Synthesis, properties, and applications of urethane-modified acrylated poly(ester-amide)s

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Abstract Epoxy resin-based unsaturated poly(ester-amide) resins (UPEAs) were treated with acryloyl chloride to afford acrylated UPEAs resins (AUPEAs). Ure-thane-based acrylated poly(ester-amide)s prepared by reaction with diisocyanate were characterized by elemental analysis, by molecular weight determination (by vapour pressure osmometry), by IR spectral study, and by thermogravimetry. The curing of interacting blends was monitored by differential scanning calorimetry (DSC). On the basis of DSC data in-situ glass-reinforced composites were prepared from the resulting materials and their mechanical, electrical, and chemical properties were characterized. Unreinforced blends were characterized by thermogravimetry.

Keywords Unsaturated bisamic acid \cdot Epoxy resin \cdot Urethane \cdot Unsaturated poly(ester-amide) resins (UPEAs) \cdot Acrylation thermogravimetry \cdot Glass-reinforced composites

Introduction

Polyesters and polyamides have specific properties which result in applications ranging from aerospace to microelectronics. They are also used as laminating resins, moulding composites, fibres, films, surface-coating resins, and fibre cushions. Polyamide materials are thermoplastics and are used, especially in the form of fibres, in engineering applications. Glass fibre-reinforced nylon plastics are now of substantial importance because of their rigidity and creep resistance. Because polyamides are also used in other fibre applications, in the automotive industry, and

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as valve covers and coatings, many researchers [1–8] have synthesized co-poly(ester-amide)s from different raw materials to obtain specific properties of different materials all in the same product.

Because of their special properties, polyurethanes are widely applied as insulating materials in the electrical industry. Coating of magnet wire with polyurethane varnish is one of the most important uses of polyurethane insulating materials. The property which has led to the popularity of polyurethane-enamelled magnet wire is solderability at 360–425 °C without the need for fluxing or stripping. Another feature of polyurethane-insulated wire is its superior Q factor (reciprocal of dissipation factor, DF).

Merging of all these unsaturated epoxy, ester, urethane, and amide groups in one polymer chain has not received academic and technical attention. Specific properties of thermoplastics may also be improved by blending. Addition to an unsaturated resin is another possibility.

To improve the specific properties of such poly(ester-amide)s it was thought interesting to study urethane modification. The work is summarised in Scheme 1.

Materials and methods

Materials

Commercially available epoxy resin, the diglycidyl ether of bisphenol-A, and vinyl ester epoxy resin were obtained locally.

The specification of the diglycidyl ether of bisphenol-A (DGEBA) was:

- 1. epoxy equivalent weight, 190
- 2. viscosity 40–100 poise at 25 °C
- 3. density at 25 °C, 1.16-1.17 g/cm

The aromatic diamines used for preparation of unsaturated poly(ester-amide) resin were:

- 1. 4,4'-methylenedianiline
- 2. 4,4'-oxydianiline
- 3. 4,4'-sulfonyldianiline

Plain-weave fibres in the form of E-glass woven fabric (poly(ester-amide)compatible) 0.25 mm thick, of mass 270 g m⁻² (Unnati Chemicals, India) were used for fabrication of composites. All other chemicals used were of pure grade.

Synthesis of unsaturated bisamic acids

Unsaturated bisamic acids were prepared by simple addition of maleic anhydride to diamines, at low temperature, in a beaker. The product was formed as a precipitate and was isolated by filtration. This method has been reported in the literature [8, 9].



Scheme 1 Synthesis steps

Synthesis of unsaturated poly(ester-amide) resins and acrylated poly(esteramide) resins

Unsaturated poly(ester-amide) resins (UPEAs) were prepared by the method reported for the reaction of epoxy resin with a carboxyl group. The diglycidylether

Composite	% Change on exposure to 25 % (w/v) NaOH		Compressive strength (MPa)	Impact strength	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight		(MPa)		
5a	0.78	1.07	460	424	111	22.65
5b	0.81	1.10	467	456	104	19.45
5c	0.79	1.02	478	447	106	23.35

Table 1 Chemical, mechanical, and electrical properties of the composites

of bisphenol-F (DGEBF) (1.0 mol) and unsaturated bisamic acid (1.0 mol) were placed in a three-necked flask equipped with a mechanical stirrer, and triethylamine (TEA), 8.0 % of the total weight, was added as basic catalyst. The reaction mixture was slowly heated to 85 °C with continuous stirring until the acid value fell below 60 mg KOH/g. The resulting resins were denoted unsaturated poly(ester-amide) resins (UPEAs); their properties are listed in Table 1. These unsaturated poly(ester-amide) resulting products were denoted acrylated poly(esteramide)s (APEAs) [1].

Synthesis of urethane-containing acrylated poly(ester-amide)s

Urethane-modified acrylated poly(ester-amide)s were prepared in accordance with Scheme 1. A stoichiometric mixture of X, Y, and the diisocyanate was placed, under an inert atmosphere, in a three-necked flask equipped with a mechanical stirrer. The flask was immersed in an oil bath and mechanical stirring was continued until the appropriate viscosity was obtained.

Analysis and thermal study

Elemental analysis

The C, H, N content of the unsaturated poly(ester-amide)s (UPEAs) and the acrylated poly(ester-amide)s (APEAs) was estimated by means of a Thermofinnigan (Italy) 1101 flash elemental analyser. The IR spectra were recorded in Kerr pellets on a Nicolet 760 D spectrometer. The number average weight of the unsaturated poly(ester-amide)s (UPEAs) and the acrylated poly(ester-amide)s (APEAs) was estimated by non-aqueous conductometric titration by use of a method reported in the literature [10]. Pyridine was used as a solvent and tetra-*n*-butylammonium hydroxide was used as titrant.

Thermal study

Curing of all the samples, with benzoyl peroxide as catalyst, was performed on a Du Pont 900 differential scanning calorimeter (DSC). The instrument was calibrated

with standard indium metal with known heat of fusion ($\Delta H = 28.45 \text{ J/g}$). Curing was performed from 30 to 300 °C at 10 ° min⁻¹ heating rate. The sample weight used for this investigation was in the range 4–5 mg; an empty reference cell was used.

Unreinforced cured samples were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermogravimetric analyser in air at a heating rate of $10 \circ \text{min}^{-1}$. The sample weight used for this investigation was in the range 4–5 mg. The TGA and DSC data are shown in Figs. 1 and 2, respectively.

IR spectral characteristics of UPEAs

The IR spectra of all the UPEAs contained an intense band at approximately $1,730 \text{ cm}^{-1}$; this band is characteristic of the >C=O stretching of A,B-unsaturated esters (Fig. 3).

- 1. The spectra of all the resins contained the characteristic >C=O stretching band of the amide group at approximately 1,690 cm⁻¹ and the characteristic –NH band of the amide group between 1,550 and 1,510 cm⁻¹.
- 2. The spectra of all the resins contained the characteristic O–H stretching band of the secondary hydroxyl group between 3,600 and 3,200 cm⁻¹.
- 3. The spectra of all the resins contained the characteristic band of the ether group at approximately $1,260 \text{ cm}^{-1}$.
- 4. The spectra of all the resins contained a band at approximately $1,655 \text{ cm}^{-1}$ which may arise from a cis C=C stretching vibration.

Thus IR spectral analysis of the resins confirmed formation of the unsaturated poly(ester-amide)s.

Composite fabrication

The composites were prepared by use of E-type glass fibre. Composite fabrication was performed by our reported method [1].

Composite characterization

Chemical resistance test

The resistance of the composites to chemicals was measured in accordance with ASTM D 543.

Mechanical and electrical testing

Flexural strength, compressive strength, impact strength, Rockwell hardness, electrical strength, and tensile elongation were tested in accordance with the ASTM.



Fig. 1 TGA curves. **a** TGA of 4a, **b** TGA of 4b, **c** TGA of 4c







Fig. 3 a IR spectrum of 2a, b IR spectrum of 2b, c IR spectrum of 2c

The C, H, and N content of all the unsaturated poly(ester-amide)s (PEAs) and acrylated poly(ester-amide)s (APEAs), estimated by means of a Thermofinnigan (Italy) 1101 flash elemental analyser, were consistent with their predicted structures. The number-average molecular weights of the unsaturated poly(ester-amide)s (PEAs) and acrylated poly(ester-amide)s (APEAs), estimated by non-aqueous conductometric titration [10], indicated that the degree of polymerization of both materials was approximately 6. The IR spectra were consistent with those expected from the structures of the PEAs (3a–c) and APEAs (4a–c).

Numbers of hydroxyl groups present per repeat unit in unsaturated poly(esteramide)s (PEAs) was also analysed by use of the acetylating method [11]. The acrylated poly(ester-amide)s (APEAs) were also characterized for the presence of double bonds per repeat unit, by use of the mercury-catalysed bromate-bromide method [12]. Satisfactory results were obtained.

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