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Material properties

Enhanced mechanical properties of unidirectional basalt fiber/epoxy composites using silane-modified Na^{+}-montmorillonite nanoclay

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ABSTRACT

This study explores the effects of 3-glycidoxypropyltrimethoxysilane (3-GPTS) modified Na-montmorillonite (Na-Mt) nanoclay addition on mechanical response of unidirectional basalt fiber (UD-BF)/epoxy composite laminates under tensile, flexural and compressive loadings. Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and simultaneous thermal analysis (STA) data confirmed the reaction mechanism between the silane compound and Mt. It was demonstrated that addition of 5 wt % 3-GPTS/Mt resulted in 28%, 11% and 35% increase in flexural, tensile and compressive strengths. Scanning electron microscopy (SEM) clarified the improvement in the adhesion between the basalt fibers and matrix in the case of Mt-enhanced epoxy specimens. Also, a theoretical route based on a Euler-Bernoulli beam-based approach was employed to estimate the compressive properties of the composites. The results demonstrated good agreement between theoretical and experimental approaches. Totally, the results of the study show that matrix modification is an effective strategy to improve the mechanical behavior of fibrous composites.

1. Introduction

Over the last century, fiber reinforced polymers (FRPs) have been widely used in structural components due to their specific characteristics such as high specific strength and specific stiffness, high fatigue and corrosion resistance, easy to fabricate and favorable price. FRPs structures undergo various loading conditions in service [1,2].

Natural fibers are increasingly being recognized as a favorable substitute for synthetic fibers. They may be obtained from plant (cotton, flax and hemp, although sisal, jute, kenaf, bamboo and coconut), animal and mineral sources. Natural fibers are nontoxic and more easily recyclable when compared with other classes of fibers [3–5]. Basalt fiber (BF), which is made from the basalt rock, is considered as a mineral fiber. BF possess outstanding properties such as good modulus, excellent stability, good chemical resistance, high mechanical strength and high temperature resistance, and easy to produce [6,7]. A scan through the literature reveals that there are many studies focusing on the different characteristics of the continuous or chopped BF polymeric composites [8–12]. Also, two comprehensive review papers on BF-reinforced composites the have been recently presented in 2015 [13,14].

Using nanoclay particles as filler within the polymeric matrix has attracted considerable attention due to the improved mechanical, thermal and physical properties of the resultant material. In recent years, intensive research efforts have been devoted to the study of the response of nanoclay-reinforced polymers to various loads (tensile, compression, bending and impact) [15–19]. It is believed that the effect of nanoclay particles on the mechanical properties of the polymers is considerable. The improvements are due to the high surface-to-volume ratio of the nanoclay particles [20].

Acceptable dispersion of nanoclay and also good adhesion at the nanoclay/polymer matrix interface are essential to improve the mechanical performance of resultant nanocomposite. For this purpose, modification of the nanoclay (especially with organo-silane compounds) was one of the most important research works in past years and some papers in this field can be found in literature [21–25]. Appropriate dispersion of the nanoclay minimizes the stress concentration regions, leading to improvement in the uniformity of stress distribution within the matrix. Silane

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grafting has proved to be a highly efficient strategy to modify the nanoclay surfaces [22,23]. In a clay/polymer system, organo-silane compound creates a bridge between two constituents by a covalent bond. This can lead to great enhancement of the mechanical properties of the resultant composite.

Recently, great efforts have been made to develop polymeric composites with a mixture of micro-scale fibers and a nano-scale filler. Such materials are termed multiscale composites [26]. There are two general methods for fabrication of multiscale composites, nanoparticle-dispersion within the matrix [27] or nanoparticle-grafting onto the fibrous reinforcement [28]. It has been well documented that a multiscale composite possesses enhanced mechanical properties compared to a FRP one [29–35]. Eslami-Farsani et al. [29] investigated the effects of thermal conditions on the tensile properties of BF-reinforced polypropylene (PP)-clay nanocomposites. They reported that the reinforcing efficiency of the nanoclay and BF for the tensile responses of PP composites is higher at low temperatures compared to room and high temperatures. Subramaniyan et al. [30] studied the compressive strength of unidirectional-glass polymeric composites containing nanoclay and reported that the addition of the nanoclay resulted a substantial increase in longitudinal compressive strength of the composites. Iqbal et al. [31] assessed impact damage resistance of carbon fiber-reinforced epoxy with nanoclay-filled matrix, and 3 wt % clay addition was shown to be an optimal content for the highest damage resistance. In Ref. [32], mechanical response of carbon fiber reinforced epoxy/clay nanocomposites was assessed. It showed that the interlaminar fracture toughness of the composites was enhanced by 85% through the addition of 4 phr nanoclay. Indeed, 2 phr of nanoclay can enhance the flexural strength by 38%. Withers et al. [33] investigated mechanical properties of an epoxy glass-fiber composite reinforced with surface organo-modified nanoclay. The results showed 11.7% improvement in the ultimate tensile strength, 10.6% improvement in tensile modulus and 10.5% improvement in tensile ductility at 60 °C in the presence of nanoclay minerals. Dorigato et al. [34] evaluated the thermo-mechanical characterization of epoxy/clay nanocomposites as matrices for carbon/nanoclay/epoxy laminates. The mechanical behavior, both under quasi-static and impact conditions, was positively affected by resin nanomodification. Gabr et al. [35] investigated the effect of organoclay on the mechanical and thermal properties of woven carbon fiber/compatibilized polypropylene composites. The results of this work demonstrated that at 3 wt % of organoclay, initiation and propagation interlaminar fracture toughness in mode I was enhanced by 64% and 67%, respectively.

Although there are a good number of published surveys on the mechanical properties of multiscale polymeric composites, to our knowledge no systematic work has been reported on the mechanical behavior of UD-BF/epoxy composites containing organoclay minerals. The focus of the study is on the effects of the Mt nanoclay modified by 3-GPTS at various contents with respect to the matrix (1–7 wt % at a step of 2 wt %) on the mechanical response of UD-BF/epoxy composites. Tensile, flexural and quasi-static compressive characteristics of the specimens were evaluated. The features of the fractured surfaces were also characterized using field-emission scanning electron microscopy (FESEM) observations.

2. Experiments

2.1. Materials

Commercially available ML-506 epoxy resin and HA-11 amine hardener were purchased from Mokarrar Engineering Materials Company, Iran. The resin-hardener ratio was 100:15 by weight, as recommended by the manufacturer. The fibrous reinforcement was basalt roving fibers (trade name: BCF13-150-KV12) which were supplied by Kamenny Vek, Russia. Sodium Montmorillonite (Na+-Mt) nanoclay particles were provided by Sigma-Aldrich Co., USA. Fig. 1 shows SEM image of nanoclay particles. 3-GPTS produced by Merck Chemical Co., Germany was used as a silane coupling agent for modification of the nanoparticles. This compound possesses epoxide groups and it is one of the most commonly used organic silane compounds in synthesis of various materials [36]. The molecular formula of the 3-GPTS is $C_9H_{20}O_5Si$ and its molecular weight is 236.4 g/mol.

2.2. Silanization of Na^+-Mt

In order to increase the chemical affinity of Mt nanoclay to epoxy matrix, surface modification of nanoparticles is necessary. The silane-modified Mt nanoclays were prepared using a method based on the following sequence: 5 g of the Na^+-Mt particles was added to 100 mL of the solution of distilled water in ethanol (5–95 ratio) and then 3-GPTS coupling agent was added to the system in a weight ratio of 1:1 with respect to the Mt. The mixture was sonicated for 10 min and then refluxed for 8 h. The pH of the system was adjusted to be ~4.5 using HCl acid (37%) [37,38]. The modified Mt powder was centrifuged, washed three times with ethanol and dried at 80 °C for 12 h.

2.3. Characterization techniques for Mt nanoclays

The chemical interactions between the Na-Mt and 3-GPTMS were evaluated using a JASCO FT-IR spectrometer (FT-IR 460 plus). Vibration bands were reported as wavenumber (cm^{-1}). The FT-IR spectra were recorded in the 400-4000 cm^{-1} range with a resolution of 4 cm^{-1}. The specimens for the FT-IR analysis were prepared by using KBr pellets.

The STA analysis (TGA+DTA – model: STA504) was carried out in a nitrogen atmosphere, with a flow rate of 50 mL min^{-1}, in the temperature range of 25–800 °C at a heating rate of 10 °C min^{-1}. The percentage of grafted silane (PGS) can be expressed by Eq. (1) as follows [39]:

$$PGS(\%) = \frac{100 \times W_{200-600}}{100 - W_{200-600}} \tag{1}$$

where, $W_{200-600}$ is the weight loss in the temperature range of 200–600 °C and M corresponds to the molecular weight of the silane coupling agent. Here, the PGS is considered as the percentage of organic 3-GPTS moieties with respect to the total mass of nanoclay. The structure of the Na-Mt and modified nanoclays and

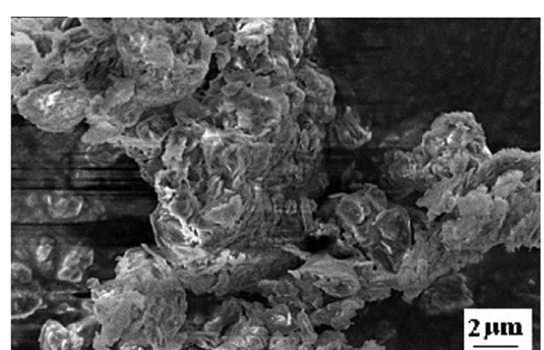
Fig. 1. SEM image of as-received Na-Mt.