Modification of Unsaturated Polyester Resin with Bismaleimide

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ABSTRACT: The modification of a commercially available unsaturated polyester resin with 4,4′-bismaleimidodiphenylmethane is presented. The properties of the modified resins were compared with those of the nonmodified resin, and the resins were characterized in the noncured state and after curing. The results indicate that the addition of bismaleimide to unsaturated polyester resin not only improves its properties but also accelerates the curing reactions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2003–2007, 2001

Key words: unsaturated polyester resins; bismaleimides; chemical modification; mechanical properties

INTRODUCTION

Unsaturated polyester resins are well known as commercially available polymeric materials with numerous applications. They are employed in the manufacturing of a broad range of products, such as structural parts of automobiles, building materials, coating materials, and engineering plastics.[1–6]

Unfortunately, these resins contain ester groups in their chains, especially maleate and phthalate groups, that are characterized by a relatively high sensitivity to hydrolysis with respect to, for instance, vinyl esters containing methacrylic esters. Additionally, acidic and alcoholic chain ends of the resins are also chemically sensitive. Consequently, an embrittlement of fiber-reinforced unsaturated polyester composites exposed to wet media occurs. Moreover, the shrinkage of polyester resins during crosslinking with a reactive solvent, such as styrene, leads to warping and cracking.[7,8]

For improving the mechanical properties of resins and the laminates derived from them, different modification methods are applied. One of them consists of blending unsaturated polyester resins with suitable polymeric or nonpolymeric additives.[9] Another is connected to the chemical blocking of functional chain end groups by reactive compounds, such as diisocyanates.[10–12] Abbate et al.[13] proposed the use of a coreactive second component to obtain resins with glass-transition temperatures and rigidity values higher than those of nonmodified unsaturated polyester resin. In their work, bismaleimide was used as a second reactive component. They concluded that the mechanism of the curing process is governed by the presence of bismaleimide.

Bismaleimides are monomers typically used in the preparation of high-temperature polymers. The obtained polymers possess excellent thermal stability, up to 300–350°C, and fatigue resistance even at high humidity.[14–17] Their main disadvantage is associated with the relatively brittle properties of the pure resin.[18–20]

In this work, the modification of unsaturated polyester resin with 4,4′-bismaleimidodiphenyl-
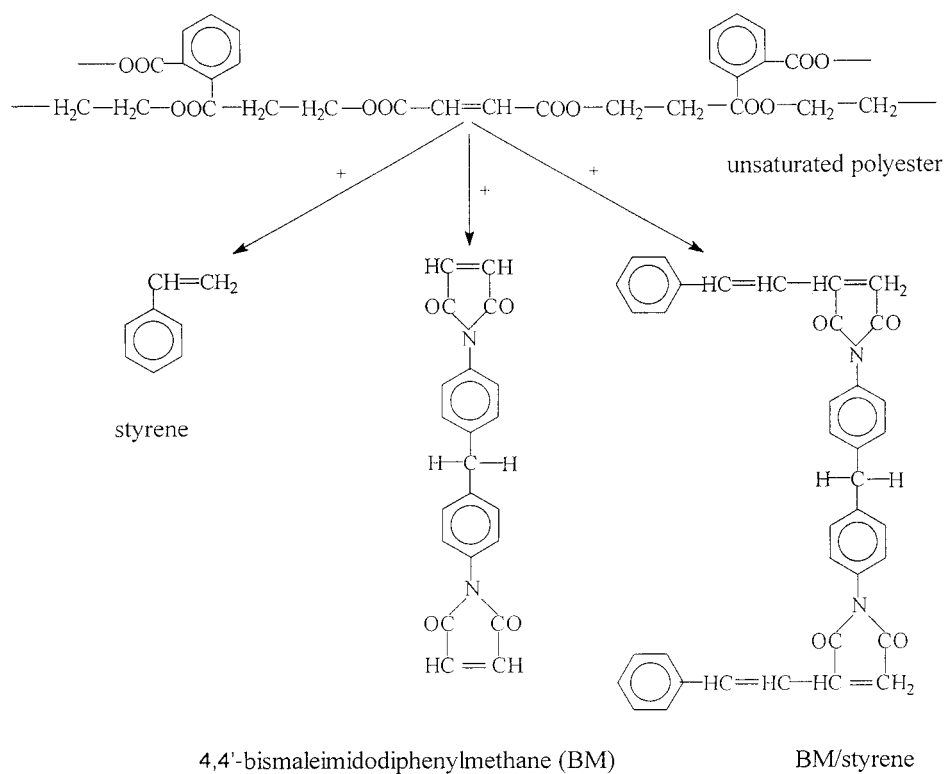
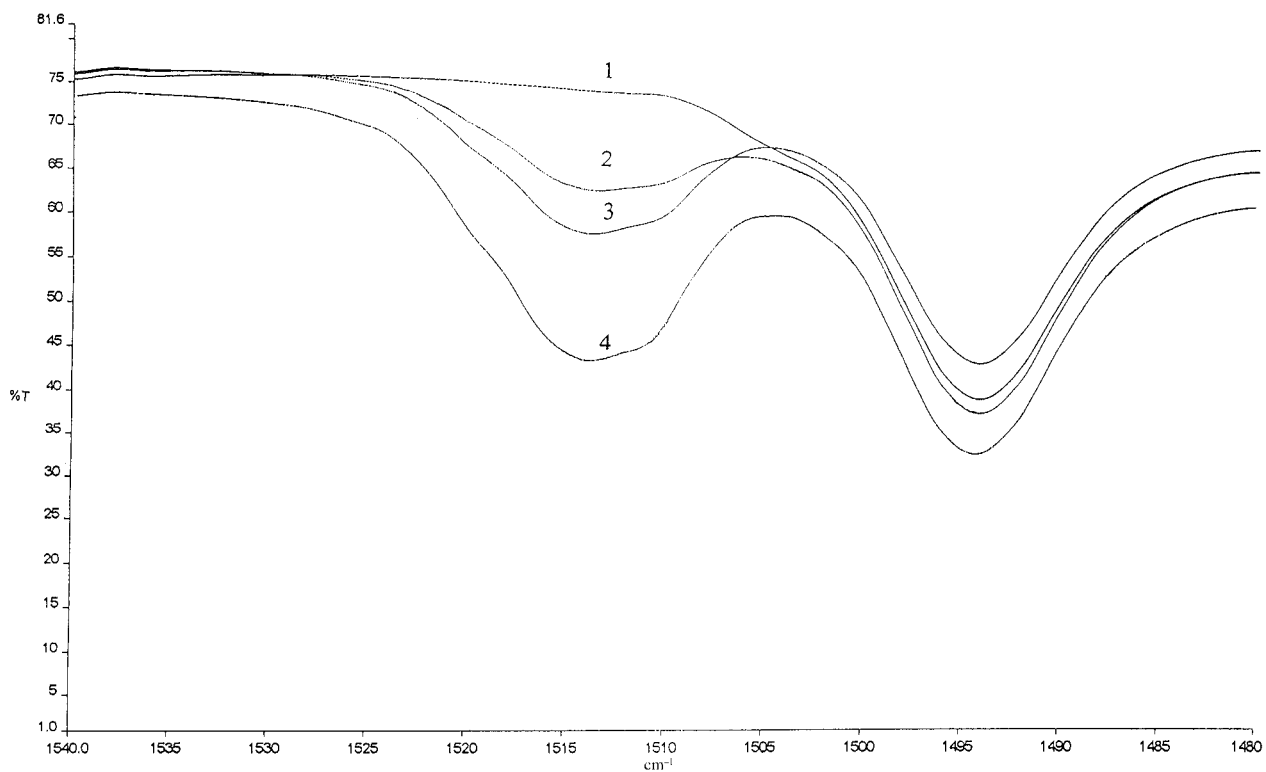**Figure 1** Possible reactions among the unsaturated polyester, styrene, and BM.

Figure 2 FTIR spectra of (1) the nonmodified resin, (2) the resin modified with 5% BM, (3) the resin modified with 10% BM, and (4) the resin modified with 15% BM.

Table I   Results of CHN Analysis

Resin Number	BM Concentration (%)	C (%)	H (%)	N (%)	N Calculated (%)
1	0	59.89	5.27	0	0
2	5	60.68	4.76	0.38	0.40
3	10	58.30	4.65	0.77	0.81
4	15	54.16	4.35	1.09	1.22

methane (BM) is presented. The properties of the resins before and after curing were studied. As a reference material, a nonmodified unsaturated polyester resin was used.

EXPERIMENTAL

Materials

The unsaturated polyester was kindly provided by the Polifarb–Becker Chemical Plant (Dębica, Poland). It is a typical orthophthalic prepolymer used for manufacturing a commercial unsaturated polyester called D-1103. BM was procured from Aldrich (Deisenhofen, Germany). Styrene and benzoyl peroxide were bought from Merck (Schuchardt, Germany), whereas Luperox (a 50% solution of methyl ethyl ketone in dimethyl phthalate) was from Luperox (Günzburg, Germany). Cobalt octoate (a 1% solution in styrene) was from POCh (Gliwice, Poland).

Preparation Procedure and Curing Conditions

A typical modification procedure was as follows. BM (5 g) was dissolved in 55 g of unsaturated polyester during its heating to 190°C. The homogeneous solution was maintained at this temperature for 0.5 h while being stirred. The hot solution was then poured into molds for solidification.

In the presence of benzoyl peroxide, BM reacts with unsaturated polyester immediately. The reaction initiated by cobalt octoate and Luperox was more gentle. In both reactions, crosslinked products insoluble in styrene were obtained. Thus, in further experiments the following procedure was applied: in the first step, homogeneous solutions of BM in unsaturated polyester were obtained, and in the second step, they were dissolved in styrene.

In this way, three polyester solutions containing 5, 10, and 15% BM were obtained. Attempts to obtain unsaturated polyester containing 20% BM failed because each time at 190°C the reactor contents gelated.

The obtained solids were dissolved in styrene; 60 wt % solutions were obtained. As a reference material, a styrene solution from pure unsaturated polyester of the same concentration was prepared.

All the studied resins were crosslinked at room temperature with 2% Luperox and 0.1% cobalt octoate for 18 h and then for 4 h at 100°C. The resins modified by BM were additionally postcured at 150°C for 4 h.

Characterization

The resins were characterized in a noncrosslinked state, during curing, and after crosslinking. In a noncrosslinked state, the density (Polish Standard PN-86/C-89082/03) and viscosity (Polish Standard PN-86/C-89082/04) were determined.

The gelation times of the resins were measured in a temperature-controlled bath (25°C) according to Polish Standard PN-75/C-89082.

The chemical structure of the resins in a crosslinked state was confirmed by elemental

Table II   Assumed and Actual Composition of the Resins

Resin Number	BM Concentration (%)	
	Assumed	Actual
1	0	0
2	5	4.7
3	10	9.5
4	15	13.3

Table III   Properties of the Resins Before Curing

Resin Number	Density (g/cm^3)	Viscosity (mPa)	Gelation Time (min)
1	1.10	220	15
2	1.11	260	6
3	1.11	300	5
4	1.12	350	4

CHN and Fourier transform infrared (FTIR) analyses. The CHN analysis was made on a PerkinElmer (Palo Alto, CA) CHN 2000 analyzer, whereas IR spectra were determined on a PerkinElmer 1700 FTIR spectrometer with KBr pellets.

Glass-transition temperatures were determined from the second run with a Netzsch DSC 200 differential scanning calorimeter (Netzsch, Germany). The conditions were as follows: a sample weight of about 10 mg, a nitrogen atmosphere, and sealed aluminum pans. As a reference, an empty aluminum pan was used. The resins were heated in a scanning mode from 20 to 300°C at a rate of 10 K/min.

The ball indentation hardness was determined according to Polish Standard PN-84/C-89030.

RESULTS AND DISCUSSION

Figure 1 shows possible reactions among BM, styrene, and unsaturated polyester.

Our results indicate that BM reacts with unsaturated polyester at high temperatures without any chemical initiator. This phenomenon is especially apparent for higher concentrations of BM. In the presence of styrene, competitive reactions take place: polyester crosslinking by BM, polyester crosslinking by styrene, and polyester crosslink-

ing by BM–styrene sequences formed in the early stages of polymerization.[13] Figure 2 shows the spectra of the parent resin and three modified resins in a cured state. In the spectra of the modified resins, a doublet band at 1500–1530 cm^{-1}, typical for the imide group, is visible, whereas in the spectrum of the nonmodified resin, this band is not present. The intensity of this band increases with the increase in the BM concentration in the resin.

The reaction between unsaturated polyester and BM was also confirmed by the CHN analysis. The results presented in Table I allow us to calculate the real composition of the resins from the nitrogen concentrations. From the data in Table II, one can see that only for the resin containing the smallest amount of BM is the real composition close to that assumed. For samples of higher BM concentrations, some differences occur. In these resins, the real concentration of BM is smaller than expected.[21]

In Table III, the properties of the resins before curing are presented. The gelation times indicate that the addition of BM accelerates the polymerization process significantly.

The properties of the resins after curing are presented in Table IV. From these data, one can see that modification with BM has an important influence on the thermomechanical properties of the resins. Glass-transition temperatures for the modified resins exceed 180°C, whereas for the nonmodified one, the glass-transition temperature is 78.4°C. Moreover, the hardness of the modified resins is greater. The observed effects are caused by the addition of BM. As a tetrafunctional compound, it increases the resin crosslinking degree. Its addition also has an influence on the final resin hardness because BM units are considerably stiffer than the styrene bridges.

The results presented here indicate that the addition of BM to unsaturated polyester resin not

Table IV   Properties of the Cured Resins

Resin Number	Ball Indentation Hardness (MPa)	Initial Decomposition Temperature (°C)	Glass-Transition Temperature (°C)
1	144.4	200	78.4
2	150.3	220	179.9
3	156.5	240	181.9
4	159.3	280	184.1

only improves its properties but also accelerates the polymerization process.

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