Novel High-Temperature Aromatic Copolyester Thermosets: Synthesis, Characterization, and Physical Properties

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ABSTRACT: An all-aromatic thermosetting copolyester has been prepared using hydroquinone, hydroxybenzoic acid, isophthalic acid, trimesic acid, and/or 1,3,5-triacetoxybenzene as key building blocks. The preparation and characterization of these materials are described. Cured resins based on these structures exhibit thermal stabilities in nitrogen to 450 °C, glass transition temperatures up to 240 °C, and moisture pickups of only 0.3 wt %. An important feature of these cross-linked aromatic copolyesters is their ability to undergo further processing in the solid state through interchain transesterification reactions.

Introduction

Thermosetting polymers find broad usage as structural adhesives, matrices for composites, protective coatings, foamed structures, binder resins with high char yield, and insulators for electronic packaging. During the past 30 years, considerable effort has been expended to design easily processible oligomers that could be cross-linked into very thermally stable polymers. The difficulties associated with these efforts become apparent with the realization that, up to now, no one has successfully prepared a general purpose, high-temperature thermoset.[1]

Conventional thermosets such as epoxy resins have been available for approximately 50 years. A major advantage of epoxies is that they can be easily processed as low molecular weight oligomers into a wide variety of forms without producing volatiles. On the other hand, the epoxies cannot be used long term at temperatures in excess of 180 °C due to thermal degradation, and they are particularly susceptible to attack by moisture and corrosive liquids.[2] Similarly, phenolic resins, which have been available since the beginning of this century, begin to oxidize at temperatures of only 150 °C. Some improvement in thermal oxidative stability has been achieved in going to aromatic oligomers capped with maleimide or acetylene units.[3] However, these end groups tend to form aliphatic or cycloaliphatic links that are susceptible to oxidation at temperatures as low as 200−235 °C.

It has been well known since their initial development in the 1960s that fully aromatic copolyesters (LCPs) possess a unique combination of outstanding chemical and mechanical properties as well as high thermal stability. However, the use of these materials is limited due to their high cost ($10−15 per lb), high temperatures required for processing (300−400 °C), and poor interlaminar shear properties due to the rodlike nature of the polymer chains. Several years ago, we set out to address these drawbacks by preparing a completely new family of thermosetting resins, based on low-cost aromatic ester units which could easily be processed as an oligomeric melt. The cured resin displays good resistance to solvents and moisture, high stiffness and strength, good dimensional stability, and excellent high-temperature properties.[1]

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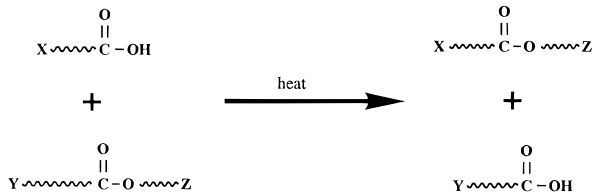

Figure 1. Interchain transesterification reaction between an ester and an adjacent acid.

In the past, systems which cure with the evolution of volatiles such as acetic acid in this case have usually led to problems of void formation in the cured polymer.[4] We have found that problems of void production during curing can be minimized and dense, nonporous structures readily obtained. Alternatively, we have found that void-free samples can be obtained by solid-state processing of cured films. Thus as shown in Figure 1, one can take advantage of interchain transesterification reactions (ITR) to form good adhesive bonds between two cured coatings.

The kinetics of these reactions have been modeled as an Arrhenius process. In thermotropic LCPs, it is estimated that each molecular chain undergoes very rapid ITR at high temperatures.[5−7] We have demonstrated somewhat earlier that ITR could be used to form an adhesive bond between two LCP coatings.[8,9] Now we have found that cured networks could be brought together, in the form of thin films or lamina, and further processed in the solid state to develop adhesive bonds across the interface without the evolution of any volatile byproducts. We introduce this concept here, and will demostrate its utility in detail in future publications.

Another important advantage of this new family of network polymers is the ability to convert the cross-linked structure back to a low molecular weight oligomer by reaction with acetic acid.[10] The resulting oligomers have been successfully repolymerized into a three-dimensional network and then depolymerized again.

In this paper, we describe our work on the synthesis of cross-linkable aromatic copolyester oligomers, the characterization and curing of these resins to form three-dimensional network polymers, and the physical properties of the cured networks.

Experimental Section

Materials. Trimesic acid [TM] (Amoco), phloroglucinol [PG] (Fluka), hydroquinone [HQ] (Aldrich), *p*-hydroxybenzoic acid

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[HBA] (Hoechst-Celanese, Aldrich), and isophthalic acid [IPA] (Amoco) were all dried thoroughly in a vacuum oven at 70 °C prior to reaction. Sodium hydroxide (EM Science), acetic anhydride (Aldrich), pyridine (EM Science), and concentrated sulfuric acid (Aldrich) were used as furnished. AS-4 (Hercules) unidirectional weave graphite fabric, 3K tow size with *G′* sizing, was used as provided.

Preparation of Monomer. Hydroquinone diacetate [HQDA] monomer was prepared from hydroquinone by reacting with acetic anhydride in a 1:2 mole ratio with slight excess (∼10%) of anhydride. Here, 440 g (4 mol) of HQ was dissolved in 920 g (8.9 mol) of hot acetic anhydride at ∼100 °C. The solution temperature was allowed to cool to 75 °C, at which point 2−3 drops of sulfuric acid was added to catalyze the acetylation reaction. The solution temperature immediately increased to 100−110 °C due to the exothermic reaction. After allowing the solution to cool to room temperature, HQDA was precipitated with distilled water. The monomer was filtered and rinsed in a Büchner funnel attached to an aspirator, dried overnight in vacuum at 70 °C, and then ground into a fine powder in a coffee grinder.

The same procedure was used to produce *p*-acetoxybenzoic acid [ABA] from hydroxybenzoic acid. In this case, the mole ratio of monomer to acetic anhydride was 1:1 with a slight excess of anhydride added to ensure full conversion. In this case, 544 g (4 mol) of HBA was dissolved in 480 g (4.7 mol) of hot acetic anhydride. The reaction mixture was again allowed to cool to ∼75 °C, at which time sulfuric acid was added dropwise. The product immediately precipitated in the form of a white paste. Distilled water was added to the ABA and the product filtered and rinsed in a Büchner apparatus. The product was dried in vacuum overnight at 70 °C and ground into a fine powder.

The trifunctional monomer, 1,3,5-triacetoxybenzene [TAB], was prepared through acetylation of phloroglucinol. Due to the large exotherm on acetylation, the above procedure for the production of HQDA and ABA was not followed. Instead, acetylation was performed in a procedure described in earlier literature.[11] Sixty grams of NaOH was dissolved in 200 mL of distilled water, and 126 g (1 mol) of PG was added to the NaOH solution. After all of the PG had dissolved, 500 g of ice and 350 g (∼3.4 mol) of acetic anhydride were quickly added to the solution. TAB immediately precipitated from solution. The product was filtered, rinsed, and dried as above. All of the reactions proceeded in high yields, although there was some loss in working up the material. No attempt was made to ensure the collection of all of the monomer from precipitation and rinsing. HQDA, ABA, and TAB monomer melting points (125, 196, and 104 °C, respectively) were determined by the DSC peak position and found to be in good agreement with known values.[12] The purity of all monomers used in the syntheses, including TM (mp ∼305 °C) and IPA (mp ∼356 °C), was found to be high (>98%) as measured by high-pressure liquid chromatography.

Synthesis of Oligomers. Carboxylic Acid Terminated Oligomer C-*x*. To produce carboxylic acid end capped oligomer C-1, 126 g of trimesic acid, 236.8 g of hydroquinone diacetate, 149.4 g of isophthalic acid, and 324 g of acetoxybenzoic acid powders were weighed and mixed in a 2000 mL reactor flask. The flask was fitted with a head containing inlets for inert gas, a mechanical stirring bar, and a thermometer to monitor distillation temperature as well as an outlet for removal of volatiles. The reactor was continuously purged with nitrogen. Initially, the outlet was fitted with a refluxing condenser. The reactor was heated to 260 °C over 15 min to get to a low-viscosity melt, at which time stirring was started. After refluxing for 1 h, the heating mantle was turned off until the distillation temperature fell below 110 °C, at which time the reflux condenser was replaced with a distillation condenser and collector flask. Heat was increased to 260 °C while stirring the melt. Acetic acid began to evolve as the reaction byproduct. The extent of the reaction was monitored by the amount of acetic acid collected. After an additional 3 h at 260 °C, the reaction was stopped. The product was a transparent, viscous melt, with 240 mL of acetic acid collected as a distillate (theoretical amount for full reaction = 242 mL). The product was ground into a fine powder and purified by Soxhlet extraction in a 3:1 methanol−water solution followed by a distilled water rinse and drying overnight at 80 °C in vacuum. The amount of oligomer collected was 560 g (∼97% yield). For calculation of MW_{av}, the carboxylic acid end groups were methylated by reaction with diazomethane in *N*-methylpyrrolidinone (Aldrich) and characterized by NMR analysis. The general reaction and methylation procedure are described extensively in the literature[13,14] and will not be discussed further here.

Table 1. Summary of Oligomer Syntheses

oligomer	molar feed ratio of monomer TM	TAB	ABA	IPA	HQDA	MW_{av} (g/mol)	functionality	softening point (°C)
C-1	2		6	3	4	1934	4	172
C-2	1		6	4	4	1890	3	143
C-3	2		4	2	3	1454	4	189
C-4	2		5	1	2	1334	4	188
C-5	1		5	2	2	1290	3	161
C-6[a]	2		3	1	2	1094	4	162
C-7[a]	2		3		1	854	4	148
C-8[a]	1		3	1	1	810	3	136
A-1	2		2	2	7	1750	4	128
A-2	1		5	2	5	1692	3	130
A-3	1		5	1	4	1452	3	160
A-4		2	4	2	1	1270	4	128
A-5		2	2	2	1	1030	4	107
A-6		2	3	1		910	4	105
A-7		1	2	1	1	732	3	81

[a] Indicates monomers initially dissolved in pyridine.

A series of carboxylic acid end capped oligomers were produced with various molecular weights and degrees of functionality (see Table 1). The same synthetic procedure was used as described above, except in the case of low molecular weight species (MW_{av} < 1100 g/mol). In the production of these oligomers, simple melt polycondensation could not be used due to the insolubility of high concentrations of the high melting point monomers (i.e. TM and IPA). To get around this problem, the initial monomer mixture was dissolved in pyridine since it dissolved all of the monomers. One such oligomer (C-6) was formed by charging 16.8 g of TM, 15.52 g of HQDA, 6.64 g of IPA, 21.6 g of ABA, and 32 g of pyridine to a 250 mL three-neck flask equipped with a mechanical stirring bar, nitrogen inlet, and condenser/nitrogen outlet. The clear reaction mixture was immersed in a 260 °C bath, at which time the pyridine began to boil off rapidly. Within 5 min, ∼30 mL of pyridine was condensed and collected from the reactor, while the solution/melt remained clear (isotropic) with a low viscosity. The remainder of the reaction and postreaction procedure was followed as described above. The reaction yield of 38.2 g (∼90%) was slightly lower in this case, most probably due to distillation of low molecular weight species with the pyridine.

Acetoxy Terminated Oligomer A-*x*. To form acetoxy end capped oligomer A-1, 126 g of TM, 432.4 g of HQDA, 99.6 g of IPA, and 108 g of ABA were reacted in the melt, as initially described. After collection of 206 mL of acetic acid (208 mL theoretical), the melt again appeared to be transparent and viscous. This is indicative of a low molecular weight (1000−2000 g/mol), isotropic melt. The product was purified and dried as previously described. Reaction yield for this oligomer was 525 g (∼98%), comparable to that of oligomer C-1.

A series of acetoxy end capped oligomers was also prepared with various molecular weights and degrees of functionality (see Table 1). For lower molecular weight analogs, as with the carboxylic acid capped oligomers, similar problems were encountered in preparing a low-viscosity isotropic melt due to the high percentage of high-melting monomers. In this case, the use of solvent in the reaction mixture was avoided by using low-melting 1,3,5- triacetoxybenzene monomer (mp ∼ 104 °C) as the trifunctional cross-linking agent. Reactions were carried out in the melt in the procedure described above.

Characterization. Softening points of oligomers were determined in a Leitz Laborlux polarizing optical microscope equipped with a Linkham hot stage. ^{1}H NMR measurements

were carried out in a General Electric GN500 (500 MHz) instrument using nondeuterated trifluoroacetic acid (Aldrich) as a solvent. Curing analysis was performed in a TA Instruments DMA 983 with resin impregnated into a glass fabric ribbon and mounted using a horizontal clamping fixture. T_g and flexural modulus for cured neat resins were measured in the DMA 983 with a vertical clamping configuration. All DMA tests were performed at 1 Hz. Ultrasonic tests to measure residual porosity were done in through-transmission at 5 MHz frequency. Liquid chromatography of monomers was done in a Waters HPLC equipped with a C18 column. Thermal analysis of cured resins was done using TA Instruments DSC10 and TGA 2950 ramped at 10 °C/min in nitrogen unless otherwise specified. Densities of cured resins were determined in a density gradient column using chloroform (EM Science) and dichloroethane (EM Science). Moisture pickup was determined by the change in dielectric constant of the cured resin after exposure to 100% relative humidity for 2 weeks at 20 °C. Dielectric measurements were carried out using a HP 4284A LC meter and measured at a frequency of 1 MHz.

Results and Discussion

Oligomeric Synthesis. A number of oligomers with different molecular weight and number of cross-linking points incorporated into the structure were prepared (see Table 1) in high yield. The average molecular weights and degrees of functionality given in the table were determined by the feed ratio of trifunctional monomer to difunctional components. The resulting softening point of the oligomers is also given. It was expected that the softening point would be determined by the oligomer molecular weight, end group, and degree of branching in the amorphous oligomer systems. However, as can be seen from the table, trends based on these variables were not always consistent. Above their softening points, the oligomers flow readily and are easily processed into a variety of forms. As expected, the viscosities of the molten oligomers appear to be related to their molecular weights.

For this paper, the properties of the system composed of a mixture of oligomers C-1 and A-1 (syntheses described in detail above) are discussed in greater depth. One likely representation of these oligomers is shown in Figure 2. In Table 1, the average molecular weight of the oligomers was given as the feed ratio of monomers, and these values were verified to be within 6% of the actual molecular weight as determined by NMR end group analysis. Also, evidence for the production of random structures is given by the NMR spectra for each oligomer shown in Figure 3. Numerous splittings corresponding to a variety of diad sequences are shown in the aromatic proton region (~7−10 ppm). Characteristic peak splittings are also shown in the end group proton regions.

The synthesis of oligomer C-1 (carboxylic end capped oligomer) as described above yielded a material with average molecular weight of 1934 g/mol and degree of functionality of 4 (483.5 g/equiv). Oligomer A-1 had a MW_{av} of 1750 g/mol and also an average degree of functionality of 4 (437.5 g/equiv). By mixing these oligomeric prepolymers in a 1.1:1 weight ratio (C-1:A-1), a stoichiometric balance of end groups was achieved. Curing of these cross-linkable oligomers into a three-dimensional network results in acetic acid being produced as the volatile byproduct.

Curing. The curing behavior was investigated by supporting the oligomeric mixtures on a glass fabric ribbon and heating isothermally in a dynamic mechanical analyzer. The fractional amount of conversion, *c*, is calculated by the technique described by Provder.[15]

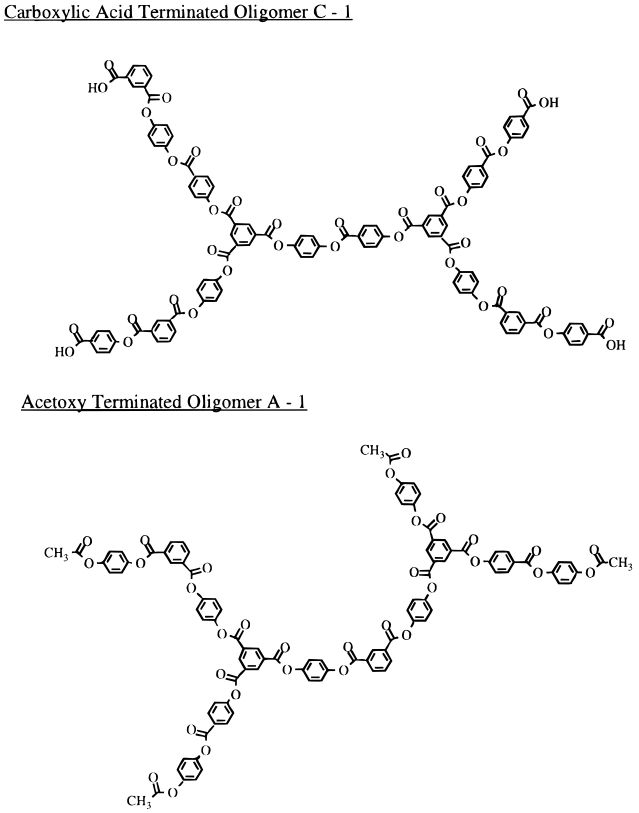

Figure 2. Representation of one possible chemical structure of aromatic copolyester oligomers. Oligomer C-1 is capped with carboxylic acid end groups. Oligomer A-1 has acetoxy ends. When heated, the oligomers react to form a three-dimensional network via a condensation reaction producing acetic acid as a byproduct.

Here, *c* was calculated from

$$c(t,T) = \frac{G(t,T) - G_0(T)}{G_f(T) - G_0(T)}$$

where $G(t,T)$ is the shear storage modulus monitored throughout the isothermal hold, $G_0(T)$ is the initial shear modulus (i.e. $t = 0$) at the isothermal temperature, and $G_f(T)$ is the shear modulus at the isothermal temperature after full cure. In this case, "full cure" was assumed to occur after an additional hold for 15 h at 320 °C for each sample. It was observed that no additional curing, as monitored by the absence of further modulus increase, could be detected in these systems past this point. The results of this analysis are shown in Figure 4.

During cure of the cross-linkable aromatic copolyester resin, the point where the material transforms from a viscous liquid to an elastic solid is defined by the gel point. Assuming an "ideal" network and using Flory's classic equation for determining the gel point in a three-dimensional network polymer,[16−18] the theoretical gel point for the system can be estimated to occur at 0.57 fractional conversion. Even though many authors have disputed the true ideality of thermosetting systems,[17,19] the assumption of an ideal network is often invoked for thermosetting systems that proceed to high conversion such as those described in this paper. As seen in Figure 4, the time to reach theoretical gelation decreases as the cure temperature is increased. Table 2 shows the gelation times at each curing temperature. The cure cycle developed to cure the cross-linkable aromatic polyester resins is given in Table 3. In order to facilitate

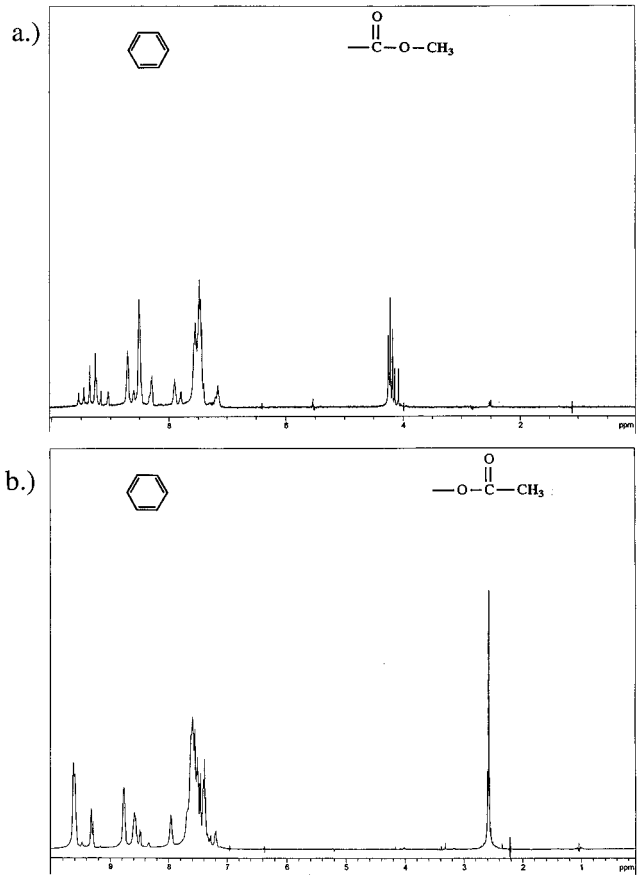

Figure 3. NMR spectra of aromatic copolyester oligomeric resins: (a) oligomer C-1 (carboxylic acid has been methylated to form a methyl ester); (b) oligomer A-1.

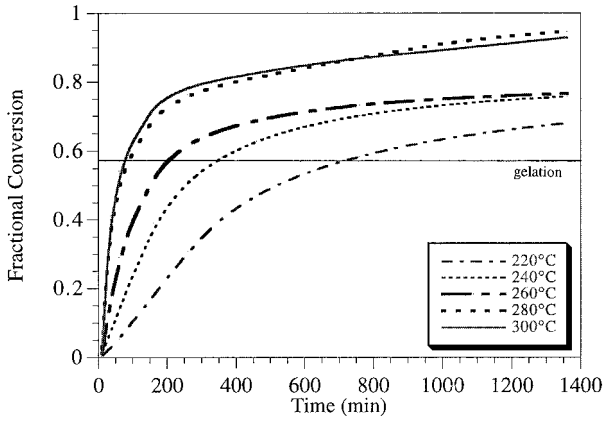

Figure 4. DMA isothermal curing data. Gelation is estimated to occur at 0.57 fractional conversion.

Table 2. Gelation Times at Various Cure Temperatures

isothermal temp (°C)	gelation time (min)
220	720
240	341
260	195
280	77
300	60

the removal of acetic acid, curing of structures was done in vacuum at −98 kPa (−29 in.Hg). Ultrasonic testing was performed to measure the residual amount of porosity due to acetic acid evolution in cured structures. The measurements show low void contents (<3%) in the final structure.

Properties. One of the distinct advantages that this cross-linkable system offers over other thermosets currently available is outstanding thermal stability. In Figure 5, TGA scans are shown of the cured resin in nitrogen and air. The material is thermally stable up to 450 °C in an inert atmosphere (measured as the point of 5% weight loss). Above 450 °C, the material degrades rapidly but still produces a char yield of approximately 40 wt %. In air, the degradation appears to start at 440 °C. However, this temperature is probably lower for extended periods of time due to oxidative degradation.[20] The thermal stabilities for these new materials represent substantial improvements over currently available high-performance thermosetting resins such as epoxies and bismaleimides.

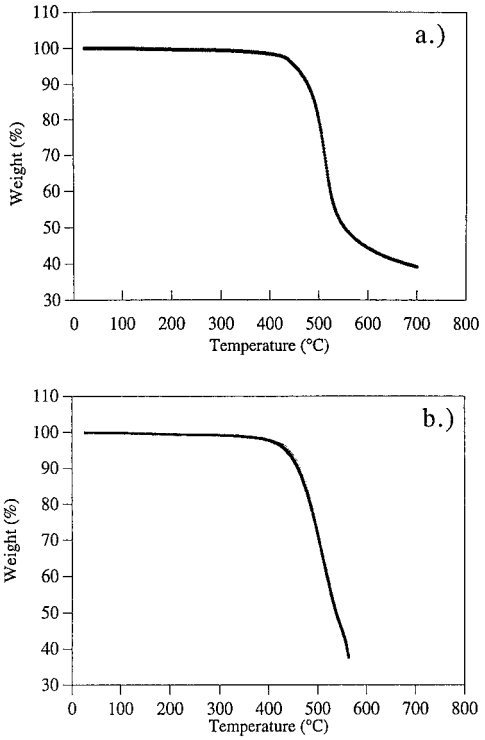

Figure 5. TGA of fully cured aromatic copolyester resin: (a) scan at 10 °C/min in nitrogen; (b) scan at 10 °C/min in air.

Table 3. Cure Cycle for Cross-Linkable Aromatic Polyester Resins

step 1: ramp 5 °C/min to 240 °C
step 2: isothermal hold for 4 h at 240 °C
step 3: ramp 5 °C/min to 270 °C
step 4: isothermal hold for 4 h at 270 °C
step 5: ramp 5 °C/min to 300 °C
step 6: isothermal hold for 4 h at 300 °C
step 7: ramp 5 °C/min to 320 °C
step 8: isothermal hold for 4 h at 320 °C
step 9: cool to room temp at approximately 2 °C/min

Another consequence of the fully aromatic structure of the network is a material which should display a high effective use temperature. In amorphous network polymers, this temperature is dominated by the glass transition. Dynamic mechanical analysis scans are shown for three formulations of cross-linkable aromatic polyesters in Figure 6. The formulations are based on the same chemistry (i.e. monomer units), the only difference being the amount of branching agent (TM or TAB monomer) incorporated into the oligomeric structure. The role of a graphite fiber reinforcement on the high-temperature properties is illustrated in Figure 7. A comparison of Figures 6 and 7 shows the profound effect of the incorporation of fibers on extending the use temperature to as high as 350 °C.

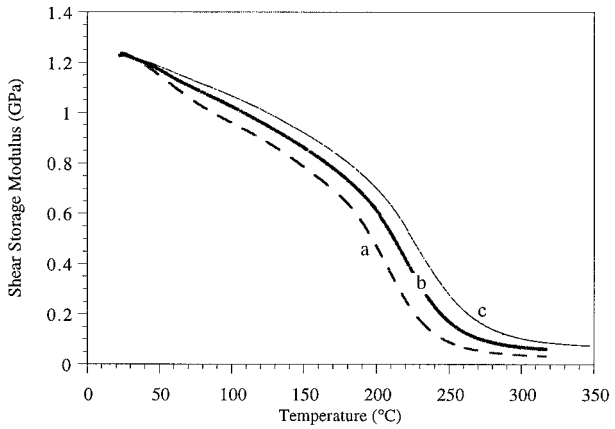

Figure 6. DMA scan showing G' for cured aromatic copolyester resins: (a) low cross-link density resin (oligomers C-2/A-2, 1.1:1 weight ratio mixture); (b) medium cross-link density resin (oligomers C-1/A-1, 1.1:1 weight ratio mixture); (c) high cross-link density resin (oligomers C-3/A-4, 1.15:1 weight ratio mixture).

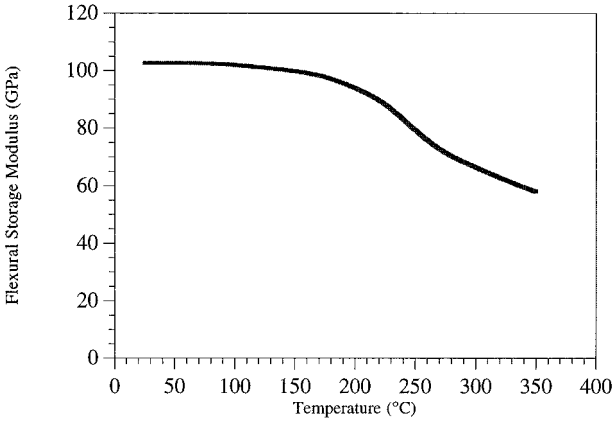

Figure 7. DMA scan showing the flexural storage modulus, E', for a composite of 40 vol % cross-linkable aromatic polyester resin (C-1/A-1) impregnated into unidirectional graphite fabric. Sample alignment was along the 0° orientation.

Returning to Figure 6, the different oligomer mixtures lead to resins with different T_g's as measured by the peak in the shear loss modulus (inflection in storage modulus curve). In Figure 6, the T_g's are found to be 209 °C for the C-2/A-2 system (curve a), 224 °C for C-1/A-1 (curve b), and 237 °C for the C-3/A-4 system (curve c). Due to the insoluble and infusible nature of thermosetting polymers, the structure of the final network is much more difficult to characterize than that of conventional thermoplastics. This structure is determined primarily by the cross-link density, typically given as the average molecular weight between cross-links (M_c). Numerous analytical techniques have been developed to evaluate this parameter, such as elastic modulus measurements above T_g, shifts in the position of T_g, swelling, and chemical methods.[21] Since the chemical structure (rodlike aromatic ester) of the material leads to a high resistance to attack by solvents and moisture, swelling and other chemical techniques are ineffective. Empirical relationships relating the degree of cross-linking and T_g have been developed, but the agreement between studies is not very good.[21,22] Thus, for this system modulus measurements would appear to have the greatest potential for determining M_c. One method frequently employed is based on the theory of rubber elasticity, where the value of the modulus in the rubbery plateau region of the thermoset is used to calculate M_c. The relationship between modulus and

Table 4. Cross-Link Density Calculations for Aromatic Copolyester Networks

	M_c (g/mol)		
	theor	rubber elasticity	empirical
oligs C-2/A-2	1040	168	849
oligs C-1/A-1	480	110	497
oligs C-3/A-4	300	81	429

cross-link density is given as[22,23]

$$M_c = \frac{\phi\rho(T)RT}{G(T)}$$

where R is the universal gas constant, T is the temperature of the modulus measurement well above T_g, $\rho(T)$ is the sample density at the test temperature, $G(T)$ is the shear storage modulus at temperature T in the rubbery region, and ϕ is termed the "front factor". The value of ϕ is given as the ratio of the size of the bridging chain between cross-linking points in the cured polymer to that of the bridge in free space. Often the value of ϕ is estimated to be unity.[22] In the case of our system, this would be a logical assumption due to the rigid, rodlike nature of the aromatic ester chains. Unfortunately, this method greatly underestimates the value of the molecular weight between cross-linking points when compared with calculations determined through monomer stoichiometry (see Table 4). This discrepancy may be explained through entropic considerations.[23] The increased stiffness incorporated in the backbone of the bridging chains due to the aromatic and ester linkages greatly limits the number of possible conformations that the chain can achieve (i.e. lowers entropy). In rubber elasticity theory, the rubbery modulus is related to the change in the number of possible chain conformations (inverse relationship). Thus, increased stiffness in the backbone of bridging chains in the network will have the same effect as increasing the effective cross-link density (i.e. lowering M_c). Similar underestimation of the effective cross-link density by rubber elasticity theory has been pointed out in numerous studies involving highly cross-linked networks, such as epoxy and bismaleimide systems.[21,22,24,25]

For materials with high modulus values (above 10 MPa) in the rubbery region due to presence of rigid bridging chains and/or tight networks, other relationships to analytically calculate the cross-link density must be used.[21−23] For highly cross-linked materials there does appear to be a relation between rubbery modulus and degree of cross-linking that gives an adequate estimation of M_c.[21,22] By the same argument presented above, this relationship should also be applicable for extremely rigid bridging chains. The equation originally given by Tobolosky is

$$M_c = \frac{293\rho}{\log_{10}G - 7.0}$$

It should be noted that this is nothing more than an empirical relationship.[21,22] However, as seen in Table 4, the results are much more reasonable than those predicted through rubber elasticity.

The physical properties displayed by this resin are summarized in Table 5. The cured resin exhibits densities of 1.35 g/cm^3. The density of the oligomers before curing is seen to be 1.38 g/cm^3. So for this thermosetting resin, curing acts to increase the specific volume (ρ^{-1}) of the system slightly. This increase is due

Table 5. Physical Properties of Cross-Linkable Aromatic Copolyester Resins

density (g/cm^3)	1.35
shear modulus at 25 °C (GPa)	1.2
glass transition temp (°C)	200−240
thermal stability	
in N_2 (°C)	450
in air (°C)	440
char yield (wt %)	38
moisture pickup (wt %)	0.3
dielectric constant[27]	4.6

to a higher free volume in the system due to the "locking in" of the rigid chemical units making up the network. This behavior differs from reports on many other systems where curing into a three-dimensional network results in a higher density and cure shrinkage.[21,25,26] The importance of the specific volume increase on curing is as a counteraction to the polymerization shrinkage due to the condensation cross-linking reaction. As stated previously, the moisture and solvent resistance of these cured materials is very good. After exposure to 100% relative humidity for 2 weeks, the moisture pickup of these networks is extremely low, as measured by the change in the dielectric constant of the resin. The water content in the polymer is calculated using a rule of mixtures calculation:

$$V_w = \frac{\epsilon - \epsilon_r}{\epsilon_w - \epsilon_r}$$

where V_w is the volume fraction of water in the resin, ϵ is the dielectric constant of the exposed resin, ϵ_w is the dielectric constant of water, and ϵ_r is the dielectric constant of the unexposed resin. At 25 °C and 1 MHz, ϵ_w is known to be 78.2. Under the same testing conditions, ϵ_r and ϵ were measured to be 4.6 and 4.9, respectively. The moisture pickup in the resin is calculated to be 0.3 wt %. Once the exposed resin is heated to 220 °C and cooled, the dielectric constant returns to its original value of 4.6.

Conclusion

In this paper, we have described the preparation, curing, and some of the properties of a completely new family of thermosetting polymer based on an all-aromatic ester structure. The network structure originates through the incorporation of a trifunctional aromatic monomer into the low molecular weight reactive oligomer. All reactions proceed in high yield (>90%). The versatility of the synthesis is easily demonstrated by the wide variety of oligomers with different molecular weights, melt viscosities, and degrees of functionality which have been produced. There are distinct advantages of this system over conventional thermosets such as epoxies, phenolics, and bismaleimides. These include extremely high thermal stabilities, high use temperatures, and excellent moisture resistance. We also discuss the utility of the rubbery plateau modulus in determining the structure of the cured network for this system. It was shown that the rigidity of the bridging chains has the same effect on the plateau modulus as increasing the cross-link density of the network.

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