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Rheological behaviour of nanocellulose reinforced unsaturated polyester nanocomposites

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ABSTRACT

Nanocellulose (NC) reinforced unsaturated polyester (UPR) composites were prepared by mechanical mixing process. Effect of isora nanocellulose on the properties of polyester composites has been studied in detail. Rheological properties of unsaturated polyester resin suspensions containing various amounts (0.5, 1 and 3 wt%) of nanocellulose were investigated by oscillatory rheometer with parallel plate geometry. Analysis of curing revealed that the time required for gelation in NC filled UPR is lower than neat resin, which describe the catalytic action of NC on cure reaction. NC reinforced polyester suspensions showed shear thinning behaviour initially and at higher shear rates they showed Newtonian behaviour. Tensile and impact properties showed superior behaviour revealing improved interfacial bonding between nanofiller and the polymer matrix. With respect to the neat polyester the percentage increase in tensile strength of 0.5 wt% NC reinforced composite is 57%. Optical and atomic force microscopic studies confirmed that the dispersion state of NC within the polyester matrix was adequate. Maximum glass transition temperature is obtained for 0.5 wt% NC reinforced composite, which showed an increase of 10 °C than neat resin.

1. Introduction

Polymer nanocomposites based on nanofillers from natural materials have attracted a great deal of interest in fields ranging from the scientific community to the industry because of remarkable improvement in properties. Cellulose nanofibrils are cellulose particles with at least one dimension equal to or less than 100 nm, having a highly crystalline nature. Cellulose nanofibrils are regarded as the promising reinforcement in polymer nanocomposites due to the combination of high aspect ratio, large surface area, and their ability to act as a significant reinforcement at low filler loading levels. In addition to its mechanical properties, the main benefit of nanosize cellulose is its biodegradability, biocompatibility, low density and non-toxic character [1–3]. Applications of nanocellulose in different forms include reinforcement material, biomaterial, membranes in drug delivery, water treatment, etc [4]. The development of nanocellulose or cellulose nanofibres (CNFs) has attracted significant interest in the last few decades due to these unique characteristics. Different raw materials used for production of cellulose nanofibres are soy hulls, pineapple, corncob, cassava baggase, hemp fibres, rice husk, sludge etc [5–11]. Of all the thermosetting polymers, unsaturated polyester resins play an important role because of their versatility in properties, flexibility in processing and low cost. Although many researchers have paid attention on the role of nanofillers in the cure reaction of thermoset based nanocomposites, most of the studies were performed on epoxy system. The number of works reported in the literature on the rheological behaviour is quite limited. In the study by Seyhan et al. the rheological behaviour of the vinyl ester/polyester resin blend suspensions containing different weight percentage of multiwalled carbon nanotube (CNT) and amine functionalized carbon nanotubes was investigated [12]. Linear dynamic viscoelastic measurements revealed that storage modulus and loss modulus values of resin suspensions as a function of angular frequency increased with respect to CNTs regardless of amine functional groups. Monti et al. investigated the cure kinetics of carbon nanofibres (CNF) filled unsaturated polyester resin by means of thermal and chemo rheological analysis [13].

Unsaturated polyesters are condensation polymers formed by the reaction of dibasic organic acids and polyhydric alcohols. They are long chain linear polymers containing a number of carbon

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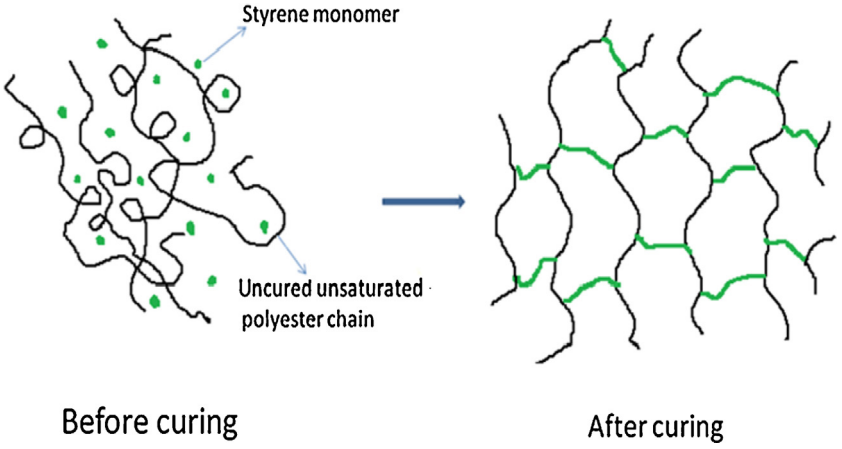

Fig. 1. Schematic representation of unsaturated polyester curing.

double bonds. Its monomer, styrene acts as a diluent, reduces viscosity and makes it easier to process. The styrene monomer also contains carbon double bonds which act as a curing agent by bridging adjacent polymer molecules at their unsaturation points. The curing or cross linking process is initiated by adding a small quantity of catalyst like organic peroxide. During the styrene-unsaturated polyester crosslinking copolymerization, the peroxide (initiator) decomposes and creates free radicals in the system. The free radicals grow and form long chain molecules by connecting styrene monomers and unsaturated polyester molecules by both inter and intramolecular reactions as shown in Fig. 1 [14,15].

Several studies have been reported on different cellulosic fibres as reinforcement in unsaturated polyester matrices. But very few studies were reported on the use of cellulose nanofibril as reinforcement in unsaturated polyester resin [16]. The main aim of the present communication is the isolation of nanocellulose from isora plant using steam explosion technique and its incorporation into unsaturated polyester matrix as reinforcement. Optical and atomic force microscopy has been used for characterising the morphology of nanocomposite. The mechanical properties were studied by tensile and impact tesing. The rheological and dynamic mechanical behaviour of unsaturated polyester suspensions containing different weight percentages of NC were also investigated. The interactions were monitored by considering rheological behaviour (liquid state) in comparison with the properties of their matching nanocomposites (solid state).

2. Experimental

2.1. Materials

The resin employed in this study was unsaturated polyester based on isophthalic acid with 40% of styrene (specific density 1.080 g/cm^3, viscosity 650 cps at 258 °C). Methyl ethyl ketone peroxide [MEKP] and cobalt naphthenate were introduced into the system as initiator and accelerator, respectively. The resin and the reagents were supplied by Sharon engineering enterprises, Cochin, India. Nanocellulose used as filler in composite was extracted from *Helicteres isora* plant using steam explosion technique. Isora fibres have a diameter of 10–20 μm, density of 1.35 g/cm^3, and a tensile strength of 500–600 MPa. Sodium hydroxide, acetic acid, sodium chlorite and oxalic acid were the chemicals used in the nanocellulose preparation and all reagents were of analytical grade.

2.2. Preparation of isora nanocellulose

Isora macro fibres were chopped into short length of about 0.5–1 cm and treated with 2wt% NaOH in an autoclave and kept under 25 psi pressure and at a temperature of 110 °C for 1 h. Then fibres were bleached for 1 h using a mixture of NaOH and acetic acid and a mixture of 1:3 sodium chlorite solution for 6 times. Fibres were then subjected to acid hydrolysis using 10% oxalic acid under a pressure of 25 psi in an autoclave for 15 min. The pressure was released immediately and the process was repeated eight times. The fibres were suspended in water and subjected to continuous stirring with a mechanical stirrer with 9000 R.P.M for 4 h. The suspension was kept in an oven at 90 °C till it was fully dried.

2.3. Preparation of composites

Isora nanocellulose/polyester composites were prepared using a three piece stainless steel mould having dimensions of 200 × 150 × 30 mm. Prior to the composite preparation, the mould surface was polished well and a mould releasing agent was applied to the surface. Isora nanocellulose (in powder form) were mixed with 100 gm unsaturated polyester resin in varying weight percentages [0.5, 1 and 3 wt%] by 20 min homogenization, followed by 10 min probe sonication. The quantity of accelerator and catalyst added to resin was 1.5% by volume of resin each and was mixed by mechanical mixing for 2 min. Then the resin mixture was poured evenly on to the mould and air bubbles were removed carefully. The closed mould was cured at room temperature for 12 h under constant pressure (1 MPa). The demoulded samples were post cured for a further period of 24 h and cured at 80 °C for 6 h. From the sheet, samples were cut according to ASTM D 5083 for tensile and ASTM D 256 for impact testing.

3. Characterization

3.1. Optical microscopy (OM)

Optical microscope (Hund mod. H600) was used to observe the dispersion of nanocellulose within the polyester matrix at room temperature. A few milligrams of the sample placed between two glass slides were observed by a Leitz Laborlux 12 Pols optical microscope. Digital micrographs were taken several times by means of a Hamamatsu TSU digital camera controller C4742-95.