Role of dry ozonization of basalt fibers on interfacial properties and fracture toughness of epoxy matrix composites

https://doi.org/10.1515/ntrev-2021-0048
received March 31, 2021; accepted June 7, 2021

Abstract: The mechanical properties of basalt fiber-reinforced epoxy composites (BFRPs) are significantly dependent on the interfacial adhesion between basalt fibers (BFs) and the epoxy matrix. In this study, we proposed a simple and efficient method for deep and stable penetration of BFs into the epoxy matrix through dry-ozone treatments. To confirm the efficiency of the proposed method, BFRPs were fabricated using two types of composites: untreated BFs and dry-ozonized BFs in varying amounts, and the optimum amount of BFs for all the composites fabricated in this work was 60 wt%. With the addition of this amount of dry-ozonized BFs, the interlaminar shear strength and fracture toughness of the composites were enhanced by 21.2 and 23.2%, respectively, as compared with untreated BFs. The related reinforcing mechanisms were also analyzed, and the enhanced interfacial adhesion was mainly attributed to the mechanical interlocking effect. This approach shows that the dry-ozone treatment of BFs is a simple and efficient method for the preparation of BFRPs with excellent interfacial adhesion, which can be a potential application in the auto parts industry.

Keywords: basalt fiber-reinforced polymer composites, interfacial properties, fracture toughness

1 Introduction

Currently, carbon fiber-reinforced polymer composites (CFRPs) are being extensively studied owing to their superior mechanical properties [1–6]. However, while CFRPs can reduce vehicle weight by 30–60%, the cost of the overall process is not currently economically viable [7, 8]. Recently, basalt fibers (BFs) have attracted considerable attention as reinforcement in polymer-based composites and auto parts industry because it is eco-friendly, nontoxic, easy to process, and costs less than carbon fibers (CFs) [9–12]. However, poor interfacial interaction of the fiber surfaces, particularly for BFs with chemically inert surfaces, makes incorporation within a polymer matrix difficult due to low wettability, resulting in poor interfacial adhesion [13, 14]. Several recent studies have confirmed that surface modification was utilized to overcome these challenges in basalt fiber-reinforced polymer composites (BFRPs) [15–17]. In this regard, Lee et al. [18] demonstrated that acid treatment can promote the chemical reaction of BFs with an epoxy matrix. In addition, Kim et al. [19] demonstrated that plasma-treated BFs enhance the interlaminar shear strength (ILSS) of BFRPs. As is well known, high concentration acid and plasma treatment has shown promising results to improve interfacial adhesions onto BFRPs. However, it has been reported that defects/damage are unavoidably introduced onto the fiber surfaces when exposing fibers to plasma irradiation [20]. In addition, the high concentration acid requires strong acids or harmful chemicals, and consequently, fibers contain traces of undesirable chemicals and thus require further purification [21]. While both of these methods have demonstrated to be efficacious, they still have some drawbacks when applied to practical applications.

Dry-ozone treatment is an eco-friendly and straightforward process as compared with the other surface functionalization techniques [22, 23]. This treatment method can be performed in an atmospheric condition and can enhance the interfacial adhesions by inducing oxygen-
containing functional groups through the O₃ oxidation process [24,25]. In this respect, Downey and Drzal [26] modified CF surfaces using ozone treatment and found the enhanced interface and mechanical properties of CFRPs. Considering the above facts, not only do various functional groups on the dry-ozonized BFAs enhance wettability with the epoxy matrix, but they can also act as reactive sites for further promotion of interfacial adhesion between the BFAs and the epoxy matrix.

The aim of the present research is to explore the potential of BFRecs fabricated from dry-ozonized BFAs, which provides new types of economical and eco-friendly composites. Herein, the chemical and morphological changes of dry-ozonized BFAs were investigated, and the effects of dry-ozonized BFAs on the interfacial adhesion and fracture toughness of the composites are evaluated. Such an effort could result in the conversion of auto parts into fiber-reinforced polymer composites (FRPs) and provide a rational solution toward determining the theoretical limits of composite interfaces.

2 Experimental

2.1 Materials

Unless otherwise stated, chemicals were obtained from a commercial company and were used without further purification. BFAs (chopped-type, a diameter of 0.5 mm and length of 4.0 mm, F260 grade) were purchased from Secotech Co., Korea. Epoxy resin (density: ~1.16 g cm⁻³ at 25°C and epoxide equivalent weight: 185–190 g eq⁻¹) was purchased from Kukdo Co., Korea. A 4,4’-diaminodiphenylmethane (DDM) curing agent was purchased from Tokyo Chemical Co., Japan.

2.2 Dry-ozone treatment of BFAs

Figure 1(a) illustrates the dry-ozone treatment process. An Ozonetech Lab-Series ozone generator was used for the production of ozone from dry and pure O₂ as the gas source. The oxygen flow rate to the generator was maintained at 0.8 L min⁻¹ and monitored with a rotameter incorporated into the ozone generator. The diffusion rate of the O₃ gas, introduced from the bottom of the ozone chamber through a sintered metal diffusion plate, was 8 g h⁻¹ and was measured at room temperature for 4 h [20]. The dry-ozonized BFAs were denoted as OBPs.

2.3 Fabrication of OBPs/epoxy composites

Figure 1(b) illustrates the OBF/epoxy composite preparation process. First, different concentrations of BFAs or
OBFs (20, 40, 60, or 80 wt%) were added to an acetone/epoxy resin suspension and sonicated for 50 min at a power of 600 W (maximum temperature: 45°C). Thereafter, the mixture was heated in a vacuum oven at 100°C for 24 h to evaporate acetone. The curing agent (DDM) was added to the OBF/epoxy mixture and planetary mixed for approximately 5 min (planetary mixing is an efficient method to fabricate bubble-free composites). When the curing agent was dissolved, the resultant suspension was degassed at 70°C in the vacuum oven for 1 h to eliminate bubbles. After the bubble removal, the resulting mixture was continuously impregnated by BFs or OBFs using a three-roll milling machine for manufacturing the prepregs. Finally, the BF or OBF prepregs were cured at 80°C for 30 min, 110°C for 1 h, and 140°C for 2 h, and post-cured at 170°C for 2 h.

### 2.4 Characterization

X-ray diffraction (XRD, D2 Phaser, Bruker Co) was performed using the Cu-Kα radiation at 40 kV 40 mA⁻¹ at scan steps of 0.02° from 10° to 80° to obtain XRD patterns of OBFs. Fourier-transform infrared vacuum spectroscopy (FT-IR, VERTEX 80 V, Bruker Co) was performed to evaluate the chemical states using KBr (radiation ranging from 500 to 4,000 cm⁻¹). X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Co) was performed to study the surface elements of OBFs using a monochromated Mg-Kα source (1486.6 eV). High-resolution scanning electron microscopy (HR-SEM, SU8010, Hitachi Co) was performed at an operating voltage of 20 kV to characterize the fracture surface of the composites after coating with platinum. Dynamic contact angles (DCAs) were tested using the sessile drop method on a dynamic contact angle meter (Phoenix 300 Plus/Touch, SEO Co). As proposed by Fowkes [27], Owens and Wendt [28], and Kaelble [29], the surface free energy can be calculated using equations (1) and (2):

\[
y = y^L + y^{SP}
\]

\[
y_L(1 + \cos \theta) = 2\left(\sqrt{y^L} \cdot \sqrt{y^{SP}} + \sqrt{y^L} \cdot \sqrt{y^{SP}}\right),
\]

where \( y \) is the total surface free energy, \( y^L \) is the London dispersion component, \( y^{SP} \) is the specific polar components, \( L \) represents a liquid, \( S \) represents a solid, and \( \theta \) represents the DCAs [30]. The basic three-liquid data of surface free energy are provided in Table S1.

The universal testing machine (UTM, Lloyd LRSk, Lloyd-Instruments Co) was used to determine the fracture toughness (\( K_{IC} \)) of the composites in terms of the critical stress intensity factor, satisfying the requirements of ASTM E399. A span-to-depth ratio of 4:1 and a crosshead speed of 1 mm min⁻¹ were considered. The fracture toughness of the specimens was calculated as follows [31,32]:

\[
K_{IC} = \frac{FL}{bd^{3/2}} \cdot Y,
\]

where \( F \) is the critical load; \( L \) is the span between the supports; \( b \) and \( d \) are the specimen thickness and characteristic length, respectively; and \( Y \) is the shape factor given by

\[
Y = \frac{3a/d^{1/2}[1.99 - (a/d)(1 - a/d)(2.15 - 3.93a/d + (2.7a^2/d^2))]}{2(1 + 2a/d)(1 - a/d)^{3/2}},
\]

where \( a \) is the crack length. The precrack was cut to approximately half the specimen depth using a diamond razor blade (LSDC, DY Co).

The interlaminar shear strength (ILSS) of the specimens was evaluated using the UTM in three-point bending tests in accordance with ASTM D-2344 [33]. A span-to-depth ratio of 5:1 and a crosshead speed of 2 mm min⁻¹ were considered. The ILSS determined from the specimens was calculated as (5)

\[
ILSS = \frac{3F}{4bd^2},
\]

where the parameters are the same as those for \( K_{IC} \).

### 3 Results and discussion

#### 3.1 Characteristics of OBFs

XRD analysis was performed to investigate the crystallographic nature of BFs and OBFs, the results of which are shown in Figure 2(a). The XRD pattern indicates that a major portion of BFs has an amorphous structure [34,35]. The XRD pattern of the OBFs was similar to that of BFs, indicating that the amorphous structure and the interplanar spacing were the same. This indicates that the dry-ozonation process did not change the amorphous structure of BFs.

Figure 2(b) shows the FT-IR spectra of BFs before and after the dry-ozone treatment. After dry ozonization, the FT-IR spectra of OBFs exhibited a decrease in the peak at 914.6 cm⁻¹ (corresponding to the Si–O–Si stretching vibrations) while new peaks appeared at 1636.7 and 3379.3 cm⁻¹, corresponding to the adsorbed water and Si–OH stretching vibrations, respectively refs. [36–38].
In dry-ozone treatment, the Si–O–Si network is attacked by OH\(^-\) and H\(^+\). The reactions are explained by the following equations (6) and (7):

\[
\begin{align*}
\text{Si} - \text{O} - \text{Si} + \text{OH}^- &\rightarrow \text{Si} - \text{OH} + \text{Si} - \text{O}^- \\
\text{Si} - \text{O} - \text{Si} + \text{H}^+ &\rightarrow \text{Si} - \text{OH} + \text{Si}^- 
\end{align*}
\]

The OBF surfaces have a uniform structure because the OH\(^-\) and H\(^+\) ions attack at ozonization.

In addition, for a detailed investigation on the surface elemental composition and chemical states of OBFs, the Si2p and O1s XPS spectra were deconvoluted, and the results are shown in Figure 2(c) and (d). There were mainly three silicate groups present in the Si2p core level spectrum (Figure 2(c)), and the corresponding binding energies were determined to be 102.5, 103.7, and 105.8 eV \([19,38,39]\). The peak at the binding energy, centered at 102.5 eV, can be attributed to \([\text{SiO}_4]^{4-}\) (tetrahedron structure). The peak at lower binding energy at 103.7 eV can be attributed to \([\text{Si}_2\text{O}_5]^{2-}\) of the layer shape structure. Similar to the FT-IR spectrum, a new peak corresponding to \([\text{Si}_2\text{O}_6]^{4-}\) (chain shape structure), derived from the oxygen end radicals, appeared at 105.8 eV \([40,41]\). To support this claim, direct evidence for the oxygen end radicals introduced on the surface of BFs can be obtained from the O1s peak deconvolution of OBFs shown in Figure 2(d). For the O1s core level spectra of BFs, only one peak was observed at 532.6 eV, corresponding to the bridging oxygen. However, the O1s core level spectra of OBFs divided into two peaks at 532.2 and 534.3 eV corresponded to the bridging oxygen and non-bridging oxygen, respectively. From the results for O1s spectra, the OBFs demonstrate the presence of non-bridging oxygen groups on the surface, which could enhance the interfacial adhesion between the fibers and the epoxy matrix. Thus, the FT-IR and XPS spectra demonstrate the presence of oxygen-containing functional groups on the surface of OBFs, which could affect the curing reaction of the epoxy resin.

### 3.2 Morphologies of OBFs

The microstructures of BFs and OBFs were observed by SEM, as shown in Figure 3(a and b). As evident in Figure 3(a), the BFs were fairly straight and highly ordered structures, and the outer surface was partially covered with a layer of metal oxide and starch. As shown in Figure 3(b), after dry ozonization, the surface of OBFs was very smooth with a few pits and grooves. This is because dry ozonization begins at the outer surface of BFs and progressively removes some of the metal oxide and starch by continuous O\(_3\) oxidation. However, the fact that the highly ordered structure of OBFs is relatively clear proves that dry ozonization does not significantly disrupt the fiber structures.
3.3 Interfacial properties of OBF/epoxy composites

The surface free energy of the composites was closely related to the wettability between the fibers and epoxy matrix [42,43]. A high surface free energy can lead to better wettability and strong interfacial adhesion. The total surface free energy results for the OBF/epoxy composites are listed in Table S2 and shown in Figure 4(a). As expected, the BF/epoxy composites exhibited a low surface free energy due to the chemically inert BF surfaces. In contrast, the surface free energy of the OBF/epoxy composites was enhanced significantly compared to that of the BF/epoxy composites. Compared to the 20 wt% BF/epoxy composites (35.4 mJ m$^{-2}$), the surface free energy values for the 20 wt% OBF/epoxy composites (37.2 mJ m$^{-2}$) increased by 5.1%. Moreover, the measured highest surface free energy value was 39.7 mJ m$^{-2}$ in the 60 wt% OBF/epoxy composites, leading to a 7.6% increase compared to that of the OBF/epoxy composites (36.9 mJ m$^{-2}$). In particular, the polar components of the OBF/epoxy composites exerted a greater influence on the surface free energy than the London dispersion components. The polar component of the BFs/epoxy composites reached roughly from $-6.4$ to a maximum of $-7.8$ mJ m$^{-2}$. In contrast, for the OBF/epoxy composites, the polar component increased significantly, ranging from $-7.5$ to $-9.8$ mJ m$^{-2}$, indicating that OBFS are more compatible with the polar epoxy matrixes. As demonstrated via FT-IR and XPS, the OBFS showed an increase in the oxygen-containing groups, which could be an important contributing factor for the improvement in the polar components [44,45].

To support this explanation, we performed a detailed study on the wetting behavior of distilled water (at 27°C for 5 min) acting on the composites. It can be seen from Figure 4(b) that the wetting behavior of the 60 wt% BF/epoxy composite indicates low wettability due to the chemically inactive surface of BFs, and the DCA is maintained at roughly 64.1°. In contrast, the wetting behavior of the 60 wt% OBF/epoxy composites decreased the DCAs rapidly and became saturated at approximately 41.8°.

![Figure 3: Surface morphology of BFs and OBFS: (a) SEM images of BFs and (b) OBFS.](image)

![Figure 4: Interfacial interaction of BFs/epoxy and OBFS/epoxy composites: (a) surface free energy and (b) optical images of the DCA of distilled water over time.](image)
This decrease is due to the oxygen-containing groups with a large number of hydrophilic surfaces on the OBFs from which water droplets could rapidly diffuse, thereby indicating enhanced wettability within the composites.

3.4 Mechanical properties of OBF/epoxy composites

The ILSS and $K_{IC}$ can lay a solid foundation for the shear and fracture properties depending on the interfacial adhesion of the fibers within the epoxy matrix [46–48]. Therefore, the mechanical properties, including ILSS and $K_{IC}$, were studied for the OBF/epoxy composites to evaluate their efficiency. As shown in Figure 5, the OBF/epoxy composites revealed good linearity in the relationship between the mechanical properties and surface free energy. In addition, the OBF/epoxy composites showed significant improvements in the ILSS and $K_{IC}$ values as compared to those of the BF/epoxy composites. Compared to the 20 wt% BF/epoxy composites, the ILSS and $K_{IC}$ values of the 20 wt% OBF/epoxy composites increased by 43.0 and 22.5%, respectively. Moreover, the measured highest ILSS and $K_{IC}$ values reached 33.8 MPa and 58.5 MPa m$^{1/2}$ in the 60 wt% OBF/epoxy composites, leading to a 21.2 and 23.2% increase compared to those in the 60 wt% BF/epoxy composites, respectively. These results indicate that the additional interfacial interlocking was active when OBFs were included within the epoxy matrix, and this enhanced the mechanical properties of the composites.

3.5 Interfacial mechanism of OBFS/epoxy composites

The schematic in Figure 6 depicts the interfacial mechanisms explaining the interfacial interlocking. As the crack opens, the cracks as shown in Figure 6(a) and (b) can occur, depending on the interfacial adhesion of the composites. For the BF/epoxy composites (Figure 6(a)), the crack paths can immediately extend to the fiber surface due to poor adhesion at the interface. Consequently, the composites could crack easily under a low load. In contrast, the OBF/epoxy composites (Figure 6(b)) prevented the cracks from contacting directly with the fiber surface, and crack paths could deviate into the interface area. This interface acted as a crack pinning that reduced the

Figure 5: Mechanical properties of BFs/epoxy and OBFS/epoxy composites: (a) ILSS and (b) fracture toughness.

Figure 6: Schematic description of interfacial mechanism: (a) BFs/epoxy composite and, (b) OBFS/epoxy composites.
internal stress concentration and enhanced the energy dissipation during deformation.

Some evidence for these interfacial mechanisms could be demonstrated on the presented fractured surfaces. Figure 7(a–d) displays SEM images of the fractured surfaces of the BF/epoxy and OBFs/epoxy composites. For the 60 wt% BF/epoxy composites (Figure 7(a) and (c)), there are distinct cracks between the BFs and the epoxy matrix. Consequently, the interfacial debonding occurred on the BF surfaces; the BFs were totally detached from the resin, and a large number of holes remained in the epoxy matrix. In contrast, the 60 wt% OBF/epoxy composites exhibited crack progression almost proprietarily along the rich interfaces and were tightly embedded within an epoxy matrix without de-bonding (Figure 7(b) and (d)). This inhibits propagation through the epoxy matrix as a crack must pass either through or fiber regions with epoxy-rich interfaces, resulting in enhanced mechanical properties.

4 Conclusion

In summary, OBFs were effectively utilized as reinforcements to enhance the interfacial adhesion of composites, thereby leading to a significant enhancement in both ILSS and $K_{IC}$. The enhanced interfacial adhesion was attributed to the oxygen end radicals introduced to the OBF surfaces, which can penetrate deep and stably into the epoxy matrix. In this regard, the measured highest ILSS and $K_{IC}$ values reached 33.8 MPa and 58.5 MPa m$^{1/2}$ with 60 wt% OBF/epoxy composites, indicating 21.2 and 23.2% enhancement compared to the 60 wt% BF/epoxy composites. Our results demonstrate that the hierarchical OBF/epoxy composites with outstanding interfacial adhesions and mechanical properties obtained through simple and commercial manufacturing are attractive candidates for fabricating new types of structural-functional integrated composites.

Funding information: This work was supported by the “Policy R&D program KPP20002.2” funded by the Korea Institute of Ceramic Engineering and Technology, Republic of Korea, and the Technological Innovation R&D Program (S2829590) funded by the Small and Medium Business Administration (SMBA, Korea).

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.
Conflict of interest: The authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analysed during the current study are available in the Supplementary material on the journal website.

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