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Resin infusion analysis of nanoclay filled glass fiber laminates

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ABSTRACT

This paper focuses on the resin flow characteristics of nanoclay filled glass fiber laminates processed by Vacuum Assisted Resin Infusion Molding (VARIM). Laminates with varying quantities of nanoclays (0–5 wt.%) were prepared and the effect of these nanoclays on the epoxy resin flow characteristics was studied. It was found that the flow rate of resin continuously decreased as nanoclay content continuously increased. The reduction in the flow rate was attributed to the rate of change of curing and the subsequent change in viscosity of the nanoclay filled resin. Analysis of infusion process by Darcy's law show that the permeability of the fiber decreased in the nanoclay filled resin system. Nanoclay filled laminates show improved static and dynamic mechanical properties than that of unfilled resin composites.

1. Introduction

Glass fiber reinforced composites are an important class of material due to their high strength to weight ratio when compared to steel, and their high corrosion and chemical resistance [1–3]. These composite laminates also consist of a range of fibers such as carbon, Kevlar and glass. They are widely used in aircraft, transportation, civil and other engineering applications [4–6].

Over the past two decades, a considerable amount of research work has been done on polymer–clay nanocomposites (PCN). Chemically treated nanolayered montmorillonite (MMT) based clays are widely used as nanofillers in these PCN based structures [7–11]. The addition of small amount of treated MMT clay (~5 wt.%) in epoxy and other polymer matrices has caused dramatic improvement in mechanical, thermal, physical and chemical properties [12–16].

The nanoparticle filled polymer reinforced with glass fibers has also been an area of research interest in past 5–7 years. In this type of composite structure, the glass fibers serve as a primary reinforcement and nanoparticles as secondary reinforcement. In such structures, the nanoparticles such as clays, carbon nanotubes, and nanosilica/TiO2 are filled in the laminate and are processed either by hand lay up, vacuum assisted infusion, hot-press or other forming techniques [17–21]. The nanoparticle infused laminates have shown improved thermal and mechanical properties [22–24] and improved fiber–matrix interface strength [25]. The study of nanoclay filled epoxy based laminate composite is a complex subject. The dispersion of clay particles in a polymer is governed by the mixing process, catalytic curing of organo-ions, the curing agent and the processing method [26–29]. From literature it is observed that the effect of clays on laminate processing is not yet fully understood. Therefore in this work we have studied the effect of clay on the processing parameters and the subsequent mechanical properties of nanoclay filled epoxy polymer reinforced with woven glass fiber. The laminates were processed using Vacuum Assisted Resin Infusion Molding (VARIM). The authors' view is that the results of this study will help the designers to control the processing properties of the laminates, namely thickness, fiber volume fraction (V_f), degree of cure (α), permeation, structure and morphology of nanoclay reinforced laminates.

2. Experimental details

2.1. Raw materials

In this study, diglycidyl ether of bisphenol-A (DGEBA) based commercial epoxy resin supplied under the trade name of LR-20 was used as the matrix. The curing agent was unmodified cyclic aliphatic amine based epoxy hardener supplied under the trade name of LH-281. Silane treated E type plain weave glass woven roving (450 GSM) was used as the primary reinforcement. All these materials were purchased from AMT Composites, Durban – South Africa. The secondary nanoclay reinforcement filler, supplied under the trade name Cloisite-30B, was purchased from Southern Clay Products, Inc., USA. Cloisite 30B is an organically modified MMT clay with MT2EtOH based Tallow compound, where MT2EtOH is

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methyl tallow bis-2-hydroxyethyl quaternary ammonium compound.

2.2. Laminate preparation

Glass fiber reinforced and nanoclay filled epoxy hybrid laminates were prepared by Vacuum Assisted Resin Infusion Molding (VARIM) process. The processing of laminates involved two steps: the first step was mixing of nanoclays in the epoxy resin and the second step was the infusion of the modified resin into the glass fiber rovings.

Six (6) layers of plain weave glass fiber (WGF) rovings were cut to size 35 cm × 35 cm, and subsequently weighed. An equivalent weight of epoxy resin to that of the 6 layers of WGF was used. Nanoclays of various weight percentages (0–5 wt.%) to that of epoxy/hardener mixture was taken and mixed with epoxy resin at room temperature. The mixing was carried out for 1 h at 500 rpm with mechanical stirrer. After mixing the resin with the clay 30 wt.% of hardener (equivalent to epoxy resin weight) was added to the epoxy-clay mixture and then processed to form a laminate. The laminates were processed by using a vacuum pressure of 0.5–2 bars. During the resin infusion process, the time taken for the resin to flow to predetermined points was taken and the corresponding viscosity and degree of cure (α) was measured.

2.3. Characterization

The viscosity of the unfilled and nanoclay filled resin system was measured using a Brookfield viscometer according to the ASTM D2393-86 method. FTIR spectra of the epoxy, the clay, the glass fiber, the unfilled and the clay filled epoxy glass fiber hybrid composite was evaluated in the Attenuated Total Reflectance (ATR) mode, in the 800–4000 cm^{-1} range. FTIR spectroscopy was performed at the different stages of processing of composite laminate to evaluate degree of cure. The laminate was water quenched periodically during processing so as to ascertain the degree of cure (α) at a given time. The degree of cure was measured using FTIR, in which the ratio of peak value of epoxide oxirane group of cured to uncured samples was measured as discussed elsewhere [30]. Three samples were used to measure viscosity and obtain FTIR spectra, and the average values were considered for discussion.

The structure of the composites was examined using X-ray diffraction (XRD) and Transmission electron microscopy (TEM). A Philips PW1050 diffractometer was used to obtain the X-ray diffraction patterns using Cu Kα lines (λ = 1.5406 Å). The diffractrograms were scanned from 3° to 16° (2θ) in steps of 0.02° with a scanning rate of 0.5°/min. Microscopic investigation of selected specimens at the various weight compositions were conducted using a Philips CM120 transmission electron microscope with an operating voltage of 120 kV.

The fiber volume fraction was determined by polymer matrix burning method. In this method, a composite laminate of size 5 cm × 5 cm was cut, weighed and then burnt in a furnace at 800 °C. The unburnt fibers were weighed and the volume fraction of fibers was calculated.

Dynamic mechanical analysis was carried out at a frequency of 10 Hz in a 3-point bending mode using the TA instruments model Q800 from 25 °C to 130 °C at atmospheric conditions. Specimen of size 5.5 cm × 1 cm × 0.3 cm was used for this test.

Tensile test of composites was carried out at room temperature according to ASTM D 3039-08 method using MTS-UTM machine. For tensile test, a constant load of 1 kN and strain rate of 1 mm/min was kept and the tensile parameters (elongation to break, failure strength and stiffness) were measured. Five samples were cut from each composite panel and then tested. The mean values were considered for graphical representation and discussion.

3. Results and discussions

3.1. Flow characteristics

The flow characteristic of the resin and the resin-clay mixture was studied by measuring the time taken for the resin to flow across the laminate during processing. Fig. 1 shows the time vs distance curve of unfilled and nanoclay filled epoxy resin. The results indicate that unfilled resin flows faster than filled resin and the flow speed decreases with increase in nanoclay content. Flow speed of unfilled resin was 1.48 mm/s and this reduced to 0.9 mm/s for 5 wt.% nanoclay filled resin. In order to better understand this finding the viscosity and degree of cure (α) of filled and unfilled resin was studied further. Fig. 2 represents the viscosity of filled and unfilled resin at various points across the length of the laminate. A uniform viscosity of 4525 cP was observed in unfilled epoxy resin across the entire laminate length. The nanoclay filled resin system on the other hand displayed a distinct initial resin mixture viscosity (η_i) and a time dependent gel viscosity (η_g) and the viscosity of resin increased as the clay content increased. The viscosity of 5 wt.% filled nanoclay increased to 5153 cP (and 5322 η_g) from 4525 cP for unfilled laminate.

The viscosity was further examined by studying the curing characteristics of filled and unfilled resin. Fig. 3 shows the degree of cure of filled and unfilled resin at various stages of laminate processing. The results indicated that α remained unchanged in the unfilled laminate, but it continuously increased across the infusion length of the nanoclay filled laminate. The degree of cure for unfilled laminate was 6% and this increased to 21% in 5 wt.% nanoclay filled laminate. One possible reason for this increase may be due to the presence of organoions in the clay. Alkyl ammonium ions (organoions) of nanoclay may have catalyzed the curing of epoxy and hence increased the degree of cure. This is consistent with the finding reported elsewhere [31,32]. To gain an understanding of this phenomenon, a series of FTIR tests was performed. Fig. 4 shows the FTIR spectrum of unfilled and clay filled epoxies during processing. The characteristic peaks of unfilled epoxy resin were observed at 3467 cm^{-1} and 1630 cm^{-1} (peaks due to primary amines), 3000–2700 (CH stretching), 1514 cm^{-1} (aromatic ring), 1293 cm^{-1} (hydroxyl ether group) and 912 cm^{-1} (epoxide group) [33]. The characteristic peaks for the glass fiber was at 1120 cm^{-1} and 930 cm^{-1} due to Al_2O_3 and SiO stretching vibrations respectively [34]. Cloisite 30B showed the characteristic peaks at 1030 cm^{-1} Si–O plane stretching, 3440 cm^{-1} and

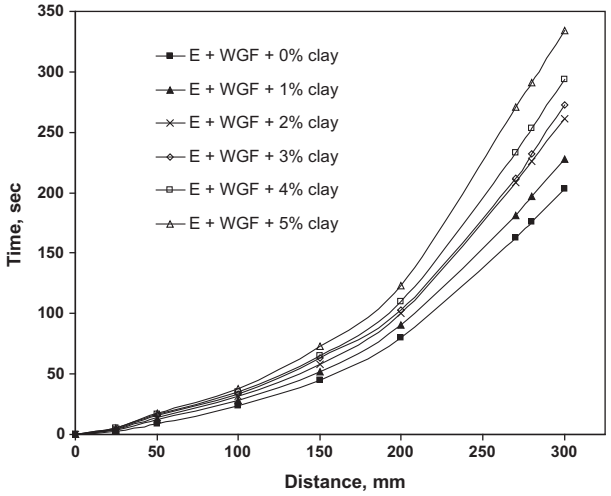

Fig. 1. Flow behavior of resin and resin-clay mixture during laminate processing.