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Plasma-induced polymerization for enhancing paper hydrophobicity

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ABSTRACT

Hydrophobic modification of cellulose fibers was conducted via plasma-induced polymerization in an attempt to graft the hydrophobic polymer chains on paper surface, this increasing the hydrophobicity of paper. Two hydrophobic monomers, butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA), were grafted on cellulose fibers, induced by atmospheric cold plasma. Various influencing factors associated with the plasma-induced grafting were investigated. Contact-angle measurement, Fourier Transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) were used to ascertain the occurrence of the grafting and characterized the changes of the cellulose fiber after modification. The results showed that the hydrophobicity of the modified paper sheet was improved significantly after the plasma-induced grafting. The water contact angle on the paper surface reached up to 130°. The morphological differences between modified and unmodified samples were also revealed by SEM observation. The resulting paper is promising as a green-based packaging material.

1. Introduction

Paper is made of cellulose fiber from green plant, which is the most abundant natural resource in the world. Cellulose fibers, as natural carbohydrate polymers, have numerous advantages, such as renewable, low cost, biodegradable, environment-friendly and nontoxic. Apart from for printing and writing, paper has been widely used as packaging materials; where, natural cellulose fibers have been utilized as reinforcements for biocomposites and other industrial applications (Bledzki & Gassan, 1999; Corrales et al., 2007; Haque & Pracella, 2010). However, the cellulose fiber is far insufficient for high-barrier applications, moisture barrier in particular, because of its hydrophilic nature. In order to improve its hydrophobic properties and widen its applications, numerous studies over the past few years have been conducted, focusing on the hydrophobic modification of cellulose fiber surfaces, preparation of superhydrophobic papers (Navarro et al., 2003; Yang & Deng, 2008), and some other fictionalizations of cellulose fibers via esterification and etherification reactions (Baiardo, Frisoni, Scandola, & Licciardello, 2001). Cunha et al. (2010) reported a simple, viable and green approach to the hydrophobic modification of cellulose fibers surface by adopting TCMS (trichloromethylsilane) as a stable and volatile reagent under mild conditions without the use of a solvent. The modification generated an inorganic coating around the fibers, which conferred a high hydrophobicity to the fibers. It was also reported that superhydrophobic cellulose nanocomposites were prepared using a multi-step nanoengineering process (Goncalves, Marques, Trindade, Neto, & Gandini, 2008). The modification called upon an aqueous LbL (Layer by Layer) system followed by siloxane hydrolysis, and the resulting cellulose–silica–silica composite materials gave rise to water contact angles approaching 150°, which also opened the way to further valorizations of a ubiquitous renewable resource in applications such as water repellence and self-cleaning.

Graft copolymerization has been applied extensively to chemical modification for cellulose fiber to achieve the desirable properties including hydrophobicity which is often achieved by grafting various hydrophobic monomers onto fibers (Cunha et al., 2007; Dahou, Ghemati, Oudia, & Aliouche, 2010; Gaiolas et al., 2009; Takács, Wojnárovits, Borsa, & Rácz, 2010). Roy et al. described the recent advances in graft polymerization techniques involving cellulose and its derivatives (Roy, Semsarilar, Guthrie, & Perrier, 2009). Some of the features of cellulose structure and cellulose reactivity as well as various techniques for grafting synthetic polymers from the cellulosic substrate were summarized. The work conducted in our group found that the hydrophobic-modified cellulose microfibrils (CMF) could be achieved via surface-initiated atom transfer radical polymerization (SI-ATRP), and the resulting CMF is of great potential as reinforcement for biocomposites (Xiao, Li, Chanklin, Zheng, & Xiao, 2011). Similar work on the initiator-modified wood pulp cellulose acting as macroinitiator for surface-initiated ATRP was also reported (Zampano, Bertoldo, & Bronco, 2009). It was

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proved that Kraft cellulose fiber was suitable as substrates for surface-initiated ATRP, thus opening the possibility to use wood fibers for value-added paper products. It was also reported that the chemical modification of jute fibers for the application of green-composites using oleoyl chloride as coupling agent could turn the hydrophilic surface of jute fibers into hydrophobic (Corrales et al., 2007).

Plasma is an attractive technique as it provides a volumetric heating process at improved heating efficiencies as compared with conventional techniques. Plasma is defined as an electrically conducting medium generally consisting of negatively charged electrons, positively charged ions, and neutral atoms or molecules or both. It contains equal numbers of ions and electrons in a sufficient density (Li, Ye, & Mai, 1997). Broadly the plasma state can be considered to be a gaseous mixture of oppositely-charged particles with a roughly zero net electrical charge (Denes & Manolache, 2004; Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006). Plasma-induced polymerization has received considerable attention in recent years and favorable results have been obtained from plasma polymerization or plasma-initiated graft polymerization on the fiber surface (Baltazar-y-Jimenez, Bistritz, Schulz, & Bismarck, 2008; Navarro et al., 2003; Nithya et al., 2011; Pertile, Andrade, Alves, & Gama, 2010;Vaswani, Koskinen, & Hess, 2005). Vaswani et al. (2005) reported that plasma-polymerized fluorocarbon films could deposit on paper and regenerate cellulose surfaces to enhance their barrier properties and hydrophobicity. The resulting paper had long-term hydrophobic characteristic. The surface of carbon fiber was modified by plasma grafting of silsesquioxane; and the results, revealed by XPS and AFM analysis, confirmed the high efficiency of plasma (Zhang, Huang, & Wang, 2006). However, the plasma-induced polymerization on paper substrates has been seldom reported.

In this study, the graft polymerization of butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) on the surface of additive-free handsheets, induced by plasma irradiation, was conducted. The paper was made up Kraft softwood cellulose fibers whereas BA and EHA are typical hydrophobic monomers. The effects of various grafting reaction variables on the grafting percentage and grafting efficiency were investigated. The as-modified hand-sheets were characterized using Fourier transform infrared spectroscopy (FTIR), XPS (X-ray Photoelectron Spectroscopy), and scanning electron microscope (SEM). Moreover, the hydrophobic properties of the grafted handsheets were revealed by contact angle measurements.

2. Experimental

2.1. Materials

The bleached kraft softwood pulps were kindly supplied by a company in China. Additive-free hand-sheets with an oven-dry weight of 60 g/m^2 were prepared according to TAPPI standard method T205 sp-95. Two hydrophobic monomers, butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) used for fiber grafting, were purchased from Sigma-Aldrich. Their purity was of ≥99% for BA and about 98% for 2-EHA; and both were used without further purification. A low pressure glow discharge plasma reactor (HPD-100C) conducted at room temperature was used throughout the experiment.

2.2. Sample preparation

The additive-free hand-sheets were soaked in monomer or mixture of monomers first for certain time at different temperatures. The samples were then treated in the plasma reactor under various conditions including the plasma power, vacuum degree, duration of plasma exposure. After plasma treatment, the samples were dried in the fume hood at room temperature for 4 h; followed by Soxhlet extraction in acetone and ethanol at 60 °C for 24 h in order to remove the residual monomers and copolymers. The hand-sheets were then dried in a vacuum oven for 12 h prior to further testing or characterization.

2.3. Sample characterization

The hydrophobic property of the modified paper sheets was determined via contact-angle measurements using a video based optical contact angle measuring instrument OCA20 (DataPhysics Instruments GmbH, Filderstadt). Each sample was measured on 5 different points and the average values and standard deviation were obtained. The FT-IR spectra were recorded on a NEXUS 670 ATR-FTIR (Thermo Nicolet, USA), in transmission mode, at 2 cm^{-1} resolution and 32 scans. The surface morphology of the modified paper was observed on a scanning electron microscope (SEM) (S-3700N, Hitachi Ltd., Japan) after gold-coated.

X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature using a Kratos Axis Ultra spectrometer (AXIS-ULTRA^{DLD}, Kratos Analytical Ltd., Japan), equipped with a monochromatic Al Kα X-ray source with a power of 150 W. Survey spectra over a binding energy range of 0–1200 eV were recorded for each sample. High resolution spectra of C 1s and O 1s were acquired for quantitative measurements of binding energy and atomic concentration. The XPSPEAK41 software was used for background subtraction (Shirleytype), peak integration, fitting and quantitative chemical analysis. The C1s (C—C) peak at 284.6 eV was used to calibrate the binding energy scale.

The grafting ratio was determined gravimetrically, i.e., based on the weight change of the paper sheets before and after grafting polymerization. The following equation was used to quantify the ratios:

$$\text{grafting ratio} = \frac{w_2 - w_1}{w_1} \times 100\%$$

where W_1 is the weight of paper sheet before grafting; W_2 is the weight of paper sheet after grafting.

3. Results and discussion

3.1. FTIR spectroscopy

In order to investigate the changes of groups on cellulose fibers in paper after plasma-induced grafting treatment, the FTIR spectra of both modified and control samples are shown Fig. 1.

The effect of plasma treatment can be assessed by observing the evolution of some new bands. It is obvious that there is a new absorption peak at 1736 cm^{-1} compared to the control sample, which is attributed to the absorption of carbonyl groups from the monomers. This literally demonstrates that a certain amount of monomers have been grafted onto the fiber surface in the hand-sheet successfully.

3.2. Contact angle of modified sample

Contact angle measurements were performed on the surface of handsheets at room temperature. The contact angle value was recorded at 10 s after the water droplet was applied on the surface of testing specimen. Fig. 2 presents the images of the water droplet held on the surface of hydrophobic-modified papersheet.

From Fig. 2, it is obvious that the contact angle for the paper after modification is increased significantly (from 0° to above 127°), which suggests the establishment of a stable hydrophobic surface

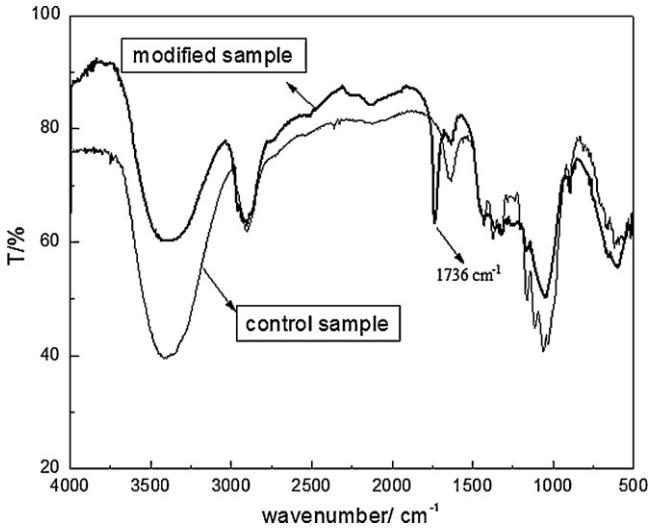

Fig. 1. FT-IR spectra for modified and control samples.

of the paper sheet compared to the unmodified one for which the water droplet absorbed quickly after water was dropped on the surface of the paper. In other words, the control sample is very hydrophilic, leading to the complete penetration of the water droplet in the paper; whereas the modified one is highly hydrophobic, preventing water droplet from flattering on the surface of the paper.

3.3. SEM morphology

The surface characterization of the fiber plays an important part in the property of paper sheet, especially for the water resistance ability. In order to test the hydrophobic property of the modified hand-sheet, the samples both unmodified (a) and modified (b) were observed using SEM (Fig. 3).

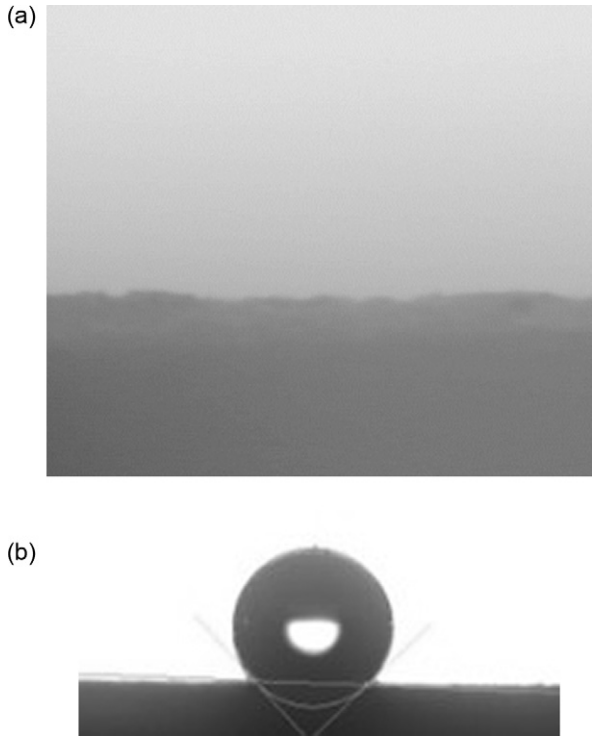

Fig. 2. Contact angle images of unmodified and modified paper. (a) Unmodified paper, the water penetrated through the paper. (b) Modified paper.

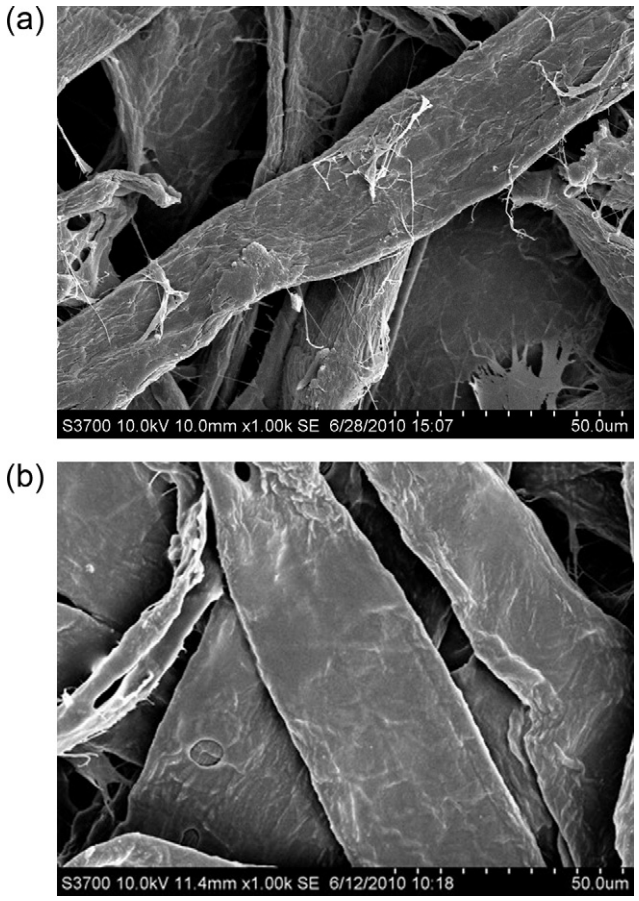

Fig. 3. SEM images of modified and unmodified samples. (a) Unmodified sample(×1000), (b) Modified sample(×1000).

From the SEM images shown in Fig. 3, it is obvious that the morphology of the fiber surface in the paper after the modification with BA and 2-EHA has been changed significantly. There were less fibrils on the surface of the modified sample than on the unmodified one. After the plasma treatment and grafting reaction, it is very likely that a polymeric film was formed on the surface of the fibers, thus increasing the hydrophobicity of the paper. This result is also supported by the fact of the high contact angle for the modified paper.

3.4. XPS analysis (elemental analysis)

The elemental analysis was conducted by XPS measurement. Fig. 4-1 shows the XPS survey spectra of the samples; whereas Fig. 4-2 presents the high resolution C1s XPS spectra for the same samples. In both figures (a) and (b) correspond to the control and modified samples, respectively. The chemical components on the surface for both control samples and modified samples are given in Table 1, which demonstrates the presence of carbon, oxygen, as expected.

As can be seen from the data shown in Fig. 4-1 and Table 1, there are some differences between the two survey spectra. The atomic concentration and mass concentration of C, as well as C/O ratios were enhanced remarkably after modification, increasing from 1.8 to 5.04 and from 1.35 to 3.78, respectively. This may be attributed to the grafting of the hydrophobic monomers onto the fiber surface, which contain more carbons compared to the cellulose fiber itself.

Table 1
Comparison of C/O ratio through XPS survey spectra.

	(a)			(b)		
	Position BE (eV)	Atomic Conc	Mass Conc	Position BE (eV)	Atomic Conc	Mass Conc
O 1s	531.1	35.67%	42.48%	530.7	16.56%	20.91%
C 1s	284.7	64.33%	57.52%	282.8	83.44%	79.09%
C/O ratio	–	1.80	1.35	–	5.04	3.78

It was reported that the peaks at binding energy of 285 eV, 286.5 eV, 288 eV and 289 eV or higher were attributed to C—C bounded carbons (alkane-type carbon atom), C—O bonds (alcohol/ether type carbon atoms), C=O group (acetyl type carbon atoms) and O—C=O (ester/ester/carboxylic acid type of moiety) group on fiber, respectively (Risio & Yan, 2009; Zafeiropoulos, Vickers, Baillie, & Watts, 2003). Evidently, there is O—C=O group corresponding to the peak in Fig. 4-2(b), which comes from the monomers, on the surface of the fiber after modification by plasma-induced grafting. Along with the changes in C/O ratio shown in Table 1, the results demonstrate that certain amount of monomers have been successfully grafted onto the fiber after plasma-induced grafting polymerization.

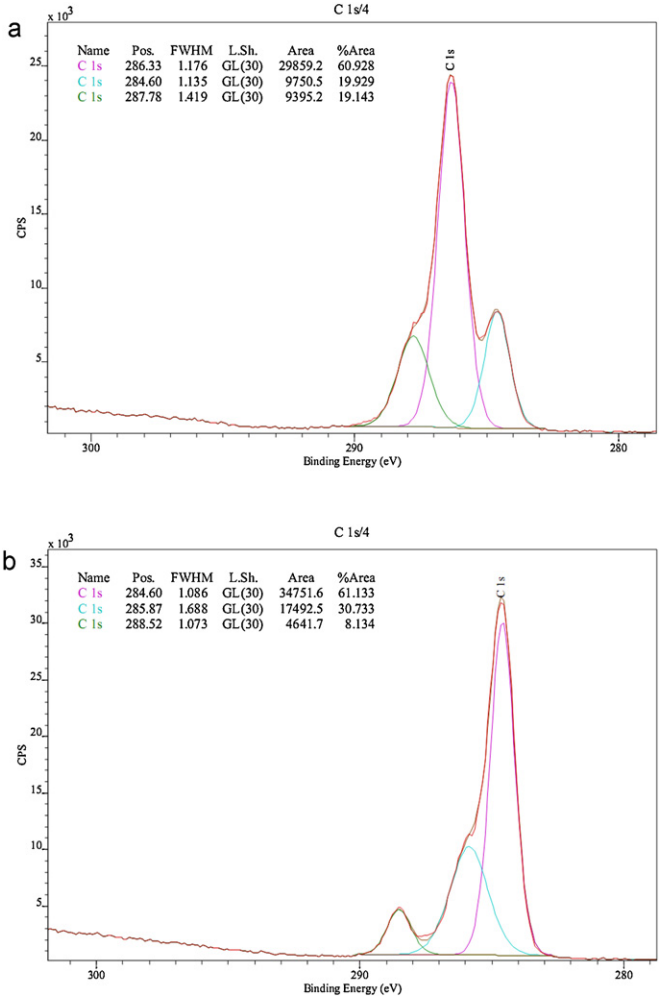

Fig. 4. (1) XPS survey spectra of samples for both unmodified and modified. (a) Control sample, (b) Modified sample. (2) High resolution C1s XPS spectra. (a) Control sample, (b) Modified sample.

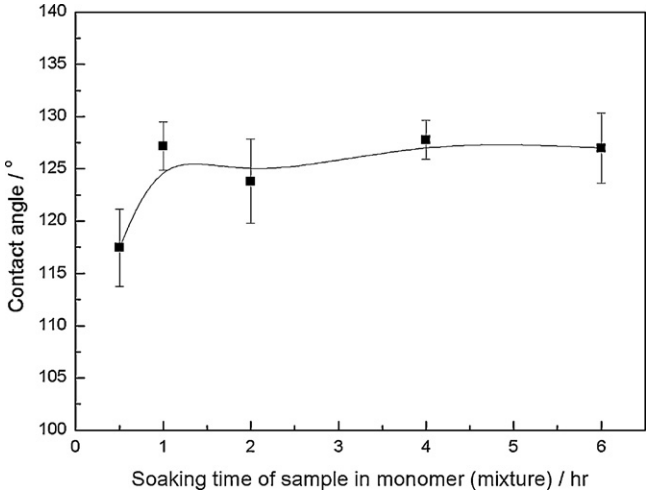

Fig. 5. Effect of monomer soaking time on contact angle.

3.5. Effect of monomer soaking time on contact angle

Fig. 5 shows the effect of soaking time on contact angle. For the handsheets tested, the reaction temperature and the plasma treatment time were fixed at 60 °C and 3 min, respectively.

As can be seen, with the prolonging of soaking time in monomers from 30 min to 6 h, the contact angle increased gradually from 118° to 125°. However, after soaking time exceeded 1 h, the curve tended to level-off as time increased, suggesting that 1 h soaking should be sufficient.

3.6. Effect of reaction temperature on grafting ratio and contact angle

The temperature also plays an important role on the modification of the samples soaked in the monomers. Fig. 6 presents

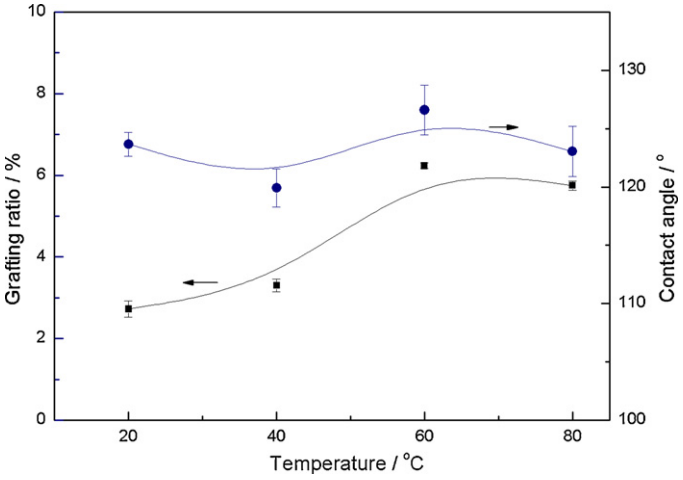

Fig. 6. Effect of temperature on grafting ratio and contact angle.

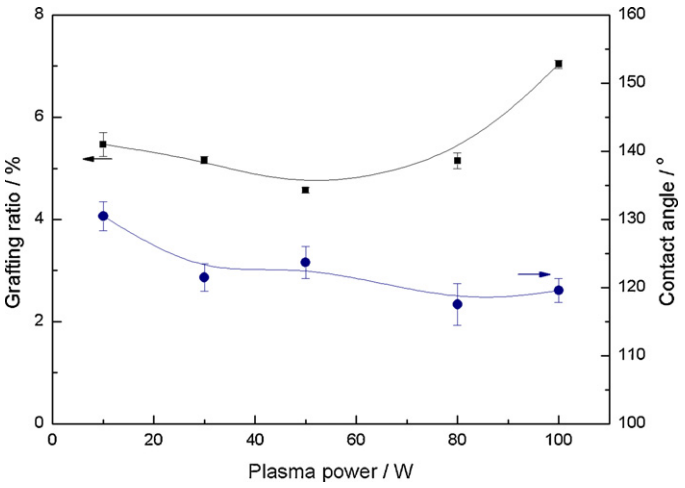

Fig. 7. Effect of plasma power on grafting ratio and contact angle.

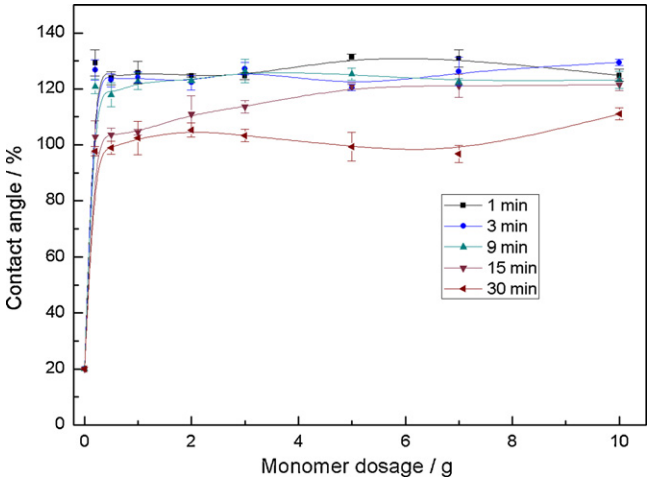

Fig. 8. Effects of monomer dosage and plasma treatment time on contact angle.

the effect of the reaction temperature on the grafting ratios and the contact angles, respectively, in which the grafting ratios were determined gravimetrically.

It can be observed from Fig. 6 that, with the change of reaction temperature, the grafting ratio increased firstly and decreased when the temperature was above 60 °C; and the grafting ratio varied from 2.4% to 6%. Similarly, the contact angle reached the maximum, i.e., 126.6°, at 60 °C. Obviously, the contact angle remained in the range from 120° to 127°, which indicated that the modified paper sheet was rendered highly hydrophobic.

3.7. Effect of plasma power on grafting ratio and contact angle

The impact of plasma power on grafting ratio and contact angle is illustrated in Fig. 7. As can be seen from Fig. 7, the contact angles show a decreasing trend from 130° to 120° as the plasma power increases; whereas the grafting ratio first decreased and then increased after the minimum at the power of 50 W. At a high level power, the high grafting ratio corresponded to a relatively low contact angle, suggesting that the high power plasma might break down the fibers or create pores on the surface of the paper, thus lowering the hydrophobicity or contact angles of the paper-sheet. To reduce the effects, the plasma power set at 10 W appeared to be appropriate.

3.8. Effects of monomer dosages and treatment duration on contact angle

The effect of monomer dosages on contact angle is shown in Fig. 8, in which the mass ratio of BA to 2-EHA was 1:1, and the reaction temperature was at 60 °C. After soaked in mixture of monomers for 1 h, the paper samples was exposed to the plasma for the duration varying from 1 min up to 30 min, at 10 W.

Clearly, the contact angles increased significantly even in the presence of a very low amount of monomers (0.2 g monomer on 5 g fiber). Further increase in monomer dosages did not change the contact angles remarkably, regardless of the treatment duration. It is also shown in Fig. 8 that, with the time of plasma treatment increased, the contact angle of the modified paper decreased particularly at the treatment time of 9 min or longer. In other words, when the treatment duration was above 9 min, the sample showed poorer hydrophobic properties compared to the other samples treated at a shorter duration. It can be concluded that the monomer dosage is not necessarily very high to render the paper surface hydrophobic; and meanwhile, the duration of the plasma does not have to be very long (less than 3 min). The results are of interest to the practical application due to the effectiveness created at a short time with a low dosage of monomers. Likely, a thin polymeric film was effectively generated over the plasma treatment under such conditions. As a result, the hydrophobicity or contact angles of the paper samples were increased significantly. The resulting paper is of great potential as green-based packaging materials for various applications.

4. Conclusions

The plasma-induced polymerization appears to be an effective approach to enhance the hydrophobic properties of paper sheet consisting of cellulose fibers. Excellent hydrophobic properties were obtained by grafting the hydrophobic monomers on the paper substrates under appropriate plasma-induced conditions. After soaked in the monomer mixture for 1 h and treated under 10 W for less than 3 min, the modified paper with the contact angle above 120° could be achieved at the monomer dosage as low as 4.0 wt% on cellulose fiber. The findings from this work are very encouraging in terms of the possibility of increasing the hydrophobic characteristic of cellulose fibers substantially through a relatively simple process. The resulting paper sheets are of great potential as green packaging materials.

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