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Full Length Article

Basalt fiber modified with lanthanum-ethylenediaminetetraacetic acid as potential reinforcement of cyanate matrix composites

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ABSTRACT

Basalt fiber (BF) is a promising material for 2,2′-bis(4-cyanatophenyl)isopropylidene reinforcement that is cost effective and has a low dielectric constant. In this study, BF was impregnated with lanthanum-ethylenediaminetetraacetic acid (La-EDTA) to improve its mechanical and interfacial properties. The properties of the La-EDTA BF and pristine BF were compared using X-ray diffraction, scanning electron microscopy, energy-dispersive spectrometry, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy to reveal the modification mechanism. The results confirmed that La-EDTA was successfully introduced on the BF surface as a crystalline lanthanum dihydrate via the reaction between various oxides and the −COOH group of La-EDTA. Moreover, the structure–property relationship of the La-EDTA BF was investigated by performing tensile strength and contact angle tests of BF monofilaments. The results showed that the average BF monofilament fracture load increased from 124.03 mN to 163.29 mN after modification; further, the contact angle between BF and 2,2′-bis(4-cyanatophenyl)isopropylidene decreased at 200 °C due to chemical compositional changes on the BF surface. This study confirms the applicability of La-EDTA BF as a reinforcement for BADCy composites.

1. Introduction

Basalt fiber (BF) has attracted increasing attention as reinforcement for polymers due to its environmental friendliness, corrosion resistance, excellent mechanical properties, marginal health hazards, and cost effectiveness [1–4]. BF has excellent application prospects in aerospace, environmental protection, military, and other fields requiring good interfacial performance [5–8]. 2,2′-Bis(4-cyanatophenyl)isopropylidene (BADCy) has outstanding dielectric properties and favorable heat resistance and process ability [9]. Commonly used in radar wave-transparent materials and insulating materials [10], the major shortcoming of BADCy is its brittleness. Inorganic fiber toughening is an effective way to decrease its brittleness [11–13]. However, carbon fillers are more expensive than BF and can result in an increase in the dielectric constant [10–13,14], which impairs the wave-transmitting capability of BADCy. Although glass fibers are cheap, their mechanical properties are poorer than those of carbon fibers and BFs [1]. In contrast, as a potential BADCy reinforcement material, BF has a low dielectric constant and price that does not increase the dielectric constant and cost of the BADCy composites. However, there are some obstacles to the application of BF-reinforced BADCy. First, research on BF-reinforced BADCy has been scarce. Second, some BF surface modification methods can degrade the mechanical properties of BF [15], thereby degrading the mechanical properties of the composites [16]. Recently, some methods have been developed to modify the basalt surface to obtain better interface properties. Coating by inorganic particles (carbon [4], graphene [17], SiO_2 [18], TiO_2 [19]) can improve the mechanical interlocking of BFs and polymer matrix, but the inappropriate selection of inorganic particles or colloids impairs the dielectric properties of the composites. Previous chemical treatments (acetone [20], NaOH and H_2SO_4 [21,22], silane coupling agents [23–25]) have been found to be beneficial to increase the chemical bonding of BF to the matrix, but these methods introduce chemical bonds on the BF surface [23–25]) or degrade the mechanical properties of BF [21,22]. Thermal treatment [20] and plasma treatment [15,26] have also been confirmed to slightly degrade the mechanical properties of BF [22]. Therefore, surface modifiers suitable for BF-reinforced BADCy composites should have multiple functionalities, should increase chemical interlocking, and should not

Abbreviations: BF, basalt fiber; BADCy, 2,2′-bis(4-cyanatophenyl)isopropylidene; La-EDTA, lanthanum-ethylenediaminetetraacetic acid; XRD, X-ray diffraction; SEM, scanning electron microscopy; EDS, energy-dispersive spectrometry; FTIR, Fourier transform infrared; XPS, X-ray photoelectron spectroscopy; IEPS, isoelectric point of solid surface; La-HEDTA, lanthanum hydroxyethyl ethylenediaminetriacetic acid dihydrate

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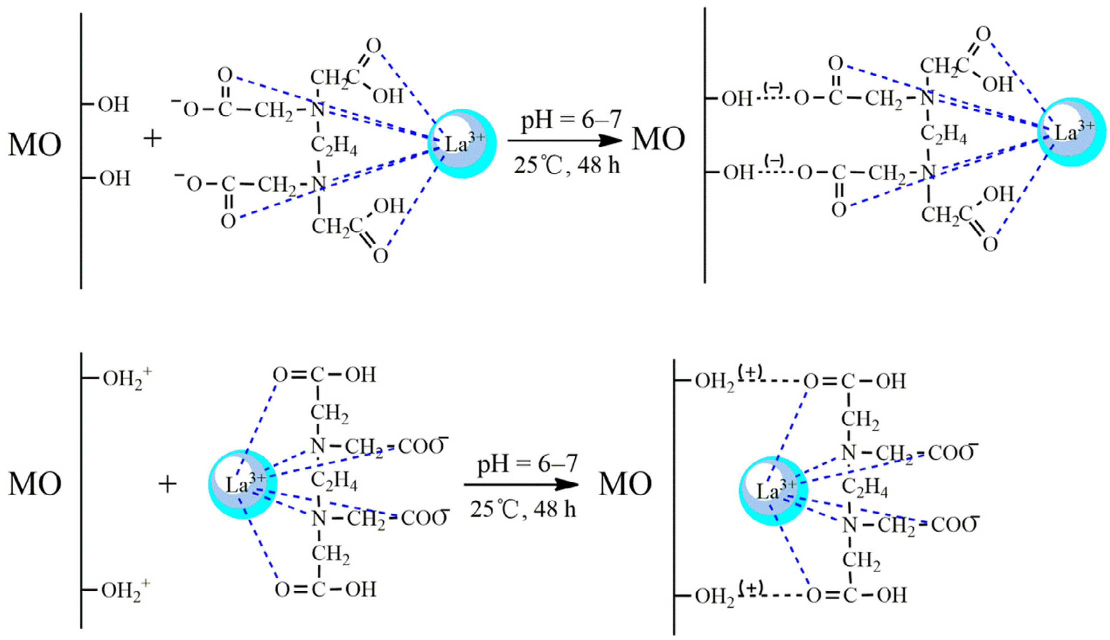

Fig. 1. Scheme of modification mechanism.

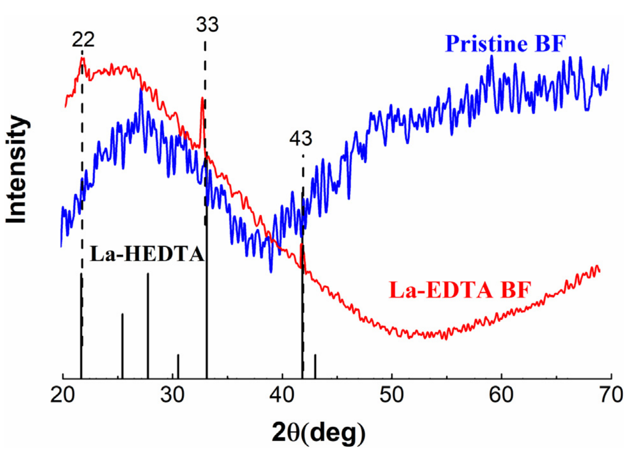

Fig. 2. XRD spectra of pristine BF and La-EDTA BF.

degrade the mechanical properties of BF.

Rare-earth ions possess diverse coordination modes and variable coordination numbers; thus, rare earth ethylenediaminetetraacetates as complexing agents [27,28] are effective surface modifiers for inorganic–organic interfaces. Lanthanum-ethylenediaminetetraacetic acid (La-EDTA) is suitable as a surface modifier for inorganic particles and fibers and can effectively improve the overall performance of composite materials [28–32] (such as thermal stability and frictional properties). The mechanisms of La-EDTA modification with silicon, silicon dioxide, carbon, alumina, and iron oxide [30–33] have been investigated previously. However, the modification mechanisms reported in these studies are applicable to only monocomponent oxides and are unsuitable to multicomponent materials such as BF [29,34,35]. On the other hand, previous research on La-EDTA-modified multicomponent oxides, such as glass fiber or BF, mainly focused on the properties and applications of fiber-reinforced composites and the modification mechanisms were rarely discussed [28,29,36]. Unfortunately, the composition of BF inevitably affects La-EDTA modification [37]. Therefore, the study of the modification mechanism is crucial for the control and design of the modification process.

In this study, to improve the interfacial properties of BF and BADCy without degrading the mechanical properties of BF, La-EDTA BF was prepared by impregnation. To reveal the modification mechanism, BF and La-EDTA BF were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Moreover, by investigating the structure–-property relationship of La-EDTA BF, the origin of the change in the wetting and mechanical properties of BF were determined.

2. Experimental

2.1. Materials

BF with an average diameter of 10 µm was obtained from Shanxi Jintou Basalt Fiber Co., Ltd., Shanxi, China. $LaCl_3{\cdot}nH_2O$ was obtained from Shanghai Shanpu Chemical Factory, Shanghai, China. C_2H_5OH, HNO_3, $CO(NH_2)_2$, EDTA, and analytical-grade NH_4Cl were obtained from Guangdong Chemical Reagent Engineering Technological Research and Development Center, China. 2,2′-bis(4-cyanatophenyl) isopropylidene (BADCy) was provided by Yangzhou Tianqi New Material Co. Ltd., China.

2.2. Sample preparation

2.2.1. Preparation of La-EDTA modifier

$LaCl_3{\cdot}nH_2O$, EDTA, HNO_3, NH_4Cl, and $CO(NH_2)_2$ were taken in an C_2H_5OH solution in concentrations of ~1 wt%, 2 wt%, 0.5 wt%, 1 wt%, and 5 wt%, respectively. The solution was blended at room temperature (25 °C) for 2 h, followed by filtration of the precipitate, and addition of only the liquid from the beaker into the alcoholic solution of the La-EDTA modifier. The pH of the La-EDTA modifier was 6–7.

2.2.2. Preparation of La-EDTA BF [28,38]

First, BF was cut into 2-cm-long fibers, washed for 5 min using alcohol to remove the surface impurities, and repeatedly washed 10 times using deionized water to obtain pristine BF. Second, the as-obtained pristine BF was added into the La-EDTA modifier and immersed for ~48 h to form La-EDTA BF. Third, the La-EDTA BF was washed thrice using deionized water for ~10 min, followed by heat treatment at 80 °C for 4 h to completely dry the La-EDTA BF.