Preparation of Hydrophobic Transparent Paper via Using Polydimethylsiloxane as Transparent Agent

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Abstract
Transparent paper with good hydrophobicity and flexibility was expected to act as an alternative substrate in fabrication of flexible electronics. However, conventional paper made of cellulose fibers was opaque and hydrophilic without undergoing special processing. Herein, cellulose fiber paper was treated by impregnating with hydrolyzed tetraethyl orthosilicate (TEOS) followed by coating with hydrophobic polydimethylsiloxane (PDMS) to prepare hydrophobic transparent paper. The results showed that silica nanoparticles produced by the TEOS hydrolysis improved the paper transparency to some extent, increased the paper thermal stability, but still remained the hydrophilicity of paper. After the paper was further coated with the PDMS and the PDMS was consolidated, the paper became clearly transparent and hydrophobic. The processed paper had a transmittance of more than 90% at 550 nm. The water contact angle of the paper reached about 110°. This work provided a new approach for the fabrication of hydrophobic transparent paper with conventional cellulose fiber paper.

Keywords: transparent paper, cellulose fiber paper, hydrophobicity, tetraethyl orthosilicate (TEOS), polydimethylsiloxane

1. Introduction

Cellulose is a cheap, renewable, biodegradable, non-toxic and environmental-friendly green material (Klemm et al., 2005; Wang et al., 2017a; Li et al., 2018). It extensively exists in plants such as wood, grass and cotton (Wang et al., 2011; Wang et al., 2017b; Reddy et al., 2018; Ewulonu et al., 2019). Therefore, the application of cellulose has always been a hot research topic (Wang et al., 2013; Ansari et al., 2014; Chen and Liu, 2016; Qin et al., 2019). Cellulose is not only used in biosynthesis and preparation of biodegradable materials with biocompatibility, but also shows great application prospects in biosensors, printed circuit boards, solar cells, membrane materials, carrier materials, functional chemicals and additives (Agate et al., 2018; Zhang et al., 2018). Cellulose fibers are hydrophilic and made into papers with interconnected network structures through hydrogen bonding. Because the hydrogen bonding is sensitive to water, the strength of paper sheet is markedly affected by moisture. By the adsorption of water, paper may even be dis-bonded. In addition, conventional cellulose fiber papers are opaque owing to their micron-sized void spaces in fiber network and the occurrence of light scattering at the interfaces among micro-sized fibers (Nogi et al., 2009). The adsorption of water also reduces the insulating property of paper. These observations limit the extensive application of cellulose papers as packaging materials, solar cell film materials and flexible printed circuit board.

The opacity of conventional paper is originated from the occurrence of fiber-air interfaces inside the paper as well as the different refractive index of cellulose and air, which results in a large amount of light scattering when light propagates through these interfaces. Therefore, reducing the opacity of a paper is required to reduce light scattering inside the paper. The most popular strategy for reducing the light scattering of paper is to make cellulose nano-paper by using cellulose nanoparticles or fabricate regenerated cellulose films by cellulose solution (Fang et al., 2014). Cellulose nanoparticles, including cellulose nanofibrils, cellulose nanocrystals and bacteria cellulose (Charreau et al., 2012), generally have poor drain-ability owning to the high water-affinity of cellulose and the large specific surface area of nanoparticles. Consequently, the manufacture of nano-paper is a
time-consuming process (Nogi et al., 2009). Meanwhile, the preparation of cellulose nanoparticles involves either a high-energy consumption process (cellulose nanofibrils) (Abdul et al., 2014; Nechyporchuk et al., 2016; Osong et al., 2016), the use of a large amount of chemicals 2,2,6,6-Tetramethyl-1-piperidine-1-oxyl free radical (TEMPO)-oxidized cellulose nanofibrils and nanocrystals) (Isogai et al., 2011; Seabra et al., 2018), or a time-consuming incubation (bacteria cellulose) (Zheng et al., 2019). The fabrication of regenerated cellulose films involves the dissolution of cellulose materials with large number of solvents, the long drying time of regenerated cellulose gel under controlled conditions and the recycling problem of the solvents (Gullo et al., 2018; Han et al., 2019). In fact, there are two traditional methods for preparing transparent paper by using conventional microsized cellulose fibers (Bachmann, 1983). One method is to use highly refined pulp to make paper and calendering paper under high pressure (Cappelletto et al., 2012; Zhu et al., 2014; Li et al., 2019). The principle is that the mechanical force in the refining process collapses the hollow cell structure of the fiber to a certain extent, makes the fiber more flexible, and produces a large number of fibrils on fiber surfaces. These fibrils on fiber surfaces can fill the gaps between the long fibers in the paper forming process. A dense paper structure is thus obtained (Li et al., 2019). To further process the paper, super-calendering is generally applied, in which strong pressure squeezed out the air inside the paper to further improve paper density and transparency (Bachmann, 1983). Another method is to treat paper with transparent agent that has a refractive index same with or similar to pure cellulose (Bachmann, 1983; Zhu et al., 2014). The generally used transparent agents are oils, resins, paraffin wax and synthetic substances, which can penetrate into the interior of the paper sheet. The transparent agents fill in the void spaces among fibers and drive out the air in the paper sheet for ensuring to make the paper sheet uniform and transparent. If hydrophobic transparent agent such as paraffin wax is used, transparent paper with water-resistance may be obtained.

In this study, polydimethylsiloxane (PDMS), a silicone elastomer, was used as transparent agent to prepare transparent paper with hydrophobicity.

2. Materials and Methods

2.1. Materials

Hydroxyl terminated PDMS with trade name of SYLGARD184 was supplied together with its curing agent by Dow Corning Corporation, USA. Tetraethyl orthosilicate (TEOS, >99.0%) was purchased from Tokyo Chemical Industry (TCI), Japan. Pristine paper used in this work was a fine paper with a basis weight of 35 g/m², which was provided by the specialty paper research group in Qilu University of Technology, China.

2.2. Methods

The TEOS was first warmed to 50 °C. Deionized water was then slowly added at a TEOS to water molar ratio of 4:1 under magnetic stirring. After reacting for 30 min to ensure the hydrolysis of the TEOS, a paper sample was dipped into the hydrolyzed TEOS dispersion. As the paper sample was completely wetted by the TEOS dispersion, it was taken out and dried at 80 °C in oven overnight.

The PDMS was mixed with curing agent at a mass ratio of 10:1 followed by stirring for several minutes to obtain a homogeneous mixture. The mixture was coated on the paper sample impregnated with the TEOS. The paper sample coated with the PDMS was placed in an oven and cured at 120 °C overnight to obtain a transparent hydrophobic paper. The coated amount of the TEOS and PDMS is about 45 g/m².

2.3. Characterization

Scanning electron microscopy (SEM, Hitachi Regulus 8220, Japan) was used to analyze the morphology of transparent paper, whose SEM images were obtained using a scanning electron microscope. Infrared (IR) technique was used to characterize the functional groups of paper samples. The IR spectra were recorded on a Fourier Transform Infrared Spectrometer (FT-IR, ALPHA, Bruker, Germany) in the range of 4000–400 cm⁻¹. The hydrophobicity of paper samples was characterized with water contact angle (Bayer et al., 2011; Wang et al., 2012), which was determined by using an optical contact angle measuring device (JC2000C1, Shanghai Powereach Co., Ltd., China). The transparency of paper samples was characterized with light transmittance, which was measured at the wavelength of 200–1000 nm by a UV-visible-near Infrared Spectrophotometer (Cary 5000, Varian, USA) with an integrating sphere attachment. The thermal stability of the paper was determined using a Q500 Thermogravimetric Analyzer with Q20 Differential Scanning Calorimeter (TA Instruments, USA) at a heating rate of 10 °C/min, where nitrogen was used as purge gas. Tensile tests were performed by using an Instron 5944 Universal Material Testing Machine (USA) equipped with a 500 N load cell. Paper samples with a width of 10 mm and a gauge length of 30 mm were tested at a cross-head speed of 10 mm/min.
speed of 5 mm/min. All samples were conditioned at a relative humidity of 50% for 24 h at 23 °C before testing.

3. Results and Discussion

3.1. The FT-IR spectra and SEM images

Figure 1 shows the FT-IR spectra of pristine paper, paper impregnated with hydrolyzed TEOS (TEOS-impregnated paper) and paper both impregnated with hydrolyzed TEOS and coated with PDMS (transparent paper). The typical absorption peaks belong to –OH of pristine filter paper do not appear in the spectrum of transparent paper due to the coverage of transparent agents. In contrast, the spectrum of transparent paper shows absorption bands of functional groups from the PDMS, curing agent and hydrolyzed TEOS. The peaks at 2961 cm\(^{-1}\) and 2904 cm\(^{-1}\) are attributed to the asymmetric stretching vibrations of –CH\(_3\) and –CH\(_2\)–, respectively (Liu et al., 2004). The absorption peaks at 1010 cm\(^{-1}\) and 1250 cm\(^{-1}\) in the spectrum of transparent paper are assigned to the asymmetric stretching vibrations of Si–O–Si and the deformation vibration of –CH\(_3\) (de Menezes et al., 2010). The IR absorption peak at 789 cm\(^{-1}\) belongs to Si–C stretching vibration (de Menezes et al., 2010). This analysis indicates that both silica, which produced by hydrolysis of the TEOS, and polycondensation-cured PDMS has been successfully introduced into transparent paper.

The variation of paper morphology before and after each step treatment was analyzed. Figure 2 shows the SEM images of pristine paper, paper impregnated with hydrolyzed TEOS and finally as-prepared transparent paper in both top view and cross-section. The SEM image of the pristine paper in top view (Fig. 2a) clearly shows the porous fiber network, in which fibers are loosely bonded. Large numbers of voids with size ranging from several ten to several hundred micrometers occur in the paper. After impregnated with hydrolyzed TEOS, the silica particles and their aggregates were hardly observed (Fig. 2b), suggesting that the SiO\(_2\) particles might be in nanosized range. This was in agreement with the previous report (Bouramtan et al., 2019). These small particles and aggregates attached on cellulose fiber surfaces, which would be beneficial for the penetration of pre-cured PDMS into the pores of fiber network and uniform distribution in fiber network and on paper surfaces. Consequently, the uniformity and transparency of paper will be improved.
By comparing the SEM image of pristine paper with that of TEOS-impregnated paper in cross section (Figs. 2d and 2e), one can find that the introduction of hydrolyzed TEOS made the paper become denser, i.e., the hydrolyzed TEOS improved the bonding between cellulose fibers in Z direction. Therefore, the thickness of TEOS-impregnated paper was lower than that of pristine paper.

The SME images of transparent paper shown in Figs. 2c and 2f confirmed the uniform coverage of polycondensation-cured PDMS on paper surfaces. After polycondensation and solidification, the PDMS completely filled in the fiber network and formed a cover layer, which made the paper have an almost smooth surface, and similar thickness with that of pristine paper.

3.2. Transparency

Figure 3 shows the transmittance and photograph of pristine paper, paper impregnated with hydrolyzed TEOS and the as-prepared transparent paper. The transmittance of paper increased with wavelength in the range of 200–800 nm, especially dramatically increased at UV region, owing to the reduction of scattering interface with increasing wavelength. The pristine paper was highly hazed and had a transmittance of 54.6% at 550 nm. After impregnated with hydrolyzed TEOS, the paper became clearer. Its transmittance increased to 64.3% at 550 nm, indicating that silica nanoparticles produced by the hydrolysis of the TEOS were filled in the pores among fibers, and reduced light scattering of paper. After further being coated with pre-cured PDMS and undergoing polycondensation and solidification, the transmittance of paper was further greatly improved compared with that of the hydrolyzed TEOS treated paper. A clear paper with high transparency was prepared. The tested transmittance was as high as 91.1% at 550 nm. This great improvement on transparency was attributed to the reduction in the fiber-air interface in fiber network by filling the space among fibers, driving out air and making the paper more uniform with poly-condensed and solidified PDMS.

3.3. Hydrophobicity

Figure 4 shows the water contact angles of transparent papers coated with different amount of PDMS as a function of time. Higher water contact angle indicates higher hydrophobicity of paper.

3.4. Thermal and mechanical properties

The thermal and mechanical properties of transparent paper were compared with those of pristine paper and paper impregnated with hydrolyzed TEOS. Figure 5 shows the thermogravimetric (TG) curves of pristine paper, paper impregnated with hydrolyzed TEOS, PDMS film and transparent paper. The water contact angle of pristine paper and paper impregnated with the TEOS was hardly measurable because the water drops quickly penetrated into the papers in the measurement process, indicating that both cellulose fiber paper and the cellulose fiber paper loaded with silica nanoparticles were highly hydrophilic owing to the occurrence of large numbers of hydroxyl groups on cellulose fibers and the porous structure of paper. By comparison, the as-prepared transparent paper (with a PMDS coating amount of 45 g/m²) had an initial contact angle as high as 105°, displaying a good hydrophobic property owing to the introduction of poly-condensed and solidified PDMS. However, the transparent paper showed a
reduced contact angle with the increase of the contact time, indicative of the anisotropic character of the paper due to the occurrences of both hydrophilic cellulose fibers and inherent hydrophobic PDMS (Abbasi et al., 2001; Bodas and Khan-Malek, 2007). Nevertheless, the contact angle did not change markedly with time, and stopped at 99°, suggesting a rather high water resistance. In addition, the contact angle decreased with the decrease of the coating amount of pre-cured PDMS, which allowed controlling the hydrophobicity of the transparent paper. The PDMS was therefore considered to be an attractive hydrophobic transparent agent in preparation of hydrophobic transparent paper (Jin et al., 2005).

As shown in Fig. 5, the PDMS film had a similar decomposition temperature with pristine paper. The weight loss at temperatures lower than 100 °C was attributed to moisture evaporation for cellulose paper (Lavoratti et al., 2016) and release of volatile molecules for the PDMS. Rapid weight loss at temperatures higher than 300 °C corresponded to the decomposition of cellulose for cellulose paper (Poletto et al., 2014) and the trimethylsilicon groups for the PDMS (Xie et al., 2018). The incorporation of the PDMS was not expected to affect the thermal stability of transparent paper markedly. However, the initial decomposition temperature of the paper after impregnation of hydrolyzed TEOS had been greatly enhanced, and the decomposition time was also increased. The reason was that silica particles produced by hydrolysis of the TEOS might fill in the spaces among fibers, resulting in an increase in the improvement of paper thermal stability. When the pre-cured PDMS was further coated on the surface of the paper impregnated with the TEOS, poly-condensed and solidified, the as-prepared transparent paper, exhibited two decomposition peaks at temperature lower than 400 °C and higher than 500 °C. The former was induced by decomposition of cellulose fibers and the PDMS, while the latter was induced by decomposition of silica particles produced by hydrolysis of the TEOS. Therefore, the as-prepared transparent paper showed much higher thermal stability than conventional paper.

Figure 6 shows the tensile stress-strain curves of pristine paper, paper impregnated with hydrolyzed TEOS and transparent paper. The impregnation of paper with hydrolyzed TEOS markedly improved the tensile strength, the elongation at break and Young’s modulus of paper. This is because the formed silica nanoparticles might fill in the spaces on fiber surfaces, which increased the stiffness of cellulose fibers, interrupted the hydrogen bonding among cellulose fibers and filled in the unboned area between cellulose fibers. After the paper was further treated with the PDMS, the tensile strength and Young’s modulus were reduced while the elongation at break was increased compared with the paper impregnated with hydrolyzed TEOS because the PDMS had a high flexibility and might interrupt the bonding of cellulose fibers. Nevertheless, the finally obtained transparent paper still showed slightly higher Young’s modulus ((2.10±0.16) GPa VS (1.85±0.23) GPa) and tensile strength ((24.5±0.11) MPa VS 24.0±0.15 MPa) than the pristine paper, indicating a higher strength and flexibility compared with pristine paper.

4. Conclusions

Transparent paper with high transparency and high hydrophobicity was prepared by treating cellulose paper with in situ formed silica nanoparticles and in situ poly-condensed and solidified PDMS. The improvement of paper transparency and hydrophobicity was originated from the filling of pores in cellulose networks with silica particles and PDMS, which might drive out air, reduce light scattering and confer hydrophobicity to the paper. The transparent paper also showed improved thermal stability, slightly higher tensile strength, greater elongation at break compared with pristine cellulose paper.
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References


