

Studies of Addition Type Polyimidesulfones and Their Composites

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Synopsis

Addition type polyimidesulfone oligomers have been synthesized from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-bis(aminophenyl) sulfone using three latent crosslinking groups as endcappers. The prepolymers were isolated and characterized for infrared spectra analysis, solubility test in various type solvents, melt flow, and cure properties. The crosslinked polyimides were characterized for thermal stability in a nitrogen atmosphere. The most promising systems, nadimide and maleimide prepolymers, were selected for the detailed study as the matrix for graphite woven cloth reinforced composites for which mechanical and other properties were tested. The differences due to various end-capped agents, including processibility, the extent of crosslinking of prepolymers, and thermal and mechanical properties of their composites, were compared.

INTRODUCTION

Over the past decade, aromatic addition polyimides have been developed both as matrix and adhesive resins for applications in future aircraft and spacecraft. Addition polyimides offer distinct processing advantages over linear polyimides.^{1,2} Initially, the linear systems developed had to be processed from the polyamic acid dissolved in a high boiling solvent and were virtually impossible to process once converted to the high molecular weight imide form. Addition polyimides, however, are easily processible in the form of short-chained oligomers end-capped with latent crosslinking groups. Grundschober and Sambeth³ reported the homo- and copolymerization of bismaleimides by heating them to temperature between 150°C and 400°C. TRW Inc. developed the first nadic capped imide of this type.⁴⁻⁶ Since then, a number of other endcappers have been investigated.^{7,8} Several of these materials have been used for the fabrication of high temperature, high performance composites for various aerospace, military, and civilian applications.

The primary objective of the present research was to synthesize and characterize three polyimidesulfone resins with various end groups for application as matrix resins in graphite woven cloth reinforced composites. Another objective was to compare three various latent crosslinking groups which could result in different processibility, the extent of crosslinking, and thermal and mechanical properties.

EXPERIMENTAL

Materials

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA), obtained from Tokyo Kasei, was recrystallized with acetic anhydride and dried in a vacuum

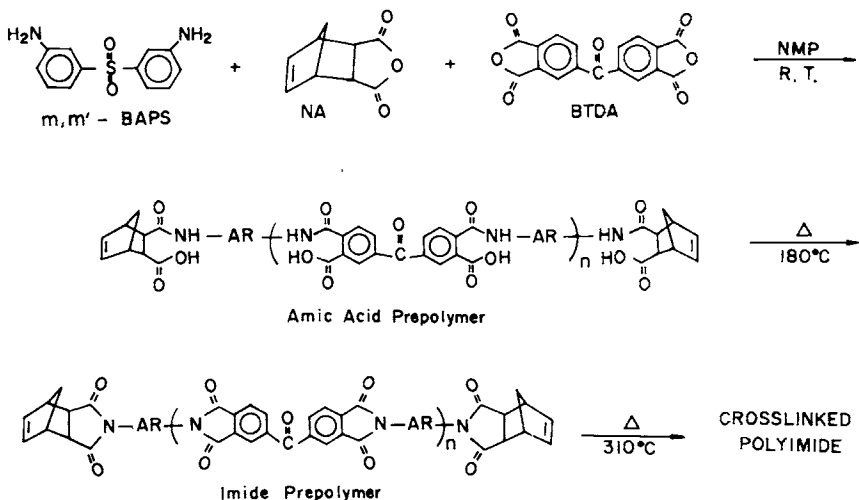


Fig. 1. The reaction scheme for the nadic-capped polyimide.

oven at 200°C for 4 h before use. The diamine monomer 3,3'-bis (amino-phenyl)sulfone (BAPS) was obtained from Tokyo Kasei and used as received. *N*-methyl-2-pyrrolidone (NMP) and *N,N'*-dimethyl formamide (DMF) from Merck were distilled before being stored in 4 Å molecular sieves. The end-capped agents used in this study, which were derived from 5-norbornene-2,3-dicarboxylic anhydride or nadic anhydride (NA), *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (CA), and maleic anhydride (MA), were obtained from commercial sources and used as received. Solvents which were used in solubility tests, including tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAC), were obtained from commercial sources and used as received.

Synthesis of Oligomers

The nadic-capped prepolymer was prepared according to the first reaction scheme outlined in Figure 1. The synthesis was performed in nitrogen atmosphere at room temperature in a three-necked flask equipped with mechanical stirring. The diamine monomer BAPS (0.4 mol) was dissolved in solvent NMP. The end-capped agent NA (0.3 mol) and dianhydride monomer BTDA (0.25 mol) were added in 10 equal portions alternately over a period of 5–6 h. The time between subsequent additions was increased since the anhydride in the

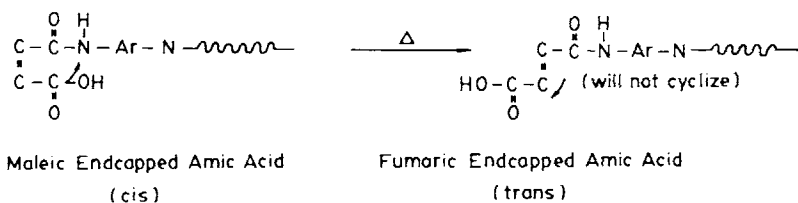


Fig. 2. Thermal conversion of the maleic-capped amic acid oligomer to the fumaric-capped amic acid oligomer.

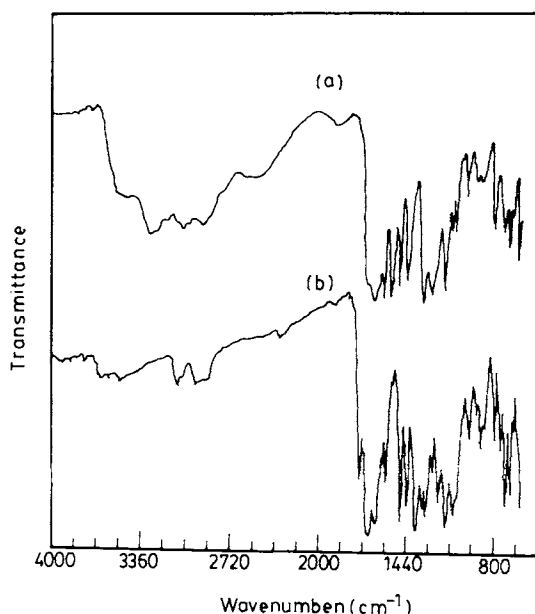


Fig. 3. Infrared spectra of the amide acid and imide for the cyclohexene end-capped prepolymers: (a) amide acid; (b) imide.

latter additions dissolved more slowly. Stirring was continued until complete solution was obtained, usually 24–36 h. The resulting amide acid solution was heated to 180°C entrapping solvent and water of imidization in a Dean-Stark receiver. The resulting imide solution was precipitated in water. Then the resulting imide powder was used for characterization or converted to the cross-linked polyimide by heating to 310°C. The prepolymer end-capped with CA was prepared similarly.

The maleic-capped amide acid was prepared as for the nadic-capped system; however, the preparation of the imide oligomer was accomplished in a slightly

TABLE I
Solubilities of Addition-Polyimidesulfone Oligomers

	NA	MA	CA
NMP	25–30%	20–25%	25–30%
DMF	25–30%	25–30%	25–30%
DMAC	20–25%	25–25%	20–25%
Aniline	30–35%	25–30%	30–35%
DMSO	20–25%	15–20%	20–25%
THF	X ^a	X	X
Chloroform	X	X	X
Toluene	X	X	X
Methyl alcohol	X	X	X
Ethyl acetate	X	X	X
Acetone	X	X	X

^a X = the oligomers were not soluble at 5 wt %.

TABLE II
Melt-Flow and Cure Properties of Addition Polyimidesulfone Oligomers

	Melt-flow range (°C)	Exotherm onset temperature (°C)	Exotherm maximum temperature (°C)
NA	147-218	296	347
MA	169-223	275	350
CA	156-194	291	413

different manner. Chemical imidization reaction was necessitated because thermal treatment of the maleic-capped amic acid resulted in partial isomerism of the maleic group to the fumaric "trans" structure as shown in Figure 2. Conversion of maleic to fumaric acid prevents cyclization from occurring, resulting in a large reduction in the thermal stability of the final polymer. Therefore, dehydration to the imide prepolymer was accomplished by using sodium acetate/acetic anhydride at 0°C. The resulting maleimide prepolymer was precipitated into water, filtered, and washed with copious amounts of the water to remove the acetic acid which was a byproduct of the cyclization step.

Characterization

Infrared spectra of the amic acid and imide oligomers were obtained using a Perkin-Elmer Model 781 infrared spectrometer. Melt-flow and cure properties of the oligomers were determined on a DuPont Model 9900 differential scanning calorimeter (DSC) at a program heating rate of 20°C/min. Tests for solubility on the imide oligomers were performed at room temperature with various type solvents. Thermal stability of the cured polymers was determined with a DuPont Model 9900 thermogravimetric analyzer (TGA) in nitrogen atmosphere.

Composite Fabrication

Graphite woven cloth (Toho 3101) was impregnated with solutions of the imide oligomers dissolved in DMF and dried at 100°C in nitrogen atmosphere.

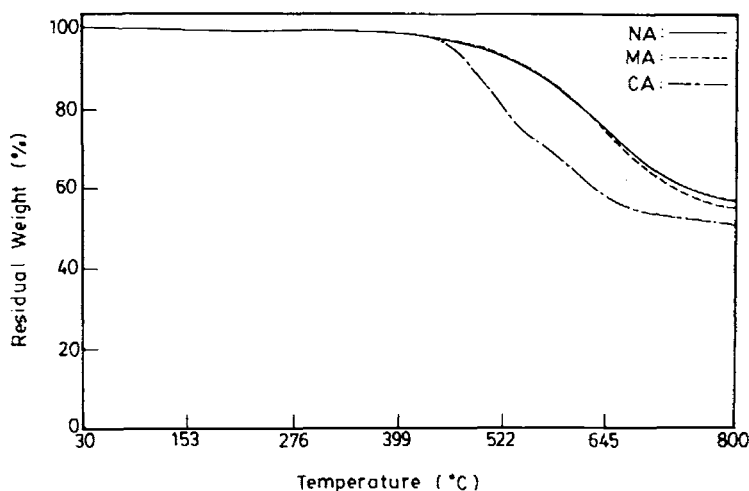


Fig. 4. TGA curves of the cured addition polyimides.

TABLE III
Tensile Properties of Addition Polyimide Composites^a

End-group [aging temperature (°C)]	Tensile strength (Gpa)	Elastic modulus (Gpa)
NA (room temperature)	0.86	23.10
NA (150)	0.79	21.10
NA (200)	0.72	19.51
NA (250)	0.61	16.89
MA (room temperature)	0.63	15.86
MA (150)	0.56	13.72
MA (200)	0.48	12.41
MA (250)	0.38	9.86

^a Fiber content was 65 wt % for all specimens. The time of aging was 1500 h. Each value was the average of five data points.

Solid content of the solution was 25%. Twelve flat laminates were molded with a compression molding machine according to the following cycle:

- (1) Preheat at 260°C for 10 min.
- (2) Apply pressure 350–500 psi.
- (3) Heat to 310°C at 5°C/min.
- (4) Hold 80 min.
- (5) Cool under pressure.

Sufficient bleedout of resin resulted in composites with approximately 65% fiber by weight.

Testing of Composites

All tests of mechanical properties were performed in an Instron testing machine Model 1123. Tensile strengths and moduli were determined according to

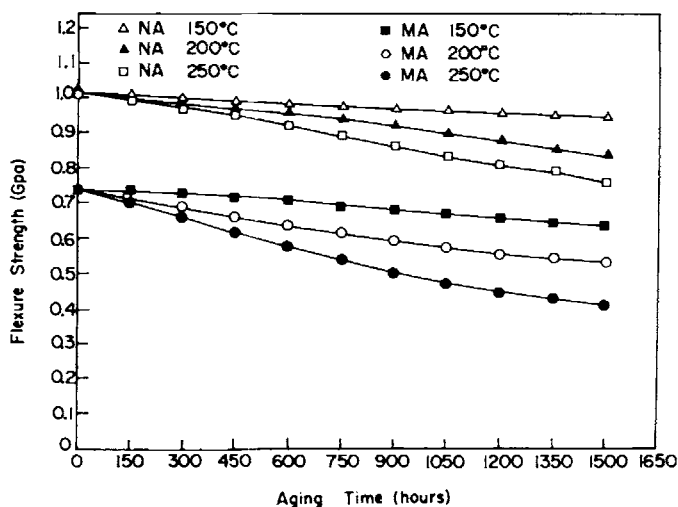


Fig. 5. Flexural strengths of composites aged at 150, 200, and 250°C.

TABLE IV
Flexural Properties of Addition Polyimide Composites^a

End-group [aging temperature (°C)]	Flexural strength (Gpa)	Flexural modulus (GPa)
NA (room temperature)	1.01	53.78
NA (150)	0.95	49.32
NA (200)	0.84	43.51
NA (250)	0.76	39.53
MA (room temperature)	0.73	35.87
MA (150)	0.63	30.63
MA (200)	0.52	28.41
MA (250)	0.41	21.13

^a Fiber content was 65 wt % for all specimens. The time of aging was 1500 h. Each value was the average of five data points.

ASTM D3039. Flexural strengths and moduli were determined using the three point loading method according to ASTM D3039. Glass transition temperature was determined by Rheometrics Model 605 rheometrics dynamic spectrometer (RDS) at a heating rate of 3°C/min. The composites were inspected under a Hitachi Model S-570 scanning electron microscope (SEM).

TABLE V
Solvents Effects on the Flexural Properties of Addition Polyimide Composites^a

	NA flexural strength (Gpa) flexural modulus (Gpa)	MA flexural strength (Gpa) flexural modulus (Gpa)
Toluene	0.99 52.86	0.70 34.21
THF	0.95 49.80	0.66 31.70
Dichloro methane	0.92 46.62	0.63 29.23
DMF	0.87 44.73	0.59 28.48
HOAc	0.87 47.06	0.61 30.88
Sulfuric acid	0.83 42.70	0.56 26.25
Sodium carbonate	0.88 44.15	0.61 29.01
NaOH	Specimen delaminating	Specimen delaminating

^a Fiber content was 65 wt % for all specimens. The time of aging was 1500 h. Each value was the average of five data points.

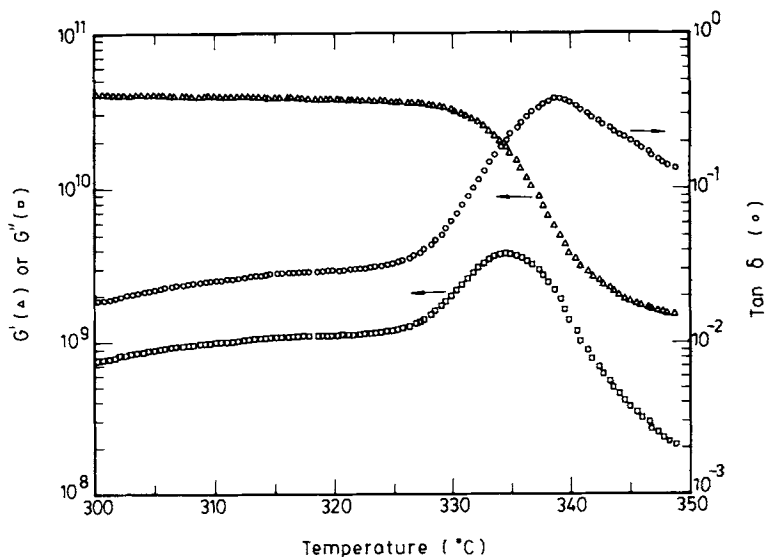


Fig. 6. Dynamic mechanical analysis of composite (the NA system).

RESULTS AND DISCUSSION

Characterization of Oligomers

All amic acids prepared from the respective end-capped agents were characterized by their IR spectra. The characteristic bands are due to $-\text{COOH}$ at 1715 and 3150 cm^{-1} and the $-\text{CONH}$ at 1665 and 3310 cm^{-1} . Other prominent absorptions are those due to unsaturation at 1620 cm^{-1} and the $-\text{SO}_2-$ group at 1300 and 1155 cm^{-1} . During the cyclodehydration process, whether thermal

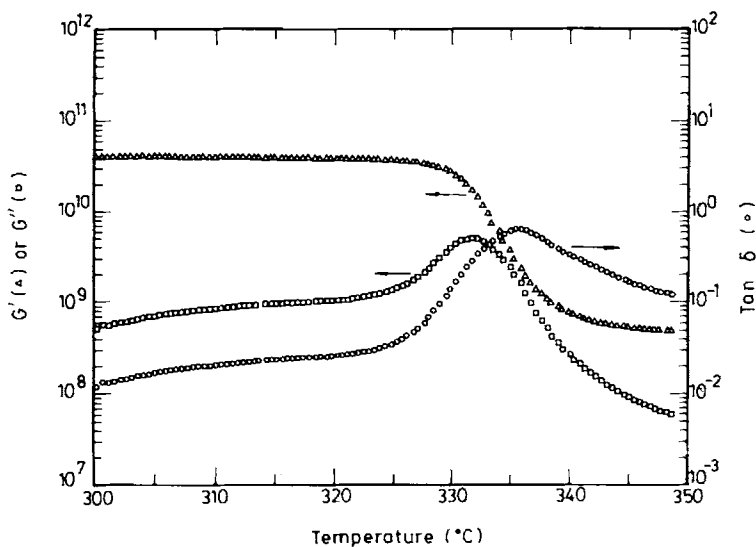


Fig. 7. Dynamic mechanical analysis of composite (the MA system).

complete imidization had occurred. Figure 3 shows a comparison of the infrared spectra of the amic acid versus the imide structure for CA end-capped prepolymer.

Solubility Tests

The results of solubility tests on the imidized prepolymers are given in Table I. All of the oligomers were readily soluble at room temperature in the amide type solvents NMP, DMF, and DMAC with 20–30% solid content. All of the oligomers were also readily soluble at room temperature in the amine type solvent (aniline) and sulfur containing solvent (DMSO). However, oligomers were not soluble at room temperature in other solvents. DMF, which has a lower boiling point and was easily removed, was chosen as the solvent for our prepolymers.

Melt-Flow Properties and Cure Studies

The melt-flow temperature ranges for the imide prepolymers listed in Table II were determined from DSC melt endotherms. The broadness of the melt-flow ranges for nadic end-capped imide may be due to a wide distribution of molecular weight species. This wider distribution for the nadimide has been shown to be due to the double end-capping of the BAPS by the nadic anhydride⁹ which has higher reactivity.

A significant lowering of melt-flow temperature ranges for NA and CA end-capped prepolymers, as compared with that for the MA end-capped prepolymer, are shown in Table II. This fact may be attributed to the first two prepolymers containing aliphatic groups which incorporate flexibility to the rigid imide structure while the maleic end-capped system lacks any aliphatic chain. A lower melting temperature range gives oligomer a distinct advantage in the process which requires a sufficient gap between the melt and "setup" or crosslinking temperature.

Table II also describes the cure conditions for each imide oligomer in terms of the onset and maximum exotherm temperatures obtained from the DSC exotherms. The cure exotherm represents the temperature range where the functional end groups react to form the highly crosslinked polymer network. The difference between onset and maximum exotherm temperature may be related to how rapidly cure is occurring. The CA end-capped system had a broad difference between the two temperatures, indicating that a relatively slow cure occurred. This fact showed that this resin required long curing period at the curing temperature in order to complete crosslinking. It led to partial degradation and hence poor properties in the polyimide and relating composites. For further studies, therefore, only NA and MA end-capped systems have been considered.

In cases where melt processing is desired, the cure exotherm onset temperature should be sufficiently separated from the melt temperature to allow time for processing. In this present study, the nadic end-capped system has a particularly wide temperature range for processing as compared with that of maleic end-capped system.

Thermal Analysis

The thermal stabilities of the cured polyimides with various end groups were evaluated from thermogravimetric studies. Figure 4 shows TGA curves of the

three crosslinked polyimides. For screening purpose, the dynamic TGA in nitrogen atmosphere for these crosslinked polymers should be taken as a potential indicator of the "short-term" heat stability of these polymers.

It is found that all cured polyimides have good thermal stability as shown in Figure 4. But NA and MA end-capped polymers have similar thermal stabilities and both are superior to the CA end-capped system. The weight loss rate between about 550 and 650°C increases greatly, which implies that polymer decomposition at this stage can be used as an indicator for the crosslinking degree of the prepolymer.¹⁰⁻¹² In this sense, the crosslinking of the CA end-capped prepolymer is not complete, which is in accordance with the fact that the CA end-capped system has a relatively slow cure rate.

Mechanical Properties of Composites

All composites tested have a composition of 35% resin by weight. Tensile strengths and elastic moduli of composites which were prepared from NA and MA end-capped resin are given in Table III. The data for composites aged at 150, 200, and 250°C for 1500 h, respectively are also listed in Table III. This table shows that composites prepared from the MA system were found to have lower tensile strengths and moduli than those of the corresponding nadimide system both at room temperature and aged at high temperature. The differences in mechanical properties and thermooxidative stability may be attributed to two reasons. One is that the MA system has higher melt-flow temperature and a narrow temperature gap between the melt-flow temperature and the onset of the exotherm as compared with the NA system. Therefore, the MA system is inferior to the NA system in processibility, and results in a heterogeneous dispersion of the resin in woven cloth. The other reason is that the byproduct of the chemical cyclization step for the MA system, acetic acid, cannot easily be removed. Acetic acid remaining in the resin may degrade the polymer, especially at high temperatures, resulting in reduced strengths.

Flexural strengths of composites aged at 150, 200, and 250°C, respectively, for various time are shown in Figure 5. Flexural strengths and moduli of two composites before and after aging at 150, 200, and 250°C for 1500 h are given in Table IV. Solvents effects on the mechanical properties are given in Table V. It appears that the flexural strengths and moduli of the NA system are also superior to those of the MA system in all conditions. Both composites will not be significantly affected by aromatic type solvent (toluene), ether type solvent (THF), and chlorinated solvent (CH_2Cl_2). But they will be profoundly affected by DMF since it can swell the polymer chain to change the arrangements of molecules, i.e., the dispersion and adhesion between resin and fiber will be destroyed. Weak acid or base solution did not have measurable influences on the properties but significant reduction was observed through the treatment of strong acid or base solution. Composites of our systems did not have any mechanical strength in the NaOH solution because delamination happened. It is possible that NaOH solution may dissolve or degrade the resin matrix.

Other Properties of Composites

Figures 6 and 7 show dynamic mechanical analyses of composites. The temperature at maximum tangent delta ($\tan \delta$) is close to the glass transition temperature (T_g). Thus, the glass transition temperatures of NA system and

MA system are 283 and 267°C, respectively. T_g of the MA system is lower than that of the NA system. Since a minor byproduct, acetic acid, of the MA system cannot be easily removed, it may act as a plasticizer and cause the difference in T_g .

Microscopy studies were performed on the side face and broken face of the composites. The resulting SEM pictures are presented in Figures 8 and 9. Figures 8(a) and 9(a) show fibers were well wetted by resin and there was no apparent evidence of void formation in the NA system. On the other hand, Figures 8(b) and 9(b) show the appearance of voids in the resin-rich areas and less good dispersion and adhesion between resin and fiber, which provides more evidence of the lower strengths in the MA system. The voids found in the MA system may be caused by the byproduct, acetic acid, and bad wetting is due to the poor processibility of MA system as proved earlier.

CONCLUSIONS

A systematic series of addition type polyimidesulfones were prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 3,3'-bis-(amino-phenyl) sulfone using various end-capped agents. Of the three investigated end-caps, the nadic and maleic endcaps show the greatest promise as matrix resins for use in composites, since the extent of crosslinking of cyclohexene end-capped system was incomplete. The maleic end-capped system showed poor processibility and had as byproduct, acetic acid, produced in the cyclodehydration step. Therefore, voids were found in laminates and decreased thermal and mechanical properties. The nadic end-capped system, as a matrix for composites, resulted in good processibility and thermal and mechanical properties.

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