins for fiber reinforced composite materials where advantage is taken of favorable properties such as high modulus, low creep and reasonable elevated temperature performance.[1,2] The desirable high glass transition temperatures of epoxy thermosets are largely attributed to their crosslink density. Unfortunately, they are limited by their lack of toughness properties. Improving the toughness of a high performance thermoset matrix without significantly affecting its mechanical properties remains a major goal in the development of these materials.

The commonly known approaches for toughening epoxies are through the addition of reactive liquid rubbers. Rubber modified epoxy resins, which have fracture energies matching that of high performance thermoplastic poly(ether sulfone)s (several kJ/m^2) have been extensively studied.[3,4,5] The rubber system that has attracted the most attention is the carboxyl

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[1] McAdams, L. V.; Gannon, J. A. in *High Performance Polymers and Composites*, Kroschwitz, J. I. ed., John Wiley & Sons, Inc., **1991**, pp 258-318.

[2] May, C. A.; ed., *Epoxy Resins Chemistry and Technology*, 2nd ed., Marcel Dekker, Inc.: New York, **1988**.

[3] McGarry, F. J. in *Polymer Toughening*, Arends, C. B., ed., Marcel Dekker, Inc.: New York, **1996**, pp 175-188.

[4] Riew, C. K.; Gillham, J. K., eds *Rubber Modified Thermoset Resins*, Advances in Chemistry Series No. 208, American Chemical Society, Washington, DC, **1984**.

terminated butadiene acrylonitrile (CTBN) liquid polymers which are commercially available with different acrylonitrile contents. However, only the highly toughenable epoxy resins modified with rubber tougheners are known to produce such an impressive toughening effect. These highly toughenable ductile epoxy resins usually exhibit rather low glass transition temperatures (below 100 °C) and low crosslink densities. They are not suitable for high performance structural applications. For high performance (high T_g, high modulus) epoxy resins, the toughening effect via rubber modification is usually only incremental. Such a disappointing result is attributed to the high crosslink densities of these epoxy resins, which greatly reduce the local molecular mobility.

As the demand for high temperature performance epoxies has increased, the effectiveness of reactive liquid rubber has diminished. Tough, high performance thermoplastic engineering polymers such as poly(ether sulfone)s and poly(ether imide)s were used as tougheners for epoxy resins.[6,7,8,9] The advantage of thermoplastics modifiers is that their incorporation into epoxy resins does not result in reduction in modulus and glass transition temperature. The addition of thermoplastics into epoxies which are believed to improve the toughness of the matrix has been the subject of a great deal of research.[6-9]

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[5] Shaw, S. J. in *Rubber Toughened Engineering Plastics*, Collyer, A. A., ed., Chapman & Hall: London, **1994**, pp 165-209.

[6] Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E. *Polymer*, **1991**, 32, 2020.

[7] Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, 30, 213.

[8] Cecere, J. A.; McGrath, J. E. *Polym. Preprints.* **1986**, 27, 299.

[9] Yoon, T. H.; Priddy, D. B.; Lyle, G. D.; McGrath, J. E. *Macromol. Symp.* **1995**, 98, 673.

It has been reported that epoxy functionalized aliphatic polyester dendrimers were used as tougheners for epoxy resins.[10] A blend with 5% of the modifiers was cured isothermally with an isophorone diamine hardener. Compared to the neat resin, a 2.5 fold increase in the K_{1C} (plane strain critical stress intensity factor) was observed. Allyl carbosilane hyperbranched polymers (1-2 weight %) were also reported by Russian workers as silicone rubber modifiers to give a 20% increase in the tensile strength and a two fold increase in the tear strength of the resultant materials.[11]

This Chapter describes modifications of epoxy resins with carboxylic acid terminated hyperbranched poly(arylene ester)s including the curing conditions, fracture toughness (K_{1C}) measurements and characterizations of modified epoxy resins.

11.2 Results and Discussion

11.2.1 Curing of Epoxy with Carboxylic Acid Terminated Branched Polyesters

A. Chemistry

The combination of high glass transition temperature and good damage tolerance is particularly desirable for high performance composite applications in aerospace. An aromatic amine, 4,4'-diaminodiphenyl sulfone (DDS), was chosen as a hardener for a diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (EPON 828, from Shell Company, MW = 380 g/mol),

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[10] Boogh, L.; Pettersson, B.; Japon, S.; Manson, J.-A. *Proced. Tenth Intern. Conf. Composite Mater.*, **1995**, vol. 4, pp. 389-396.

[11] Muzafarov, A. M.; Gorbatsevich, O. B.; Rebrov, E. A.; Ignateva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym. Sci, (USR) Engl. Tr.*, **1993**, 35, 1575.

which would give high T_g cured epoxies (> 200 °C). A “prereacted” technique[12] was used to prepare modified epoxies. Triphenylphosphine (TPP) was used as a prereaction catalyst to promote the reaction between the epoxy groups and the carboxylic acid groups of carboxylic terminated hyperbranched poly(arylene ester)s (**P1-COOH**, **10.4**) at relative low temperature (Scheme 11.1). Nucleophilic attack by triphenylphosphine opens the epoxy ring, producing a betaine. Proton abstraction from **P1-COOH** yields the carboxylic anion, forming a phosphonium salt. The carboxylic anion reacts with the electrophilic carbon attached to the positive phosphorus, regenerating the catalyst. This gives a prereacted resin that contains epoxy functionalized hyperbranched polymer and excess EPON 828. The prereacted resin was then further cured with a stoichiometric amount of DDS to form the crosslinked network (Scheme 11.2).

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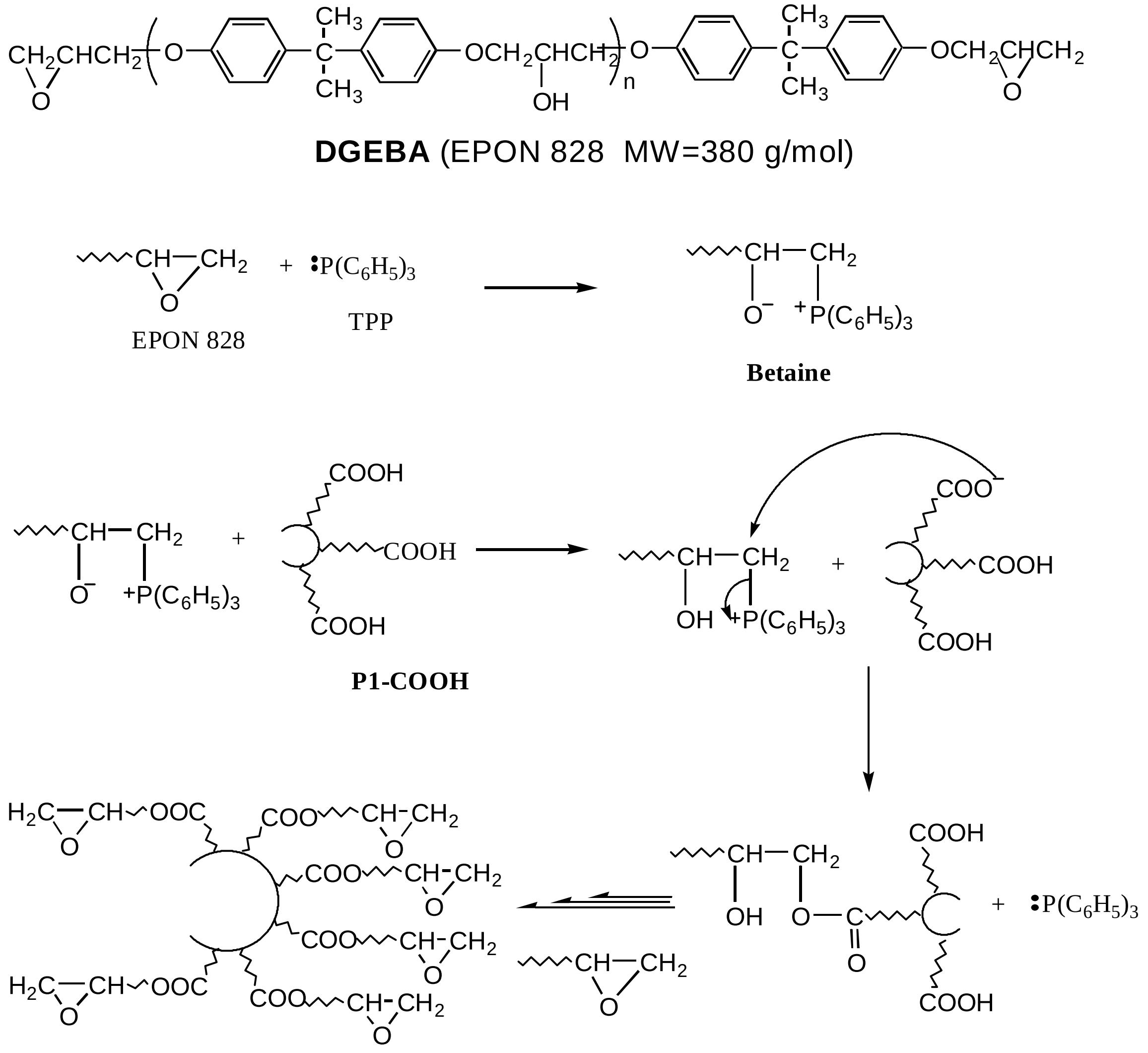
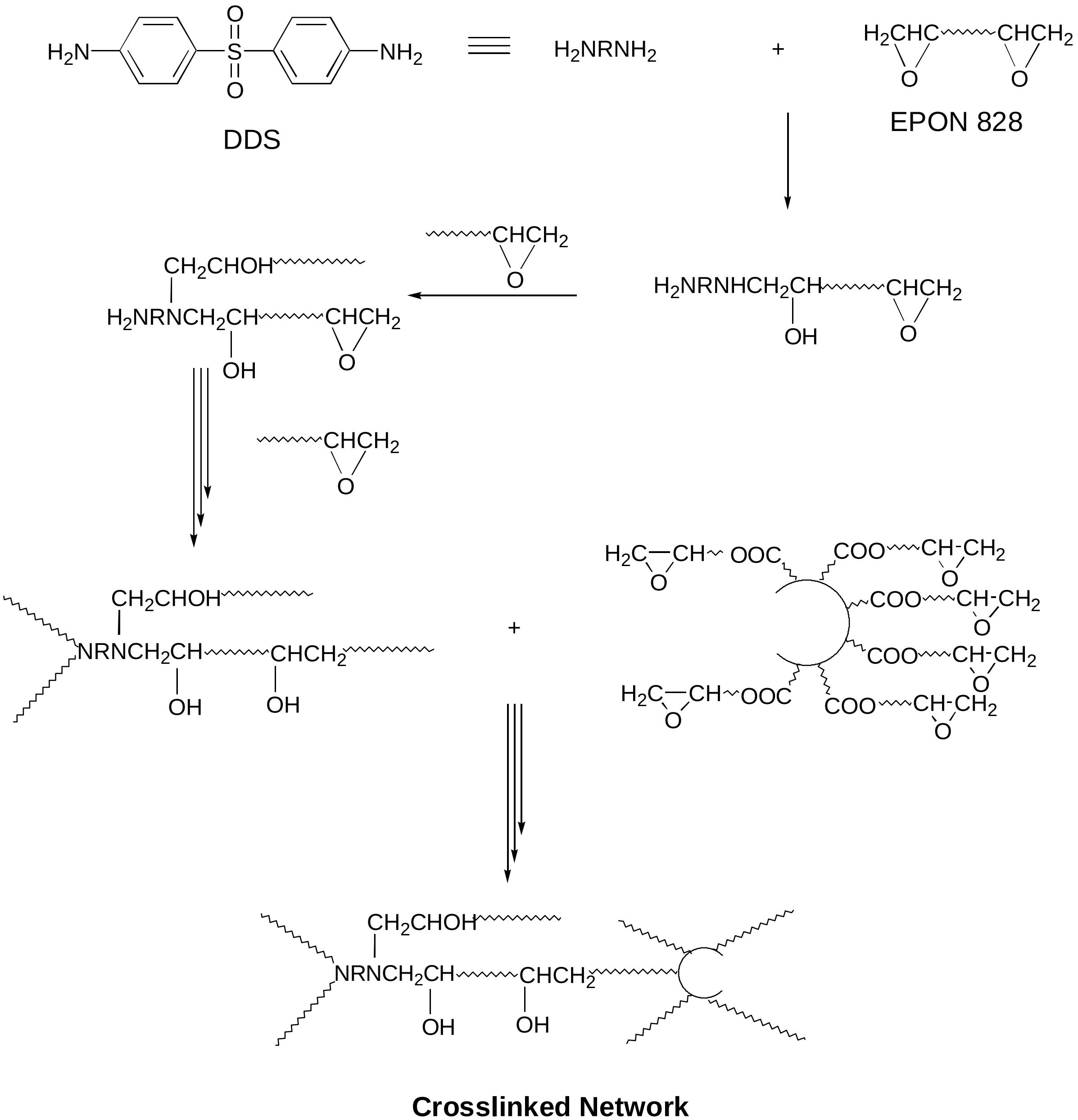
[12] Riew, C. K.; Rowe, E. H.; Siebert, A. R., In *Toughness and Brittleness of Plastics, ACS Adv. In Chem. Ser.* 1976**,** 154, 361.

Scheme 11.1


DGEBA (EPON 828 MW=380 g/mol)
EPON 828
TPP
Betaine
P1-COOH
CH₃
OH
O
n
COOH
COO⁻
OH
O⁻
P(C₆H₅)₃
CH–CH₂
OOC
COO

Scheme 11.2



B Preparation of Modified Epoxies

P1-COOH is immiscible with EPON 828 even at high temperature (200 °C). A solvent mixing method was used to mix **P1-COOH** and EPON 828 in THF. Solvent was removed by rotary evaporation and then under vacuum to give a hazy liquid. TPP (0.5 phr: parts per hundred parts resin) was then added and mixed with stirring. The preaction was carried out at 110 °C for about 30 minutes. DDS (stoichiometric amount) was then added and mixed with the prereacted resin. The absence of voids in the casting is necessary to develop the maximum fracture toughness. The system was degassed prior to cure. It was then poured into a silicone mold preheated at 175 °C and then transferred to an air convention oven. A curing schedule of 180 °C for 2 hours and 220 °C for 2 hours was used for all cured epoxies.

For proper formation of networks, it is important to maintain a 1:1 stoichiometric balance between the amine and epoxy groups. For unmodified system, the amounts of DDS and EPON 828 were calculated assuming DDS is tetrafunctional and EPON 828 (MW = 380 g/mol) is difunctional. When carboxylic acid terminated hyperbranched poly(arylene ester)s were used, the amount of each reagent was calculated assuming each carboxylic group is monofunctional since the prereaction temperature is relative low. The carboxylic equivalent weights of the hyperbranched poly(arylene ester)s were determined by potentiometric titration (see Chapter 10).

The **P1-COOH** loading varied from 1 to 9 phr. Due to the immiscibility of **P1-COOH** and EPON 828, the mixtures of **P1-COOH** and EPON 828 were viscous liquids, especially when the **P1-COOH** loading was high. The degassing and casting were difficult for modified resins containing more then 10 phr **P1-COOH**. Preliminary studies using phenolic terminated hyperbranched poly(arylene ester)s (**10.11**) as a toughening agent showed that EPON 828 is miscible with hyperbranched polymer **10.11**, this would result in better processibility.

11.2.2 Characterizations of Modified Epoxies

A Solution ^{1}H NMR Spectra of the Prereacted Epoxy Resins

To confirm the reaction between the COOH groups of **P1-COOH** and the epoxy groups, a curing sample was prepared using **P1-COOH** (LMW, 5 phr) by the solvent mixing method. After the solvent THF was removed, the ^{1}H NMR spectrum (Figure 11.1a) of the mixture of **P1-COOH** and EPON 828 showed the COOH signals of **P1-COOH** at about 13.5 ppm and a very small phenolic proton signal at 11.7 ppm. After the catalyst, triphenyl-phosphine (TPP), was added to the mixture, the prereaction between **P1-COOH** and EPON 828 was carried out at 110 °C for 30 minutes. The ^{1}H NMR spectrum (Figure 11.1b) of this prereacted mixture showed no COOH signals at 13.5 ppm, which confirms that most of the COOH groups reacted with the epoxy groups during this period. Most of the phenolic groups were also reacted with the epoxy in the presence of TPP. This experiment confirmed that the hyperbranched poly(arylene ester) was chemically incorporated into the epoxy system during the prereaction period.

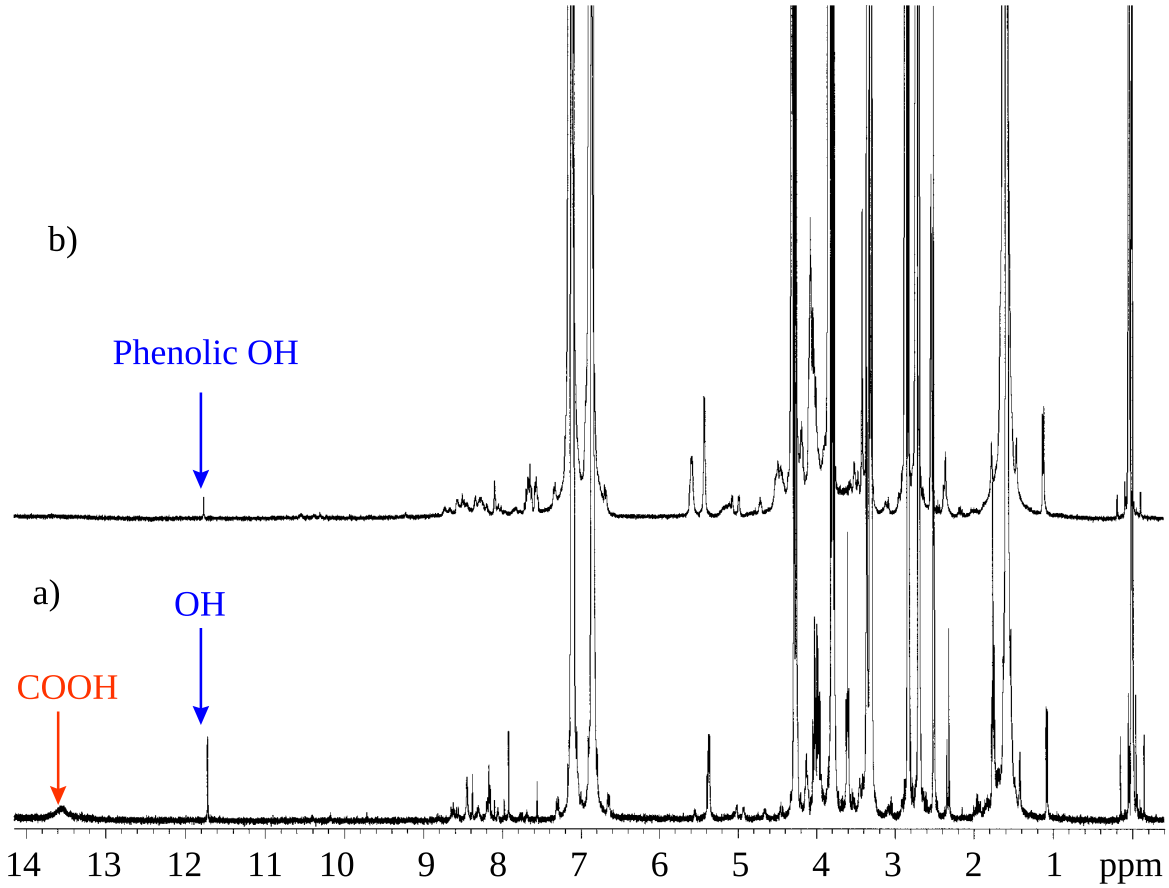


Figure 11.1 400 MHz ^{1}H NMR spectra of a) unreacted resin of **P1-COOH** (5 phr) and EPON 828, b) prereacted resin (TPP, 0.5 phr, 110 °C 30 minutes) in DMSO-d_6.

B Solid State CPMAS ^{13}C NMR Spectra of Cured Epoxy Resins

Solid state NMR is a very useful technique for analysis of thermoset materials. To further confirm the reaction between the carboxylic groups of **P1-COOH** with epoxy groups during curing, solid state ^{13}C NMR experiments were performed. The ^{13}C CPMAS (cross-polarization magic-angle spinning) NMR spectrum (Figure 11.3a) of a **P1-COOH** modified epoxy (LMW, 9 phr) showed only one signal in the carbonyl carbon region at 165 ppm corresponding to the carbonyl carbon of the ester group (C̲OOR). However, the ^{13}C CPMAS spectrum (Figure 11.3b) of the **P1-COOH** (LMW, 9 phr) modified epoxy spiked with **P1-COOH** (LMW, starting material used to modify the epoxy resin) showed two signals at 165 ppm and 170 ppm in the carbonyl carbon region, corresponding to the carbonyl carbons of C̲OOR and C̲OOH. This experiment confirmed that most of the COOH groups of **P1-COOH** reacted with EPON 828 during the curing process, i.e. the hyperbranched poly(arylene ester) was chemically incorporated into the epoxy network.

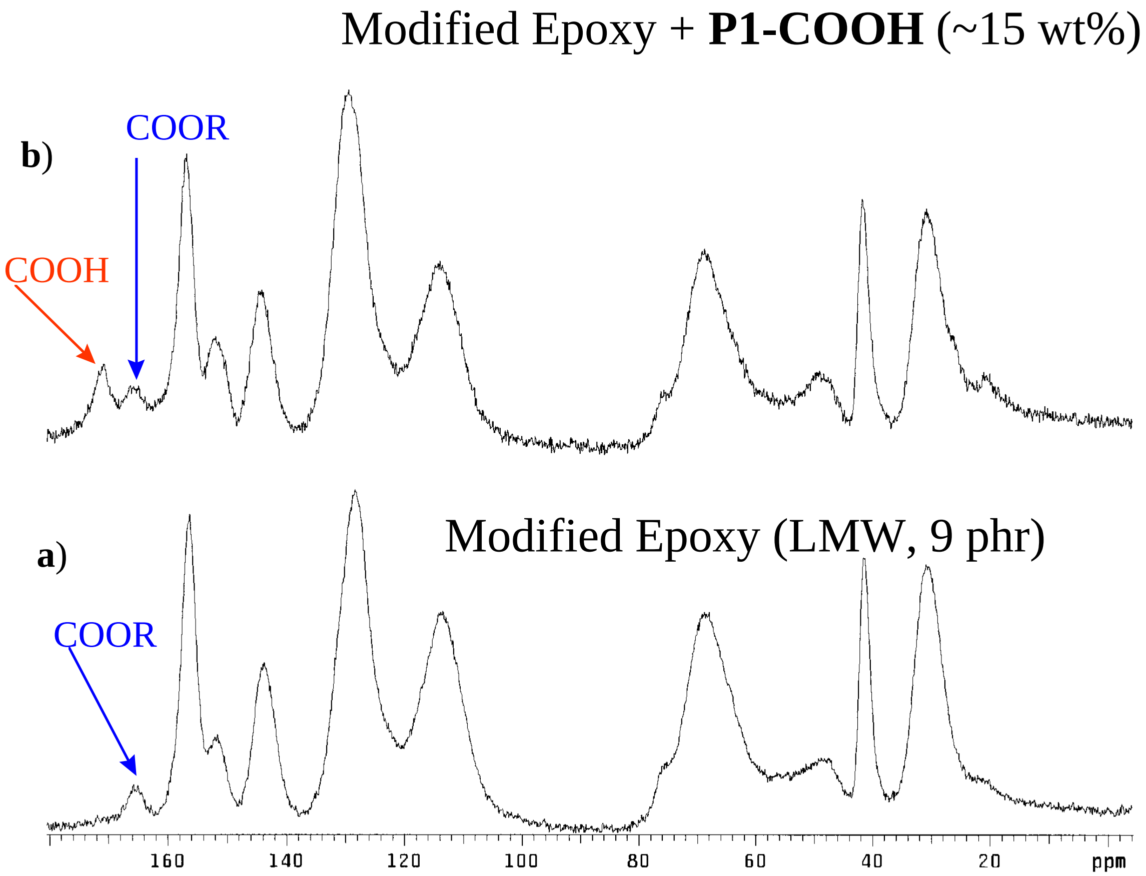


Figure 11.2 a) 90 MHz ^{13}C CPMAS solid state NMR spectrum of **P1-COOH** (LMW, 9 phr) modified epoxy, b) 90 MHz ^{13}C CPMAS solid state NMR spectrum of **P1-COOH** (LMW, 9 phr) modified epoxy "spiked" with **P1-COOH** (LMW, ~15 wt% of epoxy)

C Kinetic FTIR Studies of Epoxy Curing

Infrared spectroscopy provides a fast and accurate means for determining the extent of conversion. To gain better understanding of the curing process, first, the IR spectra of all starting materials were acquired. The FTIR spectrum (Figure 11.3) of **P1-COOH** (LMW, in KBr) showed a very broad, intense O-H stretching absorption in the region of 2500-3300 cm^{-1}, the C=O stretching bands of aryl acid and ester at about 1700 cm^{-1}. The FTIR spectrum (Figure 11.4) of EPON 828 (neat) showed small absorbing bands in the O-H stretching region (3200-3650 cm^{-1}), the aliphatic C-H stretching bands at 2860-3060 cm^{-1}, the C=C phenyl ring stretching bands at 1620 and 1462 cm^{-1}, the symmetric stretching of epoxy ring at 1250 cm^{-1}, the asymmetric ring stretching band of epoxy ring at 922 cm-1 and the out-of-plane bending band of *p*-substituted phenyl ring at 825 cm^{-1}. The FTIR spectrum (Figure 11.5, KBr) of diaminodiphenyl sulfone (DDS) showed N-H stretching vibration bands at 3060-3500 cm^{-1}, N-H bending vibrations at 1641 cm^{-1}, the strong asymmetric and symmetric SO_2 stretching bands at 1250 and 1150 cm^{-1} and the out-of-plane bending band of *p*-substituted phenyl ring at 827 cm^{-1}.

A curing sample was prepared by the solvent mixing method using **P1-COOH** (LMW, 3phr) . After the solvent THF was removed, the FTIR spectrum of the mixture of **P1-COOH** and EPON 828 was about the same as that of neat EPON 828 due to the low percentage of **P1-COOH**. After triphenylphosphine (0.5 phr) and DDS were added to the mixture, it was heated to about 90 °C until all TPP melted (mp 79-81 °C). The samples for recording spectra were prepared as thin films between two NaCl salt plates. The sample was placed in a heating cell, and the spectra were recorded at various time intervals. The curing schedule was 180 °C for 2 hours and then 220 °C for 2 hours. Absorptions at various times during cure are presented in Figure 9.6a and Figure 9.6b . The asymmetric ring stretching band of the epoxy ring at 922 cm^{-1} disappeared as the reaction proceeded (Figure 11.6a). The N-H stretching vibration bands of diaminodiphenyl sulfone (DDS) at 3060-3500 cm^{-1} also disappeared as the reaction proceeded and the absorbing bands of the O-H stretch at 3200-3650 cm^{-1} increased (Figure 11.6b). The reaction took place very rapidly at 180 °C; most of the epoxy groups were reacted during the first 30 minutes. Since the glass transition temperature of the cured epoxy is very high (>200 °C), once the glass transition temperature of cured epoxy approached 180 °C, vitrification occurred and the curing reaction proceeded very slowly. After the temperature was raised to 220 °C, small amounts of unreacted epoxy groups continued to react. At the end of the curing, only very little C-O-C band of the epoxy ring and N-H stretch bands remained. This experiment demonstrated that most of the amine and epoxy groups reacted during the curing process, which indicated the proper formation of the crosslinked network.

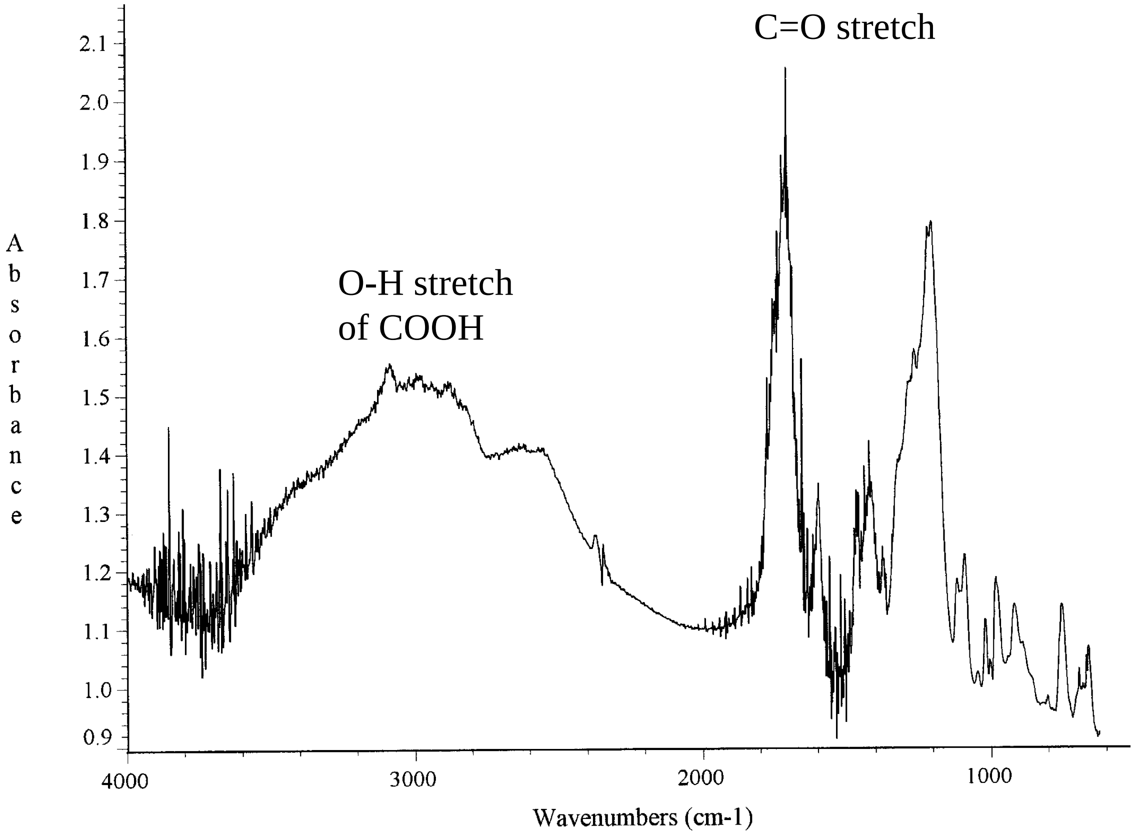


Figure 11.3 FTIR spectrum of **P1-COOH** (LMW, KBr).

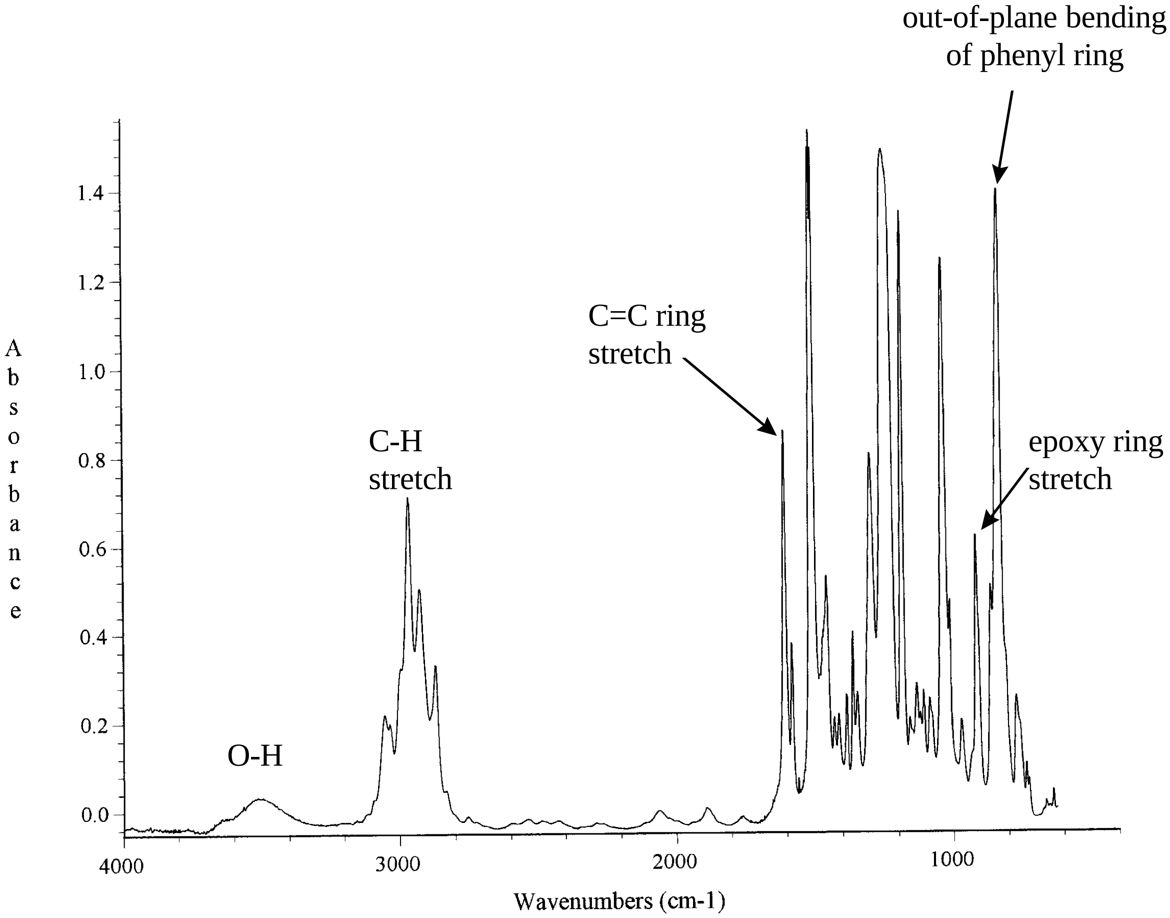


Figure 11.4 FTIR spectrum of EPON 828 (from Shell, MW = 380 g/mol, neat).

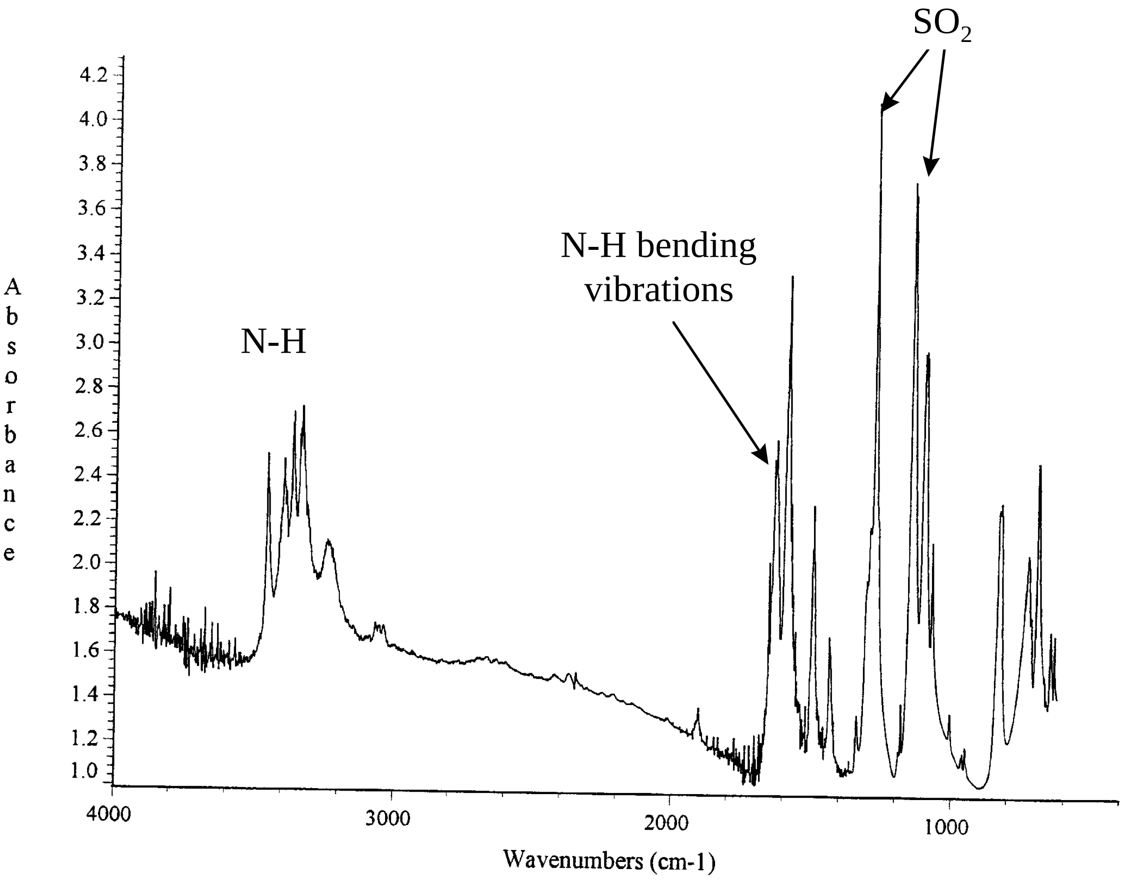


Figure 11.5 FTIR spectrum of 4,4'-diaminodiphenyl sulfone (KBr).

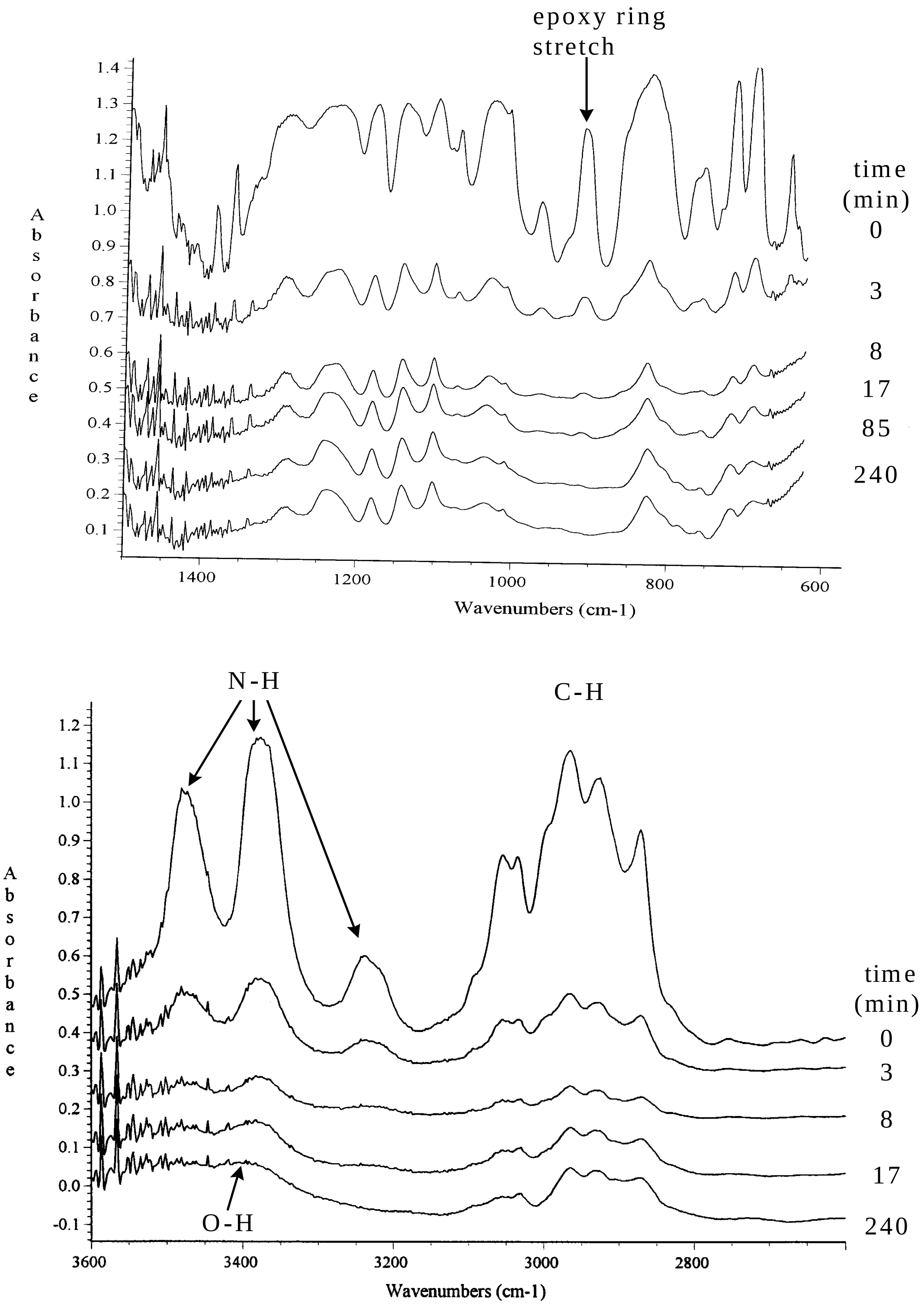


Figure 11.6 Kinetic FTIR spectra of epoxy modified with **P1-COOH** (LMW, 3 phr,) TPP (0.5 phr) and DDS (180 °C 2 hours, 220 °C 2 hours).

D Gel Fractions of Modified Epoxies

Gel fraction analysis was performed to check for complete network formation. All cured epoxies were Soxhlet extracted with THF for 3 days. After extraction, no shape deformation was observed for any specimen. All samples were then dried in a vacuum oven at 95 °C for 10 days. The gel fractions calculated were between 101% to 103%. They were then transferred to a drying pistol and dried at 110 °C (refluxing toluene) for another 7 days. Because the glass transition temperatures of modified epoxies are around 200 °C, all samples were further dried under vacuum at 200 °C for 24 hours. The final gel fractions are listed in Table 11.1.

Table 11.1 The gel fractions of cured epoxies (Soxhlet extraction with THF for 3 days)

Sample	Curing Condition	Gel Fraction (%)
JY-3-152-1	Neat DDS	97.2
JY-3-172-1	LMW 1 phr	98.0
JY-3-165-1	LMW 3 phr	96.5
JY-3-164-1	LMW 6 phr	95.8
JY-3-173-1	LMW 9 phr	99.1
JY-3-174-1	MMW 3 phr	98.3
JY-3-175-1	HMW 3 phr	97.4
JY-3-169-1	AB_2:AB/2:1 Copolymer 3 phr	99.2
JY-3-170-1	AB_2:AB/1:1 Copolymer 3 phr	97.5

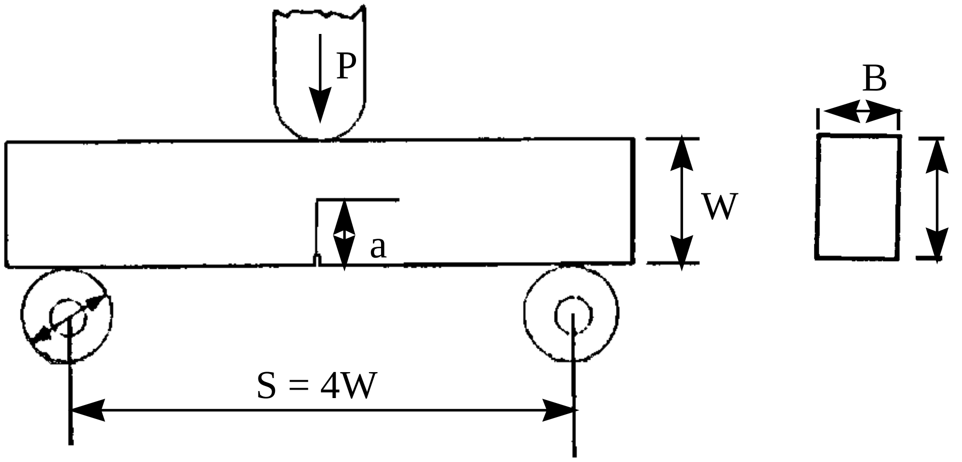
11.2.3 Fracture Toughness Measurements of Modified Epoxies

To systematically study the toughening effect of the hyperbranched polymers, EPON 828 was cured with following variables: <1> different percent loading of **P1-COOH** (LMW, 1, 3, 6, 9 phr); <2> different molecular weights of **P1-COOH** with the same percent loading (3 phr, HMW, MMW, LMW); <3> copolymers of AB_2 and AB monomers (1:1 copolymer **10.8a** and 2:1copolymer **10.8b**) with the same percent loading (3 phr). All samples were cured at 180 °C for 2 hours and then at 220 °C for 2 hours.

Fracture toughness (K_{1C}, plane strain critical stress intensity factor) was measured using the Single-Edge-Notched 3-Point-Bend (SEN-3PB) method, following ASTM-E-399-78 (Scheme 11.3). The molded samples were ground to afford a rectangular shape (3×6×48 mm). The specimens were sawed to generate a notch and then a crack was initiated by tapping a liquid nitrogen chilled fresh razor blade. The specimens were tested in an Instron Model 1123 at a rate of 2 mm/minute. Approximately 15 samples were tested and K_{1C} values were calculated according the formula provided in ASTM E-399-78.

Scheme 11.3

Single-Edge-Notch Three-Point-Bent (SEN-3PB)



Plane Strain Critical
Stress Intensity Factor:

$$K_{1C} = \frac{PS}{BW^{1/2}}\left[2.9\left(\frac{a}{W}\right)^{1/2} - 4.6\left(\frac{a}{W}\right)^{3/2} + 4.6\left(\frac{a}{W}\right)^{5/2} - 37.6\left(\frac{a}{W}\right)^{7/2} + 38.7\left(\frac{a}{W}\right)^{9/2}\right]$$

The K_{1C} values of these modified epoxy resins are summarized in Table 11.2. First, low molecular weight **P1-COOH** was chosen to study the toughening effect of hyperbranched polyesters in different percentage loadings because of its better processbility. **P1-COOH** (LMW, 1, 3, 6, 9 phr) was used to modify the epoxy resin using the same procedure for the different loadings. The fracture toughness (K_{1C}) increases as the percentage loading of **P1-COOH** (LMW) increases (Figure 11.7). To study the molecular weight effect of **P1-COOH**, the percent loading of **P1-COOH** was fixed at 3 phr. Three different molecular weight samples (HMW, MMW, LMW) were used to modify the epoxy resin under the same curing schedule. As the molecular weight of **P1-COOH** increases, the fracture toughness (K_{1C}) of the modified resins with the same percent loading increases (Figure 11.8). Branched copolyesters (AB_2:AB/2:1 copolyester **10.8a** and AB_2:AB/1:1 copolyester **10.8b**) of AB_2 and AB monomers were also used to modified epoxy resin. These copolyesters have the advantage of more linear units (compared to **P1-COOH**) to contribute to the fracture toughness and low viscosity of the hyperbranched portion for better processbility. The same percent loading (3 phr) and curing schedule were used Figure 11.9 shows that the fracture toughness (K_{1C}) of epoxy resins modified with the same percent loading increases as the number of linear units increases.

Table 11.2 The K_{1C} values of cured epoxies (0.5 phr TPP, DDS, 180 °C 2 h, 220 °C 2 h)

Sample	Condition [a]	K_{1C}(MPa/m$^{1/2}$)[b]	STD DEV (MPa/m$^{1/2}$)
JY-3-152-1	Neat DDS	0.60	0.05
JY-3-172-1	LMW 1 phr	0.65	0.03
JY-3-165-1	LMW 3 phr	0.70	0.06
JY-3-164-1	LMW 6 phr	0.76	0.09
JY-3-173-1	LMW 9 phr	0.92	0.04
JY-3-174-1	MMW 3 phr	0.80	0.05
JY-3-175-1	HMW 3 phr	1.05	0.07
JY-3-169-1	2:1 Copolymer 3 phr	0.83	0.08
JY-3-170-1	1:1 Copolymer 3 phr	0.87	0.06

a) all samples were cured at 180 °C for 2 hours and 200 °C for 2 hours.

b) the average values of about 15 individual specimens measured SEN-3PB method at a rate of 2 mm/minute.

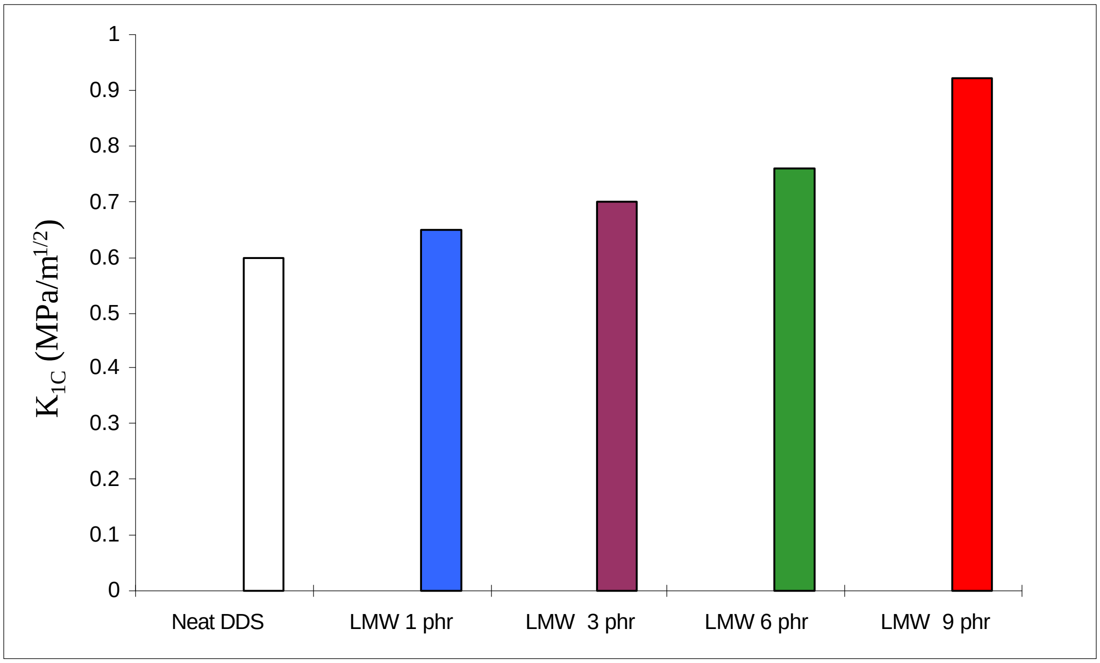


Figure 11.7 The K_{1C} values of **P1-COOH** (LMW) modified epoxies.

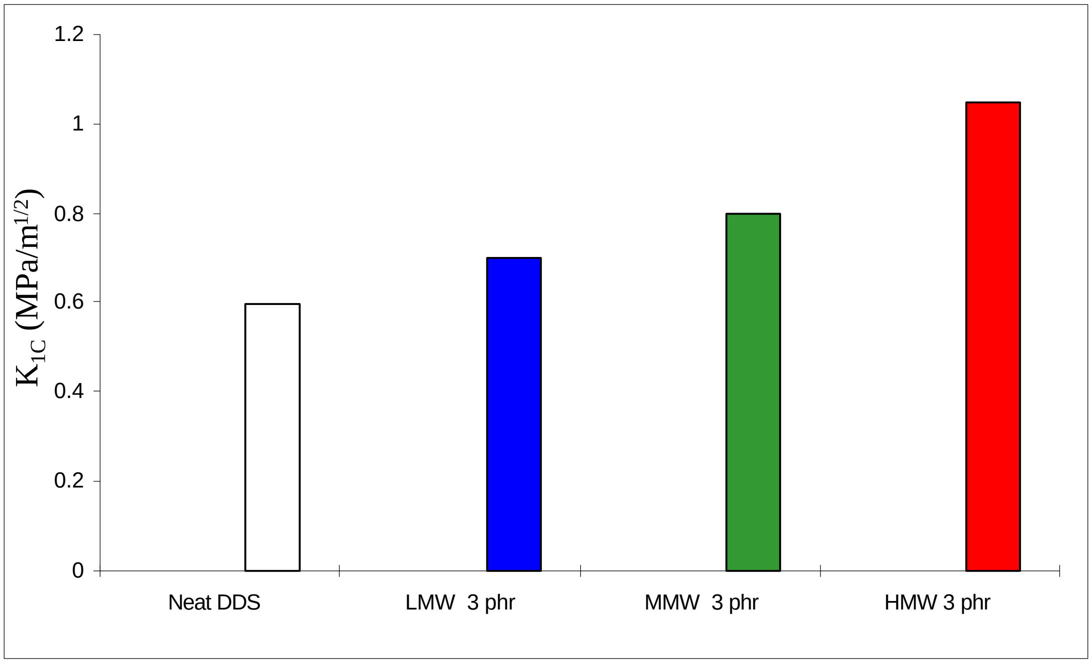


Figure 11.8 The K_{1C} values of cured epoxies modified with different molecular weights of **P1-COOH**.

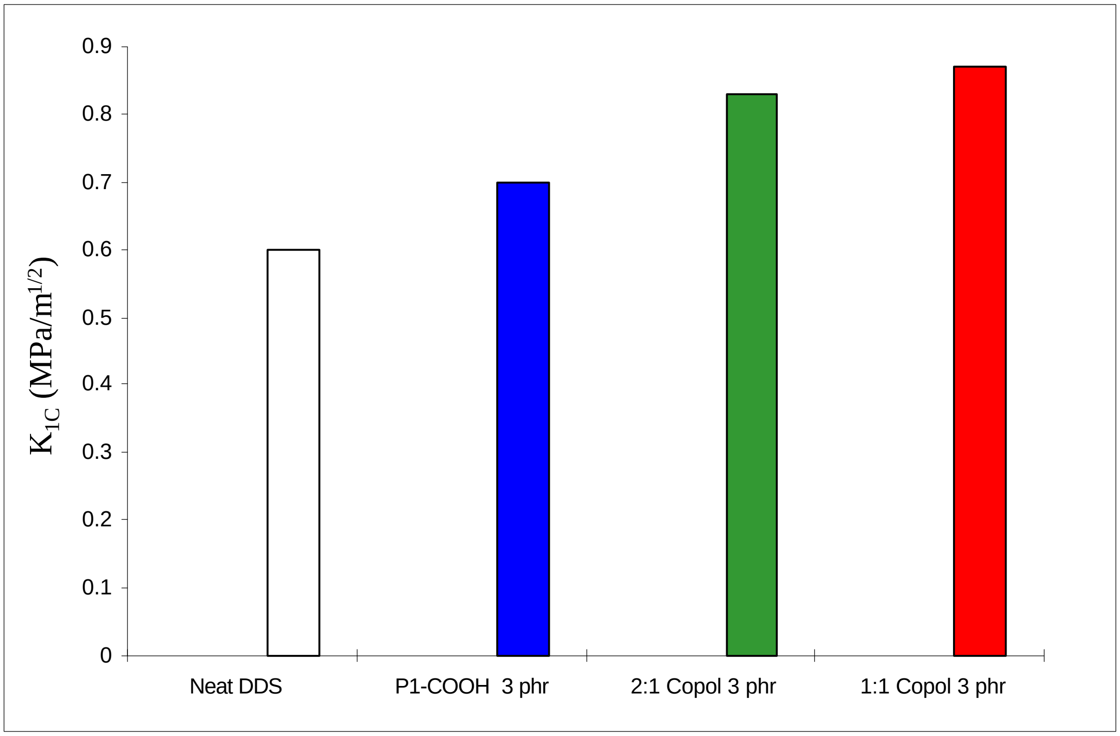


Figure 11.9 The K_{1C} values of cured epoxies modified with **P1-COOH**, 2:1 copolymer and 1:1 copolymer.

11.2.4. Thermal Properties of Modified Epoxies

The glass transition temperatures of cured epoxies were measured by DMA. The glass transition temperatures (defined as the temperatures of the loss tanδ maxima) of cured epoxies at different frequencies are listed in Table 11.3. The T_g of unmodified epoxy at 1 Hz was 201 °C and the T_g's of hyperbranched polymer modified epoxies at 1 Hz were around 195-210 °C.

Table 11.3 The glass transition temperatures (temperatures at tanδ max.)of cured epoxies measured by DMA at different frequencies

Sample	Condition	T_g (°C) at 1 Hz	T_g (°C) at 2 Hz	T_g (°C) at 5 Hz	T_g (°C) at 10 Hz	T_g (°C) at 25 Hz
JY-3-152-1	Neat DDS	201.0	203.3	206.0	208.0	212.0
JY-3-172-1	LMW 1 phr	199.0	201.0	203.0	205.0	209.0
JY-3-165-1	LMW 3 phr	--	--	--	--	--
JY-3-164-1	LMW 6 phr	195.0	198.1	200.0	203.2	206.5
JY-3-173-1	LMW 9 phr	--	--	--	--	--
JY-3-174-1	MMW 3 phr	195.5	198.5	200.5	203.5	206.5
JY-3-175-1	HMW 3 phr	--	--	--	--	--
JY-3-169-1	2:1 Copolymer 3 phr	209.0	211.0	214.0	216.0	219.0
JY-3-170-1	1:1 Copolymer 3 phr	198.5	200.5	203.5	205.5	208.5

11.3 Summary and Conclusions

The carboxyl terminated hyperbranched poly(arylene ester)s were successfully used to modify inherently brittle epoxy resins. The hyperbranched polymers were chemically incorporated into the epoxy networks using TPP as a catalyst to promote the reactions between the carboxylic acid groups and the epoxy groups. The chemistry was confirmed by solution ^{1}H NMR, solid state CPMAS ^{13}C NMR, and kinetic FTIR spectroscopies. Gel fraction analysis and kinetic FTIR indicated the proper formation of crosslinked networks. Fracture toughness was improved without sacrificing thermal properties. The K_{1C} values of the modified epoxies were found to be a function of the percentage loading, the molecular weights and the proportion of linear units of hyperbranched polymers. Because the carboxylic terminated hyperbranched poly(arylene ester)s were immiscible with EPON 828, the percent loading of hyperbranched modifiers were limited and the processibility of epoxy resins were difficult, especially at high percentage loading of hyperbranched modifiers. These problems can be eliminated by using phenolic terminated hyperbranched poly(arylene ester)s, which are miscible with EPON 828.

11.4 Experimental Section

Materials and Instrumentation.

The proton NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 399.95 MHz and reported in δ units. Tetramethylsilane was used as the internal standard. The ^{13}C NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 100.60 MHz. Spectra were proton-decoupled and recorded in deuteriochloroform (76.9) as solvent and internal standard. FTIR spectra were recorded on a Nicolet MX-1 with KBr pellets. Thermogravimetric analyses were carried out N_2 flow on a Perkin-Elmer 7700 thermal analysis system at a heating rate of 10 °C/min. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-4 at a scan rate of 10 °C/min in a nitrogen atmosphere. The thermal behaviors such as T_g's, were determined with a Netzsch Dynamic Mechanical Analyzer (DMA-242) in the double cantilever beam mode. Multiple frequency sweeps were measured at 1.0 Hz, 2.0 Hz, 5.0 Hz, 10.0 Hz and 25.0 Hz in the temperature range of -15 °C to 270 °C in a 2.0 °C isothermal steps.

Curing Epoxy Resin with P1-COOH, TPP and DDS (General Procedure)

P1-COOH (0, 1, 3, 6, 9 phr) was dissolved in THF and EPON 828 (25.0 g) was added to form a clear solution. Solvent (THF) was removed via rotary evaporation to give a hazy, viscous liquid which was placed in a vacuum oven to remove the rest of solvent at 85 °C for at least 4 hours. TPP (0.125 g, 0.5 phr) was then added and mixed with stirring. The mixture was heated in an oil bath at 110 °C for about 30 minutes. At this point the mixture was still hazy. DDS (stoichiometric amount) was then added to the beaker with stirring. It was transferred to a vacuum oven to degas at 120 °C for 30 minutes. The mixture was poured into a silicone mold preheated at 175 °C. The silicone mold was transferred to an oven and cured at 180 °C for 2 hours and 220 °C for 2 hours. About 20 specimens (48×6×3 mm) were obtained.

Procedure for Solution ^{1}H NMR Experiment

A curing sample was prepared: **P1-COOH** (LMW, 0.150 g 3phr) was dissolved in 50 mL of THF and EPON 828 (5.00 g) to form a clear solution. After the solvent THF was removed, a small amount of sample was removed for the ^{1}H NMR spectrum. After triphenyl phosphine (TPP, 0.015 g, 0.5 phr) was added, the beaker was placed in an oil bath at 110 °C and stirred for 30 minutes. The prereacted resin was soluble in DMSO. A small amount of sample was removed for the ^{1}H NMR spectrum.

Procedure for Kinetic FTIR Experiments

A curing sample was prepared: **P1-COOH** (LMW, 0.150 g 3phr) was dissolved in 50 mL of THF and EPON 828 (5.00 g) to form a clear solution. After the solvent THF was removed, a small amount of sample was removed for the FTIR spectrum. After triphenyl phosphine (TPP, 0.015 g, 0.5 phr) and DDS were added to the mixture, it was heated up to about 90 °C until all TPP melted (mp 79-81 °C). The samples for recording spectra were prepared as thin films between two NaCl salt plates. Each sample was placed in a heating cell, and the spectra were recorded at various time intervals. The curing temperature was 180 °C for 2 hours and then 220 °C for 2 hours. A spectrum was recorded every 2-3 minutes during the first 30 minutes and then every 10 minutes thereafter.

Procedure for Fracture Toughness (K_{1C}) Measurements

Fracture toughness (K_{1C}) was measured using the Single-Edge-Notched 3-Point-Bend (SEN-3PB) method, following ASTM-E-399-78. The molded samples were ground to afford a rectangular shape (3×6×48 mm). The specimens were sawed to generate a notch and then a crack was initiated by tapping a liquid nitrogen chilled fresh razor blade. The specimens were tested in an Instron Model 1123 at a crosshead transport rate of 2 mm/minute. Approximately 15 samples were tested and K_{1C} values were calculated according the formula provided in ASTM E-399-78.

Gel Fraction of Cured Epoxies

The cured epoxy resins (K_{1C} specimens, pre-weighed) were Soxhlet extracted in THF for about 72 hours. The shape of the specimens remained the same, i. e., no deformation was observed after extraction. The extracted specimens were then dried in a vacuum oven at 95 °C for 72 hours and then weighed. The gel fractions calculated for all samples were between 102% to 103%. A small amount of solvent was still trapped inside the network. The samples were dried in a vacuum oven at 95 °C for another 7 days. They were then transferred to a drying pistol and dried at 110 °C (refluxing toluene) for another 7 days. All samples were further dried in a vacuum oven at 200 °C for 24 hours prior to the final weighing.

Thesis Summary

Due to the separation of this dissertation into two distinct parts, it was suggested that a summary of the contents including major conclusions was warranted. Part I of the dissertation describes a novel approach to high molecular weight aromatic polyketones via soluble precursors derived from bis(α-aminonitrile)s. The results obtained were very promising. Bis(α-aminonitrile)s were easily synthesized from dialdehydes and secondary amines in very high yield by the Strecker reaction. Polymerization of bis(α-aminonitrile)s with activated dihalides using NaH as base in DMF yielded high molecular weight polyaminonitriles. These precursor polymers are soluble in common moderate-polarity solvents. Hydrolysis of these soluble precursors in acidic conditions produced the corresponding polyketones, which displayed excellent thermal properties and solvent resistance. A novel approach to the synthesis of high molecular weight wholly aromatic polyketones without ether linkages or alkyl substituents in the polymeric backbones was demonstrated. These new polyketones can not be obtained by other methods. Although the polymerization of 4-fluorobenzylaminonitrile was not successful, a very efficient synthesis for diphenol and activated dihalide monomers containing keto groups was developed based on α–aminonitrile chemistry. The aminonitrile intermediates and activated dihalide monomers were obtained in quantitative yields. Further chain extention was also demonstrated. This method is suitable for any activated dihalide by reaction with 2 equivalents of 4-fluorobenzylaminonitrile and NaH, followed by hydrolysis to produce a new monomer with two more *p*-fluorobenzoyl units. For the synthesis of polyaminonitriles containing ether linkages in the polymeric backbone, only low to medium molecular weight polymers were obtained. The model studies proved that the carbanions of the aminonitriles can react with ether linkages to form more stable phenoxide anions and cause the termination of the polymerization. However, the reaction between the activated fluoro sites and the carbanions of the aminonitriles is much faster than the reaction of the ether linkages with the anions of the aminonitriles.

Part II of the dissertation describes the work done since August of 1996. The general ideas are to take advantage of the special properties of hyperbranched polymers, such as low viscosity, high solubility and high degree of “surface” functionality, and use them as crosslinkable toughening agents for adhesives and composites. Functional hyperbranched poly(arylene ester)s were synthesized by thermal polymerization of 5-acetoxyisophthalic acid or 3,5-diacetoxybenzoic acid. Different molecular weights of **P1-COOH** were synthesized by controlling the reaction time and duration of the reaction under vacuum Carboxylic terminated hyperbranched copolyesters were also synthesized by copolymerization of 5-acetoxyisophthalic acid (AB_2 monomer) and 3-hydroxybenzoic acid (AB monomer) using different molar ratios of these two monomers. Both carboxylic acid and phenolic terminated hyperbranched polyesters were functionalized with different reactive groups. To demonstrate the applications of these functional hyperbranched polymers, the carboxyl terminated hyperbranched poly(arylene ester)s were successfully used to modify inherently brittle epoxy resins. The hyperbranched polymers were chemically incorporated into the epoxy networks using triphenylphosphine (TPP) as a catalyst and 4,4’-diaminodiphenyl sulfone (DDS) as a curing agent. The chemistry and the proper formation of crosslinked networks were confirmed by solution ^{1}H NMR, solid state CPMAS ^{13}C NMR, and kinetic FTIR spectroscopes. Gel fraction analysis and kinetic FTIR indicated proper formation of crosslinked networks. Fracture toughness was improved without sacrificing thermal properties. The fracture toughness K_{1C} values of the modified epoxies were found to be a function of the percentage loading, the molecular weights and the proportion of linear units of hyperbranched polyesters. Because the carboxylic acid terminated hyperbranched poly(arylene ester)s were immiscible with the commercially available epoxy EPON 828, the percentage loadings of hyperbranched modifiers were limited and the processibility of epoxy resins was difficult, especially at high percentage loadings of hyperbranched modifiers. These problems could be solved using phenolic terminated hyperbranched poly(arylene ester)s, which are more soluble in epoxy resins.

Part I and II of the dissertation may seems to be disjoined, actually they are related to each other. The main focus of the dissertation is to design and synthesize new polymers, and seek applications of these polymers as high performance materials.

VITA

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Jinlian (Jim) Yang was born to Shizhao Yang and Tiaohua Zhang on May 2, 1966 in a small village of Jinjiang County, Fujian Province, P. R. China. He received his Bachelor of Science degree in Chemical Engineering from South China University of Technology, Guangzhou, P. R. China. He continued his graduate studies in the Materials Research Institute, South China University of Technology for the next two years, specializing in Polymer Materials. In January 1990, he transferred to Marshall University, Huntington, West Virginia where he received his Master's degree in Organic Chemistry in July, 1992. He was accepted into the Ph.D. program at Virginia Polytechnic Institute and State University and joined the research group of Professor Harry W. Gibson. He was awarded a Doctorate degree in Chemistry, specializing in Polymer Science in February, 1998.