BISALLYLOXYIMIDES- NEW CO-REACTANTS FOR BISMALEIMIDES

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SUMMARY: This paper describes investigations on a new class of reactive monomer which can be used as a co-reactant in thermosetting polyimide matrix resins. The new materials offer a number of advantages over the commonly used co-reactants for bismaleimides including improved thermal stability, higher Tg and in some cases better resin flow properties. When these new materials are mixed with suitable bismaleimide monomers and applied to suitable reinforcing fibres such as carbon, they can be cured into useful composites having substantially improved thermal stabilities as judged from thermal weight loss at 204_C and 250_C. The preparation of polyimide oligomers with N-allyloxyimide end-caps for use as co-reactants or flow and toughness modifiers in other polyimide resins is also described.

KEYWORDS: Bisallyloxyimides, bismaleimide co-reactants, thermally stable polyimides

INTRODUCTION

Bismaleimide terminated compounds are well known resin types used in the preparation of thermosetting polyimides [1]. Compared with other polyimide thermosets, bismaleimides offer the advantage of having processing and curing requirements closest to those of high performance epoxy systems. In view of their generally higher thermal stability compared to epoxies, they have been attractive for advanced composite, and other applications, requiring higher temperature capability. The versatile chemistry of the maleimide moiety permits reaction with a range of other groups to make co-polymers of great value as resin matrices with special properties.

The maleimide double bond is electron deficient and highly reactive to nucleophiles. Thus amines, hydrazides and thiols readily undergo a Michael type addition across the double bond to give substituted succinimides. Dienes can undergo Diels-Alder addition with the maleimide double bond to give fused six member ring structures which can often be aromatized [1]. However the most commonly used co-reactants are carbon substituted bisallyl compounds, the allyl groups of which undergo an ene reaction with the maleimide to form styrene derivatives which react with additional maleimide to form a complex cross-linked, partially aromatized structure. The nature of this cure structure appears to limit the thermo-oxidative stability of the matrix and makes conventional bismaleimides unsuitable for really high temperature applications. Typically, a laminate made from such a system will lose from 4-10% of its weight on thermally aging at 204_C for six months . These allyl co-reactants can be as simple as 3,3'-diallylbisphenol A (MATB) as used in the Matrimid™5292 commercial bismaleimide system or larger molecular weight materials such as the bis[2-allylphenoxy]phthalimides developed by Stenzenberger and Konig [2]. The present work was

initiated as an investigation into alternative cure chemistries for bismaleimides as it was believed that given the right chemistry the above thermal stability limitations could be overcome.

Simple allyloxyimides have been studied as initiators in free radical polymerization. Thus Druliner [3] reports the use of N-allyloxyphthalimide as an initiator in acrylate polymerization. However most of the allyloxyimides reported in the literature have either been used as synthetic intermediates in the preparation of allyloxyamines or have been synthesised for biological screening programs. Diallyloxyimides do not appear to have been described previously in the scientific literature.

Some preliminary experiments with N-allyloxyphthalimide and N-phenylmaleimide showed that a reaction took place on heating these two materials which appeared to involve the formation of a polymer. Therefore the previously unknown bisallyoxyimides (Fig.1) were synthesized and investigated as potential co-reactants for bismaleimides. These compounds are the subject of Patent application [4].
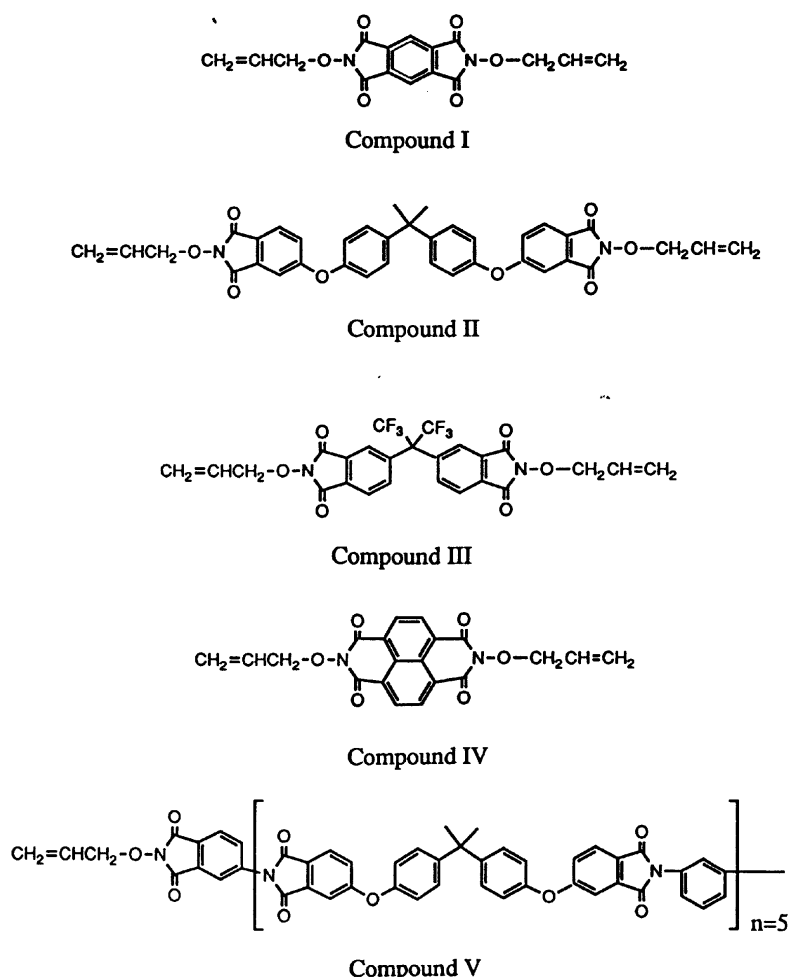

Figure 1: Structures of the new compounds

EXPERIMENTAL DETAILS

Characterization

All bisallyloxyimides were characterized by NMR, IR and MS, and also by GPC if they were soluble in THF. FTIR spectra were obtained by a variety of techniques ranging from films to reflectance methods using either a Bomem Michelson Series or a Mattson high-resolution FTIR instrument. NMR spectra were recorded in either $CDCl_3$, $CDCl_3$ containing a trace of MeOH-d_4 or in DMSO-d_6 using Bruker AC200, 250NMR or DRX500 spectrometers . Mass spectra were obtained on a Jeol JMS-DX303 mass spectrometer, using Fast Atom Bombardment or Field Desorption techniques. GPC analysis was carried out at 30°C using a Waters 150-C GPC with Ultrastyragel columns. Molecular weights were calibrated with respect to polyimide standards. HPLC analyses were performed using a Shimadzu LC-4A instrument fitted with an Altex Ultrasphere octadecyl silanized (ODS) reverse phase column using gradients of methanol/water. Mettler TA3000 and TA4000 thermal analysis instruments were used for differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC experiments were carried out under nitrogen at a scan rate of 10°C/min. Dynamic mechanical thermal analyses (DMTA) were run on a Polymer Laboratories Mk2 instrument. Fracture toughness data was obtained following the approach of Hinkley [5] or alternatively by a Double-Torsion method [6]. Neat resin static compressive properties were determined according to ASTM D695M-85, or indirectly from the laminate in-plane shear modulus using a micromechanical calculation. Flexural modulus was determined using ASTM D790M Method 1 procedure A.

Synthesis

The title compounds were made by first reacting the dianhydride with hydroxylamine in pyridine, followed by allylation. In the case of bis N-allyloxyimide end capped oligoimides, the oligomers were made by standard procedures [7] and then end-capped by a variation of the procedure described below.

2,6-diallyloxybenzo[1,2-c:4,5-c']-dipyrrole-1,3,5,7(1H,6H)-tetrone.
Compound I (DAPMI)

A solution of hydroxylamine hydrochloride (107g, 1.54 mole) in pyridine (1l) in a three knecked flask fitted with thermometer, mechanical stirrer, reflux condenser and blanketted with argon was cooled to 30°C and pyromellitic anhydride (152.7g, 0.7 mole) was added. The mixture was stirred at room temperature for 10-15 minutes during which the exotherm raised the temperature rose from 30 to 45°C. The mixture was then heated to 90°C for 45 min. At the end of this time, the reaction mixture was cooled and the fine precipitate filtered off, washed with water (the red anion is present in basic aqueous medium), dilute acetic acid and then finally with water to yield the dihydroxy compound as a cream powder, mp 300-303°C, 111.7g (64.3%).

The dihydroxycompound (74.4g, 0.3 mole) in a mixture of dry DMF (300ml) and triethylamine (0.6 mole, g, 83.7ml) was stirred at room temperature. Allyl bromide (87.12g, 62.33 ml, 0.72 mole) was added in one lot and a solution was attained while the temperature rose to 45°C. The initial red colour of the anion was dispelled after about 10 minutes and a fine precipitate formed. The mixture was stirred at room temperature for 24h and then poured into water. The precipitated product was filtered off and then washed twice with methanol and

then dried (64g, 67%). Recrystallization from dichloromethane/light petroleum yielded Compound I as colourless needles, mp 222-223°C. Mass spectrum (c.i.) 329 (M+1), 357 (M+29). ^{1}H nmr (CDCl$_3$): 4.73, m, 4H; 5.34, m, 2H: 5.42, m 2H; 6.11, m, 2H; 8.26, s, 2H. ^{13}C nmr 79.14, 118.64, 123.27, 130.81, 134.81, 134.25, 161.36.

The functionality of the oligomers was obtained by consideration of ^{1}H NMR data and the molecular weight.

Cured Neat Resin Bars

The bismaleimides used in this study (apart from the reference material Matrimid 5292A (MAT A)) were experimental materials and their preparation and properties are described fully in reference [8]. The procedure described here is only one of a number of alternative procedures used: Two experimental bismaleimides M/pPDA/UlDA/pPDA/M (M, maleimide; pPDA, p-phenylene diamine; UlDA, ultem anhydride, called CBR330) and M/Ethacure208/M (CBR328) were preheated separately at 220°C under vacuum for 30 min to remove strongly bound solvent. CBR328 (11.2g) was then placed in a resin flask and heated to 220°C where it formed a melt, a low molecular weight thermosetting polyimide (PAB, 11g) was then added, followed by the bisallyloxyimide compound I (DAPMI) (12.43g). While there is always the chance of a run-away exotherm in these blending operations this was never experienced using the quantities described here. When a full melt had been obtained, CBR330 (20.4g) was added in portions to obtain a perfect melt which was degassed under oil pump vacuum (1-2mm) for 10 min. The melt was either transferred directly into a preheated mould or cooled, ground to a powder and compressed into a mold on the hot press. The cure was carried out in three stages: 1h at 220°C; 2h at 250°C and 2h at 280°C to give a neat resin product with Tg (by DMTA) 286°C (1Hz). Some skill and attention to detail was needed to obtain cured neat resin slabs entirely free of voids by this technique.

Preparation of Laminates

A melt was produced as above, then ground up in a mortar and pestle and the micropulverized with dichloromethane to give a suitable mixture for prepregging. SP Systems RC200P plain weavecarbon fibre cloth or equivalent was coated at a rate of 1.1g of resin/g of cloth. The prepregs were dried in warm air for 60 min and "B" staged at 110°C for 2-5 min. A 10x10cm coupon for DMTA use was typically made by aligning 5 plies of prepreg in the warp direction and hot pressing between caul plates under a low initial pressure of a few psi until the platens reached 220°C, followed by 46psi at 220°C for 1h, increasing to 115psi as the temperature is raised to 250°C for 2h and then finally 280°C for 2h.

Alternatively the laminate could be partially cured under epoxy conditions: heating 180°C for 2h, followed by 200°C for 6h, and could then be removed from the press and given a free standing post-cure of 230°C for 6h. Satisfactory laminates up to 200X150mm and 12 plies were made by these procedures.

RESULTS AND DISCUSSION

Thermal Studies

All of the bisallyloxyimides were shown to self-polymerize. When the cure of Compound I was studied DSC it showed a bimodal exotherm with individual peaks at 256 and 318°C, the total energy of which represented 200 kJ/mole of allyl group. Compound II melted at 150°C and had an exotherm peaking at 292°C (180 kJ/mole of allyl group) and Compound III, mp 58°C developed a cure peak at 313°C and yielded a cure exotherm of 255 kJ/mole for the allyl group. The N-allyloxyimide endcapped oligomer CBR371 (Mn 5493) showed an exotherm peaking at 326°C corresponding to 134 kJ/mole of allyl group.

When the blend of bismaleimides and Compound I described in Section 2.4 was run on the DSC a melting endotherm was observed at 195°C followed by the onset of a large exotherm at 230°C, peaking at 285°C. The energy yield corresponded to 195 kJ/mole of maleimide. This result is typical of those obtained with all of the allyloxyimide/bismaleimide blends; that is an exotherm peaking at lower temperature than for the bisallyloxyimide alone with about the same energy yield per mole as self-polymerization.

Neat Resin Characteristics

The bisallyloxyimides tend to have considerably lower melting points than other imide derivatives derived from the same dianhydrides and this helps significantly in processing the materials intolaminates. In contrast the low minimum viscosities reached with some of these systems caused difficulty in making void-free, cured neat resin samples. The voids were generated when the low viscosities reached during cure reduced the hydraulic pressure developed within the resin inside the die thus preventing the process of squeezing out the last traces of volatiles. Table 1 summarizes some of the data obtained for selected systems. When DAPMI was used the neat resin was of comparable toughness to the commercial MATA/MATB system. The use of oligomer Compound V gave a product with higher toughness, comparable Tg and improved thermal stability. The compressive moduli that were determined by the indirect method were comparable to the values obtained for MATA/MATB by the same method.

Figure 2 shows the DMTA traces obtained from the neat resin bar made by the procedure described in Section 2.3 taken (a) immediately after cure and (b) after 14 days aging in air at 250°C. The modulus in both samples shows a marked temperature dependence. On aging there is a decrease in modulus as well as a decrease in its temperature dependence and an increase in Tg. Similar trends were observed for the other systems.

Some physical properties of cured 5 ply laminates

Table 1 summarizes properties found for some of the systems when processed into prepregs and cured into laminates. It can be seen that the oligomer CBR368 showed the best thermal stability characteristics. The Tg measured after a 7 day soak in water at 71°C is not altered significantly for the DAPMI containing system. More detailed thermal weight loss data for laminates using formulations based on Compound I (DAPMI) with the experimental bismaleimides CBR330 and M/TriMe/UlDA/TriMe/M (TriMe, 2,4,6-Trimethyl-1,3-phenylene diamine; UlDA, ultem anhydride, called CBR331), is shown in Figures 3 and 4.

The thermal aging figures of laminates at 204°C (Figure 4) showed that the CBR330/DAPMI system is superior in the long term to CBR331/DAPMI and far superior to the commercial MAT A/MAT B . Although the two former systems behave similarly for the first 6-8 weeks of aging, the weight losses on CBR331 then accelerate, whereas CBR330 maintains the steady rate. This difference is thought to be due to oxidative susceptibility of the methyl groups of backbone amine (TriMe) in CBR331 over the long term. Subsequent work on oligomeric materials is aimed at eliminating this amine.

Minimum conditions for cure

The CBR330/DAPMI system could be cured under epoxy conditions (a factor of great importance in the industry) so long as cure is completed in a free standing post cure. When two laminates were prepared from the same prepreg and one was cured according to the standard method and the other as described above, Tg values were 292 and 295°C (1Hz) respectively and the shapes of the two curves were very similar. The latter laminate did not distort on post cure and did not show any voidage.

Studies on the mechanism of the the curing reaction

A number of model systems have been examined to obtain an insight as to the nature of the interaction between bismaleimides and allyloxyimides during cure. As expected, an addition to the maleimide double bond is involved because succinimide species are produced. This was demonstrated by the observation of succinimide H3 and H4 protons in the ^{1}H NMR spectrum in the reaction product from N-n-butylmaleimide and N-allyloxyphthalimide. There is also evidence from this model system for an exchange reaction involving migration of the amine of the maleimide into the phthalimide ring. We have shown in an ESR study [9] that the onset of cure in a maleimide /DAPMI system is associated with the generation of vastly increased amounts of free radical species at around 250°C. Further work is in progress.
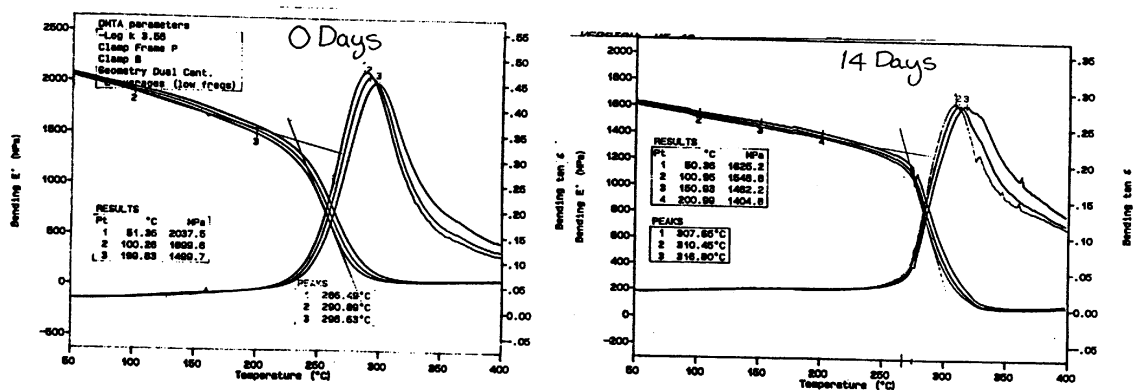

Figure 2. Changes observed in the DMTA curves obtained for cured neat resin on 14 day aging at 250°C. System: CBR330/CBR328/DAPMI/PAB see text.

Table 1. Summary of all Properties of Selected Experimental Bismaleimides With the best all round properties

	CBR330/MATB	CBR330/DAPMI	CBR331/MATB	CBR331/DAPMI	CBR330/CBR368	MATA/MATB
Tg neat resin°C	251 (220)	286 (235)	263 (225)	309 (250)	279 (240)	305
Fracture Toughness Kg MPa.m1/2		0.69			0.98	0.71
Compressive Modulus GPa			2.08±0.32			4.02±0.13
Compressive Modulus Indirect GPa		2.36+0.03	2.34±0.05			2.50±0.04
Flexural Modulus GPa	4.12+0.11		3.33 ±0.09			
Thermal Stab Wt. loss @ 250°C 1D, 7D, 14D	-1.17, 3.25, 4.68	0.3, 1.51, 2.33			0.02, 0.32, 0.77	
LAMINATE						
Tg °C (aver.)	269 (226)	265 (222)	283 (256)	304 (272)	280 (245)	299 (272)
Tg (wet) 7D at 71°C	246-241 (170)	275-269 (233)	270-263 (235)	na		307-293 (270)
Thermal Stab Wt. loss @ 250°C 1D, 7D, 14D	0.51, 1.62, 2.40	0.32, 0.73, 1.11	0.22, 1.53, 2.52	na, 0.85, 2.37	0.19, 0.24, 0.61	0.29, 1.74, 2.75
Thermal Stab Wt loss@ 204°C 1M, 3M, 6M	0.82, 1.89, 3.67	0.16, 0.77, 1.63	0.85, 3.87, 9.22	0.14, 1.63, 5.81		1.00, 3.62, 11.60
Water uptake % @71°C 1D, 7D, 14D	1.04, 1.53, 1.63	0.99, 1.35, 1.43	1.04, 1.23, 1.43			1.77, 2.27, 2.42
MEK uptake 1D, 7D, 14D	0.28, 0.65, 0.89	0.43, 0.67, 0.78	2.17, 6.76, 10.0			0.31, 0.80, 0.87
JET FUEL uptake 1D, 7D, 14D	0.11, 0.25, 0.38	0.26, 0.53, 0.73	0.51, 0.94, 1.00			0.42, 1.05, 1.33
Shear Modulus GPa		4.39 +0.06	3.86±0.11			3.70±0.07

Notes on Table

In many cases values were determined for these parameters on several laminates. In these cases the value quoted is the average value obtained.

The limits shown for mechanical properties are ± one standard deviation.

Tg is measured at 1Hz in a Polymer Labs DMTA,Tb (point of break in Modulus) is given in parenthesis values are averages where multiple determinations were available.

250°C Stabilities are quoted as weight losses after 1,7 and 14 days.

204°C Stabilities are quoted as weight losses after 1,3 and 6 months.

Indirect determination of Neat Resin Compressive modulus was via micromechanics from laminate in-plane shear modulus.
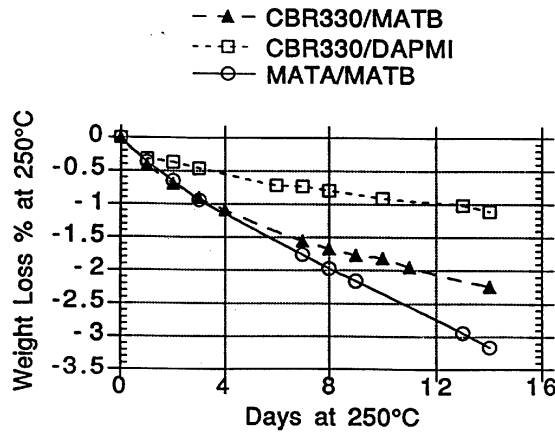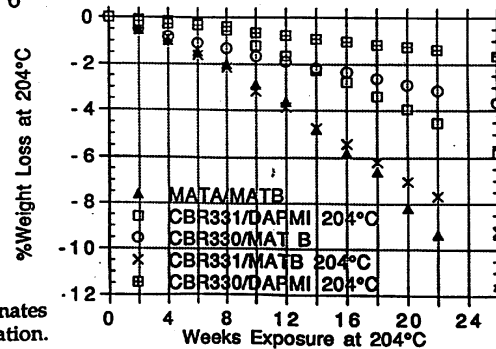
Figure 3. Comparison of weight loss data on aging of laminates at 250°C. See text for abbreviation identification.

Figure 4. Comparison of weight loss data on aging of laminates over 6 months at 204°C. See text for abbreviation identification.

CONCLUSIONS

A new class of reactive monomer with unique end groups has been developed which can be used as a co-reactant in thermosetting matrix resins for advanced composite materials. These materials offer a number of advantages over the commonly used co-reactants for bismaleimides including substantially improved thermal stability, higher Tg, in some cases better resin flow properties, and yet initial cure can still be carried out under epoxy conditions (typically 180-200°C). The new end-groups have also been incorporated into oligoimides which are still easily processible. The synthetic chemistry involved in incorporation of this end group into polyimide precursors is low cost, straight forward, high yielding and clean.

Thermal stabilities of the materials reported lie intermediate between state of the art bismaleimides and the current most highly thermally stable polyimides. Further work is in progress to improve these materials even further.

ACKNOWLEDGEMENTS

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