

The Preparation of Clay/Glass Fiber/Epoxy Hybrid Nanocomposites Using VARTM

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SUMMARY: Clay/polymer nanocomposites have received a great deal of attention recently. We prepared clay/glass fiber/epoxy hybrid nanocomposites using a vacuum-assisted resin-transfer molding (VARTM) process. A nanoclay was dispersed in a solvent with vigorous mechanical stirring and then the suspension was mixed with epoxy resin. To study the effects of fiber direction on the clay distribution, unidirectional glass fibers were placed in two directions: parallel and perpendicular to the flow direction. The micro-scale behavior of organophilic montmorillonite in an epoxy resin system was investigated using X-ray diffraction (XRD). The mechanical properties of composites with different clay loadings were measured. The morphology of the nanocomposites was also observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We found that introducing a small amount of nanoclay to the glass fiber-epoxy composites enhanced the mechanical properties. The

KEYWORDS: clay/glass fiber/epoxy hybrid nanocomposites, vacuum-assisted resin-transfer molding (VARTM), mechanical properties, impact strength

INTRODUCTION

Layered silicates are used as fillers in polymer systems because of the improved mechanical properties [1-4], thermal stability [4-8], gas barrier properties [7, 9], and flame retardant properties of the resulting polymer composites [7,11]. Conventional glass fiber-reinforced polymeric composites are also widely used as structural engineering materials in many industries. One cost-effective processing technique for producing glass fiber-reinforced composites is vacuum-assisted resin transfer molding (VARTM). VARTM is used to manufacture a wide variety of articles, ranging from small armrests for buses to large components for water-treatment plants.

Three different approaches are used to synthesize polymer/clay nanocomposites: the 1) melt intercalation, 2) solution, and 3) in-situ polymerization methods. In the melt intercalation process, a thermoplastic polymer is mixed with organophilic clay mechanically at elevated temperature. The polymer chains are then intercalated directly between layers of the clay [10]. In the solution method [11], the organoclay and polymer are dissolved in a polar organic solvent, allowing the dissolved polymer chains to penetrate the clay layers. After evaporating the solvent, uniform mixing of the polymer and layered clay is achieved. In the *in-situ* method, monomers are intercalated into clay layers directly and then polymerized within the layers. We used the solution method to synthesize epoxy/clay nanocomposites using VARTM. The morphology and mechanical and thermal properties of the nanocomposites were investigated to study the effects of nanoparticles on continuous glass fiber-reinforced polymer composites.

EXPERIMENT

Materials

The epoxy resin used was YD-128 (Kukdo Chemical Co. Ltd.). The epoxide equivalent weight (EEW) of the epoxy resin was 185-190 eq⁻¹. The curing agent was D-230 (New Seoul Chemical Co. Ltd.). The active diluting agent was butyl glycidyl ether (BGE, Kukdo Chemical Co. Ltd.). The organoclay was Cloisite 15A (Southern Clay Products Inc.) and T-800 unidirectional glass fibers (Dong-IL Industrial Co.) were used. All the components of the epoxy system were used as received without purification.

Preparation of nanocomposites

A flat rectangular mold measuring 300×200×3 mm was used to prepare the nanocomposites. A rubber gasket was placed around the perimeter of the mold halves to provide a proper seal. Fig. 1 shows a schematic of the experimental set-up used for the closed-mold VARTM process. Eight grams of organoclay (Cloisite 15A) were dispersed homogeneously in 120 mL of chloroform at room temperature. The suspension was added to epoxy resin. The mixture was stirred vigorously using a mechanical stirrer, and then the chloroform was removed by evaporation. Once the mixture had cooled to room temperature, diluted BGE and the curing agent (D-230) were added and stirred. Finally, the mixture was degassed before injecting it. Five layers of unidirectional glass fiber mat measuring 250×200×3 mm were placed in the longitudinal or transverse directions to investigate the effects of flow direction on nanocomposites. The mold was maintained at a temperature of 50°C during filling. The vacuum was maintained at 75 cm of Hg. The molded nanocomposite was cured at 80°C for 4 h and post-cured at 125°C for 3 h in the oven

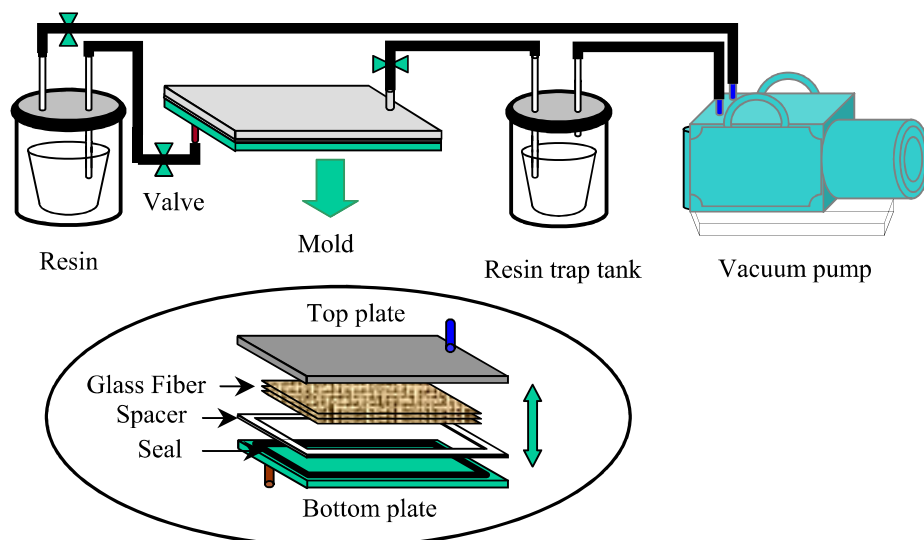


Fig. 1. Schematics of the closed-mold VARTM process

Characterization and testing

X-ray diffraction (XRD) analysis was performed using a Rigaku D/MAX 2500 diffractometer equipped with Cu-K α X-ray and operated at 40 kV and 30 mA. The scanning speed and step size used were 1° min⁻¹ and 0.02°, respectively. The diffraction patterns were collected between 1 and 10°. Cured composite samples were prepared by mounting a rectangular flat specimen in an aluminum holder. The powdered clay was compressed and smoothed into a glass holder.

Cross-sections of the composites were examined using a JEOL JSM-6400 scanning electron microscope (SEM) equipped with a PGT EDS (energy dispersive X-ray spectrometer) system. The composition of the composite was analyzed using EDS. SEM samples were cut from the composites, polished, and coated with gold.

Dynamic mechanical analyzer (DMA) tests were performed on a TA DMA-983 in fixed frequency mode at 1 HZ and an amplitude of 0.40 mm. Rectangular DMA specimens measuring 60×10×3 mm were used for the analysis.

The transverse flexural properties of the composites were measured using the three-point bending test according to ASTM D790-97. Rectangular specimens measuring 100×12×3 mm were used. The support span distance was 60 mm and the crosshead speed was 2 mm/min. The impact properties of the composites were also measured using an un-notched Izod impact test according to ASTM D4812. Specimens measuring 64×10×3 mm were used and five tests were performed for each condition.

RESULTS AND DISCUSSION

X-ray diffraction analysis was used to determine the structural characteristics of the clay dispersed in epoxy resin. Fig. 2 shows the XRD patterns of the original organoclay and the epoxy/clay nanocomposites. The basal space of the clays changed from 34.75 to 37.73 Å due to the intercalation of epoxy molecules. The degree of swelling was improved slightly when the solution was used as compared to direct mixing. When the clay content was below 3%, fully exfoliated nanocomposites were obtained. Thermogravimetric analysis (TGA) was performed at a heating rate of 10°C min⁻¹ from 50 to 700°C to investigate the thermal stability of the epoxy/clay nanocomposites. The flexural modulus and strength of the nanocomposites were measured using the three-point bending test. Table 1 summarizes the mechanical properties and thermal stabilities of nanocomposites with various clay contents. The flexural strength and modulus generally increased with the clay content. However, the flexural strength of the nanocomposites decreased suddenly above a 3% clay loading. A similar trend was

Table 1. Mechanical and thermal properties of the nanocomposites.

Clay Content (%)	Flexural strength (Mpa)	Flexural modulus (GPa)	Impact strength (J/m)	Decomposition temperature ()
0	70.89	14.63	77.9	251.19
1	70.70	14.94	74.6	256.65
3	85.33	15.20	96.7	274.99
5	58.68	15.49	100.4	286.87

reported previously [3] and it was suspected that there is a critical clay content for improving the flexural strength of a nanocomposite. Surprisingly, the impact strength increased remarkably on introducing a small amount of clay into the glass fiber-reinforced composites. Clay loading improved the thermal stability of the nanocomposites. The decomposition temperature was the temperature at which the weight loss of the nanocomposites was 1% in the TGA curves. Fig. 3 shows the storage modulus (E') and $\tan \delta$ of nanocomposites for various clay loadings. The storage modulus increased with the clay content, but no significant changes in the glass transition temperature of the nanocomposites was observed. The SEM images in Fig. 4 show that the nanoclay was distributed uniformly around the glass fiber bundles. The nanoclay particles became less dense downstream in the mold. The nanoclay particles were more uniformly distributed when the resin flows along the fiber direction compared to the flow across the fiber. EDS analysis was used to verify the clay nanoparticles in the nanocomposite.

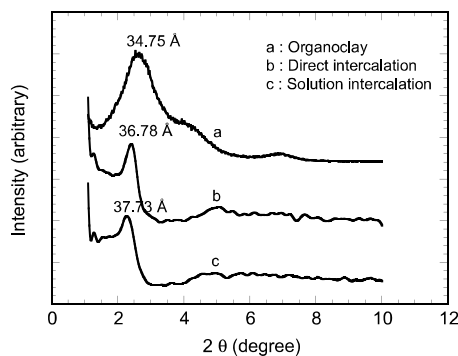


Fig. 2. XRD patterns of organoclay and epoxy/organoclay nanocomposites with 5% clay.

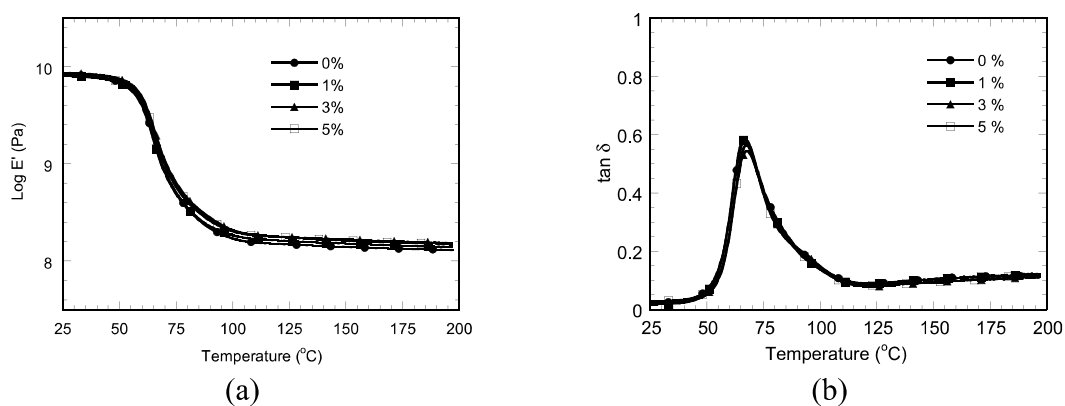


Fig. 3. (a) Storage modulus and (b) $\tan \delta$ of nanocomposites for various clay loadings.

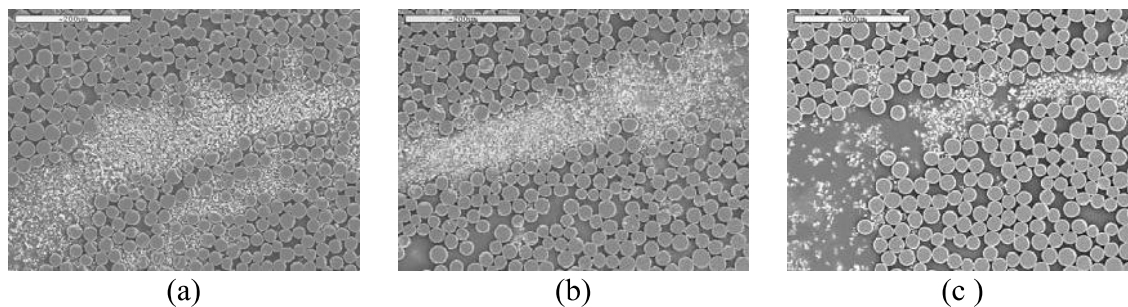


Fig. 4. SEM photographs of cross-sections of the molded part: (a) at the inlet, (b) at the middle, and (c) at the outlet regions

CONCLUSIONS

Clay/glass fiber/epoxy hybrid nanocomposites were prepared using VARTM. The mechanical and thermal properties of the conventional composites improved due to the addition of layered silicates. The impact strength of the nanocomposites was enhanced remarkably by addition of a small amount of clay. The morphology of the hybrid nanocomposites was also observed in two flow directions, parallel to the fibers and perpendicular to the fiber direction.

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