Novel maleimide functionalized oligomers: 3. Functionalization of preformed oligomers

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(Received 10 December 1990; revised 29 January 1991; accepted 14 March 1991)

Novel maleimide functionalized oligomers have been prepared by a multistage route involving the reaction of maleic anhydride with hindered primary polyamines derived from the acid catalysed oligomerization of diphenyl ether (DPE) with formaldehyde. Mixtures of maleimide and isomaleimide functionalized oligomers can also be formed depending on conditions. The oligomers have good processability and can be conveniently polymerized by heating to form crosslinked polymers exhibiting potential for service up to about 200°C. The neat resin mechanical properties are comparable with other high performance thermosets for 150–200°C performance.

(Keywords: aromatic polyamine; formaldehyde; oligomerization; maleimide; isomaleimide; characterization; mechanical properties)

INTRODUCTION

In a previous paper[1] we described the synthesis and characterization of novel maleimide functionalized oligomers by the acid catalysed copolymerization of *N*-(4-phenoxy)-phenylmaleimide (PPM) with suitably activated aromatics and formaldehyde. Such oligomers can be cured to form crosslinked networks possessing comparable thermal and mechanical properties to some commercially available bismaleimide (BMI) compositions for high performance composite applications[2].

An alternative synthesis to related oligomeric maleimides derives from the reaction of preformed oligomeric primary amines with maleic anhydride[3]. In this paper a novel synthesis of oligomeric aromatic primary amines from the reaction of aniline derivatives with pendant or terminal acetoxymethyl or hydroxymethyl functional condensates of diphenyl ether and formaldehyde is described. The derived oligomeric amines may be converted in a controlled manner to the corresponding maleimide or isomaleimide–maleimide mixture.

EXPERIMENTAL

Typical syntheses are described and are depicted in *Scheme 1*.

Preparation of acetoxymethyl functionalized oligomers (II)

Glacial acetic acid (75 ml), distilled water (115 ml) and 85% w/w sulphuric acid (25 ml) were added to formaldehyde (6.9 g, 0.23 mol, in the form of paraformaldehyde) and stirred to form a homogeneous solution, which was heated to 78°C. Molten diphenyl ether (25.5 g, 0.15 mol) was added dropwise over several minutes and the mixture was stirred at 78°C for a further 2 h. The white cloudy emulsion that formed during this period was poured into a mixture of cold water (2 l) and dichloromethane (500 ml). The resulting mixture was stirred for 15 min before allowing the layers to separate and decanting off the aqueous layer. The organic layer was washed with 10% aqueous sodium bicarbonate solution and then with water until neutral. Finally, the organic layer was dried overnight over magnesium sulphate and the dichloromethane was removed on a rotary evaporator to leave an oligomer having pendant and/or terminal acetoxymethyl groups as a clear pale yellow viscous gum. The oligomer number-average molecular weight (M_n (g.p.c.)) was 910 and functionality (number of acetoxymethyl groups per molecule, as determined by hydrolysis with 0.5 M KOH in 2-methoxyethanol) was 2.3.

^1H n.m.r. ($CDCl_3$). Broad signals at $\delta = 6.6–7.5$ (aromatics), 5.1 ($ArCH_2OCO$), 4.5 ($ArCH_2OH$), 3.9 ($ArCH_2Ar$) and 2.0 (CH_3CO_2).

^{13}C n.m.r. ($CDCl_3$). $ArCH_2Ar$ signals at $\delta = 40.3$ (4,4′-linkage), 35.4 (2,4′-linkage) and 30.3 (2,2′-linkage). Additional signals at $\delta = 65.8$ and 61.6 ($ArCH_2OCO$, bonded to the 4- and 2-positions of DPE units, respectively), 20.8 (doublet, CH_3CO_2) and 63.9 and 60.3 ($ArCH_2OH$, bonded to the 4- and 2-positions of DPE units, respectively).

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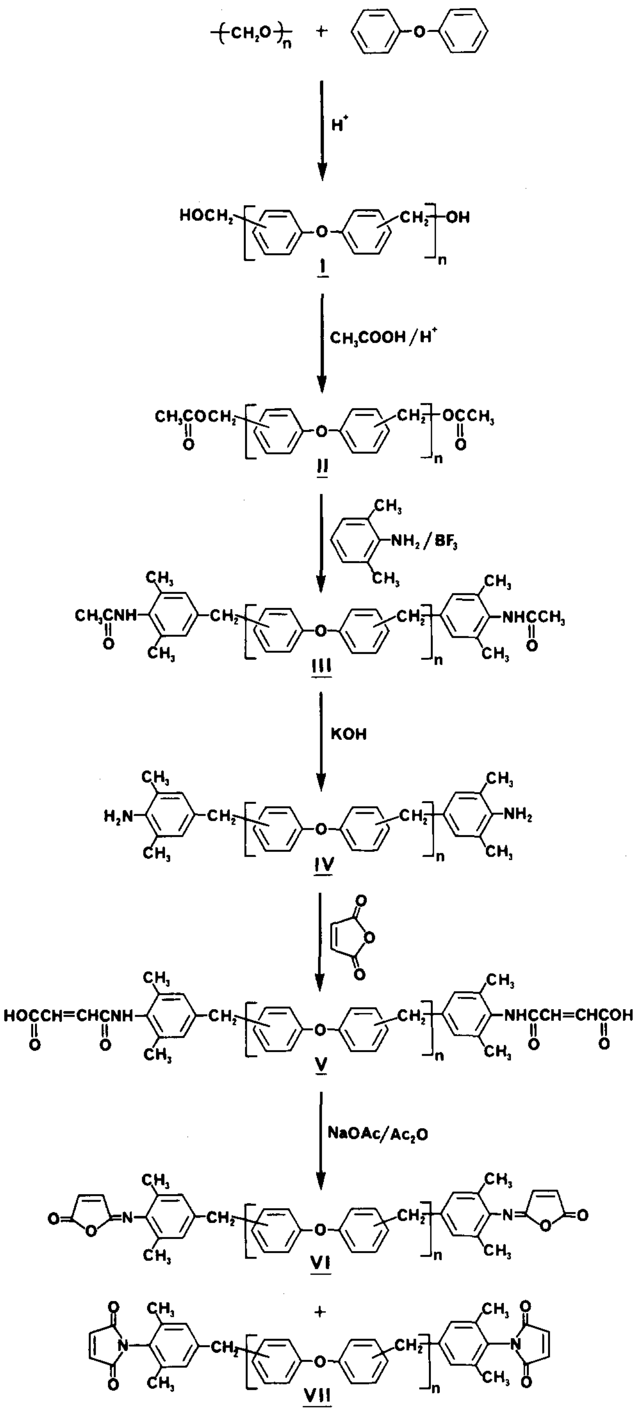


Scheme 1 Reaction pathway for the preparation of maleimide and isomaleimide functionalized oligomers

Preparation of primary amine functionalized oligomers (IV)

A mixture of 2,6-xylidine (9.68 g, 0.08 mol) and acetoxymethyl functionalized oligomer (II) ($M_n = 910$, 0.003 mol) was heated with stirring to 100°C. Boron trifluoride etherate (0.284 g, 0.002 mol) was added dropwise over 10 min while the evolved diethyl ether was allowed to escape. When the addition was complete, the mixture was stirred for a further 6.5 h at 100°C before adding potassium hydroxide (2 g) in water (0.5 ml) and diethyleneglycol monomethyl ether (10 ml), and heating to 175–180°C for 4 h. The mixture was cooled and steam distilled to remove diethyleneglycol monomethyl ether and excess 2,6-xylidine before pouring into hot water (90–100°C). The crude product was decanted and added to a further aliquot of hot water. Dilute hydrochloric acid was then added to neutralize the residual potassium hydroxide before extracting with dichloromethane. The dichloromethane extract was dried over magnesium sulphate before removing the solvent by rotary evaporator to leave primary amine functionalized oligomer with M_n (g.p.c.) = 941, functionality (number of primary amine groups per molecule, as determined by elemental analysis) = 2.2 and a softening point of 88°C.

^1H *n.m.r.* ($CDCl_3$). Broad signals at $\delta = 6.6$–7.5 (aromatics), 5.3 (NH_2), 3.8–4.1 ($Ar\underline{CH_2}Ar$) and 2.3 ($Ar(\underline{CH_3})_2$).

Preparation of isomaleimide (VI) and maleimide (VII) functionalized oligomers

Maleic anhydride powder (74.5 g, 0.76 mol) was added with stirring over 15 min to primary amine functionalized oligomer (IV) ($M_n = 941$, 0.27 mol) in acetone (1 l) cooled to below 10°C. The reaction mixture was stirred at 10°C for 60 min and then at room temperature for 75 min, during which time a precipitate of maleamic acid (V) was produced. A slurry of anhydrous sodium acetate (50 g) in acetic anhydride (230 ml) was added and the reaction mixture heated at reflux (65°C) for 2 h. The precipitate gradually redissolved during this period. The resultant solution was poured into water and the precipitated solid dissolved in methylene chloride, washed with water, aqueous sodium bicarbonate, and dried over a 4 Å molecular sieve. Removal of dichloromethane gave a yellow-orange oligomeric product found by infrared (i.r.) spectroscopy to contain a mixture of isomaleimide and maleimide functionality in the ratio 2:1. The reaction was repeated according to the procedure above except that triethylamine (5 g) was added to the reaction mixture at the same time as the anhydrous sodium acetate/acetic anhydride slurry. In this case the resultant colourless oligomeric product was found by i.r. spectroscopy to contain substantially pure maleimide functionality.

Curing and characterization of oligomers

Neat resin castings were prepared by compression-moulding portions of the maleimide and maleimide/isomaleimide functionalized oligomers in metal moulds (60 mm × 3 mm × 12.7 mm) for 30 min at 150°C followed by 16 h at 180°C under 200–800 psi (1.38–5.52 MPa) pressure with heating and subsequent cooling at 2 K min^{-1}. After demoulding, the castings were post-cured freestanding in air for, sequentially, 4 h at 220°C and 4 h at 250°C. The mechanical properties were determined according to ASTM D790 (flexural strength and modulus), ASTM E399 (K_{Ic}, plane strain fracture toughness) and Plati and Williams[4] (G_{Ic}, critical strain energy release rate). Cured oligomer glass transition temperatures (T_g) were measured by dynamic mechanical thermal analysis (d.m.t.a.) (Polymer Laboratories instrument operating in bending mode). Uncured co-oligomer molecular weights were determined by gel permeation chromatography (g.p.c.) (Waters Associates instrument with model 510 pump and model 490 multiwavelength u.v. detector equipped with a 10^3 Å (10^2 nm) pore size ultrastyragel column) calibrated with polystyrene standards and using chloroform as solvent at 25°C. Softening points were measured by Kofler bar.

RESULTS AND DISCUSSION

Oligomer synthesis

The preparation of oligomers by the acid catalysed reaction of aqueous formaldehyde with aromatics activated to electrophilic aromatic substitution (such as phenol or aniline) is well known[5]. We have studied such reactions by using diphenyl ether (DPE) as activated substrate and demonstrated the versatility of the process by functionalizing the resultant oligomer products with a variety of groups including acetoxymethyl, (meth)-acryloyloxymethyl, hydroxymethyl and carboxyl[6]. These studies were extended in the present work to include the conversion of acetoxymethyl functionality to primary amine and, subsequently, maleimide and isomaleimide (*Scheme 1*).

Acetoxymethyl functionalized oligomers. The formation of co-oligomers based on DPE and PPM with formaldehyde has been discussed in a previous paper[1]. DPE moieties are linked through methylene bridges at either the *ortho*- or *para*-positions. The reaction (*Scheme 1*) leads to the formation of branched oligomers or polymers containing hydroxymethyl functionality (I) which, in the presence of acetic acid, are converted to acetoxymethyl (II). Acetic acid has a dual role in acting as a suitable solvent and as an end-capper that contributes to molecular weight control. The acetoxymethyl concentration can be controlled to afford functionalities ranging from 1 to 5.

DPE conversion and molecular weight growth and distribution are readily followed by g.p.c. When the required M_n (typically 1000) is achieved, the reactions may be instantly quenched by pouring into water. *Figure 1* shows a typical g.p.c. trace. Nuclear magnetic resonance (n.m.r.) and infrared (i.r.) spectroscopy confirmed the structure of the oligomers. The ratio of 4,4'- to 2,4'-$ArCH_2Ar$ methylene linkages was 5:1. 2,2'-Linkages are present, but at a very low level (under 2%). A certain amount of hydroxymethyl functionality was noted (*ca.* 25% that of the acetoxymethyl functionality) and was linked to DPE units at either the 2- or 4-positions in a ratio of 1.5:1, as were the acetoxymethyl groups. Structure VIII depicts a representative oligomer form based on the above data.

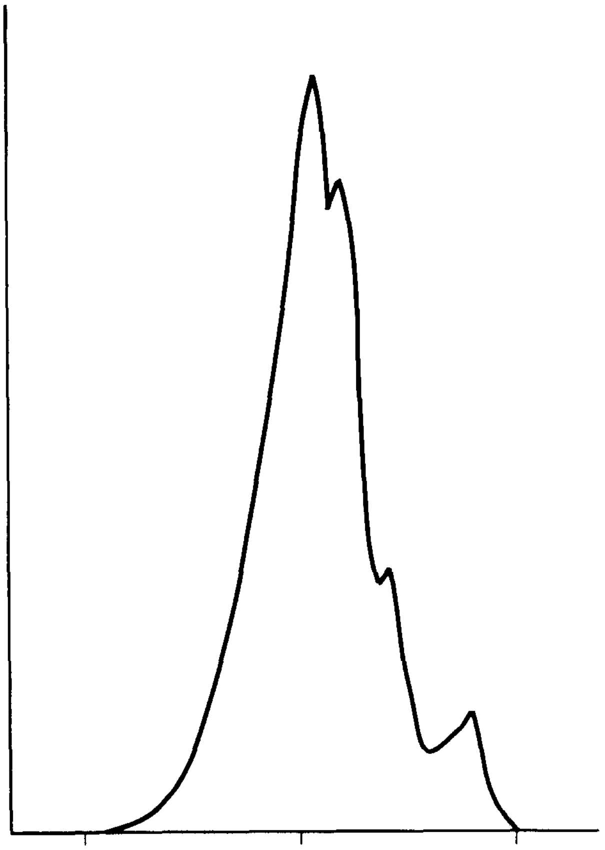
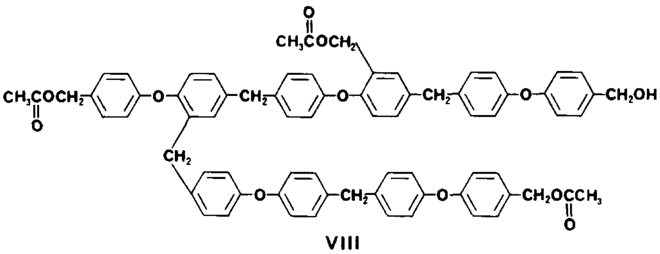


Figure 1 Typical g.p.c. trace for an acetoxymethyl functionalized oligomer



VIII

Primary amine-ended oligomers. The reaction of acetoxymethyl functionalized oligomers with the sterically hindered primary amine 2,6-xylidine, in the presence of a Lewis acid catalyst such as BF_3 (40 mol 2,6-xylidine to 1 mol BF_3) results in the near quantitative linking of the amine to the oligomer chain at the *para*-position. The released acetyl group appears as the *N*-acetyl derivative of either the oligomeric product (III) or 2,6-xylidine. Hydrolysis of this derivative leads to the primary amine (IV).

By contrast, when aniline was employed with the same low ratio of amine to BF_3, the product largely comprised secondary amine ($-OPhCH_2NHPh$) together with a smaller proportion of primary amine as the *N*-acetyl derivative. Presumably this stems from the reaction of benzylic cation intermediate with the less-hindered aromatic amine group. When a 10-fold increase in BF_3 catalyst (i.e. 4 mol aniline to 1 mol BF_3) was employed, the primary amine was formed exclusively, wherein the aniline is linked to the oligomer chain mainly *ortho* to the NH_2 group. N.m.r. evidence suggests that in this case primary amine arises, at least in part, from isomerization of secondary to primary amine during the reaction. Such rearrangements are well known and extensively studied in reactions of aromatic amines with formaldehyde[12]. It also seems likely, however, that complexation of primary amine by the higher level of BF_3 might act to hinder initial attack of the benzylic cation at that site. When low catalyst levels are used the isomerization is too slow to be of interest. Unfortunately, the larger amounts of BF_3 required to form predominantly primary amine in this way are rather impractical for routine use and the high levels of *ortho* isomer produced are undesirable. Therefore further work concentrated on reactions using sterically hindered amines.

The hydroxymethyl groups additionally present in the acetoxymethyl functionalized oligomer also react with 2,6-xylidine to form primary amine functionality, presumably via a benzylic cation intermediate. In fact, a wholly hydroxymethyl functionalized oligomer (synthesized by base hydrolysis of an acetoxymethyl-ended substrate) gave a similar product directly, thus obviating

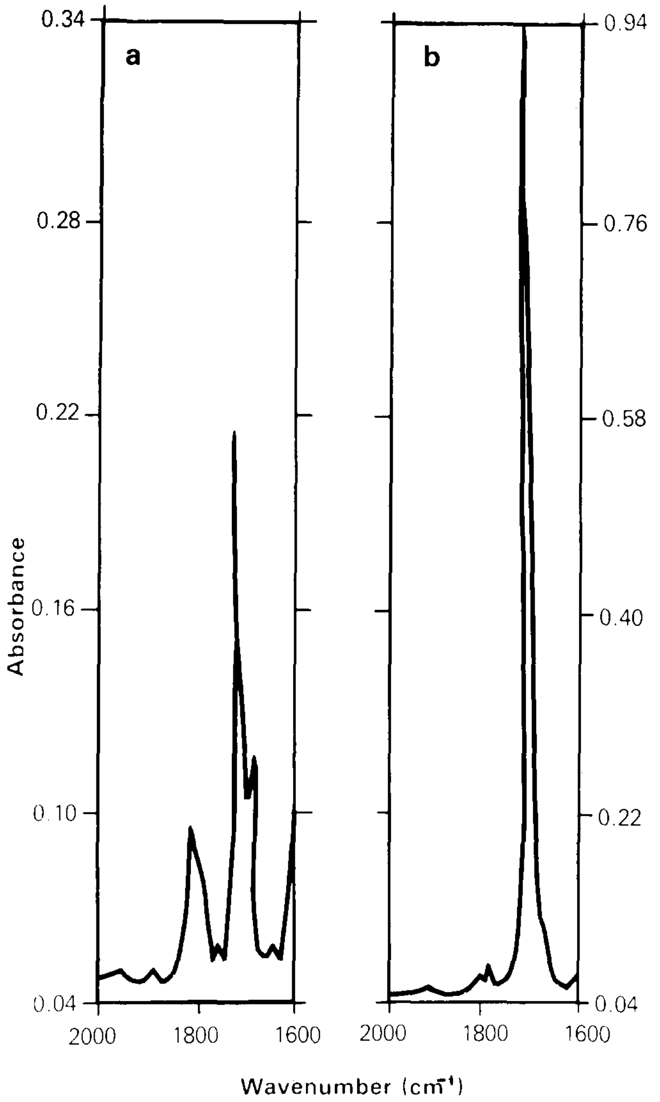


Figure 2 Typical i.r. spectra for (a) isomaleimide/maleimide functionalized oligomer and (b) maleimide functionalized oligomer (see text for peak assignments)

the need to hydrolyse the intermediate acetanilides. This behaviour is entirely consistent with some intermediate steps in the proposed mechanism for the acid catalysed condensation of aromatic amines with formaldehyde[12].

Maleimide- and isomaleimide-ended oligomers. The reaction of maleic anhydride with primary amines to form maleimides via maleamic acid intermediates is well known[7,8]. In the present work, the formation of the maleamic acid functionalized oligomer (V) is almost quantitative. The next stage in the reaction involving dehydration and ring closure was less straightforward. In the presence of acetic anhydride/sodium acetate dehydrating agent a mixture of isomaleimide (VI) and maleimide (VII) is formed, as shown by i.r. spectroscopy (1% w/v solutions in chloroform). *Figure 2a* shows the characteristic i.r. absorptions of maleimide (C=O stretch, 1715 cm^{-1}) and isomaleimide (C=O stretch, 1810 cm^{-1}; C=N stretch, 1697 cm^{-1}). Measurement of the peak height for both C=O stretches gives an estimate of the isomaleimide/maleimide ratio, which, in this case, is 2:1 in favour of isomaleimide.

Interestingly, when triethylamine is included at the dehydration stage, i.r. spectroscopy (*Figure 2b*) shows that maleimide is the predominant product with only a slight trace of isomaleimide formed. Furthermore, when a sample of the isomaleimide/maleimide mixture is dissolved in acetone and refluxed in the presence of triethylamine and acetic anhydride, the isomaleimide portion is isomerized to maleimide. This influence of choice of dehydrating agent on the synthesis of isoimides *versus* imides is well known[9,10].

Steric factors may also influence the cyclodehydration and promote isomaleimide formation. It may be that, in the presence of the adjacent methyl groups, the bulky maleimide functionality has more difficulty in forming than the slightly less bulky isomaleimide group. Certainly, an unhindered model amine, such as 4,4'-diaminodiphenylmethane, forms exclusively maleimide in the presence of acetic anhydride/sodium acetate[8], whereas in our hands 2,6-xylidine, under similar conditions, afforded the isomaleimide in high yield. A detailed discussion on the mechanism of cyclization of amic acids to imides and isoimides is provided by Angelo *et al.*[10].

The formation of an isomaleimide/maleimide mixture from the hindered primary polyamine has certain advantages. For example, isoimides are known to possess better solubility in low boiling common solvents and have lower melting points than the corresponding imides[11]. Furthermore, isoimides isomerize to the imide on heating to above 200°C, which is achieved during conventional maleimide cure schedules. The oligomers prepared in the present work certainly accord with this behaviour. For example, the isomaleimide/maleimide mixtures tend to have a greater solubility (over 50% w/v) in solvents such as acetone or dichloromethane than the corresponding maleimide functionalized oligomers and have lower softening points (110°C for mixtures *versus* 120°C for pure maleimides).

It was noted that the reaction pathway from acetoxymethyl to isomaleimide/maleimide functionalized oligomers proceeded without substantial changes in oligomer molecular weight or molecular weight distribution. For example, g.p.c. traces for both types of oligomer were virtually unchanged from that of the amine functionalized precursors or the acetoxymethyl-ended starting material.

Mechanical properties and glass transition data

The homomaleimide and isomaleimide/maleimide functionalized oligomers were polymerized to crosslinked materials simply by heating samples in metal moulds to 180°C followed by a freestanding post-cure at, sequentially, 220°C and 250°C. Good quality plaques nearly always resulted. It was found, however, that significantly improved processability and reproducibility were obtained by incorporating the low softening (80–90°C) 2,6-xylidine precursor oligomer (IV) (10% w/w) into each homomaleimide or isomaleimide/maleimide sample. The polyamine diluent would presumably react to form aspartimide units by Michael addition to maleimide[7]. From model studies of this hindered polyamine we should expect this reaction to be slow.

Table 1 provides data on mechanical properties and glass transition temperatures for the cured oligomers. Encouragingly, the property values are comparable in magnitude to those of commercially available BMI compositions. The properties of the two types of oligomer are similar, the only difference being that the cured

Table 1 Mechanical and thermal properties of cured homomaleimide and isomaleimide/maleimide functionalized oligomers

Oligomer type[a]	Flexural modulus (GPa)	Flexural strength (MPa)	K_{IC} (MN m$^{-3/2}$)	G_{IC} (kJ m^{-2})	T_g^b (°C)	T_g^c (°C)
Isomaleimide/maleimide (2:1)	3.0	84	0.75	0.27	226	274
Maleimide	3.0	126	0.66	0.23	237	279

[a] All samples contain 10% w/w, 2,6-xylidine functionalized oligomer as reactive diluent
[b] Determined by drawing tangents to the d.m.t.a. modulus *versus* temperature curve
[c] Temperature of the d.m.t.a. tan δ peak maximum

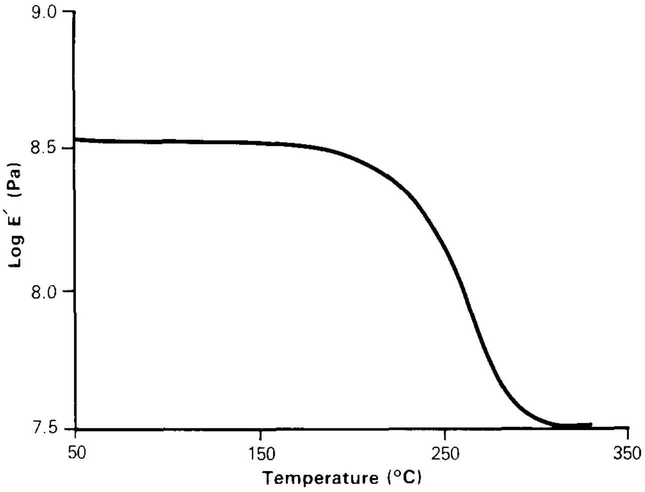


Figure 3 D.m.t.a. trace for a cured isomaleimide/maleimide functionalized oligomer

isomaleimide/maleimide functionalized oligomer has improved toughness and lower T_g than the homomaleimide although, arguably, these differences may be within experimental error. *Figure 3* displays the d.m.t.a. trace of the cured isomaleimide/maleimide functionalized oligomer and shows that the cured resin modulus remains fairly constant up to about 170°C before diminishing at higher temperatures. The cured homomaleimide gives an almost identical d.m.t.a. trace.

CONCLUSIONS

Novel maleimide functionalized aromatic oligomers can be successfully prepared from hindered polyamines derived from the acid catalysed oligomerization of diphenyl ether with formaldehyde. A mixture of maleimide and isomaleimide can also be formed, depending on conditions. Such a mixture exhibits superior processability compared to the homomaleimide. Cured oligomers possess the potential for performance up to about 200°C and have comparable mechanical performance to some commercially available BMI compositions such as those based on 4,4′-bismaleimidodiphenylmethane[7].

ACKNOWLEDGEMENTS

The authors thank ICI plc for giving permission to publish this work and also would like to acknowledge the contributions of the Characterisation and Measurement Group at ICI Runcorn.

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