



ORIGINAL ARTICLE

Glass fiber reinforced composites of phenolic–urea–epoxy resin blends

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Abstract The present work aims to modify conventional epoxy resin by blending with four different phenolic–urea oligomers. These oligomers are similar to phenolic–urea resin matrix and simultaneously function as amino curing agent for epoxy matrix. In this context, phenolic–urea oligomers were prepared respectively by polycondensation reaction of four phenols namely phenol, m-cresol, resorcinol and 1,5-dihydroxy naphthalene, respectively with formaldehyde and urea in presence of acid catalyst. The resulting oligomers were characterized by elemental analysis, spectral studies (IR & NMR), number average molecular weight (\bar{M}_n) estimated by non-aqueous conductometric titration and thermal stability by thermogravimetric analysis (TGA). Each of these oligomers was used in resin matrix as a blending component for the modification of commercial epoxy resin for fabricating glass fiber reinforced laminates. Finally these laminates were evaluated for their synergetic thermal stability, mechanical properties and chemical resistance to different reagents.

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1. Introduction

Epoxy resins, one of the most important high performance thermosetting polymeric materials are used widely as polymer matrices for fiber reinforced composites and structural adhesives. Many applications of the epoxy resins usually require a high level of cross-linking which is influenced by the stoichiometric ratio and also the cure schedule. The result is a material with a brittle behavior and poor resistance to crack propagation (Hourston et al., 1997; Beier et al., 2008). Epoxies are one of the most commonly used polymers in diversity of applications as reinforced composites in load bearing and aerospace materials. The requirements of high quality and high performance of reinforced composites have provoked a new fundamental

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research in the field of resin synthesis and curing systems. Consequently over the last few decades, a great deal of work has been reported in the area of modification of conventional epoxy resin by preparing either blends or interpenetrating network of two different types of polymers or by chemical modification in chemical structure of conventional polymer. With reference to this, blending and curing of epoxy resin has been found as a successful method for polymeric material useful for industrial applications (Elis, 1993; Nguyen and Berg, 2008).

Conventional curing agents among a great number of compounds, may react with epoxy resins gradually even at ambient temperature. Problems with the storage of epoxy resins and with the tailoring of epoxy resin processing conditions can be encountered with the low reaction temperatures of conventional curing agents (Ashcroft, 1993). Lin et al. have prepared a series of low molecular weight products by polycondensation of phenol and its derivatives with formaldehyde and secondary amine and used in curing of epoxy resin. It was observed that such oligomeric offered fast curing profile even at low temperature due to diversity of multiple functionalities of phenol and amine. Further the resulting epoxy polymers showed enhanced flexibility and improved mechanical properties. On the basis of this, present work has been undertaken with a view to investigate systematically the behavior of phenolic–urea oligomers as a blending component structurally analogous to phenolic resin and simultaneously as amino curing agent in chemical modification of the epoxy resin matrix for glass fiber reinforced composites. It includes the synthesis of phenolic–urea oligomers by polycondensation of four different phenols namely phenol, m-cresol, resorcinol and 1,5-dihydroxy naphthalene respectively with formaldehyde and urea in acid medium. The resulting low molecular weight phenolic–urea oligomers were preliminary characterized by their solubility behavior, free phenol and free formaldehyde contents and number average molecular weight (\overline{M}_n). The structure of these phenolic–urea oligomers were elucidated by elemental analysis, IR and NMR spectral studies. The thermal behavior and isothermal curing of parent phenolic–urea oligomers and their corresponding blend with commercial epoxy resin was carried out in order to optimize the temperature for fabrication of glass fiber laminates. Glass fiber reinforced laminates of epoxy resin–phenolic–urea oligomers as resin matrices were fabricated by hand lay-up method and subsequently characterized by their thermal stability, chemical resistance against 9+ different chemical reagents and mechanical properties such as flexural strength, impact strength, Rockwell hardness (Ghaemy et al., 2007; Zhou et al., 2008).

2. Materials and methods

2.1. Chemicals

All the chemicals used in the present work were of analytical grade. Commercial epoxy resin used containing epoxy equivalent value 200. The Woven glass cloth used for reinforcement was E grade.

2.2. Synthesis of phenolic–urea oligomers

Phenol (0.2 mol) in 20 ml ethanol was charged in 250 ml three neck flask equipped with a stirrer, reflux condenser and dropping funnel. This solution, ethanolic solution of urea (0.2 mol) and 1 ml concentrated hydrochloric acid as catalyst

were added and the reaction mixture was stirred for 30 min. It was then cooled to temperature 5–10 °C in ice bath. To the cold 37% aqueous solution of formaldehyde (0.4 mol) was added drop wise in a period of 30 min with stirring. It was then kept at this temperature for another half an hour and reflux for 24 h. During the reaction time period 10 ml formaldehyde solution was added after every 8 h of the time interval. After completion of the reaction, ethanol was removed under vacuum and the resulting gummy oil was soaked in 0.1 ml hydrochloric acid solution overnight. The pH of the reaction mixture was adjusted to 7–8 by using 25% ammonia solution. The precipitated polymer was filtered off and washed with water, several times to remove unreacted formaldehyde, followed by ether to remove unreacted phenol and urea. It was dried in air. The other three phenolic polymers were prepared in the same manner respectively from m-cresol, resorcinol and 1,5-dihydroxy naphthalene. They are abbreviated as PU, CU, RU and NU. The general reaction protocol for phenolic–urea oligomers are shown in Scheme 1.

2.3. Composite fabrication

A typical method of fabrication of glass fiber reinforced composites is given below:

A suspension of commercial epoxy resin (30 gm) and a phenolic–urea oligomer (30 gm) was prepared in tetrahydrofuran and stirred for 5 min. This mixture was applied with a brush on 10 sheets of 150 × 120 mm woven glass cloth (E glass, 08 mill) and dried for 2 h. These 08 dried prepregs were stacked one over another and pressed between compression steel plates using Teflon sheet as mold releasing agent. It was then kept in an oven maintained at 160–170 °C temperature. Initially normal contact pressure was maintained and at the gel point pressure of 70 psi was applied. The composite so obtained was cooled to 50 °C before releasing the pressure.

2.4. Measurements

The free phenol and free formaldehyde content of all phenolic–urea oligomers were estimated by the method reported in literature (Feigl et al., 1961). The C, H, N contents of these four oligomers were determined by means of Carlo Erba Elemental Analyzer (Italy). Number average molecular weight (\overline{M}_n) of all phenolic–urea oligomers was determined by non-aqueous conductometric titration in pyridine as solvent and standard sodium methoxide in pyridine as titrant base. The (\overline{M}_n) values of each oligomer were calculated according to the method reported in literature (Chatterji and Gupta, 1971; Chatterji and Agrawal, 1971) and shown in Table 1.

The IR spectra of phenol–urea oligomers were scanned on Perkin–Elmer Lambda-19 FTIR spectrometer using KBr cell. NMR spectra of PU, CU and RU were scanned on Hitachi, R-1500, 60 MHz. FT-NMR spectrometer in CDCl₃ using TMS as internal standard.

Thermal behavior of each of the neat phenolic–urea oligomers and their blends with commercial epoxy resin were examined by thermogravimetric analysis. For this study, the TGA of all the samples (8–15 mg) were carried out on a “Universal V2 60 TA” instrument by recording the thermogram in nitrogen atmosphere at the heating rate of 10 °C/min in the temperature range of 40–700 °C.

The mechanical properties and chemical resistance tests of glass fiber reinforced laminates were estimated according to

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