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Analysis of sulphone based organic–inorganic hybrid epoxy nanocomposites for advanced engineering applications—Study of the mechanical, thermomechanical, XRD, EDS and physical properties

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ABSTRACT

A study was made in the present investigation on sulphone containing tetraglycidyl epoxy nanocomposites to find its suitability for use in high performance applications. The synthesis and characterization of the sulphone tetraglycidyl epoxy resin denoted as 'B' was done as reported in our previous study. Nanoclay and POSS-amine nano-reinforcements denoted as N1 and N2 were incorporated into the synthesized epoxy resin. Curing was done with diaminodiphenylmethane (DDM) and bis(3-aminophenyl) phenylphosphine oxide (BAPPO) curing agents denoted as X and Y respectively. In our current research, we continue this research and study the mechanical, thermo-mechanical, X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), viscosity, epoxy equivalent weight (EEW) and gel permeation chromatography (GPC) studies.

1. Introduction

Epoxy resins are a broad class of versatile reactive compounds and are widely used in many industrial applications such as coating, adhesives, electronic devices, automobiles, marine vessels and space vehicles because of their low manufacturing cost, ease of processing, low shrinkage on cure, good chemical, electrical resistance and mechanical properties [1–12]. Nanocomposite technology, using organophilic layered silicates as nano-reinforcements, offers new opportunities for the modification of thermoset micromechanics. The dispersed phase in conventional composites is on a macroscopic (mm)-length scale, while for nanocomposites it is on a nanometer-length scale. Owing to this structural aspect, the dispersed phase has a large specific surface area and strong interaction with the matrix.

It has been proven in recent years that polymer based nanocomposites reinforced with a small amount of nanosize clay particles (<5 vol.%) significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix Clay layers nanocomposites can exhibit lighter weight dimensional stability and a certain degree of strength, stiffness, heat resistance, and barrier properties with far less clay loading than that used in conventional filled polymer composites. Hence, they have attracted considerable attention from both the scientific and the practical point of view over the past 15 years. Many aspects of clay/epoxy nanocomposites, which are regarded as one of the most promising new materials for industrial applications, have been studied. Areas such as the effect of curing processes, type of epoxy resin, type of curing agents, type of clays, intercalating and exfoliation mechanisms and corresponding morphological, physical and mechanical, thermal and rheological properties have been extensively investigated [13–15].

POSS is inorganic silica like nanocages 1.5 nm in size that has organic substituents. Inactive organic substituents make POSS physically compatible with relevant polymers and promote dispersion in the polymer at a molecular level. The polymers incorporating POSS monomers are becoming the focus for many studies due to the simplicity in processing and the excellent mechanical properties, thermal stability and flame retardation. POSS are a family of nanoscale inorganic cage structures containing a robust siloxane/oxygen framework that are intermediate between silica (SiO_2) and siloxane (R_2SiO). POSS can be easily incorporated into common plastics by means of co-polymerization, blending or grafting. Incorporation of POSS into polymers like acrylics, styryls, epoxy and polyethylene has led to enhancements in thermal stability, mechanical properties, glass transition, degradation temperatures, oxygen permeability, reduced flammability and heat evolution as

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well as modified mechanical properties relative to conventional organic systems [16–19].

In the previous paper published [1], we had discussed the development and study of the thermal and electrical behavior of TGDDS epoxy nanocomposites for high-performance applications. In this research paper we extend our study to include the mechanical, thermo-mechanical, XRD, EDS, viscosity, EEW and GPC studies.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and were used without further purification. 4,4′-Diamino diphenyl methane (DDM) was obtained from Huntsman, USA. Epichlorohydrin and sodium hydroxide were obtained from SD Fine chemicals, India. Triphenylphosphine oxide, 4,4′-diaminodiphenylsulphone (DDS) were obtained from Alfa-Aaser, Germany. Aminopropyltrimethoxysilane (γ-APS), stannous chloride and sulphuric acid were obtained from Merck (Germany). Tetrahydrofuran (THF) and benzene were obtained from Sisco research laboratories, India. Nanoclay was obtained from Nanocor, USA. Hydrochloric acid was obtained from Hi-pure, India.

2.2. Synthesis of N,N′-tetraglycidyl diamino diphenyl sulphone (TGDDS)

The synthesis is carried out as reported in our previous research study. The structure of the synthesized *N*,*N*′-tetraglycidyl diamino diphenyl sulphone (TGDDS) is shown in Scheme 1.

2.3. Preparation of nanocomposites

In order to study the properties of the epoxy resins, neat resin laminates were prepared by curing the synthesized TGDDS (B) by DDM (X) and BAPPO (Y) curing agents as shown in Table 1. For the fabrication of nanocomposites, the nanoclay (Nanocor 1.30 E) was dried at 24 h at 50 °C under vacuum. The epoxy resin was mixed mechanically in a reaction vessel with the nanoclay at 50 °C for 3 h. Then it was further mixed in an ultrasonic bath for 30 min to disperse the clay in the resin. Later the mixture was cooled to room temperature in 30 min. The curing agent was then added. After mixing mechanically for 10 min, the mixture was degassed by a vacuum pump to remove the air bubbles and poured into molds. The nanocomposites were cured for 3 h at 120 °C and post-cured for 2 h at 200 °C. After that the resin plaque was cooled to room temperature naturally. The nano-reinforcement N2 was mixed with the epoxy resin and then cured. Blends of epoxy, N2 and curing agent were held molten at 100 °C for 25 min and then poured into a mold coated with release agent on the inner walls of the mold that was preheated to 120 °C. The curing cycle was 180 °C for 3 h and 220 °C for 2 h. After that the resin plaque was cooled to room temperature naturally, and it was cut into specimens of the required dimensions, required for the different testing and evaluation studies.

Table 1
Fabrication of resin laminates.

Type of epoxy	Matrix name	Nano-reinforcement	Curing agent
TGDDS	BX	–	X
	BXN1	N1	X
	BXN2	N2	X
	BY	–	Y
	BYN1	N1	Y
	BYN2	N2	Y

2.4. Characterization

Various characterization studies like spectral analysis (FT-IR, NMR), thermal, water absorption and flame retardant behavior were carried out and their results presented in the previous research paper [1]. In this study, we extend our study to further characterization studies like Mechanical, Thermo-mechanical, and XRD, EDS, viscosity, EEW and GPC studies.

2.4.1. Mechanical studies

The mechanical properties such as tensile strength and tensile modulus were carried out as per ASTM-D3039 using Instron testing machine (Model 6025 UK), at 10-mm/min crosshead speed, using specimen with a width of 25 mm, length of 200 mm, and thickness of 3 mm. The epoxy resins have been tested at different strain rates ranging from $5.9 \times 10^{-5}\ s^{-1}$ to $0.03\ s^{-1}$. The flexural strength and flexural modulus were studied as per ASTM D790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length using Instron testing machine (Model 6025 UK), at 10 mm/min cross-head speed. The Izod impact strength was studied as per ASTM D256-88 using testing machine (Model 6025, UK) using specimens having thickness 3.2 mm with 10 mm cross-section and 64 mm long and hardness of matrix was studied as per ASTM D2240 standards using durometer-type D as per ASTM D2240, the sample specimens were 3 mm in thickness.

2.4.2. Thermo-mechanical analysis

2.4.2.1. Heat distortion temperature (HDT). Determination of heat distortion temperature was carried out as per ASTM D648-72 using heat distortion temperature apparatus. The specimens of size 120 mm in length, 13-mm in thickness and 5 mm in width were kept in an oil bath under a load of 1.82 MPa. The temperature was raised at a rate of 2 °C/min and the temperature was noted when the specimen deflected by 0.25 mm.

2.4.2.2. Dynamic mechanical analysis (DMA). The dynamic mechanical behavior of both unmodified and modified epoxy resins was studied in a Metravib viscoanalyser. Each sample of size 10 mm was scanned from 0 °C to 300 °C at a heating rate of 276.15 K/min in an inert atmosphere. During heating the samples were subjected to strain at a frequency of 10 Hz while the storage modulus (E') and the damping factor ($\tan\delta$) were recorded. The temperature corresponding to the maximum in $\tan\delta$ versus temperature plots was recorded as the measurement of glass transition temperature (T_g).

2.4.3. X-ray diffraction technique

The X-ray diffraction technique is the most direct and simple method to evaluate the spacing between the clay layers. XRD patterns were obtained using an X-ray diffractometer (X'pert, Philips) equipped with Cu, Kα radiations and a curved graphite crystal monochromator.

Diffraction data was collected at 0.001°/S steps between 10 °C and 70 °C, and were used to determine changes in gallery heights in the before and after the addition of nanoclay and POSS-amine in the polymer matrices.

2.4.4. Flame and water absorption tests

UL 94 vertical burning flame test was carried out to analyze the flammability of the sample. Test specimens prepared as per ASTM D 570 were immersed for 24 h at 30 °C and the percentage of water absorbed by the specimen was calculated using the equation given below

$$\%\ \text{water absorption} = \frac{(w_2 - w_1) \times 100}{w_1}$$