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New Materials

Bismaleimide-Bisvinylether Copolymers: A New Class of Thermosetting Resins

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Summary

The free radical network copolymerization of bismaleimides with bisvinylethers containing aromatic groups gives rise to a new class of thermally stable imide-containing thermosets. The chief assets of these thermosetting materials are their ability to cure rapidly at low temperatures without the evolution of volatile byproducts.

Introduction

Motivated by the ever increasing demands of the aerospace industry for new higher performance composite materials, there currently is considerable effort in many laboratories directed toward the development of new thermosetting resins for use in this application. Among the primary requirements of candidate thermosetting resins are their ability to rapidly develop excellent thermal and mechanical properties at as low a cure temperature as possible. It is also essential that crosslinking take place without the elimination of volatile products to avoid the formation of voids which seriously limit the mechanical properties of the cured matrix. Although polyimide resins have the required thermal and mechanical properties for advanced composite applications, their poor processing characteristics and high cure temperatures have precluded their use in all but the most demanding applications. Bismaleimide resins developed by Rhone-Poulenc (GRUNDSCHOBER and SAMBETH 1969) are an attempt at a compromise to obtain materials which process and cure at low temperatures without the formation of volatiles while at the same time maintaining a reasonably good level of thermal performance. Nevertheless, these materials still require temperatures of 250°C from eight to twenty-four hours for complete cure.

Maleimides and bismaleimides are examples of electron poor monomers which undergo inefficient radical polymerization. Similarly, vinyl ethers are electron rich monomers which do not undergo free radical initiated homopolymerization. In contrast to the reluctance of these two types of monomers to homopolymerize is the great facility with which maleimides and vinyl ethers copolymerize to give 1:1 alternating copolymers (APONTE and BUTLER 1984). It occurred to us that this free radical copolymerization might serve as the basis for an interesting new class of imide-containing thermosets. We report in this communication the results of our investigations into the preparation and characterization of these new copolymer matrix materials.

Experimental

All reagents and starting materials used in the course of this work were reagent grade and were used without purification. Preparative methods for the synthesis of bisvinyl ethers (CRIVELLO and CONLON 1983), the bispropenyl ethers (CRIVELLO and CONLON 1984) and the bismaleimide monomers (CRIVELLO 1976) were as described in the previous publications.

Gel Time Studies

Gel time measurements were conducted with the aid of a Sunshine Gel Meter equipped with a constant temperature bath. Measurements were made at 150°C using equimolar (0.01 mol) amounts of bismaleimides and 2 weight % of various free radical initiators.

Reactivity Ratios

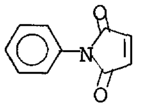
Into polyethylene lined screw cap vials there were placed varying ratios of N-phenyl maleimide and (2-vinyloxyethoxy)benzene keeping the total concentration of the two monomers at 0.02 mol. To the monomers there were added 0.001 mol benzoyl peroxide and 5 mL benzene. The samples were immersed in a constant temperature bath at 100°C for 5 minutes and then quenched in an ice bath. The polymers were isolated by pouring the samples into methanol followed by filtering the precipitated polymers, washing with fresh methanol and drying overnight at 60°C in vacuo. The composition of the polymers was determined by ^{1}H-NMR using a Varian EM 390 Nuclear Magnetic Resonance Spectrometer. From the areas of the band at 3.8 ppm assigned to the methine protons and the band at 6.7-7.5 ppm due to the aromatic protons of both monomers, the content of both monomers in the polymer can be calculated.

Molding Compounds Studies

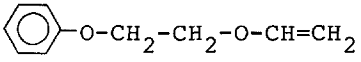
Combined together were equimolar quantities of the bisvinyl or bispropenyl ethers and the bismaleimide. The two materials were heated together at 80-100°C on a 2 roll mill to form a homogeneous melt, and then, respectively, 1 and 50 weight % t-butylperbenzoate and inorganic filler were added. The resulting melt was cooled and then granulated to form the molding compound. Test specimens were transfer molded using a 12 ton Hull press. Property measurements were carried out on the test specimens according to ASTM standards. HDTUL measurements were performed on standard bar specimens at 264 psi with a heating rate of 2 degrees per minute. A Du Pont 950 Thermal Analyzer was employed for the thermogravimetric analysis measurements at a heating rate of 10 degrees per minute.

Results and Discussion

As a prototype of our intended matrix forming system, the copolymerization of the model compounds N-phenylmaleimide (M_1) and (2-vinyloxyethoxy)benzene (M_2) was carried out.



M_1



M_2

Using the method of Fineman and Ross (FINEMAN and ROSS 1950), the respective copolymerization parameters were determined and were, respectively, $r_1 = 4.3$, $r_2 = 0.01$. Since the value of the product of r_1r_2 is very near zero, one can expect essentially an alternating copolymerization to occur between these two monomers.

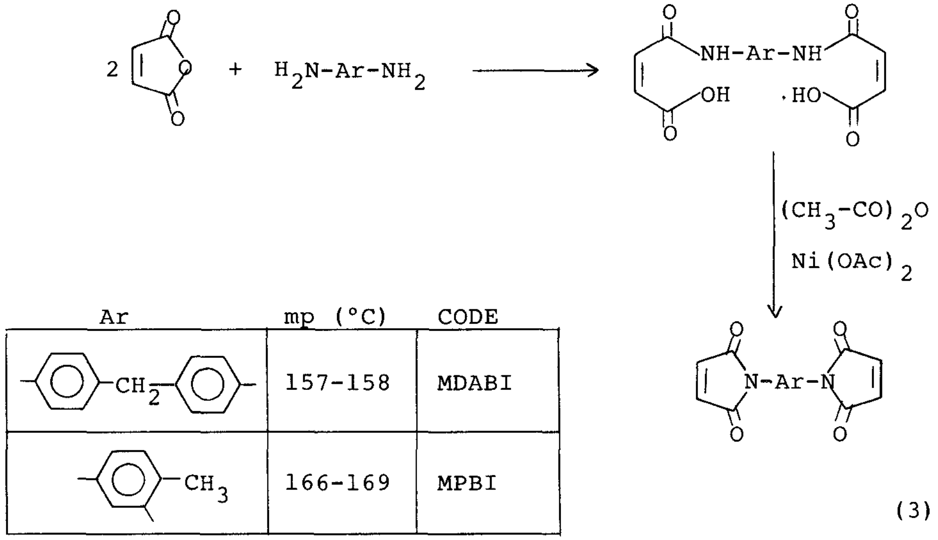
In two recent publications we have reported the synthesis and characterization of aromatic containing bisvinyl ethers (CRIVELLO and CONLON 1983) and bispropenyl ethers (CRIVELLO and CONLON 1984). The former compounds can be readily prepared as shown in equation 1 by the phase transfer catalyzed condensation of bisphenols with 2-chloroethyl vinyl ether (GALLUCCI and GOING 1983).

$$HO\text{-}Ar\text{-}OH \;+\; 2\,Cl\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CH_2 \xrightarrow[NaOH]{(n\text{-}Bu)_4N^+\;Br^-} CH_2{=}CH\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Ar\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CH_2 \tag{1}$$

Aromatic containing bispropenyl ethers can be obtained by isomerization of the corresponding bisallyl ethers in the presence of a strong base or certain transition metal catalysts as depicted in equation 2.

$$(CH_2{=}CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O)_2Ar \xrightarrow{cat.} (CH_3\text{-}CH{=}CH\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O)_2Ar \tag{2}$$

In the present communication, we have elected to limit our investigation to only two monomers: the bisvinyl ether (BPADVE) and bispropenyl ether (BPADPE) derived from bisphenol-A. BPADVE is a pure crystalline monomer with a melting point of 57-58°C, while BPADPE is a mixture of all three geometric isomers (cis-cis, cis-trans and trans-trans). The two bismaleimide monomers used in this work were prepared as shown in equation 3 (CRIVELLO 1976) by the nickel acetate catalyzed cyclodehydration of their bismaleamic acid precursors.



Ar	mp (°C)	CODE
$-C_6H_4-CH_2-C_6H_4-$	157-158	MDABI
CH_3	166-169	MPBI

(3)

Mixtures of bismaleimides and bisvinyl ethers or bispropenyl ethers can be copolymerized together using a wide variety of free radical initiators. At temperatures greater than 100°C, homogeneous melts of these monomers were obtained which in the presence of AIBN or benzoyl peroxide rapidly polymerized to hard glassy masses. These observations suggested potential applications for these materials as high temperature casting, molding and laminating resins. To obtain some semiquantitative data on the rate of polymerization in these systems, a study of the influence of various free radical initiators on the gel time of equimolar mixtures of MDABI and BPADVE were conducted. The results of this study are shown in Table 1.

TABLE 1

The Polymerization of Equimolar Mixtures of BPADVE and MDABI Using 2% Various Radical Initiators at 150°C

Experiment	Peroxide	Gel Time (min)
1	AIBN	1.0
2	benzoyl peroxide	2.9
3	benzopinacole	4.5
4	t-butyl hydroperoxide	4.3
5	t-butyl perbenzoate	3.0

At 150°C, crosslinking occurs very rapidly in the presence of these initiators. Clearly, those initiators (AIBN and benzoyl peroxide) having the lowest decomposition temperatures give the shortest gel times. These data suggest that it should be possible to adjust the rate of crosslinking in such resins by appropriate selection of the initiator and polymerization temperature. All the resins shown in Table 1 were pale yellow, hard, glassy materials which were completely insoluble in all solvents. Figure 1 depicts the thermogravimetric analysis curve of a cast sample of one of these resins which was determined in air and nitrogen. The results indicate that these materials have good stability up to 300-350°C.

Since cast samples were extremely brittle and too glassy to obtain reproducible mechanical properties, it was decided to combine these resins with various fillers and evaluate them as molded samples. Accordingly, formulations were compounded on a 2 roll mill at 80-100°C and then molded for 2 minutes under 600 psi pressure in a 12 ton Hull transfer press. Specimen bars were initially test molded to determine processibility and also to measure the heat distortion temperatures (HDTUL) of the copolymer resins which were taken to be an indication of the crosslink density. These results are given in Table 2.

TABLE 2

Heat Distortion Data on Several Vinyl Ether-Maleimide Molding Compounds*

Molding Cmpd.No.	Vinyl Ether	Maleimide	Filler	HDTUL(°C)
1	BPADVE	MDABI	Silica	> 220
2	BPADVE	MDABI	$CaCO_3$	> 220
3	BPADVE	MPBI	Silica	> 220
4	BPADPE	MDABI	Silica	180

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*Molding compound composition: 48% resin, 50% filler and 2% t-butyl perbenzoate

The above test data were especially encouraging for molding compounds 1 and 3, and these materials were selected for further evaluation. A number of molded test specimens were then prepared from these materials for thermal and mechanical property evaluation. The data gathered in these studies are entered in Table 3.

TABLE 3

Mechanical Data on Vinyl Ether-Maleimide Silica Filled Molding Compounds

Temp(°C)	Flex (psi) Str.	Flex (psi) Mod.	Tensile (psi) Str.	Tensile (psi) Mod.
Molding Compound 1				
25	8,843	2.02×10^6	2,554	9.04×10^5
150	-	-	2,027	-
180	-	-	2,077	-
Molding Compound 3				
25	10,099	1.69×10^6	4,947	1.22×10^6
150	-	-	3,066	-
180	-	-	2,017	6.98×10^5

As noted, the mechanical properties remain essentially the same even at 180°C. At the same time, the isothermal weight loss studies conducted in air at 250°C show a weight loss of only 1% after 4 hrs. From these data it may be concluded that these copolymer resins are a new class of polyimide based materials with very good mechanical properties and thermal capabilities which exceed those of epoxy resins and are at least on a par with commercial bismaleimide resins. In addition, the low melting points of the monomer mixtures together with their excellent solubility in a wide variety of common low boiling solvents give these new copolymer matrix resins the advantage of excellent processing characteristics and suggest potential applications, particularly in fiber reinforced composites. Work is currently in progress at this laboratory to explore the use of these new materials in several application areas.

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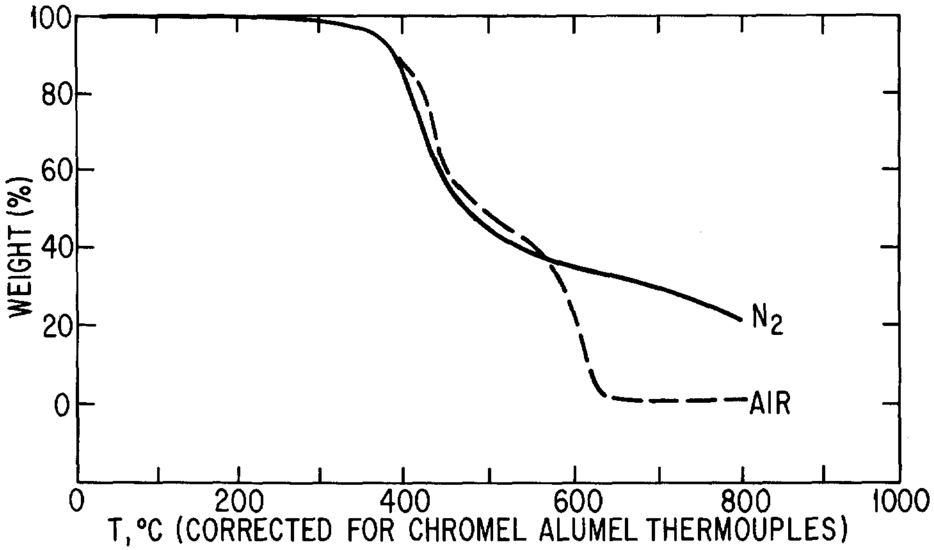

Figure 1. Thermogravimetric analysis curve of cast sample of an equimolar mixture of BPADVE and MDABI containing 1.8% by weight t-butylperbenzoate. Cured 5 h at 130°C and 1.5 h 180°C.

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