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Formation and application of hierarchical calcium silicate-calcium sulfate whiskers

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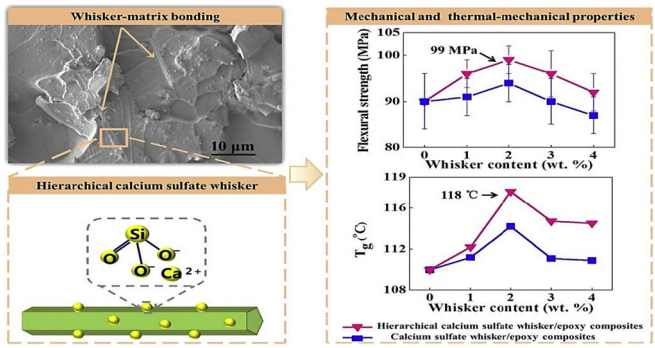
HIGHLIGHTS

- The hierarchical calcium silicate-calcium sulfate whiskers were prepared and used as reinforcements for epoxy composites.
- The hierarchical whiskers were formed via anchoring calcium silicate nanoparticles on whiskers in sodium silicate solution.
- The hierarchical whiskers with high surface roughness improved the mechanical interlocking among whiskers and resin matrix.
- The addition of 2.0 wt% hierarchical whiskers increased the flexural strength (10%) and T_g (8 °C) of epoxy composites.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile method was designed for synthesizing hierarchical calcium silicate-calcium sulfate whiskers (H-CSW) via treatment of the calcium sulfate whiskers (CSW) in sodium silicate solution. Calcium silicate nanoparticles with a size of 70–100 nm were uniformly anchored on H-CSW surfaces and the specific surface areas of the whiskers increased from 6.0 $m^2 \cdot g^{-1}$ to 29.1 $m^2 \cdot g^{-1}$. The addition of 2.0 wt% of H-CSW in epoxy composite led to the increase of 10% in flexural strength, 16% in flexural modulus, 18% in storage modulus (30 °C) and 8 °C in glass transition temperature owing to the enhanced mechanical interlocking among H-CSW and the epoxy matrix.

1. Introduction

Calcium sulfate whiskers (CSW) were often prepared via moderate hydrothermal route from the cheap and rich raw materials as commercial dihydrate calcium sulfate, natural gypsum, phosphogypsum, and flue gas desulfurization gypsum, et al. [1]. Compared with the conventional inorganic fillers as clay, silica, and calcium carbonate, etc., CSW were fiber-shaped single crystals with many desirable properties such as high aspect ratio, high strength and stiffness, non-toxicity and low cost, making them the excellent fillers for polymers [2–10].

Epoxy resins were thermosetting materials intensively used as the polymer matrix owing to their excellent mechanical strength, thermal stability and chemical resistance [11]. The addition of inorganic fillers as CSW in an epoxy resin can improve the mechanical and heat-resistance properties to match the next-generation electronics,

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coatings, and fiber-reinforced composite applications [12,13]. However, the reinforcing effect of CSW on epoxy matrix was often limited by the smooth surfaces of CSW due to the inadequate interfacial interaction among CSW and the tridimensional crosslinking network [14]. The former researchers often use coupling agents as silane and polyether titanate to increase the number of hydroxyl groups on CSW surfaces so as to improve the interactions among CSW and resin matrix. For example, the modification of CSW with silane coupling agent led to the increase of the strength of the modified CSW/polypropylene composite by 11.6% [15]; the modification of CSW with polyether titanate led to the increase of yield strength and Young's modulus of the modified CSW/PVC composite by 33.8% and 20.7%, respectively [16].

Recently, some hierarchical structures based on the one-dimensional materials were synthesized and exhibited perfect multi-scale reinforcing effects on the epoxy composites owing to the improved interfacial interactions. For example, the use of the hierarchical multi-walled carbon nanotubes composed of polyhedral oligomeric silsesquioxanes and polydopamine transition layers rather than the normal multi-walled carbon nanotubes led to the increase of 20.6% in compressive strength and 33.3% in the compressive modulus for the carbon nanotube/epoxy composite [17]; the coating of the SiC whiskers with iron oxide nanoparticles via polymer-polymer (poly(acrylic acid)/poly(2-vinyl pyridine)) complexation route led to the increase of 20% in the dynamic storage tensile modulus of the SiC/epoxy composite [18].

A facile anchoring method was designed in the present work to synthesize hierarchical CSW (H-CSW) composed of CSW and $CaSiO_3$ nanoparticles by treatment of the naked CSW in Na_2SiO_3 solution. The effects of CSW and H-CSW on the mechanical and thermal-mechanical properties of the epoxy composites were studied and the corresponding strengthening mechanisms were discussed. The objectives of this study not only provided a method for high-value utilization of CSW, but also offered a method for designing, fabricating, and optimizing high-performance polymeric composites.

2. Experimental methods

2.1. Preparation of CSW and H-CSW

2.1.1. Preparation of CSW

Commercial chemicals with analytical grade were used in the experiments. 0.60 g of $CaSO_4 \cdot 2H_2O$ and 60.0 mL of deionized water were mixed at room temperature in a small Teflon-lined stainless steel autoclave with an inner volume of 120.0 cm^3, then the autoclave was heated (5.0 °C·min^{-1}) to 135 °C and kept in isothermal condition for 4.0 h. After hydrothermal treatment, the suspension was cooled down to about 80 °C and filtrated. The product was washed with ethanol and dried at 105 °C for 2.0 h. Finally, the whiskers were sintered in a muffle oven at 600 °C for 2.0 h.

2.1.2. Preparation of H-CSW

0.40 g of CSW was mixed with 40.0 mL of 0.05 mol·L^{-1} Na_2SiO_3 at 100 °C in 100.0 mL beaker and kept in isothermal condition for 15.0 min. Then the suspension was filtrated, the product was washed with ethanol and dried at 105 °C for 2.0 h.

2.2. Preparation of CSW/epoxy composites

The 1.0, 2.0, 3.0, and 4.0 wt% of CSW or H-CSW were premixed with tetrahydrophthalic acid diglycidyl ester using mechanical stirring at 500 rpm under room temperature for 1.0 h. Then, the curing agent methylphthalic anhydride and accelerator 2-ethyl-4-methylimidazole were added into pure tetrahydrophthalic acid diglycidyl ester or the above mixed whisker/epoxy resin suspensions with a resin/anhydride/accelerator weight ratio of 100:67:1. The mixture was next degassed at 80 °C for 20.0 min under vacuum. Finally, the resin system was poured into a steel mold and cured via a thermal cycle regime of 80 °C for 1.0 h, 130 °C for 3.0 h, and 180 °C for 1.0 h. The same method was used to create neat epoxy composites without any filler as control samples.

2.3. Characterization

The morphology of the samples were detected by the scanning electron microscopy (SEM, JSM 7401F, JEOL Ltd., Japan) and the high-resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL Ltd., Japan). The composition of the samples were characterized by the powder X-ray diffractometer (XRD, D8 advanced, Bruker, Germany) using Cu Kα radiation (λ = 1.54178 Å),with a scanning rate of 5.0°·min^{-1} and a scanning 2θ range of 5° to 90°. The surfaces of samples were characterized by the X-ray photoelectron spectroscopy (XPS, Model PHI-5300, PHI, USA) with a Mg-Kα photon energy of 1253.6 eV and the atomic force microscope (AFM, Dimension, Bruker, Germany). The specific surface areas of the samples were analyzed by the N_2 adsorption–desorption analyzer (Quadrasorb-S1, Quantachrome,USA) and evaluated by the Brunauer-Emmett-Teller (BET) model. The soluble [Ca^{2+}] and [SO_4^{2-}] were detected by ion chromatography (CIC-300, ShengHan Chromatography Technology Co., Ltd., China).

According to the standard test method ASTM D790, the flexural performances of resin casts were analyzed using a universal testing machine (WDS-10, Beijing Guance Jingdian Instrument Inc., China) with a testing speed of 2.0 mm·min^{-1}. Ten samples with a span-to-depth ratio of 32/1 were tested for each sample type. The morphology of the fracture surfaces of the resin casts were observed using SEM and a scanning white-light interferometer (WLI, MicroXAM-100, KLA-Tencor Corp., USA). Before the SEM observation, the specimen surfaces were sputter-coated with platinum for electrical conductivity. Dynamic mechanical analysis tests for the epoxy casts were analyzed using a dynamic mechanical analyzer (DMA, TA Q800, TA Instruments, USA) with a double cantilever mode. The testing frequency was set at 1.0 Hz from room temperature to 250 °C with a heating rate of 5.0 °C·min^{-1}.

3. Results and discussion

3.1. Composition variation in the presence of Na_2SiO_3

The dissolution and precipitation behaviors of CSW in 0.05 mol·L^{-1} Na_2SiO_3 at 100 °C are shown in Fig. 1. Soluble [SO_4^{2-}] increased from 0.013 mol·L^{-1} to 0.050 mol·L^{-1} while [Ca^{2+}] kept at 1.1 × 10^{-5} mol·L^{-1} as the reaction time increased from 10.0 min to 60.0 min (Fig. 1a), which was connected with the dissolution of CSW and the precipitation of $CaSiO_3$:

$$CaSO_{4(s)} \rightarrow Ca^{2+} + SO_4{}^{2-} \quad K_{100\,°C} = 10^{-5.87} \qquad [1]$$

$$Ca^{2+} + SiO_3{}^{2-} \rightarrow CaSiO_{3(s)} \quad K_{100\,°C} = 10^{9.77} \qquad [2]$$

$$CaSO_4 + Na_2SiO_3 = CaSiO_3 + Na_2SO_4 \quad K_{100\,°C} = 10^{3.90} \qquad [3]$$

Soluble [Ca^{2+}] was 10^3 times lower than [SO_4^{2-}], indicating that the precipitation of $CaSiO_3$ was much faster than the dissolution of CSW. With the increase of reaction time from 10.0 min to 60.0 min, the weight percent of the dissolved CSW increased from 15.4 wt% to 64.2 wt% in Na_2SiO_3 solution while kept nearly constant at 6.0 wt% in water (Fig. 1b), indicating that the precipitation of $CaSiO_3$ accelerated the dissolution of CSW. The weight percent of $CaSiO_3$ in the products increased from 17.7 wt% at 10.0 min to 67.8 wt% at 60.0 min (Fig. 1b), indicating that most of the CSW was converted to $CaSiO_3$ after 60.0 min of reaction. The anchoring process was described in Fig. 1c.