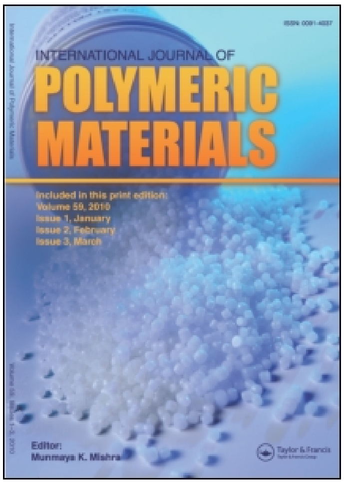

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Patel, H. S. and Panchal, K. K.(2005) 'Novel Unsaturated Polyester Resins Containing Epoxy Residues', International Journal of Polymeric Materials, 54: 1, 1 — 7

To link to this Article: DOI: 10.1080/00914030390224247

URL: http://dx.doi.org/10.1080/00914030390224247

International Journal of Polymeric Materials, 54:1–7, 2005
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390224247

NOVEL UNSATURATED POLYESTER RESINS CONTAINING EPOXY RESIDUES

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Novel unsaturated polyester resins (UPEs) were prepared by reaction of diglycidyl ether of bisphenol–A (DGEBA) with unsaturated bisamic acids. These UPEs were characterized by elemental analysis, molecular weight determination by non-aqueous conductometric titrations, and thermogravimetry. The curing of these UPEs was carried by using benzoyl peroxide (BPO) as catalyst and monitored by differential scanning calorimetry (DSC). Based on DSC study, glass fiber reinforced composites (i.e., laminates) of these UPEs have been fabricated and their chemical, mechanical, and electrical properties evaluated.

Keywords: DGEBA, UPE, bisamic acid

INTRODUCTION

It is well known that epoxy resins, polyamides, and unsaturated polyester resins (UPEs) are independent polymer candidates for a wide range of industrial applications like composites, inks, paints, films, and so on [1–10]. Merging of all the three,—epoxy, amide, and UPE—segments into the polymer chains has not received attention academically and technically. Merging of all three segments into the polymer chains may alter the properties of polymer to some extent. Hence it was thought interesting to study the novel unsaturated polyester resin. The present article comprises the study of UPEs based on epoxy

Received 4 April 2003; in final form 15 April 2003.

The authors thank Dr. R. M. Patel, Head of the Department, for providing research facilities. The authors are grateful to Atul Ltd., Valsad, India for sanctioning the grant for the work as well as fellowship to one of the authors (KKP).

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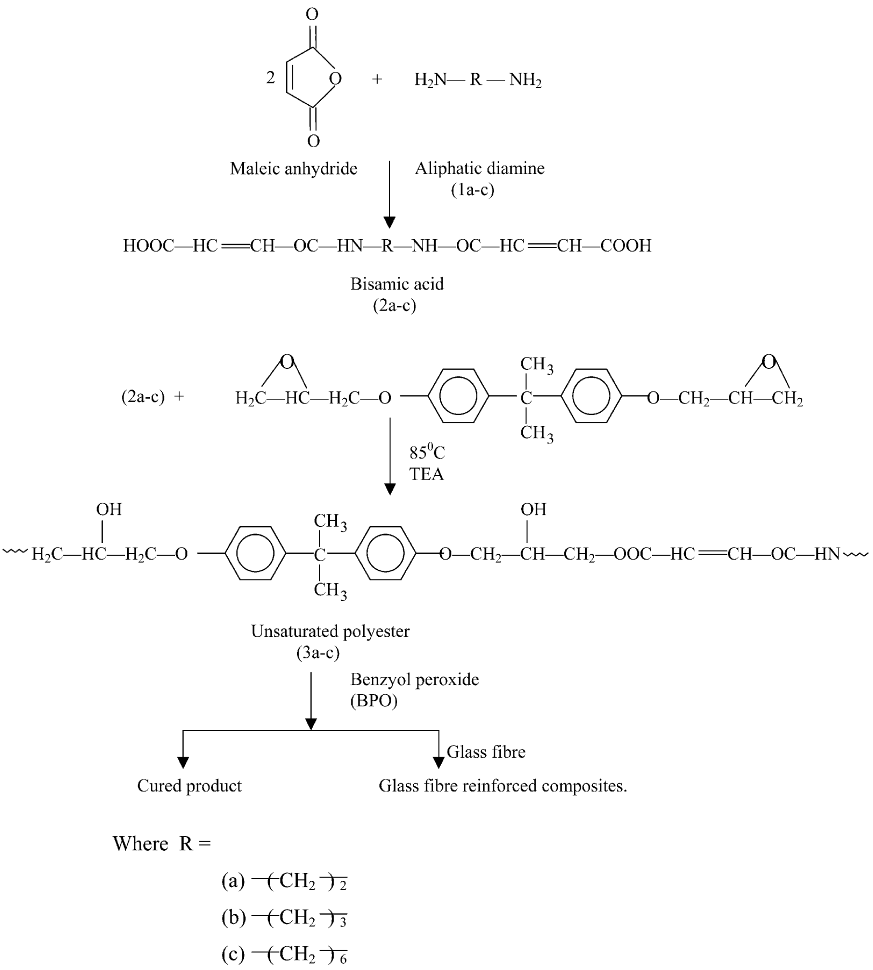

SCHEME 1

resin and bisamic acid obtained from maleic anhydride and aliphatic diamines. The synthetic steps are shown in Scheme 1.

EXPERIMENTAL

Materials

Commercial epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) was obtained from Synpol Products Ltd.

The specifications of DGEBA are as follows.

1. Epoxy equivalent weight, 190.
2. Viscosity 40–100 poise at 25°C.
3. Density at 25°C, 1.16–1.17 $g \cdot cm^{-1}$

The diamines used for bisamic acids are

1. Ethylene diamine,
2. Propylene diamine, and
3. Hexamethylene diamine.

All other chemicals used were of laboratory grade.

Synthesis of Unsaturated Bisamic Acids

These were prepared by using a method reported in the literature [11–12]. The general procedure is as follows:

To a well-stirred solution of maleic anhydride (2.0 mole) in acetone, a solution of diamine (mentioned earlier) (1.0 mole) in acetone was gradually added at 0–5°C. The addition of diamine is completed within half an hour. The resulting bisamic acid was filtered, washed with acetone, and air-dried. The structures of all three bisamic acids (now designated as unsaturated bisamic acids) are given in Scheme 1.

Synthesis of Unsaturated Polyester Resin (UPE)

Epoxy resin (DGEBA) (1.1 mole) and unsaturated bisamic acid (1.0 mole) (2a–c) were mixed well by vigorous agitation. A little ether solvent was added for good suspension. Then, triethyl amine (TEA) (8% of total weight) was added as a catalyst. The resulting mixture was heated to 85°C with continuous stirring. Samples were taken at regular intervals to check the acid value. The reaction was continued till the acid value fell below 55 mgKOH/gm. The resin was then discharged.

The three resins were obtained in the form of semi-solid mass and their details are furnished in Table 1.

COMPOSITE FABRICATION

The composites were prepared by using glass fiber. The glass fiber: resin ratio is 60:40. (30% UPE resin + 10% DGEBA.)

TABLE 1 Characterization of UPEs

UPE sample	Elemental analysis (wt%) Calc./(Found) %C	%H	%N	No. of double bonds	IR spectral features (cm^{-1}) –OH	–CH2	–COO	Number average molecular weight ($\overline{M}n$)
3a	62.41 (62.25)	4.96 (4.50)	6.04 (5.95)	1.9	3500–2600	2850–2920	1680	3755
3b	62.95 (62.80)	4.59 (4.50)	6.23 (6.20)	1.9	3500–2600	2850–2920	1680	4085
3c	64.42 (64.30)	4.29 (4.10)	6.75 (6.65)	2.0	3500–2600	2850–2920	1680	4240

A suspension of UPEs (3a–c) was prepared in terahydrofuran (THF). To this syrup 1% of ethylene dimethacrylate and 0.05% of benzoyl peroxide (BPO) was added. This syrup was well stirred for about 5 min. The suspension mixture was applied with a brush to a 15 cm × 15 cm glass fiber mat and the solvent was allowed to evaporate. The dried prepregs were stacked on top of one another and pressed between steel plates coated with a Teflon film release sheet and compressed in a flat press under 70 psi pressure. This prepreg stack was cured by keeping it in an autoclave oven at 140°–150°C for about 8 h. The composites so obtained were cooled to 50°C before the pressure was released. The composites were then machined to final dimensions. The unreinforced material, which spread outside the fabricated composite, was collected and crushed into fine powder.

MEASUREMENTS

The C, H, N contents of all the UPEs were estimated by means of Carlo Erba elemental analyzer (Italy). The IR spectra were recorded in KBr pellets on a Nicolet 400 D spectrophotometer. The data are presented in Table 1.

The number of average molecular weights of all the UPEs were estimated by nonaqueous conductometric titration following the method reported in the literature [13]. Pyridine was used as a solvent and tetra-n-butyl ammonium hydroxide was used as a titrant.

Curing

Curing of UPEs was carried out in a differential scanning calorimeter (DSC). A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H = 28.45$ J/g). Curing was carried out from 30°–300°C at 10°C min^{-1} heating rate. The sample weight for this investigation was in the range of 4–5 mg and an empty cell was used as a reference.

Unreinforced cured samples were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermogravimetric analyzer in air at a heating rate of 10°C min^{-1}.

Chemical Resistance Test

The resistance against chemicals of the composite sample was measured according to ASTM D 543.

Mechanical Testing

All mechanical testings were performed using three test specimens.

- The compressive strength was measured according to ATM D 695.
- Impact strength was measured using Izod type impact tester at room temperature, according to the method of ASTM D 256.
- The Rockwell hardness was measured according to the ASTM D 785.
- Measurement of the dielectric strength was carried out on a high voltage tester machine oil test set.

RESULT AND DISCUSSION

The bisamic acids were obtained by the reaction of maleic anhydride and diamine following the reported method [11–12]. The bisamic acids were then treated with DGEBA (a commercial epoxy resin) according to the method reported for reaction of epoxy group and carboxylic group [14]. The resultant UPEs were then characterized by elemental analysis. The values of C, H, N of each of the UPEs were consistent with its predicted structure. The unsaturation was also determined and confirmed the two double bonds in a repeating unit. The number average molecular weight ($\overline{M}n$) of these resins were determined by nonaqueous conductometric titration and their values of ($\overline{M}n$) are furnished in Table 1. This indicates that the D_p of these polymers is about 6. The IR spectra, not shown, of all UPEs show the prominent positions of important segments in the polymer chain. The broad band from 3600–2500 cm^{-1} with inflexions at 2850–2920 cm^{-1}. The broad band mainly due to secondary –OH groups. This is supported by the strong band at 1100 cm^{-1}. The inflexions are raised from $-CH_2$ groups present in both epoxy and aliphatic diamines. The bands due to

TABLE 2 DSC Curing of Unsaturated Polyester Resins

	Curing temp. (T°C)		
UPE sample	T_k	T_p	T_f
3a	100	128	148
3b	98	126	146
3c	95	123	140

presence of aliphatic segments are at their respected position. The only discernible difference between spectra of epoxy resin and UPE reveals that the band at 910 cm^{-1} appeared in the spectrum of epoxy group is almost vanished in the spectra of UPEs and a new band appeared at 1680 cm^{-1} from ester group. This confirms the reaction between DGEBA and bisamic acid.

The UPE resins (3a–c) were cured by using benzoyl peroxide as a catalyst. The data of DSC thermograms of all the resins are furnished in Table 2.

The unreinforced cured UPE resins (3a–c) products were also analyzed by thermogravimetric analysis (TGA). TGA data of all the cured samples are shown in Table 3. The results reveal that the cured samples start their degradation at about 150°C and their initial weight loss is about 2%. This small weight loss may be due to either insufficient curing of components used or due to the catalyst used. A weight loss of about 10% is found at 300°C. However, the rate of decomposition increases very rapidly between 300°C to 450°C and the products are lost completely beyond 750°C.

Glass fiber reinforced composites of all UPE resins (3a–c) were cured at temperatures based on DSC data. The laminates have good chemical resistivity. The mechanical strength of the laminates is also good. Their details are furnished in Table 4.

TABLE 3 TGA of Unreinforced Cured Sample of UPE's Resins

	% Weight loss at various temp. (°C) from TGA				
UPE sample	150	300	450	600	750
3a	2.00	9.00	73.50	80.50	84.00
3b	2.05	8.90	73.00	80.10	84.00
3c	1.95	9.00	73.00	80.10	83.50

TABLE 4 Chemical, Mechanical, and Electrical Properties of Glass Fiber Reinforced Composites of Unsaturated Polymer Resins

UPE composite	Chemical resistance* % change in Thickness	Weight	Impact strength (MPa)	Compressive strength (MPa)	Rockwell hardness (R)	Electrical strength in air (kV/mm)
3a	0.9	1.2	410	400	79	19.7
3b	0.9	1.1	405	395	75	20.3
3c	0.88	1.0	390	386	64	21.9

*Chemical resistance to alkali (25% w/v NaOH); composites are unaffected by common organic solvent and concentrated mineral acids (25% v/v). Conditions reinforcement; E type glass cloth, plain weave, eight layers; resin content; 40% curing temperature: 140°C; curing time; 84°C; curing pressure 70 psi.

The results of these novel unsaturated polyester resins suggest that these resins can be competitors to commercial unsaturated polyester resins. Further work in connection with the blending of UPEs with vinyl monomers is under progress.

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