Mechanical performance of multiscale basalt fiber–epoxy laminates containing tourmaline micro/nano particles

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\textbf{A R T I C L E   I N F O}

\textbf{Article info}
Received 7 November 2012
Received in revised form 7 October 2013
Accepted 25 October 2013
Available online 5 November 2013

\textbf{Keywords:}
A. Particle-reinforcement
B. Mechanical properties

\textbf{A B S T R A C T}

In this study, the effect of different tourmaline (TM) micro/nano particle loading (i.e., 0.5–2 wt\%) on the tensile and flexural properties of a basalt fiber-reinforced epoxy composite laminate (BFRP) was investigated. The TM/basalt/epoxy laminates were fabricated by impregnating woven basalt fibers into epoxy resin mixed with TM particles via vacuum assisted resin transfer molding. Tensile and flexural tests were performed according to ASTM standards. Fracture surfaces were characterized by scanning electron microscopy and energy dispersive spectroscopy. The results showed significant improvement in both tensile and flexural strength and modulus when tourmaline particles where incorporated in the basalt/epoxy composite. The best result was obtained at 1 wt\% TM loading with surfactant (i.e., C4) showing an increase of \~16\% in both tensile and flexural strength, and 27.4\% and 153.3\% increase in tensile and flexural modulus, respectively, compared to neat basalt/epoxy composite. The enhanced performance of TM/basalt/epoxy laminates is attributed to a good dispersion of TM particles in the epoxy matrix providing increased surface area for strong interfacial interaction and good load transfer.

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1. Introduction

Fiber-reinforced polymeric composites (FRCs) are used in many applications such as in aerospace, automotive, marine, recreational equipment, construction, and other high performance applications due to their high stiffness to weight ratio and their ease of processing [1,2]. For epoxy-based laminates, fibers such as carbon fiber, glass fiber, and basalt fiber have been used as filler materials to improve the overall properties of the composite laminate. Due to environmental concerns, recent research has been on the use of natural fibers for polymer reinforcement [3]. Flax and hemp fibers are good natural fiber reinforcement materials having acceptable mechanical properties and low cost, however, there is difficulty in maintaining their properties when exposed to high temperature. They are also sensitive to humidity, as well as some experiencing adhesion problem with a polymer matrix [4]. Among the natural fibers, basalt fiber (BF) has been considered as a potential reinforcement of composite materials because of the following properties: good strength, excellent fiber–resin adhesion, sound insulation properties, low water absorption [5], good resistance to chemical attack, ecologically friendly, free from carcinogens and health hazards, high operating temperature range, and can be produced at considerably lower cost than carbon fiber [6–9]. Basalt fibers offer an excellent alternative to carbon fibers in different applications. BF is known to have higher tensile strength than E-glass fiber and has larger strain-to-failure than carbon fiber [7]. The excellent heat resistance and low water absorption of basalt fibers make them suitable as thermal insulation materials and hot fluid conduits [6]. Basalt fibers also showed potential as reinforcement for concrete mixture, which could provide high fire resistance. A recent study showed an increase in load-carrying capacity and deflection ductility of timber beams when reinforced with natural fibers including basalt fibers [10]. BFRPs can be utilized in heat shield, thermal insulating barriers and as fire protection [8,11]. Moreover, BFRPs showed good potential as an alternative to glass FRP bars for reinforcing concrete structures, especially those structures exposed to repeated load during service such as bridges and parking garages [12]. Additionally, BFRPs can be used as a jacket bonded around concrete columns to enhance their seismic performance [13]. Thus, BFRPs can potentially replace glass fiber...
reinforced polymers for various applications such as in aerospace, construction, transportation, automotive, and shipbuilding.

In recent years, the use of multiple reinforcement length scales has been extensively explored in the design of composite laminates with improved properties [1,14–17]. Research in nanocomposites, where micro or nanoparticles (NPs) are incorporated in the polymeric matrix has generated vast interest in the past two decades [18]. It opens a new paradigm to tailor the polymer matrix to have optimized properties [19]. Organic or inorganic nanoparticles that have high surface-to-volume ratio are used as filler materials, and when incorporated in a polymer matrix can provide synergistic properties that are difficult to obtain separately from their individual components [20,21]. Studies using carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as fillers in polymer composites have reported improved mechanical, electrical and thermal properties of the resulting composites [19,22–25]. Bekyarova et al. [15] selectively deposited CNTs on woven carbon fabric by electrophoresis, and fabricated a CNT/carbon fabric/epoxy composite via a vacuum-assisted resin transfer molding (VARTM) process. The multiscale composite showed a ~30% enhancement in interlaminar shear strength relative to carbon fiber-reinforce composite polymer (CFRP) and demonstrated significantly improved out-of-plane electrical conductivity. Other reports also indicated that surface chemical modification of nanoparticles significantly helps in the better dispersion of NPs in the polymeric matrix resulting in enhanced properties of the composite [14,26,27].

Many studies have attempted to enhance the properties of composite materials by incorporating nanoclays in the polymeric matrix. Inorganic nanoparticles such as nanoclays have gained wide interest as potential reinforcing materials because of their low cost and ease of fabrication [28]. In the present study, nonwoven basalt fiber/epoxy laminates dispersed with 0.5–2.0 wt% tourmaline micro/nanoparticles were fabricated by vacuum assisted resin transfer molding (VARTM). Tourmaline (TM) is a polar crystalline material belonging to a group of silicate minerals compounded with many elements called cyclosilicates [29,30]. In a previous study [31], the incorporation of tourmaline NPs in polyurethane nanofibers increased the mechanical properties of the nanocomposites. Furthermore, since TM is hydrophilic in nature, the resulting TM/PU nanofibrous mats showed increased hydrophilicity with the increase of TM NP content in the nanofiber. Here, we investigated the effect of the incorporation of tourmaline micro/nano particles in a basalt fiber-reinforced-epoxy matrix on the mechanical properties (i.e., tensile and flexural properties) of the composite laminates. The fractured surfaces were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Materials

Basalt fiber (EcoB4-F210, woven, 210 ± 10 g/m²) and tourmaline powder (TM, 325 mesh) were purchased from Seco-Tech, Korea and UBS Inc., Co., Ltd., Korea, respectively. The size of as-received TM particles was about 900 nm–8 lm. The epoxy resin (HTC-667C) and modified aliphatic amine hardener were provided by Jet Korea Co., Korea. Acetone (Junsei, Japan) was used to initially disperse the TM NPs before mixing with epoxy resin. Triton X-100 was used as a surfactant and was purchased from OCI Company, Ltd., Korea. All chemicals and materials were used as received.

2.2. Fabrication of composite laminate

Tourmaline particles were first dispersed in 50 ml acetone by using a homogenizer operating at 10,000 rpm for 30 min. The high shear force from the homogenizer helps in breaking down the agglomerated TM particles and reduces their size, and properly

Table 1

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Name convention</th>
<th>Concentration of TM particles with respect to epoxy resin (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt-fiber reinforced plastic (composite)</td>
<td>BFRP</td>
<td>0</td>
</tr>
<tr>
<td>Basalt/epoxy composite with 0.5 wt% TM (no surfactant)</td>
<td>C1</td>
<td>0.5</td>
</tr>
<tr>
<td>Basalt/epoxy composite with 1.0 wt% TM (no surfactant)</td>
<td>C2</td>
<td>1.0</td>
</tr>
<tr>
<td>Basalt/epoxy composite with 2.0 wt% TM (no surfactant)</td>
<td>C3</td>
<td>2.0</td>
</tr>
<tr>
<td>Basalt/epoxy composite with 1.0 wt% TM (with surfactant)</td>
<td>C4</td>
<td>1.0 + surfactant</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic layout of the preparation and fabrication process of the BFRP and composite laminates.
disperses the TM particles in the solution. The TM solution was then mixed with the epoxy/acetone solution (without hardener) and was stirred overnight. The TM/epoxy/acetone solution was degassed in a dry oven at 60°C for 30 min to evaporate the acetone. A hardener was then added to the solution and was mixed by manual stirring and then was again degassed for 45 min in a dessicator yner vacuum to release the trapped bubbles. The concentration of TM particles was varied from 0.5 wt% to 2 wt% with respect to the epoxy/hardener solution. Additionally, to check the effect of surfactant in the dispersion of TM particles, one sample was prepared with Triton X-100 added to the TM/expoxy/acetone solution containing 1 wt% TM particles. The Triton X-100 to TM ratio in solution was 5:1.

Fig. 1 shows a schematic of the preparation and fabrication process of the present samples. Composite laminates were fabricated via a VARTM process. First, 10 layers of basalt fabric with a size of 250 mm × 250 mm were stacked in the VARTM stainless steel plate mold (size: 300 mm × 300 mm), and were wrapped with vacuum bagging film using a sealant tape (AT200Y). The TM/epoxy solution was then injected into the mold through a vacuum pump (–80 kPa) for 30–40 min. The prepared panel (i.e., molded material) was cured in an autoclave at 65°C for 2 h. For comparison, neat basalt/epoxy laminate (BFRP) was also prepared as the control. Table 1 shows the composition and name conventions of the samples prepared in this study.

2.3. Measurements and characterization

Tensile test was performed according to ASTM D 3039M-00 using a universal testing machine (Unitech–M, R&B). The composite plates were cut into dog-bone shape test specimens (L = 165 mm) by water jet cutting. At least five specimens were tested for each sample and the average of which is reported here. The test was conducted at a crosshead speed of 2 mm/min at room temperature.

Flexural (three-point bending) test was carried out according to ASTM D970. The average of at least five measurements of each laminate sample is reported here. Rectangular shape (L = 76.2 mm, W = 12.7 mm) specimens were used. The crosshead speed was maintained at 3 mm/min.

Scanning electron microscopy (SEM, JEOL JSM-5900) was utilized to characterize the morphological structure of the tourmaline particles and the cross-section of the fracture surface of the composite laminates. The elements at the cross-section of the samples were analyzed by energy dispersive X-ray spectroscopy (EDS) attached to SEM machine.

3. Results

Fig. 2 shows typical tensile stress–strain curves of BFRP and composite samples. Here, the stress linearly increased with increasing strain until reaching failure for all samples. BFRP

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile properties</th>
<th>Flexural properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>% Gain/loss in strength (±)</td>
<td>Modulus (GPa)</td>
</tr>
<tr>
<td>BFRP</td>
<td>307.5 ± 8.8</td>
<td>0</td>
</tr>
<tr>
<td>C1</td>
<td>325.7 ± 4.9</td>
<td>+5.9</td>
</tr>
<tr>
<td>C2</td>
<td>311.0 ± 11.1</td>
<td>+7.6</td>
</tr>
<tr>
<td>C3</td>
<td>318.9 ± 22.1</td>
<td>+10.2</td>
</tr>
<tr>
<td>C4</td>
<td>357.2 ± 3.1</td>
<td>+16.1</td>
</tr>
</tbody>
</table>

Fig. 3. Average tensile strength and modulus of the BFRP and TM particle-reinforced composite laminates.
showed the lowest tensile strength, while the incorporation of TM particles has increased the tensile strengths of the composites. Fig. 3 shows the average tensile strength and Young’s modulus of the present samples. The basalt/epoxy laminate (i.e., BFRP) shows a tensile strength and modulus of $308 \pm 9$ MPa and $14 \pm 0.5$ GPa, respectively. The incorporation of tourmaline particles in the composite laminate showed increasing trend for both tensile strength and modulus with the increase of TM content. The composite laminates showed an increase in tensile strength of 5.9%, 7.6%, 10.2%, and 16.1% for C1, C2, C3, and C4, respectively compared to that of BFRP (see Table 2). The modulus of elasticity is shown to continually increase with the increase of the TM content. One interesting result is that with the increase in tensile strength and modulus of composite laminates, there was negligible effect on the tensile strain of the composites (see Fig. 4). From among the samples, C4, i.e., with the use of surfactant to disperse TM particles, showed the best results in the improvement of tensile strength and Young’s modulus. The surfactant helped in making the TM particles more hydrophilic, thus improving their dispersibility in the epoxy matrix.

Flexural (3-point) bending tests were performed to check the effect of TM filler particles on the stiffness and strength of composite laminates. Fig. 5 shows the average flexural strength and Young’s modulus of the present samples. The flexural strengths of the composite laminates increased by 1.3%, 4.5%, 10.3%, and 16% for C1, C2, C3, and C4, respectively relative to BFRP (see Table 2). The composite laminates also showed significant improvement in the Young’s modulus from bending. The modulus of BFRP was 6.5 GPa, but when different concentrations of TM particles were loaded, the modulus of composite laminates was

Fig. 5. Average flexural strength and modulus of the BFRP and TM particle-reinforced composite laminates.

Fig. 6. Representative SEM images of the fracture surfaces after tensile test of: (a) BFRP, (b) C1, (c) C2, (d) C3, and (e) C4. The EDS spectra of the boxed area (i.e., TM particle on basalt fiber) in (d) is shown in (f).
13.6 GPa, 14.7 GPa, 15.4 GPa, and 16.4 GPa, for C1, C2, C3, and C4, respectively. This translates to an increase of 110–153% in modulus relative to BFRP. Similar to the results in tensile test, C4 showed the highest improvement in flexural properties from all the samples. The increased flexural properties signify that TM particles were homogeneously dispersed in the epoxy matrix.

Fig. 6 shows the SEM images of the fractured surfaces of the BFRP and composite laminates after tensile test. In BFRP (Fig. 6a), a fracture at the resin was observed, with fiber-matrix interfacial debonding, and separation and fracture of fibers. The composite laminates with different TM particle contents without surfactant (Fig. 6b–d) showed better fiber-matrix bonding. A few fiber delamination in C2 was found. Some TM particle agglomeration could be seen at C3 (Fig. 6d) and voids as well. In C4 (Fig. 6e, i.e., with surfactant), the fibers were observed to be between the basalt fiber filaments and were tightly packed with very good fiber-matrix interfacial bonding. The EDS spectra (see Fig. 6f) of the boxed area in Fig. 6d confirmed the presence of TM particles on the surface of basalt and the epoxy matrix showing the elemental components of TM. Fig. 7 shows the fracture surfaces of the present samples after flexural test. BFRP (Fig. 7a) showed some fiber pull-outs and voids, and fiber-matrix debonding. In C1 (Fig. 7b), some delamination and cracks were seen to occur in the composite. Some broken fibers are observed in C2 (Fig. 7c), which relates to strong interfacial bonding with TM/epoxy matrix, i.e., less fiber pull-outs. A good epoxy-fiber bonding and well-impregnated TM particles were observed in C4 (Fig. 7d).

4. Discussion

The technology in micro/nano particle reinforcement in polymer matrix can be categorized into inorganic layered clay technology, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and metal particle technology [34–37]. Due to lower cost and ease of fabrication, several inorganic particles have been used for composite reinforcement such as silica NPs, alumina NPs, boron nitride, and nanoclays to improve the properties of the composite materials [34]. Dean and colleagues [1] reported an increase of 31% and 24% in flexural modulus and flexural ultimate strength, respectively when they incorporated 2% silicate loading in carbon fiber-reinforced epoxy laminate. Shahid et al. [38] investigated the effect of chemically-functionalized alumina nanoparticles (carboxylate–alumoxanes) on the performance of CFRP materials. They concluded that the miscibility of alumoxane nanoparticle in the resin is of prime importance in the mechanical performance of the composite. They also suggested that <5% loadings must be used to provide enhanced performance.

In this study, we used tourmaline micro/nano particles to improve the properties of basalt fiber-epoxy composite laminates. To the authors’ best knowledge, no one has reported yet on the use of tourmaline particles for reinforcement in composite laminates. Here, the increase in mechanical properties of composite laminates is attributed to the efficient stress-transfer from epoxy to TM particles and basalt fibers, originating from the homogeneous dispersion and the strong interactions between epoxy matrix and TM particles, and fiber-epoxy interfacial interaction. For an effective load transfer of polymer matrix to filler particles, a good dispersion of filler particles is necessary. Studies show that the load-transfer mechanism happens due to the mobility of filler particles, wherein the particles orient themselves under tensile stress, forming temporary cross-links with polymer matrix, thus creating a local region of enhanced strength [39]. At high filler concentration, the TM particles tend to aggregate, which results to less homogeneous dispersion in the epoxy matrix, thereby decreasing the surface area for interfacial adhesion, and decreasing the free volume for particles to move around [34,40]. The aggregated particles lead to the formation of stress convergence points or as crack initiation sites [41], thus leading to lower tensile strain [42,43]. Especially at the highest TM concentration (C3), clusters of particles were observed (see Fig. 6d), which reflected that some particles agglomerated with each other. This suggests that even after high shear sonication process, the TM particles were not easy to disperse in the epoxy matrix. Similar observation was reported by Lam et al. [40] using nanoclays subjected to sonication. Basalt fiber is mainly composed of SiO₂, Al₂O₃, CaO, MgO, Fe₂O₃, TiO₂, MnO, and K₂O [44]. The structure of basalt fiber is similar to glass fiber, and its main structure is the network structure of Si–O–Si–[45]. Tourmaline is a silicate-based compound, which also has similar composition with basalt. In the present study, some of the TM nano-microparticles could have reacted with the silicon hydroxyl
groups at the basal fiber surface forming a new –Si–O–Si– bonding, which results in more uniform silicon-oxide network structure leading to improve mechanical properties [45]. In this study, the addition of surfactant (i.e., C4) lead to the better dispersion of TM particles in the epoxy matrix. This better dispersion provided more surface area for load transfer of epoxy matrix to TM particles, resulting in increased mechanical properties. Davis et al. [46] attributed the improvement in their composite laminate strength and stiffness to the enhanced fiber–matrix interfacial strength due to fiber–epoxy–f-CNT interfacial covalent bonding.

5. Conclusion

This study investigated the effect of tourmaline micro/nanoparticle-loading of 0.5–2 wt%, with and without surfactant on the mechanical properties of basalt fiber-reinforced epoxy composite laminate fabricated by a vacuum assisted transfer resin molding. Tensile and flexural tests and fracture surface characterizations were performed. The composite laminates with different TM loadings showed improved tensile and flexural properties compared to the neat basalt fiber–epoxy composite (BFRP). The tensile and flexural strengths increased by 5.9–10.2% with negligible effect on tensile strain, and 1.3–10.3%, respectively with increasing TM particle loading. The best result was obtained with C4, i.e., at 1 wt% loading + surfactant, wherein the tensile and flexural strengths increased by 16% and 16.1%, respectively compared to BFRP. Furthermore, the flexural modulus increased by as much as 153.3% when loaded with TM particles. SEM images exhibited good epoxy-fiber bonding and well-impregnated TM particles. The enhancements in mechanical properties are attributed to the good dispersion of TM particles in the epoxy matrix, which lead to high surface area for strong interfacial bonding. This study shows that the mechanical properties of neat BFRP can be further enhanced by the homogenous dispersion of TM particles in the epoxy matrix. The good interfacial adhesion between the polymer matrix and basalt fibers as well as the effective load transfer from the polymer matrix to the nanoparticles has led to the improvement of the mechanical properties. Proper dispersion of micro/nano fillers is an important requisite for effective mechanical property enhancement. The expanding applications of BFRPs in industries would benefit from this study and could provide additional information on the exploitation of micro/nano particles to further enhance the properties of epoxy-based composite materials.

Acknowledgements

This research was financially supported by the Ministry of Education, Science and Technology (MEST) and the National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation. I.D.G. Ary Subagia acknowledges the support from the Degree General High Education (DGHE) postgraduate abroad scholarship of the Republic of Indonesia for his Ph.D. program at Chonbuk National University in Republic of Korea.

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