

Novel composite matrices from crosslinked aromatic polyamides

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A novel class of matrix polymer based on amorphous crosslinkable aromatic polyamides has been developed. These polymers possess an attractive combination of good moisture resistance, high glass transition temperature (T_g) and reasonable toughness. The polyamide synthesis utilizes the ring opening reaction of bis(2,2'-diphenic imides) with multi-functional aromatic primary amines at elevated temperatures. The mechanical properties of the resultant polyamides are strongly influenced by the ratio of imide to amine. Optimum properties are obtained with a non-stoichiometric ratio of 1:1.2 equivalents of imide/amine.

(Keywords: synthesis; crosslinked polyamide; diphenic imide; composite matrix; tough)

INTRODUCTION

Since the early 1970s continuous fibre reinforced composites have become increasingly important as structural materials for, in particular, aerospace applications. A large number of polymer matrices for such composites, both thermosetting and thermoplastic, have been studied. Important developments in recent years have been directed towards higher temperature performance matrices with 180°C service temperature for the next generation of aircraft. For example, ICI have recently introduced a thermoplastic aromatic polymer composite with a high temperature crystalline matrix, APC (HTX), which exhibits excellent toughness and damage tolerance¹. The main drawback with thermoplastic matrices is that they commonly require demanding processing conditions.

Thermosetting matrices on the other hand are relatively easy to process. Typical high temperature systems include bismaleimides², nadimides³ and acetylenes⁴. Although these polymers exhibit good high temperature performance, they tend to be brittle in the cured state and have poor damage tolerance.

This paper presents data on novel crosslinked amorphous polyamides which combine good toughness and high temperature performance with reasonable processability⁵. Previous work at this laboratory⁶ has shown that some novel linear amorphous polyamides can be produced by the ring opening polymerization of bis(diphenic imides) (I) with aliphatic diamines. This reaction has the major advantage of not involving loss of volatiles⁶ (Scheme 1), and this work was therefore extended in an attempt to prepare crosslinked products.

These might be made if a bis-imide such as I was reacted with an amine having a functionality of >2. Similarly, crosslinked polyamides would result from the reaction of a diamine with a molecule containing >2 imide group or a polyfunctional amine with a

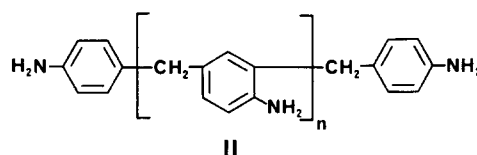
polyfunctional imide. The investigation of these synthetic approaches is the basis of this paper.

EXPERIMENTAL

Materials

2,2'-diphenic anhydride (Lancaster Synthesis), 1,3-phenylene diamine (1,3-PD) (BDH), triethylamine (BDH-Analar) and acetic anhydride (BDH-Analar) were used as supplied.

4,4'-Diaminodiphenylmethane (4,4'-DDM) (Fluka), 4,4'-diaminodiphenyl sulphone (4,4'-DDS) (Fluka) and 3,3'-diaminodiphenylsulphone (3,3'-DDS) (Lansdowne Chemical Co.) were dried at 60°C under vacuum for 2 h before use.



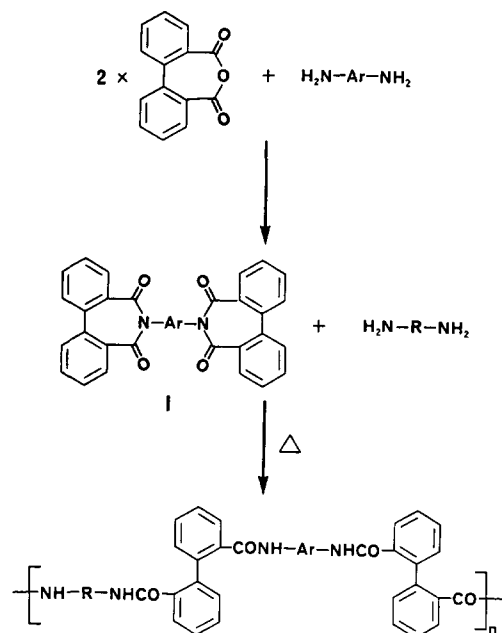
Oligomeric DDM (oligo-DDM) (II) is an aniline/formaldehyde condensation product supplied by ICI. It consists of a mixture of amine products where n varies principally from 0 to about 4. The average ratio of diamine to higher functionality amine in the oligo-DDM mixture can be altered simply by either adding more 4,4'-DDM or removing 4,4'-DDM by molecular distillation. All solvents were dried over 5 Å molecular sieve before use.

Preparation of imides from 2,2'-diphenic anhydride

A typical procedure for the preparation of a bis-imide is as follows using 4,4'-DDM as diamine.

2,2'-Diphenic anhydride (95 g, 0.42 mol) was added over 90 min to a stirred solution of 4,4'-DDM (42 g, 0.21 mol) in *N,N'*-dimethylacetamide (DMAc) (300 ml) cooled to below 10°C. The temperature of the mixture was then allowed to rise to 20°C and stirring was maintained for a further 60 min. Triethylamine (4 ml) and

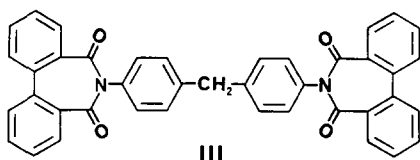
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Scheme 1 Preparation of linear amorphous polyamides

acetic anhydride (143 ml) were added in one portion and the temperature raised to 80°C over 30 min. During this time a thick precipitate formed which was broken up and a further portion of DMAc (300 ml) was added. Stirring was continued for an additional 45 min at 80°C before allowing the mixture to cool to room temperature. The precipitate was filtered, washed thoroughly with several 500 ml aliquots of distilled water followed by two aliquots (200 ml) of methanol before drying under vacuum at 50°C.

The yield was 121 g (94%) of an off-white powder (m.p. 312–314°C). This was further purified by recrystallization from dimethylsulphoxide or *N*-methyl-2-pyrrolidone. The mass spectrum and ¹³C n.m.r. spectrum of the product were consistent with that of 4,4'-bis (2,2'-diphenic imido) diphenylmethane (III).



Preparation of polyamide prepolymers

A typical procedure was as follows. Bis-imide (III) (6.1 g) and an equivalent amount of oligo-DDM (2.1 g) were heated under vacuum in separate nitrogen purged tubes until molten (m.p. of III = 312°C, m.p. of oligo-DDM = 40–60°C). The oligo-DDM was then poured under nitrogen into the tube containing the bis-imide and the mixture was agitated (mechanical stirrer) at 300–320°C under vacuum for 3 min. The mixture was then cooled to room temperature to yield a brittle glassy prepolymer which was ground down into a free flowing powder (m.p. = 240–260°C).

Preparation and characterization of crosslinked polyamide mouldings

Portions of the polyamide prepolymer powders were placed in metal moulds (60 × 12.7 × 3.2 mm) and

compression moulded at 300°C for 1 h. Good quality test strips were obtained by this procedure. The mechanical properties of the resultant samples were measured according to ASTM D790-71 (flexural strength and modulus), ASTM E399-83 (K_{IC} , plane strain fracture toughness) and Plati and Williams⁷ (G_{IC} , critical strain energy release rate). The glass transition temperatures (T_g) were determined by a Du Pont 982 Dynamic Mechanical Analyser (DMA).

RESULTS AND DISCUSSION

Synthesis of diphenic imides

The synthesis of the bis-imides is a facile reaction resulting in a good yield of reasonably pure product. The preparation of the polyfunctional imides, however, is not so straightforward because the oligomeric nature of the oligo-DDM starting material makes the tedious procedure of purification by reprecipitation necessary. Details of the resultant imides are shown in Table 1.

All the bis-imides (A–D) have high melting points varying from 280–320°C. The polyfunctional imides E and F have lower melting points, presumably due to their heterogeneity. Imide F, which has a relatively low 4,4'-DDM content, (<20% w/w) has a m.p. of 160–180°C whilst imide E (containing 45–50% w/w 4,4'-DDM) melts over the range 240–280°C.

Preparation of crosslinked polyamides

A number of the imides described in Table 1 were reacted with either oligo-DDM or 4,4'-DDM to form prepolymers and subsequent crosslinked polyamide mouldings. The combinations employed and the T_g values of the resultant crosslinked polyamides are presented in Table 2. Equivalent ratios of imide to amine were employed in each case. Table 2 shows that, as anticipated, all the crosslinked polyamides synthesized have a high enough T_g to operate at a proposed continuous service temperature target of 180°C.

Table 1 Imides of 2,2'-diphenic anhydride

Sample	Amine	Imide m.p. (°C)
A	4,4'-DDM	318–20
B	4,4'-DDS	314–19
C	3,3'-DDS	306–10
D	1,3-PD	280–81
E	Oligo-DDM ^a	240–80
F	Oligo-DDM ^b	160–80

^a As supplied, contains 45–50% w/w 4,4'-DDM

^b Fractionated sample, contains <20% w/w 4,4'-DDM

Table 2 T_g values of crosslinked polyamides^a

Sample	Imide ^b	Amine	T_g (°C)
1	A	oligo-DDM ^d	240
2	B	oligo-DDM ^d	265
3	D	oligo-DDM ^d	201
4	E	4,4'-DDM	248
5	F	4,4'-DDM	250

^a Equivalent ratios of imide to amine employed in each case

^b From Table 1

^c Determined by d.m.a.; defined as the intersection of tangents to modulus–temperature curve

^d As supplied, contains 45–50% w/w 4,4'-DDM

At this point it was decided to concentrate on assessing the mechanical properties and cure behaviour of one imide/amine combination. Factors taken into account in selecting the preferred combination were imide/amine reactivity, polymerization temperature/time, ease of scale up, etc. These factors are discussed below.

The ring opening reaction of 2,2'-diphenic imides with aromatic amines is a relatively slow reaction and a temperature of greater than 200°C in the melt is required to achieve acceptable rates. However, due to the high melting points of the bis-imides (typically above 300°C; see Table 1), temperatures much higher than 200°C are needed to achieve effective melting and mixing of the two components. As a result, the formation of prepolymer can be a rapid process and reasonably high prepolymer molecular weights are attained within short formation times (0.5–10 min).

Differences in bis-imide reactivity as a function of molecular structure are observed. For example, due to the electron withdrawing effect of the sulphone group, the bis-imide of 4,4'-DDS ring opens more easily than the other bis-imides studied. Hence the initial reaction of the sulphone-containing bis-imide with aromatic amines is difficult to control.

Lower melting imides are obtained from oligo-DDM and these prove significantly easier to handle in the mixing operation because the lowest melting samples E and F could be mixed with the aromatic amine coreactant at temperatures where virtually no reaction occurs. Unfortunately, the problems associated with purifying imides E and F make scale-up for a full mechanical property evaluation impractical.

After considering all these factors it was decided to concentrate further work on the reaction of oligo-DDM with the bis-imide of 4,4'-DDM and to optimize the cure conditions as a function of mechanical and thermal properties. It would be expected that the structure of the fully cured polymer prepared from these two reactants would be that of an aromatic polyamide with linear segments (IV) derived from the 4,4'-DDM present in the oligo-DDM mixture and crosslinks (V) originating from the oligo-DDM polyamines. For such structures, the crosslink density would be inversely proportional to the concentration of diamine (i.e. 4,4'-DDM) in the oligo-DDM mixture. This simple relationship provides a means of progressively varying crosslink density by either

adding 4,4'-DDM to the mixture or removing it by fractionation or molecular distillation.

A detailed structural characterization of the cured crosslinked polyamides was not possible due to their insolubility. The infra-red spectra of cured films and model compounds were, however, both consistent with the proposed structures IV and V.

Optimization of cure conditions

The mechanical and thermal properties of most cured thermosetting systems are strongly influenced by the cure schedule and resin stoichiometry. These factors were studied in this work, utilizing the bis-imide of 4,4'-DDM (III) and oligo-DDM as a model imide/amine combination. In particular, work was directed at optimizing the conditions under which the polyamide prepolymer was synthesized and the effect of altering the imide/amine ratio.

It was found that control of the intermediate prepolymer formation was crucial to the preparation of tough crosslinked polyamides. Mouldings prepared simply by mixing and curing imide/amine combinations directly in moulds (thus omitting the prepolymer formation step) were always less tough. It is believed that the mixing procedure employed in the prepolymer formation favours reaction of the terminal amine groups of the oligo-DDM mixture with the imide functionality, thus forming an essentially linear prepolymer. A gel permeation chromatography (g.p.c.) study of the prepolymers (DMF solutions) as a function of prepolymer formation time at constant temperature and stirring rate provides evidence for their linear nature (Table 3).

If crosslinking reactions were an important event (through the reaction of the in-chain primary amine groups derived from oligo-DDM segments) the polydispersity (M_w/M_n) would be expected to rise with formation time due to the rapid increase in M_w of the prepolymers. However, Table 3 shows that the polydispersity is invariant with formation time; $M_w/M_n = 2.3$ for all prepolymers studied.

It thus seems likely that in-chain primary amine participates in crosslinking only during the final cure stage in the mould when terminal and in-chain amine groups possibly react at similar rates. Hence, when imide and amine are mixed and cured directly in a mould, crosslinking occurs at the expense of chain extension resulting in a strained, less tough network which may not be fully cured. In the case of the prepolymers, essentially linear chain extended systems are moulded and these can achieve full cure to form unstrained tough networks.

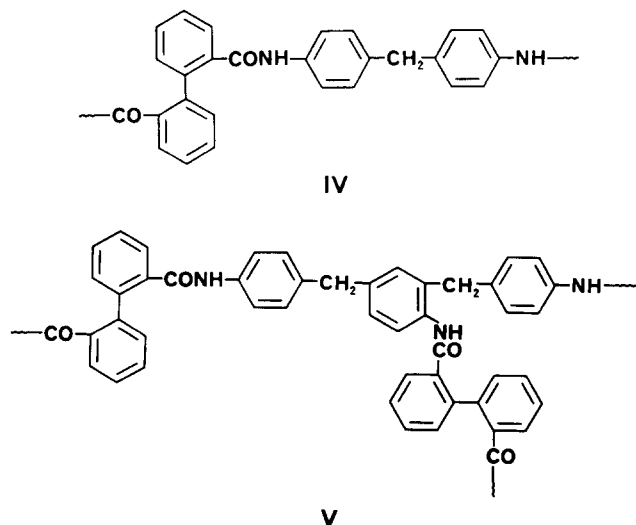


Table 3 G.p.c.^a data of polyamide prepolymers^b

Formation time (min)	M_n	M_w	M_w/M_n
1	6700	15600	2.3
3	8000	18200	2.3
5	9300	21800	2.3

^a Calibrated against polystyrene standards

^b Prepared from bis-imide III and oligo-DDM (45–50% w/w 4,4'-DDM content)

Table 4 Effect of prepolymer formation time on crosslinked polyamide^a mechanical properties

Formation time (min)	Flexural strength (MPa)	Flexural modulus (GPa)	K_{Ic} (MN m ^{-3/2})	G_{Ic} (kJ m ⁻²)
0.5	32	2.6	0.97	0.57
1	83	3.2	1.07	0.73
3	88	3.1	1.20	0.74
5	43	2.8	0.96	0.59
8	24	2.3	0.66	0.47
10	28	2.6	0.60	0.38

^a Prepared from bis-imide III and oligo-DDM (45–50% w/w 4,4'-DDM content). 1.15 equivalents of oligo-DDM were used in each experiment

Table 5 Effect of imide/amine ratio on crosslinked polyamide^a mechanical and thermal properties

Equivalents of oligo-DDM	Flexural strength (MPa)	Flexural modulus (GPa)	K_{Ic} (MNm ^{-3/2})	G_{Ic} (kJm ⁻²)	T_g^b (°C)
1.00	78	2.8	0.66	0.35	248
1.05	89	2.7	0.78	0.61	243
1.10	109	2.9	0.95	0.65	244
1.15	110	2.9	1.02	0.72	252
1.20	94	3.1	1.11	0.71	234
1.25	75	2.9	1.30	0.87	246
1.30	64	3.0	0.88	0.55	246
1.35	63	2.7	0.42	0.21	228

^a Prepared from bis-imide III and oligo-DDM (45–50% w/w 4,4'-DDM content). Prepolymer formation time of 3 min was used in each experiment

^b Determined by d.m.a.

Effect of prepolymer formation time on mechanical properties

It was shown that the prepolymer formation time at a given temperature, and hence prepolymer molecular weight, has an important effect on the resultant mechanical properties of the cured polyamides. This effect was quantified by studying the properties of mouldings prepared from prepolymers which had been produced by varying formation times from 0.5–10 min at 320°C. In each experiment 1.15 equivalents of oligo-DDM were used. The results are presented in Table 4. This shows that flexural strength, flexural modulus, K_{Ic} and G_{Ic} all reach maximum values at prepolymer formation times of 1–3 min. This corresponds to an optimum prepolymer M_n value of about 8000 (from Table 3). At lower prepolymer molecular weights (< 1 min formation time), a significant proportion of unreacted functional groups exist and it is suggested that these crosslink at the expense of chain-extension during moulding to form relatively strained, brittle materials. In the case of higher prepolymer molecular weights (> 3 min formation time), the melt viscosity of the prepolymers is relatively high and it becomes progressively more difficult to make good quality mouldings and the mechanical properties deteriorate as a result.

Effect of imide/amine ratio on mechanical and thermal properties

In other resin systems which can be cured with amines (such as epoxides or maleimides) the amount of amine employed can have an important effect on the final cured

resin properties. Optimum mechanical properties are not necessarily obtained when an equivalent amount of amine is employed. Thus, it was deemed necessary to determine the optimum imide/amine ratio with respect to mechanical and thermal properties.

Using the optimum prepolymer formation time of 3 min various prepolymers containing 1.0–1.35 equivalents of oligo-DDM were prepared and cured. The mechanical properties of the resultant polyamides are detailed in Table 5. The results indicate that the flexural strength reaches a maximum value when 1.1–1.15 equivalents of oligo-DDM are employed while flexural modulus, K_{Ic} and G_{Ic} reach optimum values using 1.2–1.25 equivalents oligo-DDM.

Little is known so far of the exact structure of the crosslinked polyamides or how the imide/amine ratio changes during cure. Attempts were made to ascertain the proportion of any unreacted amine or imide groups in the cured polymers by Fourier transform infra-red (FTi.r.) spectroscopy. However, little knowledge could be gained as any primary amine or imide absorbances are swamped by the strong amide bands.

A d.m.a. study of the cured polyamides was carried out to determine the effect of imide/amine ratio on the polyamide T_g . Table 5 summarizes the results, whilst Figure 1 illustrates a typical d.m.a. trace. It can be seen that over the composition range studied, the polyamide T_g is relatively independent of the amount of oligo-DDM used and has a value of 235–255°C. Furthermore, a good modulus retention is displayed up to at least 230°C (Figure 1) and this temperature performance appears to be adequate for a proposed service temperature of 180°C.

In summary, optimum resin properties are obtained when employing an imide/amine ratio of about 1:1.2 with a prepolymer formation time of 3 min. Under these conditions crosslinked polymers possessing a useful combination of good toughness, stiffness and temperature performance can be prepared.

Moisture resistance and thermal stability

In addition to good mechanical and thermal properties, the crosslinked polyamides also possess surprisingly good moisture resistance. For example, the equilibrium water uptake at 25°C of a crosslinked polyamide prepared from equivalent amounts of bis-imide III and oligo-DDM is 2.45% w/w. The thermal stability is also good, i.e. the same polyamide shows an

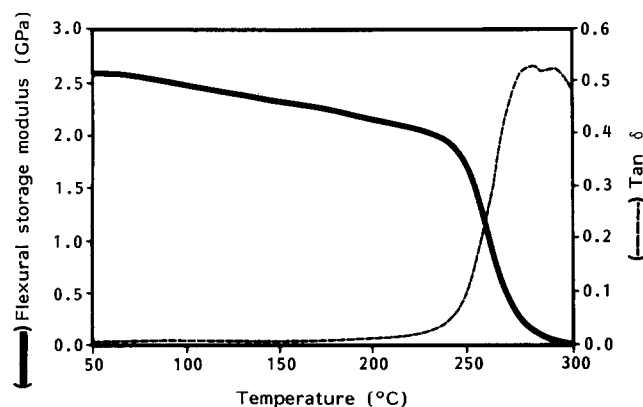


Figure 1 Typical d.m.a. trace of a crosslinked polyamide prepared from bis-imide III and oligo-DDM (1.15 equivalents)

onset of thermal degradation in air at about 360°C, as determined by thermal gravimetric analysis.

These figures compare favourably with, for example, commercial bismaleimide systems which generally have room temperature equilibrium water uptakes of about 4–5% w/w and an onset of thermal degradation at 380–400°C.

CONCLUSIONS

The work detailed in this paper describes initial investigations on the reaction of diphenic imides with primary amines and shows that polymers demonstrating a useful combination of properties can be prepared. An assessment of these polymers as composite matrices has still to be completed, but results to date show that this system has some potential.

Several other aspects have still to be studied. For example, catalysis could be employed to lower the temperature of the imide/amine reaction and to achieve better control over the prepolymer formation process. Many other combinations of diphenic imide and amine could be employed which might lower the prepolymer melting point and hence yield a more processable system.

Ring opening of diphenic imides can be achieved using nucleophiles other than amines. For example, initial observations have shown that phenols will also react to yield polymeric structures and this is another area worth investigating.

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