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Helium plasma treatment of ethanol-pretreated ramie fabrics for improving the mechanical properties of ramie/polypropylene composites

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ABSTRACT

When cellulose fibers are ethanol pretreated followed by plasma treatment, their surfaces become more hydrophobic, resulting in better interfacial adhesion to hydrophobic thermoplastics. How much the improvement of composite mechanical properties could be achieved using this method is still unknown. In this study, ramie fabrics are ethanol-pretreated followed by an atmospheric helium plasma treatment for 15 s, 30 s and 45 s, respectively, in order to reveal the degree of improvement in mechanical properties of ramie-fabric-reinforced polypropylene composites. Scanning electron microscopy shows that the fiber surfaces of the treated groups become rougher and are covered with PP resin after interlaminar shear strength (ILSS) tests. X-ray photoelectron spectroscopy shows that the 30 s treated group has a 50% reduction in atomic ratio of oxygen to carbon. Water contact angle measurement demonstrates that the wettability of the surfaces of the treated fibers significantly decreases. The mechanical tests show increases of up to 39, 28 and 20% in ILSS, flexural strength and tensile strength of the treated composites compared to the control group, respectively, which may be attributed to the combined effects of the increased surface hydrophobicity due to the reaction of ethanol molecules to cellulose in plasma treatments and the roughened surface from plasma etching.

1. Introduction

In recent years, vegetable fibers like jute, flax, ramie, hemp, sisal and bamboo have attracted increasing attention in light of growing environmental awareness, since they have the potential to be widely used as eco-friendly and low carbon emission alternatives to non-renewable man-made fibers for reinforcement materials in green composites (Martin et al., 2013). Among these, ramie fiber has been considered as one of the most promising candidates for the green composite industry because of its biodegradability, recyclability, low cost, high specific strengths and specific modulus as well as commercial availability (Goda et al., 2006; Nam and Netravali, 2006; Li et al., 2012; Liu et al., 2013; Zhou et al., 2013). In China, the renewable cellulose fibers are abundant, especially ramie fibers, which are called "Chinese plant" (Li et al., 2013).

One of the major problems limiting the application of vegetable fibers to composites is that the hydrophilic fiber surfaces are incompatible with relatively hydrophobic polymer matrices (Bledzki et al., 1996; Ragoubi et al., 2010), leading to poor mechanical performance of the corresponding composites due to low interfacial adhesion. To solve this problem, many surface modification methods have been employed such as alkaline treatment (Ray et al., 2001a,b; Li et al., 2007; Zhou et al., 2012), silane treatment (Seki, 2009; Sever et al., 2010; Xie et al., 2010), acetylation treatment (Bledzki et al., 2008), isocyanate treatment (George et al., 1999) and stearic acid treatment (Kalaprasad et al., 2004; Torres and Cubillas, 2005). Although some of these treatments have been shown effective in improving interfacial adhesion, problems regarding the disposal of pollutant waste, high water and energy consumption and damage of fiber strength still exist.

A more eco-friendly and effective approach to modify fiber surfaces is the use of plasma treatment which can modify chemical and physical structure of material surfaces without altering their bulk properties (Kusano et al., 2011). In our previous studies, atmospheric pressure plasma treatments in conjunction with ethanol pretreatment of ramie fibers have shown to be effective in hydrophobize ramie fiber surfaces, leading to a substantial enhancement of interfacial bonding strength between the fiber and hydrophobic polypropylene (PP) matrix (Zhou et al., 2011).

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However, no one has reported how much improvement due to this treatment to a fabric can be transferred to the enhancement of the mechanical performance of ramie/PP composites.

In this work, we aimed to study how much improvement in the mechanical properties of ramie-fabric-reinforced PP composites could be achieved through ethanol pretreatment followed by a helium plasma treatment to the ramie fabric. Ramie fabrics were surface treated for various durations using an atmospheric pressure plasma system. The SEM, XPS, water contact angle analyses and mechanical tests (shear, flexure and tensile) were employed to study the modification effect.

2. Experimental

2.1. Materials

The desized plain weave ramie fabric having warp and weft counts of 33 ends/cm and 26 picks/cm and an areal density of 150 g/m^2 was used as the reinforcement fabric. The matrix PP was provided by Shanghai Lizi Chemical Engineering Co. Ltd. in the form of films with a density of 0.9 g/cm^3. The ethanol (≥99.7% purity) was supplied by Jiangsu Yangyuan Chemical Company. Helium gas (≥99.99% purity) was used as the treatment gas.

2.2. Helium plasma treatment of ramie fibers

The desized ramie fabrics were cleaned successively with acetone and deionized water and then dried in a vacuum oven. Then the cleaned ramie fabrics were randomly divided into six groups: the control group containing fabrics without any further treatment, the ethanol-pretreated only group containing fabrics only treated with ethanol for 10 min, the plasma-treated only group containing fabrics treated with plasma only for 30 s and three ethanol-pretreated plus plasma-treated groups containing fabrics ethanol-pretreated followed by plasma treatments for 15 s, 30 s and 45 s, respectively. The fabrics had 5% weight gain after soaking in ethanol for 10 min. A pulse plasma machine, model ST/RI (Shanghai Textile Science Institute, China), was used as the plasma source which has an effective area of exposure about 25 cm × 25 cm between two copper electrodes. Each copper electrode is embedded in a glass dielectric barrier with a thickness of 6 mm. Then, the ramie fabrics were exposed to 60 W helium plasma at atmospheric pressure with treatment duration of 15, 30 and 45 s, respectively. The diagram of the experimental set up for helium plasma treatment is shown in Fig. 1.

2.3. Composite preparation

Twelve layers of ramie fabrics and thirteen pieces of PP films were stacked alternately to make the laminates. The weight percentage of ramie fibers in the composites was kept at 35%. Then the whole assembly was processed in a two-step heating cycle to ensure sufficient penetration of PP into the ramie fabrics. First, the assembly was preheated at 183 °C without any pressure. Then, it was pressed between two steel plates at 185 °C under 2 MPa for 10 min. A stainless steel spacer frame with a thickness of 3 mm was placed between two steel plates in order to obtain the desired uniform thickness of the composites. Finally, the composite was cooled down naturally to ambient temperature.

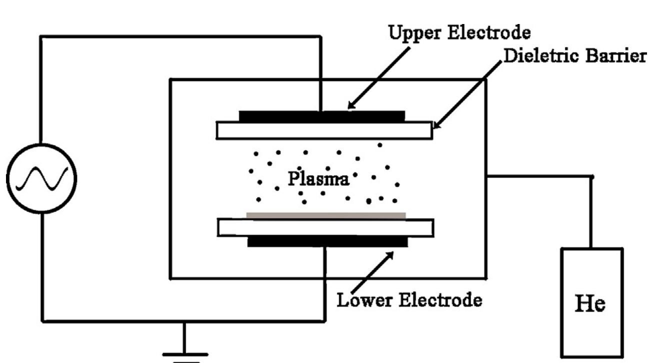

Fig. 1. Schematic of the helium plasma treatment system.

2.4. Scanning electron microscopy (SEM)

The surface morphology of the ramie fibers and the fracture surfaces of the composites after shear test were observed by SEM (JSM-5600LV Model, Japan) at the magnification of 10,000× and 500×, respectively. The surfaces were gold sputtered prior to the SEM examination to ensure good conductivity.

2.5. X-ray photoelectron spectrometer (XPS)

The XPS analysis was carried out with ESCALAB 250 photoelectron spectrometer (Thermo Electron VG Scientific, USA), equipped with an Mg source at a power of 150 W. The pressure within the chamber was 10^{-7} to 10^{-8} Pa and the take-off angle was 45°. The deconvolution analysis of C1s peaks was performed using XPSEAK software with Gauss–Lorenz functions.

2.6. Wettability

The static water contact angle of the fabric surfaces were measured on an OCA40 contact angle tester (Dataphysics Company, Germany) using the sessile drop method. A 5 μL drop of distilled water was placed on the fabric surface by a microliter syringe. A digital image capturing and processing system was used to record the image of the water droplet immediately after it landed on the fabric to calculate the contact angle. Each value reported here was the average of at least five measurements.

2.7. Mechanical tests

The composites were stored at 20 °C and 65% relatively humidity for 48 h prior to the tests. The mechanical tests including interlaminar shear test (ILSS), flexure test and tensile test were conducted on a Universal Testing Machine (Hualong Co. Ltd., China) fitted with a 20 kN load cell.

2.7.1. ILSS test

The ILSS test for the composites was performed following the double-notched shear test method according to ASTM D3846-08. The specimens (79.5 mm × 12.7 mm × 3 mm) were tested at a constant cross-head movement rate of 1.3 mm/min. Two parallel slots 6.4 mm apart were machined into the opposite faces of the specimen (see Fig. 2). The slots were cut deep enough to pass the center line of the laminate to guarantee pure in-plane shear loading. The width of the slots was maintained at approximately 1.5 mm wide. A supporting jig was used to hold the specimens during the test to prevent them from buckling. The interlaminar shear stress is given by

$$\alpha_i = \frac{P_{max}}{ab} \quad (1)$$

where P_{max} is the maximum load detected in shear failure, a is the length of the failed area and b is the width of the specimen. The data reported here was the average of at least five runs.