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MULTIFUNCTIONAL CROSSLINKING AGENTS ON THE
THERMOMECHANICAL PROPERTIES OF POLYIMIDE
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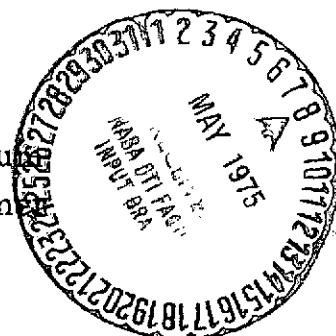
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**EFFECTS OF MULTIFUNCTIONAL CROSSLINKING AGENTS ON
THE THERMOMECHANICAL PROPERTIES OF POLYIMIDE FILMS**

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ABSTRACT

Three new polyfunctional amines were synthesized. Polyimide films containing varying amounts of the amine crosslinking agents were prepared. Their thermomechanical properties were compared with those of control film samples prepared from difunctional amines. The effect of crosslink density on isothermal weight loss, polymer softening, and glass transition temperature is discussed.

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INTRODUCTION

One of the potential applications of high temperature resistant polymers is their use as matrix resins in fiber-reinforced composites for turbojet engine components such as blades and vanes. However, the potential of high temperature resistant polymers such as polyimides (PI) and polyphenylquinoxalines (PPQ) as matrix resins in fiber-reinforced composites has not been fully realized to date. One of the problems associated with these resins is that they exhibit creep, or thermoplastic yielding under load at temperatures approaching 316° C (600° F). A commonly used method to reduce or eliminate thermoplastic behavior is to induce crosslinking into the polymer structure by post-curing the composites at temperatures up to 454° C (850° F). However, such inordinately high post-cure temperatures significantly reduce the long-term thermo-oxidative stability of the polymer by initiating reactive sites for degradation (Ref. 1). A more desirable approach for introducing cross-links is by means of chemical reactions having lower activation energies that would reduce the post-cure temperature or time. One such approach was developed by investigators at the Systems Group of TRW, Inc., using low molecular weight amide acid prepolymers end-capped with norbornene rings (Refs. 2-3). The cure proceeds by a complex set of reactions involving chain extension and some degree of crosslinking. Subsequent studies in our laboratory led to an improved method for preparing addition-cured polyimides (Refs. 4-5). In this approach in situ Polymerization of Monomer Reactants (PMR) occurs on the surface of the reinforcing fibers.

The purpose of this investigation was to further reduce thermoplastic behavior of polyimide resins by substituting a controlled amount of the diamine monomer with crosslinking agents having a higher amine functionality. The knowledge gained from a study of the thermomechanical properties of the crosslinked resins would then be used in the fabrication of fiber-reinforced polyimide composites.

This report describes the synthesis and characterization of three new polyfunctional amines. Polyimide films containing varying amounts of the cross-linking agents were prepared, and their properties compared with those of control samples prepared with difunctional amines. The effect of cross-link density on isothermal weight loss, polymer softening, and glass transition temperatures is discussed.

RESULTS AND DISCUSSION

Monomers

The monomers and crosslinking agents used in the preparation of polyimide films are shown in Fig. 1. The two dianhydrides, 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) were recrystallized from acetone. 4,4'-Methylenedianiline (MDA) was recrystallized from 2-propanol.

2,2', 3,3'-Tetra(p-aminophenyl)-6,6'-diquinoxaline (TABQ) was synthesized by the following method: two moles of 4,4'-diacetamidobenzil (Ref. 6)

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was condensed with one mole of 3,3'-diaminobenzidine in refluxing glacial acetic acid to yield the tetraacetyl derivative of TABQ, m.p. 344-349° C. This material was hydrolyzed with conc. HCl on the steam bath. The cooled mixture was diluted with water and made basic with conc. NH₄OH. After isolation and drying, the crude material was crystallized from DMF/EtOH to give pure TABQ in 89% yield, m.p. > 360° C. Anal. - Calcd. for C₄₀H₃₀N₈: C, 77.15%; H, 4.86%; N, 18.00%. Found: C, 77.42%; H, 4.47%; N, 17.86%.

6,6'-Bis [2,3-di(p-aminophenyl) quinoxalyl] ketone (TABK) was synthesized by a reaction sequence analogous to that used for TABQ, with 3,3', 4,4'-tetraaminobenzophenone as the tetraamine component. The intermediate tetraacetyl derivative of TABK, m.p. 231.5-233.5° C, was hydrolyzed as before. Crystallization from DMF/EtOH gave an 81% yield of pure TABK, m.p. 281-283° C. Anal. - Calcd. for C₄₁H₃₀N₈O: C, 75.67%; H, 4.65%; N, 17.22%. Found: C, 75.99%; H, 4.35%; N, 17.01%.

3,3',5-Triaminobenzophenone (TABP) was prepared by hydrogenation of 3,3',5-trinitrobenzophenone (Ref. 7) in a Parr apparatus with Raney nickel in EtOAc at a pressure of 40-50 psi. Crystallization from water gave a 75% yield of pure TABP, m.p. 130-131.5° C. Anal. - Calcd. for C₁₃H₁₃N₃O: C, 68.70%; H, 5.77%; N, 18.49%. Found: C, 68.81%; H, 5.46%; N, 18.11%.

Polymer Synthesis

Two polyimides, used as control samples in this investigation, were prepared from MDA/BTDE and MDA/PMDA in a 1:1 stoichiometric ratio. The two step method of Sroog, et.al. (Ref. 8) was used. In the first step, a polyamide acid solution in dry N,N-dimethylacetamide (DMAc) was prepared under a nitrogen blanket. The solution was cast onto a glass plate, and the resulting thin film partially dried at 80° C under nitrogen for 0.5 hr. In the second step, the film was converted to the polyimide by heating to 300° C at a rate of 10° C/minute, then holding the film at 300° C for 1 hour.

In the preparation of polyamide acid solutions, the order of addition of the reactants is important. The preferred method for achieving high molecular weights is a gradual addition of the solid dianhydride to a solution of the diamine in DMAc calculated to give a total solids loading of 10-15% (Ref. 9). However, in the synthesis of polyamide acid solutions where the multifunctional amine crosslinking agents were partially substituted for the difunctional amine MDA, the order of addition had to be changed to obtain stable solutions. If the dianhydride was added to a solution of a mixture of MDA and the crosslinking agent, gelation occurred within 10-15 minutes, even at solids concentrations as low as 5%. Similar results were obtained upon addition of a mixture of MDA and the crosslinking agent to a slurry of the dianhydride in DMAc. Stable polyamide acid solutions were obtained by the following method: solid dianhydride was added during 5 minutes to a solution of MDA in DMAc. The solution was stirred for 2 hr. at temperatures up to 50° C. The crosslinking agent was added, and the mixture stirred for an additional 2 hours. In this manner 12 different polyamide acid solutions containing up to 20 mole% of the multifunctional amines were prepared. As the proportion of the crosslinking agent was increased, the solids content had to be decreased to a value of 4% in some cases. At crosslinking agent concentrations much above 20 mole%, gel formation became a serious problem even at very low solids concentrations, and synthesis of the polyamide acids was impractical.

Thermomechanical Properties of Polyimide Films

The thermo-oxidative stability of polyimide films was determined by isothermal exposure at 316° C (600° F) in a forced draft oven with an air change rate of 100 cm³/min. The film weight loss after 600 hours for the various

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polyimides is summarized in Table I. Film samples 1-9 are prepared from the dianhydride BTDA. Comparison of samples 2-4 (containing the tetraamine TABK) with the control sample 1 shows that the weight loss of the films decreases as the molar ratio of TABK is increased. A similar trend is apparent for tetraamine TABQ (samples 5-7) and triamine TABP (samples 8-9). The improved thermo-oxidative stability could perhaps be attributed to crosslinking or to reaction with the ketone carbonyl groups. On the other hand, in the series of film samples 10-14, made from the dianhydride PMDA, the opposite trend prevails. As the molar ratio of the tetraamines is increased, the film weight loss increases as well. While increasing crosslink density should promote a higher thermo-oxidative stability, the decreasing content of the rigid PMDA units apparently is sufficient to counteract the benefits of increased crosslink density and to cause an overall increase in film weight loss.

Compression properties of the polyimide films such as softening and penetration under load were determined with a DuPont 942 Thermomechanical Analyzer (TMA) using a penetration probe. The TMA runs were conducted on 4 x 4 mm film samples, 0.0254-0.0508 mm (1-2 mils) thick, at a heating rate of 10°C/min. under a load of 10 g. The sensitivity of the probe displacement was 4.6×10^{-4} cm/cm of chart paper. Figure 2 shows the TMA curves for the linear MDA/BTDA polyimide (sample 1) and two polyimides containing various mole fractions of the tetraamine TABK (samples 3 and 4). As the temperature is increased, all curves show an initial upward displacement of the probe due to thermal expansion of the films. The temperature at which the probe has reached its maximum upward deflection on the ordinate scale is arbitrarily defined as the onset of penetration temperature. This temperature of course depends on variables such as film thickness, heating rate and applied load. However, since all TMA runs were performed under identical conditions, this permits one to make at least qualitative comparisons of film softening and creep characteristics. It is seen in Fig. 2 that the onset of penetration temperature increases from 275°C for the MDA/BTDA film (sample 1) to 295°C for sample 3 (containing 8 mole% of TABK) and to 307°C for sample 4 (containing 16 mole% of TABK). The glass transition temperatures (T_g) correspond to the point where the penetration curve exhibits a change of slope. The T_g values were determined from a separate first derivative plot of the TMA curve, where the second derivative is zero. Compared with a value of 300°C for sample 1, the T_g also increased significantly with increasing crosslink density: to 327°C for sample 3, and to 342°C for sample 4.

Figure 3 shows the TMA curves for the control sample 10 (MDA/PMDA film), sample 11 (containing 8 mole% TABK), and sample 12 (containing 16 mole% TABK). Here the onset of penetration temperature increases even more dramatically than in the MDA/BTDA polymer series, from 285°C in the control sample to 385°C in sample 12. While sample 10 exhibits a discrete T_g value of 362°C , the T_g values of the crosslinked film samples 11 and 12 were not observed in the temperature range investigated. It should be noted that none of the film samples used in the TMA studies were subjected to an elevated temperature post-cure. It can also be seen in Figs. 2 and 3 that the depth of penetration decreases as the crosslink density of the film samples is increased.

Table II summarizes the onset of penetration temperatures and T_g values for all polyimide films investigated. It can be seen that in the series based on the MDA/BTDA polyimide a significant increase of both T_g and onset of penetration is obtained with increasing crosslink density, although films with a low tetraamine content (samples 2 and 5) exhibited only a small T_g increase (5°C) compared with control sample 1. Film samples 8 and 9, containing the triamine TABP, exhibited considerably lower T_g values compared to

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the films containing the tetraamines TABK and TABQ with a comparable mole percent of MDA.

In the MDA/PMDA polymer series, films prepared using the tetraamine TABQ (samples 13 and 14) showed a very pronounced increase in the onset of penetration temperature with increasing tetraamine content, up to 435° C for sample 14.

In summary, this investigation has shown that substitution of polyfunctional amines into the polyimide structure significantly decreases thermo-plasticity without subjecting the polymers to an elevated temperature postcure. These polyfunctional amines are currently being investigated as crosslinking agents in graphite fiber/PMR polyimide composites.

CONCLUSIONS

The results of this investigation show that the use of tetrafunctional amines for introducing crosslinks into the BTDA/MDA polyimide structure resulted in a significantly higher thermo-oxidative stability. Substitution of tetraamines in the PMDA/MDA polyimide had an adverse effect on the polymer thermo-oxidative stability. The substitution of tri- and tetra-functional amines into the polymer molecular structure significantly increased the polyimide softening temperature and glass transition temperature. The increases were obtained without subjecting the polymers to an elevated temperature postcure. This suggests that incorporation of the tetrafunctional crosslinking agents in the polyimide matrix of graphite fiber-reinforced composites would significantly increase the creep resistance of the composites without the need for long-time elevated temperature postcure schedules.

REFERENCES

1. J. T. Hoggatt, S. G. Hill, and J. G. Shdo, "Development of Polyphenylquinoxaline Graphite Composites," Boeing Aerospace Company, NASA CR-134674, 1974.
2. H. R. Lubowitz, E. R. Wilson, W. P. Kendrick, and E. A. Burns, French Patent 1,572,798 (U.S. Patent 3,528,950), June 1969.
3. E. A. Burns, R. D. Jones, R. W. Vaughan, and W. P. Kendrick, "Thermally Stable Laminating Resins," TRW Systems Group, TRW-11926-6013-RO-00, NASA CR-72633, 1970.
4. T. T. Serafini, P. Delvigs, and G. R. Lightsey, J. Appl. Polym. Sci. 16, 905 (1972).
5. T. T. Serafini, P. Delvigs, and G. R. Lightsey, U.S. Pat. 3,745,149, July 1973.
6. H. L. Gee and J. Harley-Mason, J. Chem. Soc., 251 (1947).
7. F. Bardone, C. R. Hebd. Seances Acad. Sci. 236, 828 (1953).
8. C. E. Sroog, L. A. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, J. Polym. Sci. Part A, 3, 11373 (1965).
9. C. E. Sroog, J. Polym. Sci. Part C, 16, 1191 (1967).

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TABLE I. - PERCENT WEIGHT LOSS OF POLYIMIDE FILMS

Film sample	Monomer stoichiometry	Percent weight loss after 600 hr at 316° C (600° F) ^a
1	1.00 MDA/1.00 BTDA	17.1
2	0.92 MDA/0.04 TABK/1.00 BTDA	17.0
3	0.84 MDA/0.08 TABK/1.00 BTDA	13.6
4	0.68 MDA/0.16 TABK/1.00 BTDA	10.6
5	0.92 MDA/0.04 TABQ/1.00 BTDA	16.5
6	0.84 MDA/0.08 TABQ/1.00 BTDA	12.5
7	0.68 MDA/0.16 TABQ/1.00 BTDA	11.9
8	0.85 MDA/0.10 TABP/1.00 BTDA	13.7
9	0.70 MDA/0.20 TABP/1.00 BTDA	11.2
10	1.00 MDA/1.00 PMDA	15.0
11	0.84 MDA/0.08 TABK/1.00 PMDA	15.2
12	0.68 MDA/0.16 TABK/1.00 PMDA	19.8
13	0.84 MDA/0.08 TABQ/1.00 PMDA	16.8
14	0.68 MDA/0.16 TABQ/1.00 PMDA	20.0

^aIn circulating air; flow rate 100 ml/min.

TABLE II. - THERMOMECHANICAL ANALYSIS OF POLYIMIDE FILMS^a

Film sample	Monomer stoichiometry	Onset of penetration, °C	Tg, °C
1	1.00 MDA/1.00 BTDA	275	300
2	0.92 MDA/0.04 TABK/1.00 BTDA	275	305
3	0.84 MDA/0.08 TABK/1.00 BTDA	295	327
4	0.68 MDA/0.16 TABK/1.00 BTDA	307	342
5	0.92 MDA/0.04 TABQ/1.00 BTDA	275	305
6	0.84 MDA/0.08 TABQ/1.00 BTDA	292	321
7	0.68 MDA/0.16 TABQ/1.00 BTDA	310	335
8	0.85 MDA/0.10 TABP/1.00 BTDA	283	305
9	0.70 MDA/0.20 TABP/1.00 BTDA	297	317
10	1.00 MDA/1.00 PMDA	285	362
11	0.84 MDA/0.08 TABK/1.00 PMDA	315	>450
12	0.68 MDA/0.16 TABK/1.00 PMDA	385	>450
13	0.84 MDA/0.08 TABQ/1.00 PMDA	325	>450
14	0.68 MDA/0.16 TABQ/1.00 PMDA	435	>450

^aPenetration probe; 10 g load; heating rate 10° C/min; sample size 4 x 4 mm.

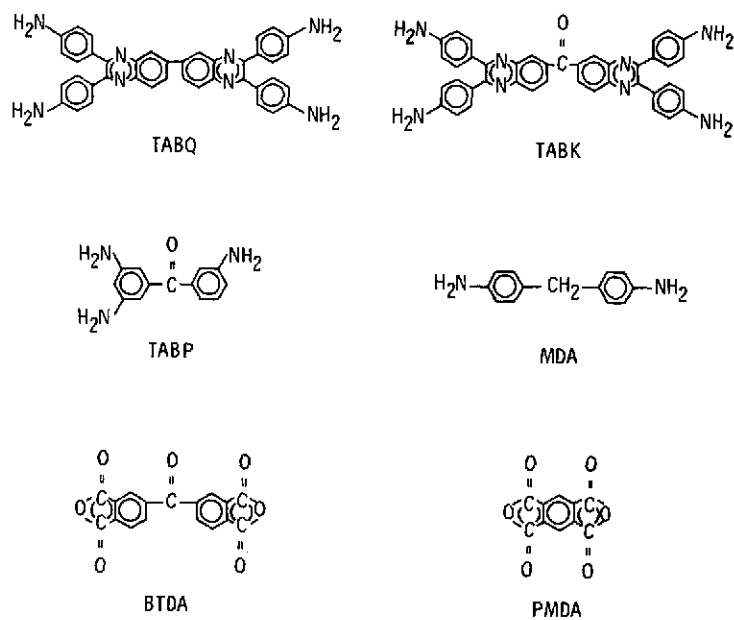
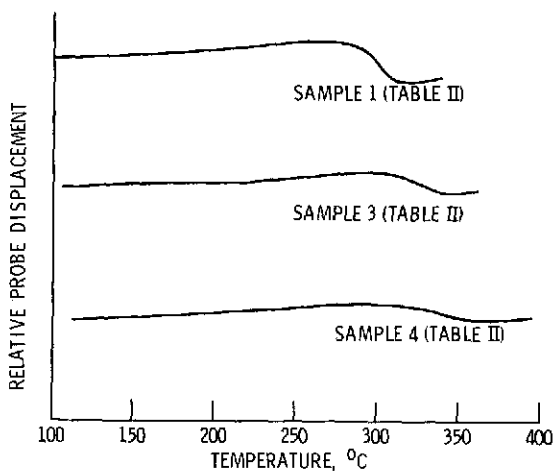
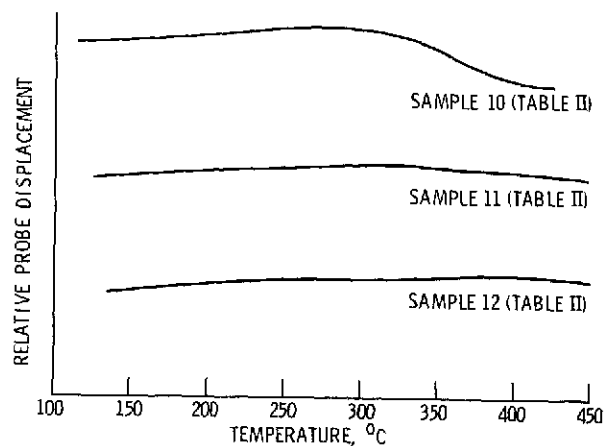


Figure 1. - Monomers used for polyimide synthesis.

Figure 2. - Thermomechanical analysis of polyimide films. Penetration probe; 10g load; heating rate 10^0 C/min.; sample size 4x4 mm.Figure 3. - Thermomechanical analysis of polyimide films. Penetration probe; 10g load; heating rate 10^0 C/min.; sample size 4x4 mm.