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Note

Curing studies and mechanical properties of glass fiber reinforced composites based on silanized clay minerals

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ABSTRACT

A commercial organically modified montmorillonite Cloisite® 15A was modified via a new silanization route by two different silane coupling agents: 3-Aminopropyltriethoxysilane and 3-Glycidyloxypropyltrimethoxysilane. This method enables the use of very high concentration of silanes for functionalization of clay minerals. The ratio of weight of silane coupling agent to that of weight of clay mineral (X) was varied from 0.1 to 6. Small angle X- ray scattering and thermogravimetric analysis were carried out on silane modified clay minerals to quantify the grafting of silanes as a function of ratio of weight of silane agent to that of clay mineral. Fiber reinforced epoxy nanocomposites containing silylated clay minerals were manufactured using vacuum assisted resin infusion molding method. Also, curing studies were carried out on fiber reinforced epoxy nanocomposites containing Cloisite® 15A at different cure temperatures, e.g. 70 °C, 80 °C, 85 °C, 95 °C and for two different curing time periods, e.g. 7 h and 10 h. Significant improvements in mechanical properties of fiber reinforced nanocomposites were obtained with incorporation of clay minerals silanized using high concentration of silanes in solvent and chosen curing schedule. The tensile modulus, tensile strength, flexural modulus and bending strength increased by 30%, 37%, 139% and 146% respectively, in nanocomposites containing clay mineral modified using 4X aminopropyltriethoxysilane. An attempt has been made to correlate the results with the morphology of nanocomposites by transmission electron microscopy and that of fractured surfaces by scanning electron microscopy.

1. Introduction

The modification of clay minerals makes it possible to achieve good dispersion of clay minerals into polymer matrix, and to take advantage of its high aspect ratio and large surface area for interaction of clay mineral layers with the polymer molecules. A lot of research have been done to modify the clay minerals using different techniques (Bergaya et al., 2006; de Paiva et al., 2008; He et al., 2013; Kango et al., 2013; Kotal and Bhowmick, 2015; Varadwaj et al., 2016) in order to make them compatible with polymers. The modification of clay minerals using organofunctional silanes has attracted interest of many researchers because grafting of silane molecules on clay mineral surfaces improve their dispersibility (Chen et al., 2005a,b; Ha et al., 2008; De Maria et al., 2011; Park et al., 2009; Qian et al., 2009), wettability (Ianchis et al., 2011; Park et al., 2009), interfacial adhesion (Ha et al., 2007; Kráčalík et al., 2007; Park et al., 2009), and promotes exfoliation (Chen et al., 2005a; Ha et al., 2007, Ha and Rhee, 2008; Sharma et al., 2016; Silva et al., 2011; Wang et al., 2006) in polymers. The exfoliated morphology leads to improvements in mechanical properties on addition of a small amount of clay mineral in polymer matrix (Chen and Yoon, 2005b; Ha et al., 2007, 2008, 2010; Ha and Rhee, 2008; Huskić et al., 2013; Ianchis et al., 2015; Piscitelli et al., 2012; Wang et al., 2006) because of improved reinforcement effect of clay mineral. Based on our knowledge, the silane grafting reaction is dependent on the nature of clay minerals used (Daitx et al., 2015; He et al., 2005; Romanzini et al., 2015a,b; Wan et al., 2008; Wang et al., 2005), the number of reactive sites available at broken edges, interspace or external surface of clay mineral (Herrera et al., 2004; Varadwaj et al., 2016; Zhang et al., 2006), the grafting temperature (Piscitelli et al., 2010; Yang et al., 2012), the chain length of silane moieties (He et al., 2013; Ianchis et al., 2012; Piscitelli et al., 2010), quantity of silane (Huskić et al., 2013; Piscitelli et al., 2010), solvent and method used for silanization of clay minerals (Bertuoli et al., 2014; Shanmugharaj et al., 2006; Shen et al., 2007; Su et al., 2013; Yang et al., 2012).

Chen and Yoon (2005a) concluded that silane treatment of different organically modified clay minerals with glycidyloxypropyltrimethoxysilane increased the hydrophobicity of clay minerals in the order: Cloisite® 15A < Cloisite® 20A < Cloisite® 30B. Further, the synthesized clay-poly(l-lactide) nanocomposites had intercalated/exfoliated morphology as a result of silanization of clay minerals and extent of

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intercalation increased with increase in order of hydrophobicity of silane modified clay minerals. Ianchis et al. (2012) functionalized Cloisite® 30B with four different alkoxysilanes and studied the effect of chain length of organofunctional groups on degree of functionalization of clay mineral and properties of clay-polystyrene nanocomposites. The grafting of silanes decreased with increase in chain length but expectedly the hydrophobicity of Cloisite® 30B increased. The glass transition temperature of clay-polystyrene nanocomposites was also influenced by modification of Cloisite® 30B with different silane coupling agents. Piscitelli et al. (2010) modified sodium montmorillonite (Na-Mt) using three different amino silanes and observed that the degree of silyation of Na-Mt increased with increase in chain length of silane moieties, concentration of silane, and reaction temperature. However, silanization of Na-Mt with long chain length silane moieties resulted in decrease in interlayer distance of clay mineral which was attributed to strong tendency of longer and more mobile chains having two -NH groups to interact among themselves and decrease the number of silane molecules, which could enter the interlayer space. Huskić et al. (2013) carried out silylation of montmorillonite (Mt) with different amount of silanes for different reaction periods. Small angle X ray scattering (SAXS) showed that an increase in the concentration of silane used during reaction resulted in an increase in d_{001} spacing of Mt. Also, the clay-epoxy nanocomposites containing silylated Mt had slightly higher glass transition temperature (T_g) and increased elastic modulus in comparison with the nanocomposites containing other commercial OMt/neat epoxy nanocomposites. Shanmugharaj et al. (2006) had observed that grafting of aminopropyethoxy silanes on Mt was influenced by the nature of solvent used in silanization reaction. The hydrolysis of silane in solvents having high surface energy than Mt. decreased the grafting of aminosilane on Mt.

Not much literature is available on fiber reinforced epoxy composites containing silyated clay minerals. Zulfli and Shyang (2010) observed an increase in flexural modulus and flexural strength of the glass fiber reinforced clay-epoxy nanocomposites containing Nanomer 1.30E treated with aminopropyltrimethoxysilane. In our previous study (Sharma et al., 2016), the effect of incorporation of clay minerals, treated using different concentrations using a new silanization method was reported. The tensile properties, flexural properties and extent of curing increased in nanocomposites containing clay minerals modified using 200 wt% silane (with respect to weight of clay mineral). However increasing the amount of silane above this, led to a decrease in mechanical properties, which was attributed to clustering of silane treated clay minerals which resulted in visually poor dispersion in epoxy resin.

In the present study, we report that complete curing of nanocomposites as evidenced by DSC study, containing clay minerals functionalized using silanes, even in very small amount resulted in significant improvement in tensile and flexural properties in comparison with those containing commercial OMt. A new method of silanization on nanodispersed clay mineral was studied and this led to an increase in the swelling of clay mineral, which would significantly increase grafting of silanes on the clay mineral.

2. Materials and methods

2.1. Materials

The E-glass woven roving, WR360 made of Advantex® glass was purchased from Owens Corning, India. A commercially available organically modified clay mineral, Cloisite® 15A was purchased from Nanoshel limited, India. Cloisite® 15A (Montmorillonite treated with dimethyl, dehydrogenated tallow, quaternary ammonium salt) had a cation exchange capacity of 125 meq/100 g. The silane coupling agents: 3-Glycidyloxypropyltrimethoxysilane (GPS; Purity >97%) and 3-Aminopropyltriethoxysilane (APS; Purity >98%) were purchased from Tokyo chemicals industry, Japan. The solvents used for hydrolysis of silane coupling agents (SCAs) were acetone (Purity = 99%) or a mixture of ethanol (Purity = 99.9%) and distilled water. Acetone and ethanol were purchased from Loba Chemie Pvt. Ltd., India. The epoxy system consisted of liquid diglycidyl ether of bisphenol-A and an amine hardener. The Airstone epoxy system (Airstone 780E resin and Airstone 786H hardener) was supplied by Dow Chemical International Limited, India. The epoxide equivalent weight of resin was 172 g/eq and the amine content in hardener was 9.5 meq/g. Airstone epoxy system is suitable for production of large, fiber reinforced parts that require long infusion time and is used in manufacture of structural composites for diverse applications including construction, marine and infrastructure.

The terminology used for silane modified clay minerals, consists of a prefix A (for aminosilane) or G (for glycidyl silane) followed by the concentration of silane in parentheses. A suffix GFRC is added to the symbol of silane modified clay minerals to denote nanocomposites containing silanized clay minerals.

2.2. Methods

2.2.1. Silane functionalization of clay mineral

The amount of Silane coupling agents (SCAs) used was 0.1X, 0.5X, 2X, 4X and 6X with respect to the weight of clay mineral (X). Each SCA was mixed in a solvent and hydrolysis was carried out for 30 min with continuous stirring of the solution. 5 g of Cloisite® 15A was immersed in a dilute solution containing different quantities of silanes. The hydrolysis of aminopropyltriethoxysilane was done in acetone, and glycidyloxypropyltrimethoxysilane was hydrolyzed in a solution containing 95% ethanol and 5% distilled water (Choi et al., 2009; Ha and Rhee, 2008; He et al., 2005; Zhang et al., 2006). Further, the Cloisite® 15A was nanodispersed in silane solution by using a high shear homogenizer operated at 12,000 rpm for 3 min and ultrasonic mixing using a probe sonicator operated at an amplitude of 80% for 10 min. The solvent was then removed using a Heidolph rotary evaporator. The modified clay minerals were washed twice with the solvent used for hydrolysis to remove soluble homocondensates (Chen et al., 2005a,b; Huskić et al., 2013; Ianchis et al., 2011, 2015; Zhang et al., 2006). Thin layers of silane modified clay minerals were laid in petri plates to avoid large aggregations and then were dried in a vacuum oven at 60 °C for 48 h. The dried clay minerals were ground in a pestle mortar to obtain a fine powder. Silylated clay minerals were heated for 15 min at 120 °C prior to mixing in epoxy resin to remove residual solvent and moisture. To remove free water from the clay minerals, drying temperature was kept below the degradation temperature of quaternary ammonium modifier and organic moieties of silane coupling agents. The onset degradation temperature of organic modifier in Cloisite® 15A was 230 °C as determined from TGA. The results of thermogravimetric analysis of Cloisite® 15A and silylated clay minerals are reported in Section 3.1.1. Drying at 120 °C was unlikely to cause the degradation of organic moieties as both APS and GPS are gamma-substituted silane coupling agents and can withstand long term continuous exposure to 160 °C (Gelsest, 1967).

2.2.2. Fiber reinforced clay-epoxy nanocomposites

Clay minerals at 2 parts per hundred resin were added to epoxy resin and dispersed using a high speed homogenizer operated at 20,000 rpm for 3 min and ultrasonic mixing using probe sonicator operated at an amplitude of 80% for 10 min. A stoichiometric amount of hardener was added to the homogeneous mixture and degassing was done using a vacuum desiccator for 30 min. Finally, epoxy was infused into the fiber preforms to manufacture high quality two ply laminate using vacuum assisted resin infusion set-up. Further, curing of laminate was carried out on the heated mould. The temperature of mould was controlled by a proportional–integral–derivative controller.

2.3. Characterization

Thermogravimetric analysis (TGA) of clay minerals was carried out using Shimadzu TGA 50 thermogravimetric analyzer. The clay mineral