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Helium plasma treatment voltage effect on adhesion of ramie fibers to polybutylene succinate

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ABSTRACT

Plasma modification effect on fiber surfaces is closely related to the plasma treatment voltage. In this study, ramie fibers with ethanol pretreatment were treated by helium plasma under four different applied voltages of 1.5, 3, 6, and 9 kV, respectively, to study the influence of plasma voltage on treatment effect. Scanning electron microscopy (SEM) showed rougher fiber surfaces with increasing plasma voltage. Dynamic contact angle analysis and X-ray photoelectron spectroscopy revealed that the fiber surface wettability decreased and more C—C bonds were incorporated to ramie fiber surface by plasma treatment when the voltage was above 3 kV. Microbond pullout test showed that interfacial adhesion between ramie and polybutylene succinate for 1.5, 3, 6, and 9 kV group increased by 9.6, 29.6, 45.5, and 19.4%, respectively. Single fiber tensile strength test confirmed no significant strength loss for all groups after the plasma treatments. This study showed that proper selection of treatment voltage was critical for optimal improvement of bonding between cellulose fiber and thermoplastic resin using ethanol pretreatment followed by plasma treatment.

1. Introduction

Vegetable or natural cellulose fibers have many advantages such as biodegradability, recyclability, high specific mechanical performance, low cost, less tool wear, and no dermal and respiratory irritation (Angelini and Tavarini, 2013; Arbelaiz et al., 2005; Cordeiro et al., 2011; Huda and Yang, 2009; Jayaraman, 2003; Li et al., 2000, 2013; Liu et al., 2013; Martin et al., 2013; Zhou et al., 2011, 2014). These fibers are promising candidates to partially replace glass fibers for reinforcement materials in polymeric composites (Le Moigne et al., 2014; Ragoubi et al., 2010; Zhou et al., 2013). One of the major problems in this application, is that their hydrophilic surfaces are incompatible with hydrophobic polymer matrices (Bledzki et al., 1996), resulting in poor mechanical performance of composite due to insufficient interfacial adhesion. Even though many conventional chemical modification methods (Bledzki et al., 2008; Cordeiro et al., 2011; George et al., 1999; Kalaprasad et al., 2004; Li et al., 2007; Ray et al., 2001a,b; Seki, 2009; Sever et al., 2010; Torres and Cubillas, 2005; Xie et al., 2010; Zhou et al., 2012) have been somewhat successful in improving the interfacial adhesion, concerning environment pollution, energy consumption, and fiber damage, better technologies are still needed in this field.

Over recent decades, some remarkable new energy-efficient technologies have been developed in cellulose modification (Adeel et al., 2013, 2014; Batool et al., 2013; Khan et al., 2014; Rehman et al., 2013; Zhou et al., 2011), among which plasma treatment has attracted much attention as a clean, more efficient surface modification technique with little or no damage to substrate bulk properties (Li et al., 2013; Sun and Qiu, 2012). As reported in literature (Chen et al., 2008; Gogoi et al., 2011; Kang et al., 2002), plasma modification effects on fiber surfaces are closely related to plasma treatment parameters. Improper plasma treatment parameters may even deteriorate substrate surface properties. Our previous work (Li et al., 2013; Zhou et al., 2011), found that ethanol pretreatment followed by atmospheric plasma treatment did significantly improve the compatibility between ramie fiber and polypropylene (PP) matrix and the treatment effect was associated to the treatment duration. However, plasma treatment voltage is also critically important for the effectiveness of plasma treatment. Without enough voltage, some of the plasma induced reactions may not occur or may not be sufficient; while an over voltage plasma treatment could induce harmful reactions or suppress beneficial

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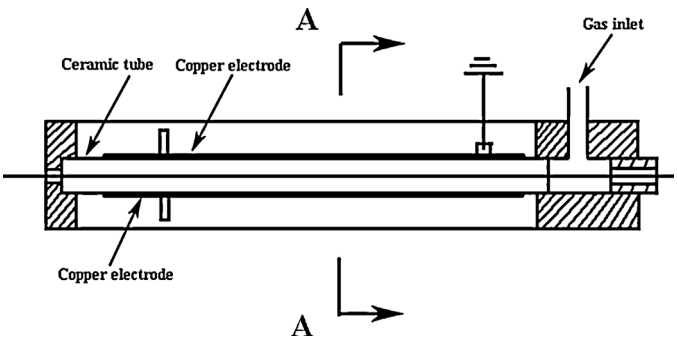

Fig. 1. The schematic of the atmospheric pressure dielectric barrier glow discharge (DBD) system.

reactions to the fiber surfaces. This work aims at investigating how plasma voltage influences the surface treatment effect of ramie fibers as well as ramie/poly(butylene succinate) (PBS) adhesion. PBS is a thermoplastic aliphatic polyester with excellent biodegradability, high processing capability and good thermal resistance (Chrissafis et al., 2005; Han et al., 2006; Kim et al., 2006). Its tensile strength is in between polyethylene (PE) and PP; its stiffness is in between low density PE and high density PE (Han et al., 2006). It is also one of the commercially available polymers with a cost lower than poly(lactic acid) and poly(3-hydroxybutyrate) (Han et al., 2006). In this work, helium plasma treatment was employed to modify ethanol pretreated ramie fiber surfaces in order to improve their compatibility with PBS matrices. Four voltages were selected as operating parameters to treat four groups of samples. The surface topology, chemical composition and wettability were analyzed using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and dynamic contact angle analysis (DCAA), respectively. Microbond pullout test was performed to determine the interfacial adhesion of the ramie/PBS interface. The single fiber tensile strength test was carried out to determine if plasma treatment could have any negative effect on fiber tensile strength.

2. Experimental

2.1. Materials

Ramie fiber was supplied by Mahua Technology Co., Ltd. (Suzhou, China) in the form of degumming fibers with a tensile modulus of 25 GPa. The diameters of the single fibers were differed from 15 μm to 40 μm. The matrix PBS film was provided by Mitsubishi Chemical Corporation (Japan) with a Young's modulus of 500 MPa. Ethanol with 99.7% purity was obtained from Yangyuan Chemical Company (Jiangsu, China).

2.2. Sample preparation and plasma treatment

The fibers were washed successively with acetone and distilled water followed by drying in an oven. These fibers were then soaked in ethanol for 10 min with a mass gain of 5.0% before plasma treatment. The schematic of the atmospheric pressure dielectric barrier glow discharge (DBD) system is shown in Fig. 1. The DBD discharge was generated between two parallel copper electrodes. The main chamber was made of ceramic with a dimension of 45 mm × 15 mm × 15 mm. A power supply of 15.9 kHz frequency was applied to generate the plasma between the electrodes within a gap of 10 mm. The applied voltages were measured by a high voltage probe (Tektronix P5100) and a digital oscilloscope (Tektronix TDS 3024B). The helium (≥99.99% purity) was used as the treatment gas with a flow rate of 2 L/min and treatment time of 30 s. Four

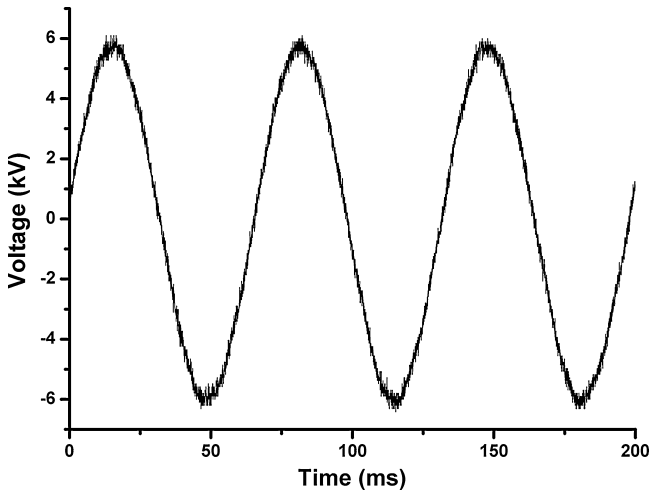

Fig. 2. A model waveforms of applied voltage in atmospheric pressure DBD system.

voltages of 1.5 kV, 3 kV, 6 kV and 9 kV were chosen to treat four groups of samples, namely, 1.5 kV group, 3 kV group, 6 kV group and 9 kV group for short. Fig. 2 is a model waveform of applied voltage in the experiment. All samples were prepared and treated at 20 °C and 65% relative humidity.

2.3. Scanning electron microscopy (SEM)

Surface morphologies of ramie fibers were observed by SEM (JSM-5600LV Model, Japan). The magnification of the images was set at 10,000× and the fiber samples were gold coated for better surface conductivity prior to the SEM analysis.

2.4. X-ray photoelectron spectroscopy (XPS)

Surface chemical compositions of the control and the treated fibers were analyzed by ESCALAB 250 photoelectron spectrometer (Thermo Electron VG Scientific, USA) with an Mg Kα (1253.6 eV) X-ray source and a power of 300 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 spectra was carried out using XPSEAK4.1 software.

2.5. Wettability measurement

The wettability of ramie fiber surface was examined by the modified Wilhelmy technique using a dynamic contact angle analysis system (Tensiometer DCAT 11, Dataphysics Company, Filderstadt, Germany). The test liquid used for the measurement was distilled water. The mass change of a single ramie fiber during the measurement was too small, so five fibers were aligned parallel with each other to increase the mass change. An average of five measurements was performed for each sample.

2.6. Microbond pullout test

Microbond pullout test was performed to determine the interfacial adhesion of the ramie/PBS interface. PBS film was cut into V-shape to clamp onto the ramie fiber and then the specimens were heated at 130 °C for 30 s, nearly uniform micro beads were formed. A typical specimen is shown in Fig. 3. The embedded length, the fiber diameter and the bead width were measured with a polarized light microscope (LV100P, Nikon Ellipse).

The microbond test was performed on a single fiber tensile testing machine (XQ-2, Shanghai Lipu Research Institute, China)