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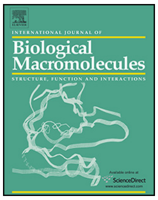

Effect of a silane coupling agent on the mechanical properties of a microfibrillated cellulose composite

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ABSTRACT

Composite materials reinforced with microfibrillated cellulose (MFC) fibers were prepared and characterized in terms of their mechanical properties. The surface of the MFC fibers was treated with a silane coupling reagent having an NH_2 functional group to improve fiber–matrix adhesion. Due to the unique structure of the MFC, which consists of nano-order-scale interconnected fibrils and microfibrils with greatly expanded surface area and submicron pore size compared to conventional cellulose, it was possible to enhance the effect of silane coupling agent and thereby improve the compatibility between the fibers and matrix and also the dispersibility of fibers. The Young's modulus was significantly increased to more than 70%.

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1. Introduction

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Across the globe, there has been increasing interest in preservation of the environment and sustainability of resources. Thus, the utilization of natural fibers is receiving renewed attention as an alternative to inorganic counterparts in materials technology. Particular consideration has been paid to cellulose fibers, which are the most abundant biomass resource on Earth [1].

The plant cell wall consists of nanofibers 4 nm in width and thickness, called cellulose microfibrils [2]. Because the nanofibers are bundles of semi-crystalline extended cellulose chains, the Young's modulus and tensile strength are as high as those of aramid fibers (trade name: Kevlar) [3,4], a well-known high strength fiber, and surprisingly the thermal expansion in the axial direction is as small as that of quartz [5,6].

In the early 1980s, a new type of cellulose morphology, called microfibrillated cellulose (MFC), was developed [7]. This was a new form of expanded, high-volume cellulose in which the fibers were moderately degraded and greatly expanded in surface area via a homogenization process. Because of their unique characteristics and efficient mechanical properties, MFC fibers showed great potential as reinforcing elements in composite materials based on polymeric matrices [1,5,6].

Although MFC has extraordinary potential as a reinforcement material, the composites made with MFC exhibit disadvantages because of the hydrophilic character of the MFC fibers, which is attributable to the presence of several hydroxyl groups on the fibers. The hydrophilicity of MFC leads to low affinity with widely used hydrophobic polymer matrices such as acrylic resin, and can spoil the advantages of the mechanical properties of MFC, because the low compatibility between the cellulosic fiber and matrix reduces the load transfer efficiency from the matrix to the fibers and the dispersibility of the fibers within the matrix [9,10].

Hence, surface modification of MFC fibers is very important to reduce the hydrophilic property and to increase the affinity between the MFC filler and matrix. Several approaches to modifying the surface to improve the compatibility have been studied [11–13].

Commercially available silane coupling agents are widely used for surface modification of inorganic fillers such as glass fiber [14]. The silane coupling chemicals have the general formula ($R{-}Si{-}(OR')_3$). In this formula, the R′ group is an alkoxysilane group that is capable of reacting with OH-rich surfaces after hydrolysis. The R group is chosen according to the property of the matrix. Thus, the R and R′ groups can improve the compatibility between the components of the composite [15].

Recently, Gandini et al. showed that silane coupling agents that include an amino group at the R group display a good affinity toward cellulosic substrate [16,17]. Previously hydrolyzed trialkoxysilane was physically adsorbed onto the fiber surface, and the chemical grafting was shown to occur followed by a thermal treatment. Furthermore, some studies showed that composite

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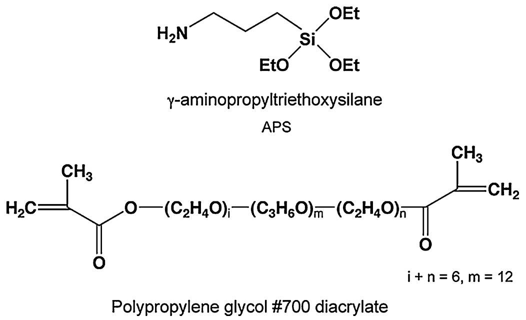

Fig. 1. The silane coupling agent and acrylic resin used in this work.

materials prepared using both matrices and cellulose fibers treated with silane coupling agents displayed good mechanical properties [15,18].

However, despite its attractive structure, there have been no attempts to employ MFC treated with silane coupling agents in the production of composites. Due to the unique characteristics of MFC, such an application would be expected to afford considerable mechanical improvement in the reinforcement–matrix interface interactions. Therefore, in this study we examined the effects of treatment with a silane coupling agent on the mechanical properties of an MFC-reinforced polymer composite.

2. Experimental

2.1. Materials

Microfibrillated cellulose (MFC; Celish KY-100G) was purchased from Daicel Chemical Industries, Ltd. (Tokyo, Japan). The silane coupling agent (γ-aminopropyltriethoxysilane (APS)) was provided by Shin-etsu Chemical Co., Ltd. (Tokyo, Japan). Acrylic resin (polypropylene glycol #700 diacrylate; APG-700) was provided by Shin-nakamura Chemical Co., Ltd. The molecular structures of the commercial silane and acrylic resin are shown in Fig. 1. A cotton fiber sheet was used as a reference (commercially available filter paper, Advantech No. 1).

2.2. MFC sheet production

13.3 g of Celish (MFC content 10%, water 90%) was suspended in 650 mL ethanol and homogenized by a high-performance disperser (T25 ULTRA-TURRAX, IKA) with a dispersing element (S25N-25F, IKA) at 13,500 rpm for 5 min. The ethanol suspension of MFC was vacuum filtered, producing a thin sheet 185 mm in diameter. The sheet was hot-pressed at 0.6 MPa and 120 °C for 4 min to obtain a dried flat sheet. The obtained MFC sheet was cut to about 40 mm long and 30 mm wide for silane coupling treatment.

2.3. Fiber treatments

Fibers were treated according to the procedure described in Ref. [17]. The treatment of MFC sheets with different amounts of the APS was carried out in 80/20 (v/v) ethanol/water medium under stirring for 2 h. Then the sheets were taken out of the solutions, dried at room temperature for 2 days, and heated at 120 °C under a vacuum for 2 h in order to promote condensation between the OH groups of the hydrolyzed silanes and OH groups present at the surface of the cellulose, resulting in the permanent chemical modification of the surface. All heat-treated samples were submitted to a 24 h Soxhlet extraction with ethanol to wash off the residual unreacted APS and hot-pressed at 0.6 MPa and 120 °C for 4 min for drying.

2.4. Composites preparation

Silane-treated and untreated MFC sheets were impregnated with neat acrylic resin (polypropylene glycol #700 diacrylate) under a reduced pressure of −0.09 MPa for 12 h. The resin-impregnated sheets were cured (20 J/cm^2) using UV curing equipment consisting of a F300S UV lamp system and an LC6 bench-top conveyer (Fusion UV Systems, Tokyo, Japan). The silane-treated and untreated MFC/resin composites thus obtained were about 135 μm thick, and the fiber contents of the nanocomposite were about 34 wt%.

2.5. Fourier transform infrared (FT-IR)-attenuated total reflection (ATR) spectroscopy

Infrared spectra of the BC samples were recorded with an FT-IR spectrometer (Spectrum One; Perkin-Elmer Japan Co., Ltd.) equipped with an ATR attachment (Universal ATR; accumulation of 16 scans, with a resolution of 4 cm^{-1}). Under our measurement conditions, the depth of the FT-IR-ATR was about 1.5–15 μm at 400–4000 cm^{-1}.

2.6. Scanning electron microscopy (SEM)

The silane-treated and untreated MFC sheets were coated with platinum by an ion sputter coater and were observed with a field-emission scanning electron microscope (JSM-6700F; JEOL Ltd.).

2.7. Tensile test

Specimens having dimensions of about 40 mm long and 4.5 mm wide were manufactured and subjected to a tensile test using an Instron 4411 universal materials testing machine. Young's modulus (E) and tensile strength (σ) were thus determined. The span was set to 20 mm and the crosshead speed to 1.0 mm/min.

3. Results and discussion

3.1. Preparation of MFC sheets and the silane coupling treatments

Fig. 2 shows scanning electron microscopy (SEM) images of a cotton fiber sheet (Fig. 2a) and MFC sheet (Fig. 2b and c). Fig. 2a and b was taken at 250-fold magnification, and Fig. 2c was taken at 20,000-fold magnification. All fibers of dried MFC sheets existed separately without coagulation as shown in Fig. 2c, since the surface tension was reduced by the addition of ethanol when the MFC suspension was vacuum filtrated. Thus, the greatly expanded surface area of MFC fibers was preserved. The differences in element dimensions are evident. Most of the cotton fibers are some tens of micrometers wide with tens μm pore size, and the MFC appears as an interconnected web-like structure of thin fibrils and microfibril bundles having diameters on the order of a nanometer with submicron pore size. As a consequence of this unique structure, the ratio of the surface area to the volume of MFC elements is dramatically increased [8]. Q3

MFC sheets were treated by APS according to the procedure in Ref. [17]. Surface modification of APS was accomplished through a physical absorption of the hydrolyzed silane followed by a thermal treatment of modified fibers at 120 °C under a vacuum. This treatment induced the chemical bonding of silanes onto the MFC surface, which was not removed by Soxhlet extraction with ethanol. The increase in the weight of modified MFC after heat treatment at 120 °C followed by Soxhlet extraction, was used to determine the relationships between the initial concentration of APS and the amount adsorbed onto the MFC surface as shown in Table 1. The results indicated that the adsorption of APS increased as the initial

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