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Hydrophobic surface modification of ramie fibers with ethanol pretreatment and atmospheric pressure plasma treatment

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ABSTRACT

Incompatibility between hydrophilic natural cellulose fibers and hydrophobic thermoplastic polymer matrices leads to poor interfacial bonding in their composites. This study investigates how atmospheric pressure plasma jet (APPJ) treatment with ethanol pretreatment may improve ramie fiber surface properties for better adhesion to polypropylene. After soaking in ethanol for 10 min, ramie fibers are treated by helium plasma. For the plasma treated fibers, scanning electron microscopy shows increased fiber surface roughness due to plasma etching, which favors mechanical interlocking of the interface; X-ray photoelectron spectroscopy analysis indicates increased carbon contents and hydrophobic C–C bonds. Larger advancing water contact angles are found in dynamic water contact angle measurement. Microbond test shows an up to 50% increase of the interfacial shear strength of the fibers to polypropylene compared to the control, which may be attributed largely to the combined effects of the roughened fiber surface due to plasma etching and increased hydrophobicity of the fiber surface resulting from the reaction of ethanol molecules to cellulose in plasma treatment, thus improving their compatibility to polypropylene matrix.

1. Introduction

Cellulose natural fibers have been emerging as low cost, widely available, renewable, and environmentally friendly substitutes to non-renewable manmade fibers such as glass and synthetic fibers in composites [1–3]. Thermoplastic composites reinforced with natural fibers are enjoying a rapid growth with advantages such as light weight, reasonable specific strength and stiffness [4]. However, the hydrophilic nature of natural fibers affects negatively their adhesion to hydrophobic polymeric matrices [4,5]. Physical and chemical methods have been used to modify the interface [4,6–10] and traditional surface modification methods like mercerization, acetylation, coupling agents, polymer grafting, have the disadvantages of using polluting organic solvents and producing hazardous waste.

An environmentally favorable alternative is plasma treatments, which have been applied effectively in inducing surface modifications such as cleaning, etching, deposition and polymerization [10–12]. Atmospheric pressure plasma treatments have the advantages of low operating costs, short treatment times and greater flexibility since it does not require a vacuum-chamber [13]. Moreover, atmosphere pressure plasma can treat materials with absorbed liquid [14].

In case of cellulose fibers, modification of the hydroxyl groups and decrease of the polarity of the surface may increase the affinity to hydrophobic polymers. However, previous studies have shown that using oxygen, argon, helium or air plasma tend to increase the hydrophilicity of fiber surfaces [15–18]. Plasma fluorination can enhance surface hydrophobicity [10,19,20], but the use of fluorocarbon gas has potential harmful effect on the environment. Thus efforts are still being made to find better ways to modify the fiber surface. Jiang et al. [21] have found that atmospheric pressure plasma treatment does not improve hydrophilicity of polyethylene fibers when these fibers are pretreated with ethanol. In light of the study, and given that high energy particles activated in plasma could react with ethanol to form aliphatic compounds on fiber surface [22,23], this paper is intended to investigate the combined effect of ethanol pretreatment and atmospheric pressure plasma on hydrophilic cellulose fibers. The advantage of using ethanol is that it has been used as a pretreatment agent for surface cleaning as well as relatively low cost and low impact on the environment.

In the present study, ramie fibers were soaked in ethanol for 10 min and treated by plasma. The interfacial adhesion between ramie fibers and polypropylene matrix was investigated in terms of surface modification and fiber/matrix interfacial shear strength (IFSS). Surface morphology, wettability and chemical composition of the fiber surface were characterized using scanning electron microscopy (SEM), dynamic water contact angle measurement and X-ray photoelectron spectroscopy (XPS) analysis, respectively and fiber/matrix IFSS was measured by micro-bond test. The mechanical properties of the ramie fibers were also examined using single fiber tensile strength test.

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2. Experimental

2.1. Materials

The ramie fibers were provided by Ma Hua Technology Co. Ltd. (Suzhou, China) in the form of degumming fibers with a tensile modulus of 25 GPa. The mean diameter of a single fiber ranges from 15 to 40 μm. The matrix polypropylene was provided by Shanghai Great Eastern Garden Chemical Fiber Co. Ltd. (Shanghai, China) in the form of a yarn composed of monofilaments with a Young's modulus of 1.75 GPa and a single fiber diameter around 50 μm. The ethanol was 99.7% pure provided by Changshu Yangyuan Chemical Company (Jiangsu, China).

2.2. Sample preparation and plasma treatment

The ramie fibers were randomly divided into three groups: control or untreated, plasma treated only, ethanol pretreated for 10 min followed by a plasma treatment. The fibers had 4.8% weight gain after soaking in ethanol for 10 min. The plasma treatment was carried out using an atmospheric pressure plasma jet (APPJ) system (Model Atomflo^{TM-R} 250, Surfx Company, USA) with a frequency of 13.56 MHz and discharge power of 40 W. Helium gas with a purity of 99.99% was introduced into a nozzle at a flow rate of 20 L/min and the plasma jet system covered an active area of 2×10 mm^2. The single ramie fibers were fixed on a frame with distance of 2 mm from the nozzle and were moved on a conveying belt vertical to the nozzle at a rate of 6 mm/s. The stationary treatment time was equivalent to 8, 16 and 24 s in choice. All the sample preparation and treatment were performed in an environment of 20 °C and 65% relative humidity (RH).

2.3. Wettability measurements

The surface wettability was characterized by the measurement of dynamic contact angles based on Wilhelmy technique [24] and distilled water was used as the test liquid. The test was performed on a DCAT11 Dynamic Contact Angle Analyzer (Dataphysics Company, Germany) with the line voltage of 12 VDC and input power of 55 W (Fig. 1). In order to magnify the mass change, five fibers were fixed parallel to each other on a measuring carrier. The testing length of each specimen was about 3 mm. Weight changes were recorded by an ultramicro-electrobalance (MP8, Sartorius, Göttingen, Germany; accuracy = 0.1 mg, reproducibility = 0.2 mg). The immersion and emersion of ramie fibers into and from water were controlled through a reversible elevator, driven by a DC motor with a constant-current source (Philips Power Supply Unit PE1507) and moving at a velocity of 0.01 mm/s.

The contact angle measurements were performed in an environment of 20 °C and 65% RH.

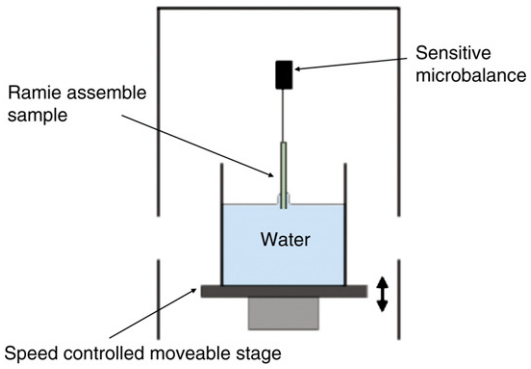

Fig. 1. Schematic diagram of Dynamic Contact Angle Analyzer.

2.4. Microbond specimen preparation and test

Single PP fibers were tied on ramie fibers and then the specimens were heated at 180 °C for 30 s, then cooled down and balanced in an environment of 20 °C and 65% RH. Upon melting of thermoplastic PP knots on ramie fibers, nearly uniform beads were obtained. The embedded length, the beads width and the fiber diameter were measured using an LV100P polarized light microscope (model Nikon Ellipse) with a digital photographic system. A typical specimen is shown in Fig. 2. The microbond test was conducted on an XQ-2 Fiber Tensile Testing Machine with a microwave. The rate of the upper clamp displacement was 20 mm/s.

The interfacial shear strength (IFSS), τ_i, was calculated using the following equation derived from the shear-lag model [25]:

$$\tau_i = \frac{np_{max}\coth(nL/r)}{2A} \tag{2}$$

where p_{max} is the peak load, L is the embedded length. r is the radius of the fiber, A is the cross-sectional area of the fiber, and n is defined as [25]

$$n = \left[\frac{E_m}{E_f(1+\nu_m)In(R/r)}\right]^{1/2} \tag{3}$$

where E_m is the Young's modulus of the matrix (1.75 GPa), E_f is the tensile modulus of the fiber (25 GPa), ν_m is the Poisson's ratio of the matrix (0.35), R is the radius of the PP beads and r is the same as defined previously.

2.5. XPS

The surface chemical composition of the control and the treated fibers was evaluated with a Thermo ESCALAB 250 X-ray photoelectron spectrometer. The spectra were collected using Mg Kα, ($h\nu = 1253.6$ eV) with a pass energy of 20 eV. The X-ray source power was 300 W and the take-off angle was 45°. The pressure within the XPS chamber was between 10^{-7} and 10^{-8} Pa. The C1s and O1s core level spectra were recorded to determine the surface composition of the fibers. Deconvolution curve fitting was performed for the C1s peaks and the spectra were fitted using Gaussian peak profiles and a linear background.

2.6. Scanning electron microscopy

The surface morphology of the control and the treated ramie fibers were observed by a JSM-5600LV Scanning Electron Microscopy (SEM)

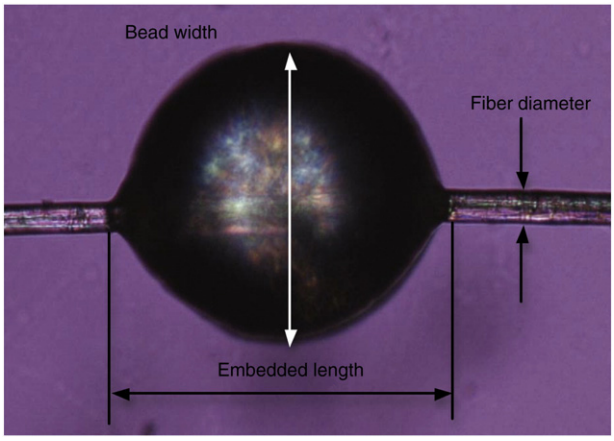

Fig. 2. Polarized light microscope photograph of microbond specimen.