SMART ADHESION BY SURFACE TREATMENT
Experimental and Theoretical Insights

by

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To investigate how plasma treatment affected the surface structure and adhesion to polypropylene matrix and unsaturated polyester matrix, green abaca fibers were treated by low temperature plasma under different plasma processing parameters including treatment time, output power, and working gas. Abaca fibers were characterized by atomic force microscope, X-ray photoelectron spectroscopy, contact angle and interfacial shear strength. The results of contact angle and interfacial shear strength were consistent with the changes in surface roughness and the atomic ratio of the plasma treated abaca fibers with treatment time, output power, and working gas. It was concluded that the surface roughness and atomic ratio played a major role in the adhesion improvement of the plasma treated abaca fibers to polypropylene matrix and unsaturated polyester matrix due to the mechanical interlocking and chemical bonding, respectively. The geometrical potential theory was adopted to elucidate the mechanism of the adhesion property.

Key words: *abaca fibers, surface treatment by excited gases, adhesion by mechanical interlocking, adhesion by chemical bonding, geometrical potential*

Introduction

The green composites reinforced by natural fibers have been used in various fields to replace many of their synthetic partner [1, 2]. However, the poor interfacial adhesion between natural fibers and polymer matrix limited their applications because the properties of natural reinforced composites were determined by the properties of fibers and polymer matrix and their interfacial adhesion [3]. To provide appropriate interfacial interactions, proper surface modification of natural fibers should be performed accordingly, which can make them stronger bonding to the polymer matrix. A variety of surface treatment methods have been developed for natural fibers mainly including chemical treatment (alkaline, silane, acetylation, isocyanate, and stearic acid) [4, 5] and physical treatment (electron beam irradiation, corona, plasma) [6]. Compared with other methods, plasma treatment has attracted much attention as a more eco-friendly and high efficient approach to modify physical and chemical structure of substrate surface without affecting bulk properties [7]. In previous studies, plasma surface treatment of natural fibers has shown high efficiency in improving the interfacial adhesion between natural fibers and polymer matrix such as jute [8], flax [9, 10], ramie [11], hemp [12], sisal [13, 14], bamboo, and so on [15]. However, there are no related reports on surface modification of abaca fibers by plasma treatment technique.

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In this study green abaca fibers were treated by low temperature plasma to improve the interfacial adhesion between abaca fibers and polymer matrix such as polypropylene (PP) and unsaturated polyester (PET). The influence of plasma treatment time, output power and working gas on the surface structure and properties of the plasma treated abaca fibers was investigated. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used to analyze the changes in surface morphology and chemical composition.

The effects of plasma treatment on abaca fiber properties were detected by the changes in wettability and adhesion, which were characterized by contact angle and interfacial shear strength, respectively.

Experimental insight

Materials

The fiber linear density of abaca fibers was 4.8 dtex with the density of 1.45 g/cm^3. The PP matrix was provided by Shanghai Great Eastern Garden Chemical Fiber Co. Ltd., Shanghai, China in the form of a yarn composed of monofilament with the Young's modulus of 1.75 GPa. The PET matrix with the density of 1.11 g/cm^3, isophthalic acid type resin, was supplied by Jiangyin Thousands Chemicals Co., Ltd., Jiangsu, China.

Plasma treatment

The HD-1B cold plasma modification treatment instrument, produced by Changzhou Zhongke Changtai Plasma Processing Apparatus Plasma Technology Co., Ltd., Jiangsu, China, was applied to perform the plasma treatment of abaca fibers. They were treated by Ar and O_2 for different treatment times at different output powers, respectively.

Wettability measurement

Water contact angle was applied to determine the wettability of abaca fibers. Contact angle test was performed on a JC2000D3 Angle Analyzer produced by Zhongchen Digital Technic Apparatus Co., Ltd., Shanghai, China. According to drop technique, abaca fibers were fixed on the fiber support and a droplet of distilled water (2 μL) was put on the fiber surface by a microsyringe. Initial contact angle was recorded as soon as the water droplet was on the surface of abaca fibers. Five measurements were averaged.

Adhesion measurement

Adhesion between abaca fibers and polymer matrix was determined by interfacial shear strength (IFSS) through micro-bond pull-out technique [16, 17]. For PET matrix, the specimens were cured for 3 hours at 80 ℃ after placing the PET resin on the fibers. For PP matrix, the specimen were cured for 3 hours at 80 °C after placing the PET resin on the fibers. For PP matrix, PP filaments were tied to form PP knots on abaca fibers. The specimens were heated at 180 ℃ for 30 seconds and the thermoplastic PP knots on abaca fibers were melted to form the PP matrix beads [13]. The IFSS between abaca fibers and matrix, τ_i, was calculated by eq. (1) derived from the shear-lag model [18].

$$\tau_{\mathrm{i}} = \frac{np_{\max} \coth \dfrac{nL}{r}}{2A} \tag{1}$$

where $p_{\max}$ is the peak load, L – the embedded length, r – the fiber radius, A – the fiber cross-sectional area, and n – determined by eq. 2 [19].

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

where E_m is the Young's modulus of the matrix (1.75 GPa and 25 GPa for PP and PET, respectively), E_f – the tensile modulus of the fiber (25 GPa), ν_m – the Poisson's ratio of the matrix (0.35), and R – the radius of the matrix beads.

Characterization

Miltimode Nanoscope IIIa Controllor (Veeco, American) was used to observe surface morphological changes of abaca fibers [19]. The surface chemical composition analysis of abaca fibers was carried out by on Thermo ESCALAB 250XI system (Thermo Fisher Scientific, USA) to confirm the surface chemical changes.

Results and discussion

The AFM analysis

Figure 1 shows the AFM images of surface topography for the control and the abaca fibers modified by O_2 plasma and Ar plasma for 2 min and 4 min at 100 W, respectively.

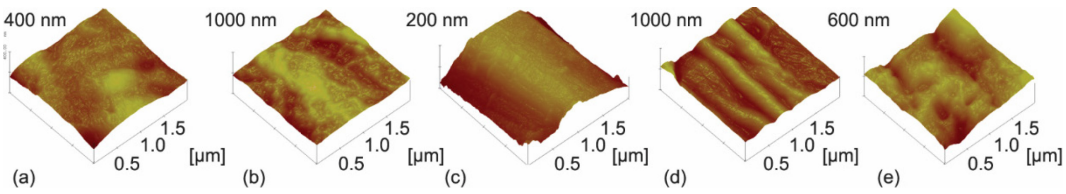

Figure 1. The AFM images of surface topography for the control and the abaca fibers modified by different working gases for different times at 100 W; (a) control, (b) O_2, 2 minutes, (c) O_2, 4 minutes, (d) Ar, 2 minutes, and (e) Ar, 4 minutes

It could be seen that there were quite differences in surface morphology of the control and the plasma treated abaca fibers. As can be seen from fig. 1(a), the control had a relatively smooth and homogenous surface with some natural longitudinal grooves. However, in figs. 1(b)-1(d), there exhibited tiny grains on the slightly rough fiber surface of the plasma treated abaca fibers due to the plasma etching. The bombardment of ions and electrons in plasma caused polymer degradation reaction to form pits or fragments [20]. There were more grooves and micro-pits on the surface of the Ar plasma treated abaca fibers than those on the surface of the O_2 plasma treated abaca fibers. The difference in surface morphology between the Ar plasma treated abaca fibers and the O_2 plasma treated abaca fibers became smaller with the increasing of treatment time.

Figure 2 illustrates the effect of treatment time and output power on the surface mean roughness of abaca fibers modified by Ar plasma and O_2 plasma, respectively.

It was found that the surface mean roughness of the plasma treated abaca fibers increased quickly and then slowly with the increasing treatment time and output power. When the treatment time and output power increased to 4 minutes and 400 W, respectively, the surface mean roughness showed no significant change. It was also observed that the surface mean

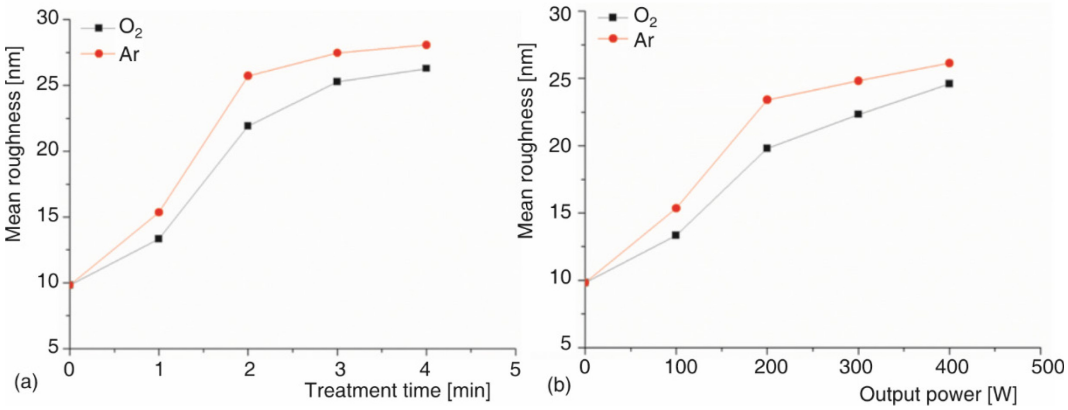

Figure 2. Effect of plasma processing parameters on the surface mean roughness of abaca fibers; (a) treatment time and (b) output power

roughness of the Ar plasma treated abaca fibers was higher than that of the O_2 plasma treated abaca fibers, implying that the surface of the Ar treated abaca fibers was rougher than that of the O_2 plasma treated abaca fibers due to the higher etching tendency of Ar plasma because Ar plasma was more invasive in plasma etching than O_2 plasma [12].

The difference in the surface mean roughness between the Ar plasma treated abaca fibers and the O_2 plasma treated abaca fibers increased firstly and then decreased with treatment time and output power. The surface mean roughness of the Ar plasma treated abaca fibers was much higher and slight higher than that of the O_2 plasma treated abaca fibers when abaca fibers were treated for 2 minutes and 4 minutes, respectively, which was consistent with the AFM images as shown in figs. 1(b)-1(d). Similarly, the difference in the surface mean roughness between the Ar plasma treated abaca fibers and the O_2 plasma treated abaca fibers was the biggest and smallest at 200 W and 400 W as shown in fig. 2(b), respectively. All these results indicated that the surface of the Ar plasma treated abaca fibers was much rougher than that of the O_2 plasma treated abaca fibers for the shorter treatment time or at the lower output power, while there was nearly no difference in the surface roughness between the abaca fibers treated by Ar plasma and the O_2 plasma, respectively, for the longer treatment time or at the higher output power.

The XPS analysis

Figure 3 presents the effect of plasma processing parameters on the atomic ratio (O/C) of abaca fibers obtained by XPS analysis.

The control and the plasma treated abaca fibers contained oxygen and carbon elements. The O/C ratio for the plasma treated abaca fibers was higher than that for the control about 0.149, namely the decrease of carbon content and the increase of oxygen content, which implied an effective modification of abaca fibers and the occurrence of oxidation. In addition, the O/C ratio increased quickly and then slowly with the increasing treatment time and output power. When the treatment time and output power increased to 4 minutes and 400 W, the O/C ratio showed almost no obvious change. For the different working gases, the O/C ratio and the variation for the O_2 plasma treated abaca fibers were higher than those for the Ar plasma treated abaca fibers. In O_2 plasma, oxygen was excited into a high energetic and reactive atomic and diatomic molecular state, leading to the higher oxygen content and O/C ratio on the surface of the O_2 plasma treated abaca fibers [21].

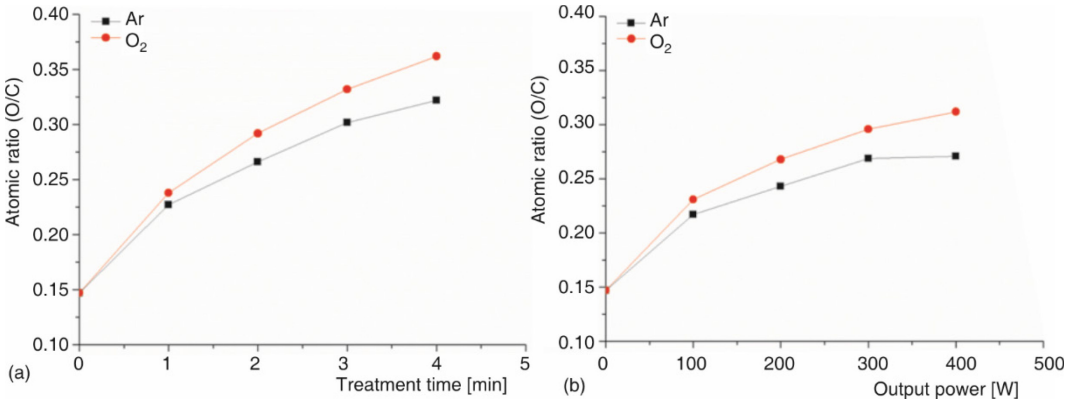

Figure 3. Effect of plasma processing parameters on the atomic ratio (O/C) of abaca fibers determined by XPS; (a) treatment time and (b) output power

Contact angle

Figure 4 illustrates the effect of plasma processing parameters, namely treatment time, output power, and working gas, on the contact angle of abaca fibers.

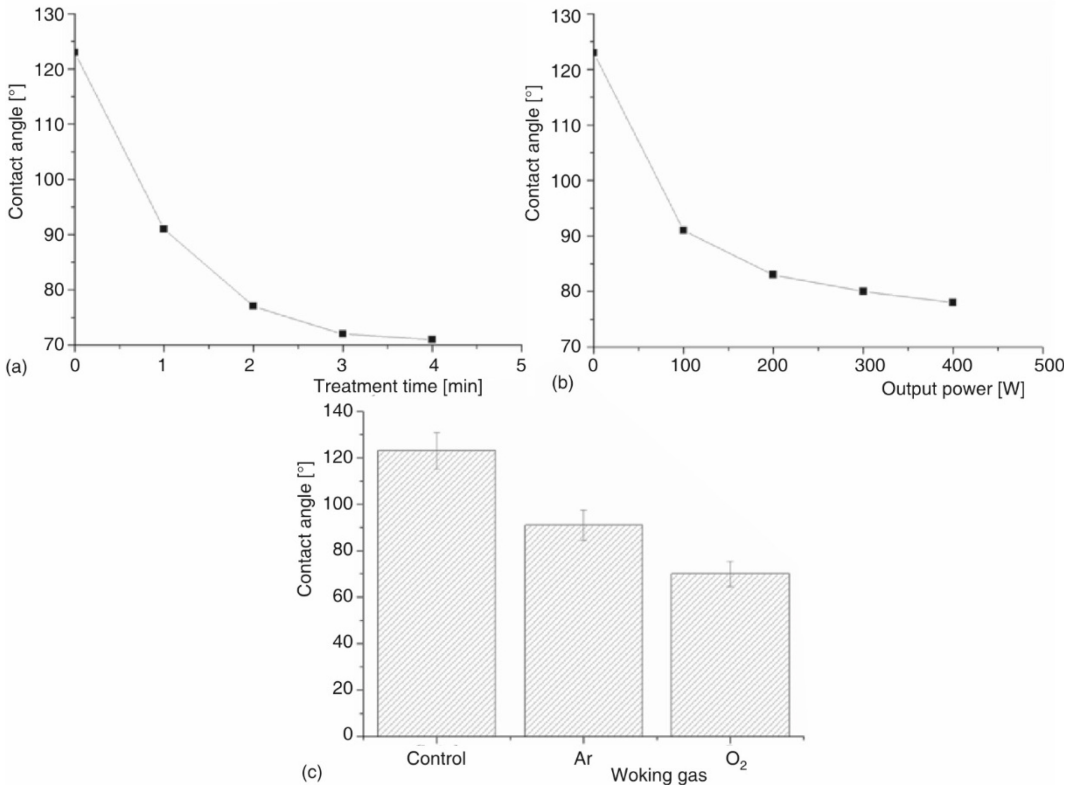

Figure 4. Effect of plasma processing parameters on contact angle of abaca fibers and matrix; (a) treatment time, (b) output power and (c) working gas

The contact angle of the control was 124°. The contact angle of the plasma treated abaca fibers, much smaller than that of the control, decreased to different degrees due to the different plasma processing parameters manifesting the surface wettability improvement of abaca fibers. The contact angle of the plasma treated abaca fibers decreased with the increasing treatment time and output power and the decreasing rate gradually slowed down. When treatment time and output power reached 4 minutes and 400 W, respectively, the contact angle showed no distinct change, which indicated that the longer plasma treatment time or the higher output power no longer increased the surface wettability of abaca fibers. The decreasing rate of contact angle with treatment time was higher than that with output power. The contact angle of the plasma treated abaca fibers decreased to about 70° and 80°, respectively, with the increasing treatment time and output power. It could be inferred that treatment time had more important influence on contact angle of abaca fibers. The contact angle of the O_2 plasma treated abaca fibers was smaller than that of the Ar plasma treated abaca fibers, which demonstrated that the decrease of the contact angle of the plasma treated abaca fibers was mainly determined by the number of oxygen-containing groups.

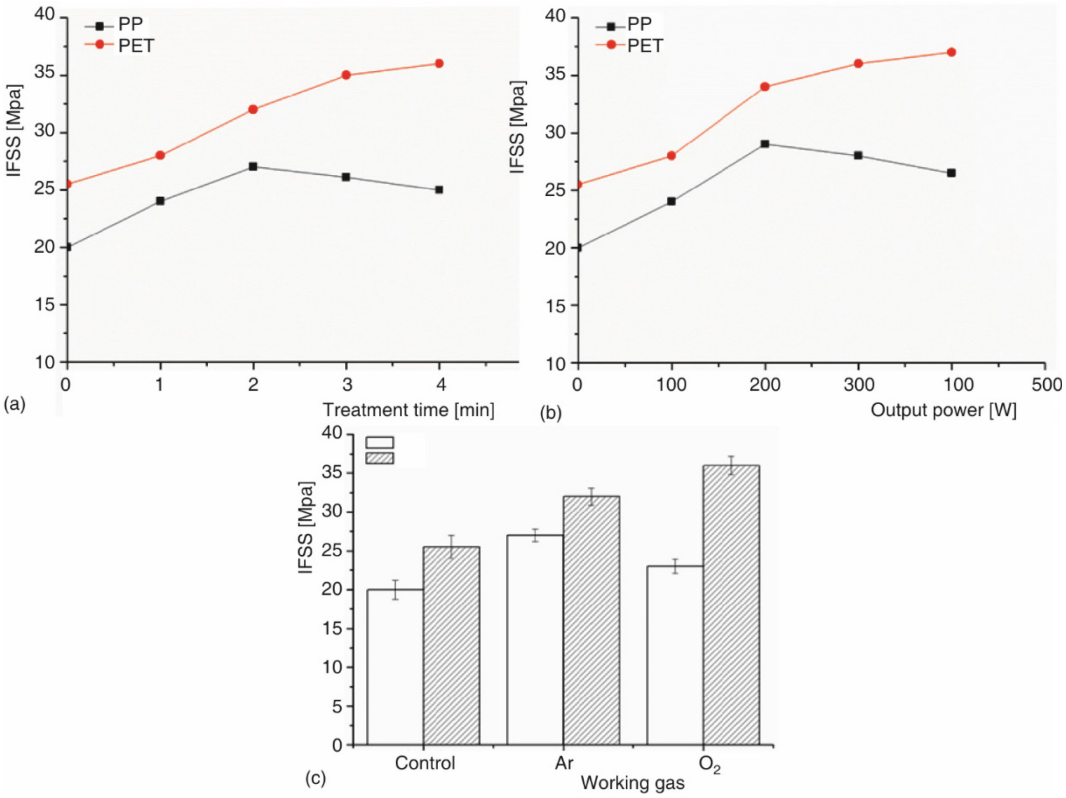

Figure 5. Effect of plasma processing parameters on IFSS between abaca fibers and matrix; (a) treatment time, (b) output power and (c) working gas

The IFSS analysis

Figure 5 gives the effect of plasma processing parameters on IFSS value between abaca fibers and polymer matrix.

It could be seen that IFSS value of the plasma treated abaca fibers became higher than that of the control. It was also detected that plasma processing parameters, namely treatment time, output power and working gas, had different influences on IFSS value between the plasma treated abaca fibers and different polymer matrices. For PP matrix, IFSS value increased and then decreased with the increasing treatment time and output power. When plasma treatment and output power were 2 minutes and 200 W, respectively, IFSS value was the highest. IFSS value for the Ar plasma treated abaca fibers was higher than that for the O_2 plasma treated abaca fibers. For unsaturated PET matrix, IFSS value enhanced quickly and then slowly with the increasing treatment time and output power. When treatment time and output power increased to 4 minutes and 400 W, respectively, IFSS value almost remained constant. IFSS value for the O_2 plasma treated abaca fibers was higher than that for the Ar plasma treated abaca fibers.

It is well known that there are mainly two factors affecting the adhesion between fibers and polymer matrix, namely surface roughness and O/C ratio. The increase of surface roughness of fibers enlarges interfacial area, which may improve the adhesion by mechanical interlocking between fibers and polymer matrix. The increase of O/C ratio introduces polar groups, which may improve the adhesion by chemical bonding between fibers and hydrophilic polymer matrix. For hydrophobic PP matrix surface roughness and O/C ratio have positive and negative effect on the adhesion, while for hydrophilic unsaturated PET matrix surface roughness and O/C ratio have positive effect on the adhesion. The changing trend of IFSS value between the plasma treated abaca fibers and PP matrix with plasma processing parameters was similar to that of the surface roughness of the plasma treated abaca fibers. However, the changing trend of IFSS value between the plasma treated abaca fibers and unsaturated PET matrix with plasma processing parameters was the same as that of O/C ratio of the plasma treated abaca fibers. Therefore, it could be said that surface roughness was the dominant factor for the adhesion between abaca fibers and PP matrix while O/C ratio was the dominant factor for the adhesion between abaca fibers and unsaturated PET matrix.

Theoretical insight

Adhesion strongly depends upon surface morphology. This can be explained by the geometrical potential theory [21-26]. According to this theory, any surface can produce a potential called the geometrical potential. A convex surface produces an absorbing force like Earth's gravity, while a concave surface results in a repelling force. The smart adhesion is to balance the absorbing force and repelling force by surface roughness on a nanoscale, which can be achieved by plasma treatment.

Figure 2 shows the surface roughness change after plasma treatment, according to the geometrical potential theory [21-26], the tiny grains on the slightly rough fiber surface of the plasma treated abaca fibers as shown in fig. 1 can produce a boundary-induced force, which can attract water molecules, as a result, the water contact angle becomes smaller than the smooth surface without plasma treatment. Similarly the micro and nanoscale tiny grains on the plasma-treated surface can attract a contacted surface, and the interfacial shear strength between two surfaces can be remarkably improved. The smart adhesion theory is to control

the interfacial shear strength by controlling the surface morphology by the plasma treatment. A detailed theoretical model will be published in a forthcoming paper.

Conclusion

The influence of low temperature plasma processing parameters including treatment time, output power and working gas on the surface structure and properties of green abaca fibers was studied. The surface roughness and O/C ratio increased quickly and then slowly with the increasing treatment time and output power. Almost no obvious changes in the surface roughness and O/C ratio were observed when treatment time and output power increased to 4 minutes and 400 W, respectively. The results were nearly agreement with the changes in the wettability and adhesion to PP matrix and unsaturated PET matrix with treatment time and output power. The surface roughness of the Ar plasma treated abaca fibers was higher than that of O_2 plasma treated abaca fibers, while the O/C ratio of the Ar plasma treated abaca fibers was lower than that of the O_2 plasma treated abaca fibers. The adhesion to PP matrix of the Ar plasma treated abaca fibers was better than that of the O_2 plasma treated abaca fibers, while the wettability and adhesion to unsaturated PET matrix of the Ar plasma treated abaca fibers was poorer than that of the O_2 plasma treated abaca fibers. All these results indicated that the surface roughness and O/C ratio of abaca fibers could be considered as the main constraint on the adhesion to PP matrix and unsaturated PET matrix, respectively.

References

[1] Saheb, D. N., *et al.*, Natural Fiber Polymer Composites: a Review, *Advances in Polymer Technology, 18* (1999), 4, pp. 351-363
[2] Bogoeva-Gaceva, G., *et al.*, Natural Fiber Eco-Composites, *Polymer Composites, 28* (2007), 1, pp. 98-107
[3] George, J., *et al.*, A Review on Interface Modification and Characterization of Natural Fiber Reinforced Plastic Composites, *Polymer Engineering and Science, 41* (2001), 9, pp. 1471-1485
[4] Li, X., *et al.*, Chemical Treatments of Natural Fiber For Use in Natural Fiber-Reinforced Composites: a Review, *Journal of Polymers and The Environment, 15* (2007), 1, pp. 25-33
[5] Corrales, F., *et al.*, Chemical Modification of Jute Fibers for the Production of Green-Composites, *Journal of Hazardous Materials, 144* (2007), 3, pp. 730-735
[6] Mukhopadhyay, S., *et al.*, Physical Modification of Natural Fibers and Thermoplastic Films for Composites-a Review, *Journal of Thermoplastic Composite Materials, 22* (2009), 2, pp. 135-162.
[7] Bucek, A., *et al.*, Glass Bond Adhesive Strength Improvement by DCSBD Atmospheric-Pressure Plasma Treatment, *International Journal of Adhesion and Adhesives, 78* (2017), Oct., pp. 1-3
[8] Bozaci, E., *et al.*, Effect of the Atmospheric Plasma Treatment Parameters on Surface and Mechanical Properties of Jute Fabric, *Fibers and Polymers, 10* (2009), 6, pp. 781-786
[9] Marais, S., *et al.*, Unsaturated Polyester Composites Reinforced with Flax Fibers: Effect of Cold Plasma and Autoclave Treatments on Mechanical and Permeation Properties, *Composites Part A: Applied Science and Manufacturing, 36* (2005), 7, pp. 975-986
[10] Bozaci, E., *et al.*, Effects of The Atmospheric Plasma Treatments on Surface and Mechanical Properties of Flax Fiber and Adhesion between Fiber-Matrix for Composite Materials, *Composites Part B-engineering, 45* (2013), 1, pp. 565-572
[11] Zhou, Z., *et al.*, Hydrophobic Surface Modification of Ramie Fibers with Ethanol Pretreatment and Atmospheric Pressure Plasma Treatment, *Surface and Coatings Technology, 205* (2011), 17-18, pp. 4205-4210
[12] Gulati, D., *et al.*, Surface Characteristics of Untreated and Modified Hemp Fibers, *Polymer Engineering and Science, 46* (2006), 3, pp. 269-273
[13] Jayaraman, K., *et al.*, Plasma Treatment of Sisal Fibres and Its Effects on Tensile Strength and Interfacial Bonding, *Journal of Adhesion Science and Technology, 16* (2002), 6, pp. 703-727
[14] Jayaraman, K., *et al.*, Mechanical Properties of Plasma-Treated Sisal Fibre-Reinforced Polypropylene Composites, *Journal of Adhesion Science and Technology, 18* (2004), 9, pp. 1027-1045

[15] Thomas, S., *et al.*, the Role of Fibre/Matrix Interactions on the Dynamic Mechanical Properties of Chemically Modified Banana Fibre/Polyester Composites, *Composites Part A: Applied Science and Manufacturing, 37* (2006), 9, pp. 1260-1269
[16] Wang, C. X., *et al.*, Surface Modification and Aging Effect of Polysulfonamide Yarns Treated by Atmospheric Pressure Plasma, *Fibers and Polymers, 14* (2013), 9, pp. 1478-1484
[17] Wang, C. X., *et al.*, Influence of Twist and Filament Location in a Yarn on Effectiveness of Atmospheric Pressure Plasma Jet Treatment of Filament Yarns, *Surface and Coatings Technology, 202* (2008), 12, pp. 2775-2782
[18] Wang, C. X., *et al.*, Surface Modification of Aramid Fiber by Plasma Induced Vapor Phase Graft Polymerization of Acrylic Acid. I. Influence of Plasma Conditions, *Applied Surface Science, 349* (2015), Sept., pp. 333-342
[19] Li, Y., *et al.*, Helium Plasma Treatment Voltage Effect on Adhesion of Ramie Fibers to Polybutylene Succinate. *Industrial Crops and Products, 61* (2014), Nov., pp. 16-22
[20] Fakirov, S., *et al.*, *Handbook of Engineering Biopolymers: Homopolymers, Blends and Composites*, Carl Hanser Verlag, Munich, Germany, 2007
[21] Zhou, C. J., *et al.*, What Factors Affect Lotus Effect? *Thermal Science, 22* (2018), 4, pp. 1737-1743
[22] Liu, P., *et al.*, Geometrical Potential: an Explanation of Nanofibers Wettability, *Thermal Science 22* (2018), 1A, pp. 33-38
[23] Tian, D., *et al.*, Self-Assembly of Macromolecules in a Long and Narrow Tube, *Thermal Science, 22* (2018), 4, pp. 1659-1664
[24] Tian, D., *et al.*, Strength of Bubble Walls and the Hall-Petch Effect in Bubble-Spinning, *Textile Research Journal*, *89* (2019), 7, pp. 1340-1344
[25] Tian, D., *et al.*, Geometrical Potential and Nanofiber Membrane's highly Selective Adsorption Property, *Adsorption Science & Technology*, (2018), On-line first, https://doi.org/10.1177/0263617418813826
[26] Tian, D., *et al.*, Hall-Petch Effect and Inverse Hall-Petch Effect: A Fractal Unification, *Fractals, Fractals, 26* (2018), 6, ID 1850083

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