Preparation of Aromatic Poly(1,3,4-oxadiazoles) Pulps and Their Paper Properties

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ABSTRACT: To improve the paper properties of the poly(1,3,4-oxadiazoles) (POD), the POD pulps were prepared by prechemical and mechanical methods to increase their polarity, contact area, and interaction. The fibrillated degree of the staple fibers was evaluated by the Canadian Standard Freeness and the specific surface area, while the surface free energy was calculated by the Micro–wilhelmy method. Meanwhile, the functional groups and compositions on the surface of the POD fibers were confirmed by the FTIR–ATR and the X-ray photoelectron spectroscopy, and the surface morphological structure and the crystalline structure of the POD fibers were observed by the fiber analyzer, scanning electron microscope, and Wide-angle X-ray diffraction, respectively. It was found that the pronounced abrasive and distinctive grooves were formed on the surface of the POD fibers after prechemical and mechanical treatment. The surface free energy of POD fibers increased 8.41%, and the polar part increased by 32.10% after treatment. It was confirmed that the polar functional groups and fibril were formed after chemical and mechanical treatment, so the interaction of the POD fibers was highly enhanced, and as a result the apparent density, tensile strength, fold endurance, and tear strength of the paper formed by those treated fibers were all improved apparently. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39818.

INTRODUCTION

Aromatic poly(1,3,4-oxadiazoles) (POD) is a kind of rigid polymer with excellent heat resistance, high glass transition temperature, good hydrolytic stability, electroluminescence, electrical insulation, and good mechanical properties.[1] POD fibers are generally used to reinforce the advanced composite materials, such as honeycomb structure materials, protective products, hot gas filtration materials, and electrical insulating paper.[2] It has been reported that POD fibers are industrialized with small scale in Russian and used as friction materials.[3–5] Huang et al.[6,7] used the POD fibrids, which were obtained by precipitation methods, to prepare the insulation paper with polyester fibers. In our previous work,[2,8] POD was synthesized by one step with three stages and its fibers were prepared by wet spinning. However, similar to other high performance polymers, POD fibers with round cross-section have dense and regular structure, smooth surface, and strong chemical inertness, so the POD fibers are difficult to disperse in water and the interaction between fiber–fiber and fiber–matrix is weak. As a result, the strength of the paper or paper-like composites is low.

Papers are generally thin and fibrous sheets comprised a network of randomly oriented and short fibers or pulps laid down from a water suspension and bonded together by their own chemical attraction, friction, entanglement, binder, or a combination thereof.[9,10] The mechanical performances of papers are mainly determined by the properties of fibers. For the moment, there are two methods for production of synthetic pulps.[11–25] The precipitation method is adding the solution of the wholly synthetic polymer to the precipitant, and the fibrillation method is abrading the staple fibers mechanically to reduce their sizes and provide many fibrils. The fibrids formed by the precipitation method have high specific surface area (SSA) and high absorptive water capacity, which is in favor of fibrids adhesion and dispersion. However, the tearing and burst strengths of its paper are very low because of the losing of the fibrous morphology. Pulp is defined as fiber stem, which is highly fibrillated. The pulp has fibrillated fibrous structure, namely particles of the material having a stalk and fibrils, which contributes to the fiber–fiber bonding. To form strong contacts between the fibers, it is important to have both a large molecular contact area between the fibers and a large interaction between the

fibers in this contact zone.[26] Possibility of forming mechanical and chemical bonding at the interface is mainly dependent on the surface morphology and chemical composition of the fibers. Chemical modifications may activate these groups or introduce new moieties that can effectively interlock with the fiber. Surface characteristics such as wetting, adhesion, surface tension, etc. can be improved by modifications. The irregularities of the fiber surface play an important role in the mechanical interlocking at the interface. Parameters such as Van der Waals force, dipole–dipole interaction, hydrogen bond etc. determine the extent of physical bonding.[27]

Thus, making POD pulp by fibrillation method, improving morphological structure and surface properties of fiber is a key to improve dispersing and adhesion of fiber, which is a method for improving the formation and strength of paper or paper-like composites.

In the present work, POD fibers were immersed in the sulfuric acid solution at room temperature in some time, and then washed to neutral. The fibers after treatment in sulfuric acid were further treated by high-speed refining to etch the surface, reduce the size, and provide many fibrils. The effect of sulfuric acid concentration, immersed time, refining time on the Canadian Standard Freeness (CSF), SSA of POD pulp, and the surface of the POD fibers were studied in detail. The morphology, structure, composition, and surface free energy of the POD fiber were characterized by the scanning electron microscopy (SEM), fiber analyzer, Wide-angle X-ray diffractometer (WAXD), X-ray photoelectron spectroscopy (XPS), and dynamic wetting methods, respectively. The pulp treated by prechemical and mechanical method with 10 L water was poured into the 100-mesh screen to make handsheet. The surface structure of the sheet was characterized by SEM, and the physical properties (thickness, basis weight, tensile strength, Elmendorf tear strength, and fold strength) of the sheet were also studied.

EXPERIMENTAL

Materials
The POD fibers were prepared by wet spinning as was described in our previous works.[2,8]

Preparation of the POD Pulp
The POD staple fibers with 6 mm length were immersed into the 60%, 65%, 70%, and 75% sulfuric acid at room temperature for 30 min, and then washed the fibers to neutral. After that, 10–30 g treated staple fibers were dispersed in 1000 mL water (refining consistency 1–3%), and fibrillated by a high-speed PFI type refiner (T07-PF1, Xianyang Tongda light industrial instruments) subsequently. The 1000 mL mixture of POD and water was divided into four sections and refined, respectively. The POD fibers at different immersed time and refined time were collected to analyze.

CSF and SSA Analysis
CSF of POD pulp is conducted on a PL26 (Xianyang Pulplabtest) freeness tester according to TAPPI test T227. The SSA of the POD pulp is determined by using the BET SSA method on a SSA-4200 (Beijing Builder) SSA and aperture

tester according to ISO test 9277-1995 with the absorption the nitrogen. The wet pulp samples were dried at 120°C for 12 h, and further dried at 200°C for 1 h under nitrogen atmosphere.

Surface Free Energy Analysis
The fiber surface energy may be determined by measurement of the contact angles on the fiber using liquids of known polar and dispersive characters. Contact angles (both advancing and receding) on single fibers are determined by a Micro–wilhelmy technique on the JK99B (Powereach, China) surface tension tester using distilled water and diiodomethane (GR, Sinopharm Chemical Reagent) as probe liquids.

The surface energy of POD fibers was calculated according to the following equations[28]:

$$\gamma_S = \gamma_S^D + \gamma_S^P \tag{1}$$

$$\gamma_L = \gamma_L^D + \gamma_L^P \tag{2}$$

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^D \gamma_L^D} + 2\sqrt{\gamma_S^P \gamma_L^P} \tag{3}$$

$$\gamma_{L_1}(1+\cos\theta_1) = 2\sqrt{\gamma_S^D \gamma_{L_1}^D} + 2\sqrt{\gamma_S^P \gamma_{L_1}^P} \tag{4}$$

$$\gamma_{L_2}(1+\cos\theta_2) = 2\sqrt{\gamma_S^D \gamma_{L_2}^D} + 2\sqrt{\gamma_S^P \gamma_{L_2}^P} \tag{5}$$

where θ is the contact angle between fibers and liquid; γ_s is the solid surface energy; γ_L is the liquid surface energy; γ_L^D and γ_L^P are the dispersion and polar parts of the liquid surface energy, respectively; γ_{L1} and γ_{L2} are the two liquid surface energy, respectively; γ_s^D and γ_s^P are the dispersion and polar parts of the POD fibers' surface energy, respectively.

XPS Analysis
POD pulp had been successively extracted in the solvent of ethanol for 48 h and dried. XPS experiments were conducted on a XSAM800 (KRATOS) with the 14 kV and 250 W Mg Kα monochromatic X-ray sources. The base pressure of vacuum chamber was set at 1.33×10^{-6} Pa. The pass energy and energy step were 20 and 0.05eV, respectively.

Fourier Transform Infrared-Attenuated Total Reflection (FTIR–ATR) Spectroscopy Analysis
The Infrared spectra were recorded on a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer in the range of 4000–650 cm^{-1}.

Surface Morphology and Structure Analysis
The effect of the prechemical and fibrillating treatment on the POD fibers surface morphology was observed with the JSM-5900LV SEM and the XWY-VI (Zhuhai Hualun papermaking technology) fiber analyzer. For fiber analyst, the samples were prepared according to QB/T2597-2003.The surface of the POD sheet was observed by using the JSM-7500F SEM. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature on a X'pert Pro (Philip) X-ray diffractometer with the range of 10°–45° and the scanning rate was 12°/min with nickel-filtered Cu Kα radiation.

The Properties of Sheet Materials Analysis
The pulp treated by prechemical and mechanical method with 10 L water was poured into the 100-mesh screen on the PL6–
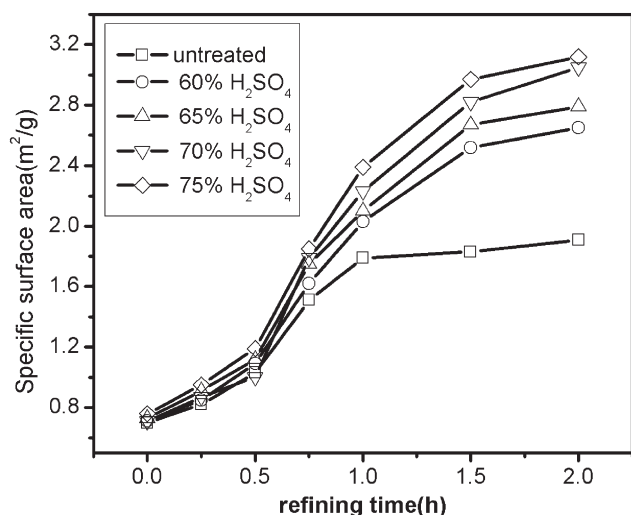
Figure 1. Dependence of specific surface area on refining time at different concentrated sulfuric acid solution.

300(Xianyang Pulplabtest) sheet machine of paper to make handsheet. The thickness and basis weight (grammage) of the sheet were determined by the thickness tester and basis weight scale, respectively. The tensile strength and elongation of the sheet were tested on the DCP-KZ300 (Sichuan Changjiang Papermaking instruments) tensile strength tester and the specimens were all 15 mm width and 250 mm length. The TAPPI test T515 OM was adopted here to test the fold endurance by using the DCP-MIT135A (Sichuan Changjiang Papermaking instruments) MIT folding strength tester. Elmendorf tear strength was measured on the DCP-SLY1000 (Sichuan Changjiang Papermaking instruments) Elmendorf tear tester according to the TAPPI test T419 OM.

The limiting oxygen index (LOI) of the POD handsheets were measured based on ASTM-D2863-00 with JF-3 oxygen index tester (Jiangning Nanjing Analytical Instrument Factory).The relative dielectric constant and dielectric loss index of the handsheets were measured according to GB/T1409–2006 with micro-
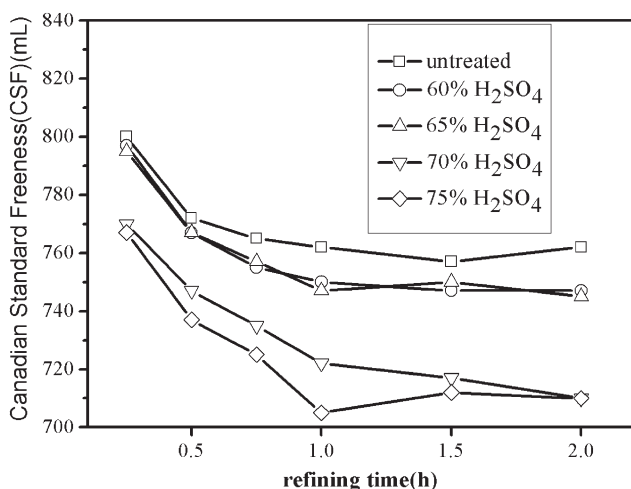
Table I. The Distribution of Fiber Length and Curl Index of POD Pulp

Fiber length (mm)	Content (%)	Curl index	Content (%)
0–0.5	1.2	0-0.1	6.0
0.5–1.0	2.4	0.1-0.2	22.6
1.0–1.5	9.5	0.2-0.3	15.5
1.5–2.0	10.7	0.3-0.4	11.8
2.0–2.5	7.2	0.4-0.5	10.7
2.5–3.0	7.1	0.5-0.6	9.5
3.0–3.5	17.9	0.6-0.7	2.4
3.5–4.0	19.0	0.7-0.8	4.8
4.0–4.5	9.5	0.8-0.9	3.6
4.5–5.0	9.5	0.9 up	13.1
5.0–5.5	4.8		
5.5–6.0	1.2		

wave dielectric measurement system (WY2855, Shanghai Wuyi Electronics). The volume resistivity of the handsheets was measured according to GB/T1410–2006. Thermal stability of handsheets were evaluated by the thermogravimetric analysis on thermogravimetric analyzer (NETZSCH TG 209F1 Iris) with the heating rate of 10°C/min. The tested temperature was in the range of 30–700°C.

RESULTS AND DISCUSSION

The Effect of Prechemical and Abrading Treatment on CSF and SSA POD Pulp and Fiber Length of POD Pulp

The CSF numbers were the volumes of the water that drained from aqueous slurry under the specified conditions. And it is determined by the fineness, flexibility, and the fibrillated degree of the fibers. The CSF number will decrease as the fibrillated degree of the fibers increase, because the numerous fibrils will reduce the rate at which water drains through a forming paper mat. The SSA numbers also can be used to indicate the fibrillated degree of the fibers. The changes of the SSA numbers and CSF numbers after treated under different conditions are shown in Figures 1 and 2, respectively. We can see from Figure 1 that the SSA of the fibers treated by sulfuric acid increases more rapidly with the increase of refining time than that of the untreated fibers. It can also be found that the increase of the SSA becomes slowly after refining for 1 h. The CSF, as is shown in Figure 2, shows the similar trend of variability that the CSF of the treated fibers decreases more rapidly with the increase of refining time than that of the untreated fibers and the decrease becomes slowly after refining for 1 h. Besides, the CSF numbers of the fibers treated by 70% and 75% sulfuric acid solution decrease much more than that of the others. It is considered that the fibrils will become membranous when the fibers are treated in the more concentrated sulfuric acid and the membranous fibrils will reduce the draining rate of water. The fiber length and fiber curl of the POD pulp after treatment with 60% H_2SO_4 together with refining through a fiber analyzer are shown in Table I.

The Morphology of POD Fibers

The coagulation process of the POD fibers was studied in details and the optimal condition, which was coagulating in
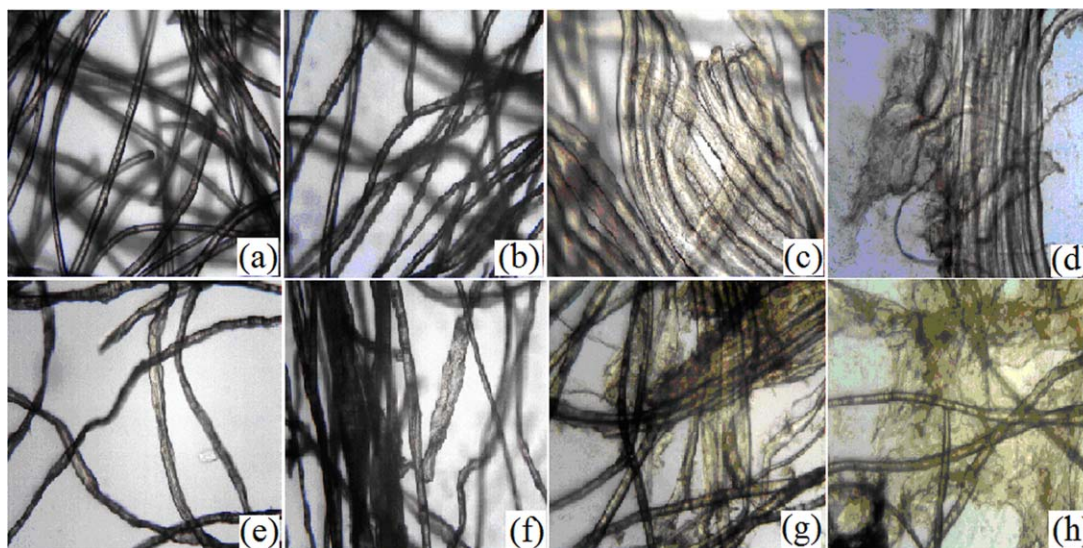

Figure 2. Dependence of Canadian Standard Freeness (CSF) on refining time at different concentrated sulfuric acid solution.

Figure 3. The micrographs of POD fibers: (a–d) are the POD fibers after treatment with 60, 65, 70, and 75% H_2SO_4 for 30 min, respectively, (e–h) are the POD fibers after treatment with 60, 65, 70, and 75% H_2SO_4 for 30 min together with refining for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

45% H_2SO_4 at about 50°C, was explored to prepare the POD fibers. The post-stretching process of the POD fibers was then carried out under the acid conditions at a specified temperature. POD hydrolyzes obviously in 25–70% sulfuric acid at room temperature.[29] Figure 3 is the micrographs of the POD fibers treated by sulfuric acid with and without refining treatment. We can see from it that the changes of the POD fibers are indistinctive after being treated by 60%, 65% H_2SO_4 within 30 min, and the POD fibers become winding and flat after refining for 1 h. The POD fibers treated by 70%, 75% H_2SO_4 become swelling and bind to each other within 30 min, and the POD films form among the POD fibers after refining for 1 h, and exceptionally, the POD films become bigger after being treated with 75% H_2SO_4. To retain the morphology and strength, the 60% sulfuric acid was chosen to treat the POD fibers. The surface morphologies of the POD fibers before and after treatment by 60% sulfuric acid are shown in Figure 4. The surface of the untreated POD fibers is almost smooth with a few grooves, as is shown in Figure 4(a). The surface of the POD fibers treated in 60% sulfuric acid for 30 min is rough with numerous grooves, as is shown in Figure 4(b). This suggests

that the surface of POD fibers is corroded by the sulfuric acid severely in a short time. From Figure 4(c), it can be found that the on-shedding fines appear after immersing the POD fibers in 60% sulfuric acid for 30 min and refining for 1 h, which indicates that the POD fibers are fibrillated and the POD pulps are formed.

The Crystallization Structure of POD Fibers
The POD fibers with three-layer skin-core microstructure are composed of the giant fibril, fibril, microfibril, and the amorphous region. The degree of crystallinity of the microfibril region is the highest among these regions. After chemical and mechanical treatment, the amorphous region of the fibers is destroyed, and then the microfibril region comes out. Figure 5 is the WAXD spectra of the POD fibers before and after treatment. It shows that the degree of the crystallinity increases indistinctively after treatment by 60% sulfuric acid for 30 min. However, the increase becomes significant after further treatment by refining for 1 h. It illustrates that the amorphous region is damaged slightly in sulfuric acid and severely destroyed after refining.
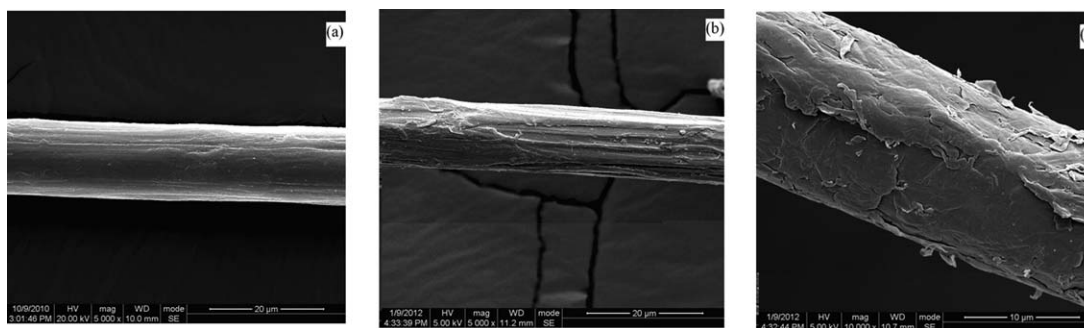

Figure 4. SEM micrographs of POD fibers: (a) original, (b) treated with 60% sulfuric acid, and (c) treated with 60% sulfuric acid together with mechanical treatment.
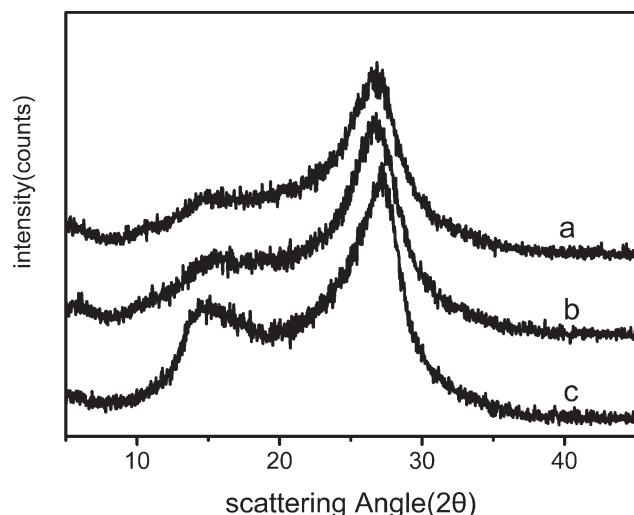
Figure 5. X-ray diffraction patterns of POD fiber: (a) original; (b) after treatment with 60% H_2SO_4 in 30 min; (c) after treatment with 60% H_2SO_4 together with refining.

The Surface Free Energy of POD Fibers

As regard to the surface free energy of the fiber γ, and thus the work of adhesion W_A, as being made up of the sum of components associated with the types of bonding appropriate to the chemical nature of the POD fibers involved.[30] By measuring the contact angles of a number of different probe liquids on the same surface, the components for the solid surface can be evaluated. The Micro–wilhelmy testing results are shown in Table II. It can be seen that the surface free energy of the POD fibers increases by 5.04% and the polar part increases distinctively by 17.28% after treatment with 60% sulfuric acid. After further treatment by refining for 1 h, the surface free energy increases by 8.41% and the polar part increases by 32.10%. The high surface free energy will benefit the impregnation of water and improve the adhesion of fibers between each other.

FTIR Analysis and Surface Component of POD Fibers

There are 1,3,4-oxadiazole rings, which were derived from dihydrazide dewatering in the structural unit of macromolecular chains of POD, and 1,3,4-oxadiazole rings were prone to open especially in alkali aqueous solution, while 1,3,4-oxadiazole rings were more difficult to open in acid solution.[31]

The FTIR–ATR spectra of the fibers before and after treatment are shown in Figure 6. The broad absorption peak from 3500 to 3200 cm^{-1} is the stretching vibrations of N—H and O—H groups. The absorption peaks at 1269 and 963 cm^{-1} are the vibrations of the

Table II. The Surface Free Energy of POD Fibers After Different Treatments

Samples	Γ (mN/m)	γ^D (mN/m)	γ^P (mN/m)
a	41.6	33.5	8.1
b	43.7	34.2	9.5
c	45.1	34.4	10.7

a is the original fibers, b is the fibers after treatment with 60% H_2SO_4 in 30 min, and c is the fibers after treatment with 60% H_2SO_4 together with refining for 1 h.
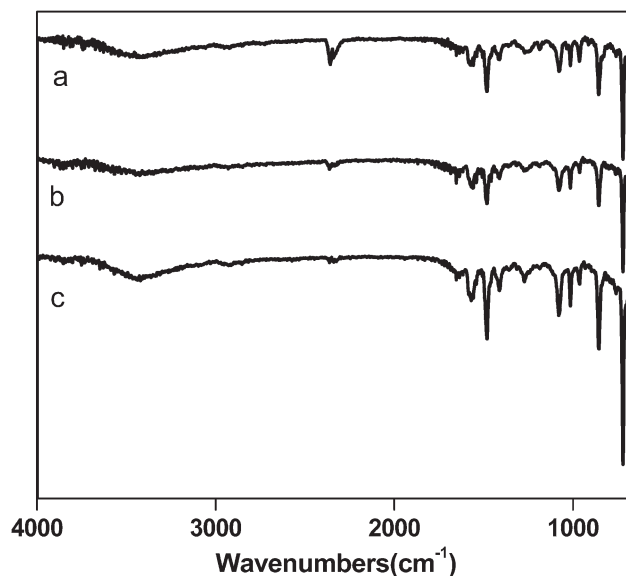

Figure 6. The ATR–FTIR spectra of POD fibers: (a) original; (b) after treatment with 60% H_2SO_4 for 30 min; (c) after treatment with 60% H_2SO_4 together with refining for 1 h.

1,3,4-oxadiazole rings and the peaks at 1635 and 1481 cm^{-1} are induced by C=N and N—N, respectively, while peaks at 1014 and 1073 cm^{-1} are the vibrations of C—O—C. The weak peak at 1568 cm^{-1} is the vibration of the remained hydrazide groups, which have not converted into the oxadiazole rings in the process of dehydration cyclization. It can be concluded that the broad peak from 3500 to 3200 cm^{-1} of the active groups is enhanced and the peaks from 1569.5 to 963 cm^{-1} and from 855 to 719 cm^{-1} are the attributed to the protonation of oxygen and nitrogen atom of 1,3,4-oxadiazole rings, respectively. The protonation mechanism was shown in Scheme 1. The intensity change of absorption peak of POD fiber after treatment with 60% H_2SO_4 together with refining for 1 h is very pronounced in Table III.

The surface composition of POD fibers before and after chemical–mechanical treatment is determined by XPS and the results are shown in Table IV and Figure 7. It can be seen that the content of oxygen and carbon on the fiber surface increases and the content of nitrogen decreases after treatment with the sulfuric acid. However, the content of the oxygen and nitrogen increases and the content of carbon decreases after treatment by sulfuric and refining. The variations of the ratios of N/C and O/C indicate that the molecules on the surface of the chemical–mechanical treated fibers are disrupted by chain scission and crosslinking. To evaluate the chemical interaction during

Table III. The Functional Group Change

Wave numbers (cm^{-1})	Intensity	Possible reason
3500–3300	Increase	νN—H, νO—H
1482	Increase	νN—N
853	Increase	νC—N
719.5	Increase	δN—C=O
2370–2320	Decrease	νas-N=C=O, or reagent

Table IV. The Surface Component of POD Fibers Before and After Chemical–Mechanical Treatments

Samples	C (at %)	O (at %)	N (at %)	O/C	N/C
a	74.26	14.48	11.27	19.50	15.18
b	81.4	15.5	3.1	19.04	3.80
c	57.9	29.7	12.4	51.30	21.42

a is the original fibers, b is the fibers after treatment with 60% H_2SO_4 for 30 min, and c is the fibers after treatment with 60% H_2SO_4 together with refining for 1 h.

chemical and chemical–mechanical treatment, the resolved analysis of C1s peak is performed and the results are shown in Figure 8. The peaks at 284.7, 285.55, 287, and 288.1 eV are due to C—C, C—O—C, C=N, N—C=O, respectively. As is shown in Figure 6(b,c), the changes of the content of C—C, C—O—C, C=N and N—C=O after treatment with 60% H_2SO_4 for 30 min indicate that the C—C, C—O—C are broken and the C=O are generated during the chemical–mechanical treatments.
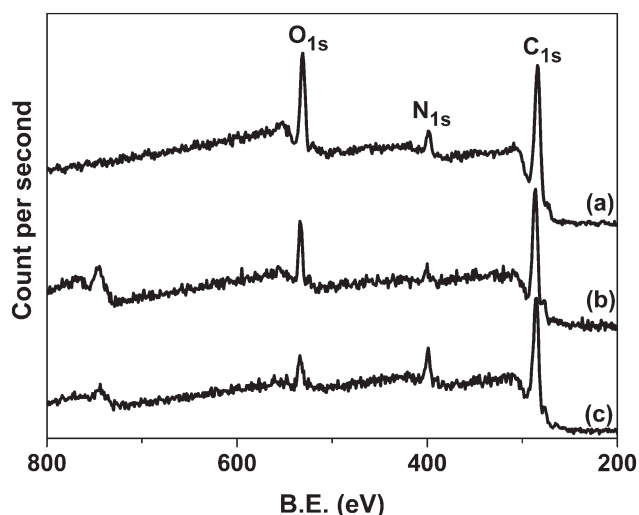

Figure 7. The XPS spectra of POD fiber: (a) original, (b) after treatment by 60% H_2SO_4, and (c) after treatment by 60% H_2SO_4 together with refining for 1 h.
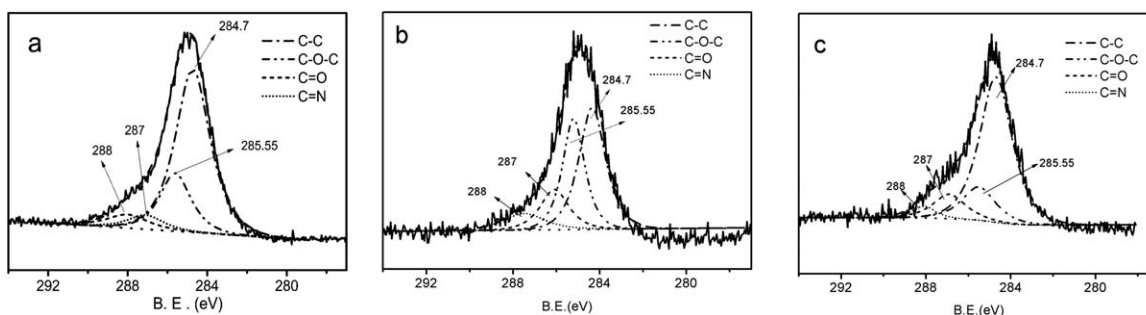

Figure 8. XPS C_{1s} spectra of POD fiber surface: (a) original; (b) after treatment by 60% H_2SO_4 for 30 min; (c) after treatment by 60% H_2SO_4 together with refining for 1 h.
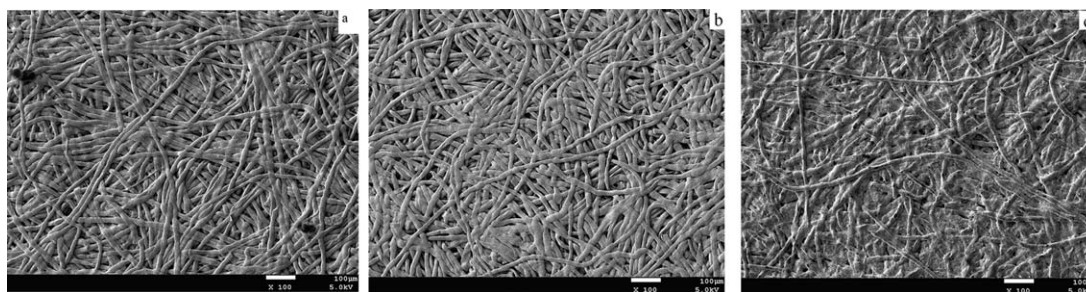

Figure 9. The SEM of the hand sheet surface: (a) original fibers; (b) the fibers after treatment by 60% H_2SO_4 for 30 min; (c) the fibers after treatment by 60% H_2SO_4 together with refining.

Table V. Physical Properties of the POD Handsheet

Samples	Thickness (mm)	Basis weight (g/m^2)	Tensile strength (N/cm)	Elongation (%)	Fold strength (times)	Tear strength (mN)
a	0.069	58.3	22.42	2.6	49	725
b	0.058	57.9	27.19	3	43	821
c	0.061	59.1	30.35	2	44	854

a is the original fibers, b is the fibers after treatment by 60% H_2SO_4 for 30 min and c is the fibers after treatment by 60% H_2SO_4 together with refining.

Table VI. Comparison of Electrical Property and Flame Retardant Between POD Handsheet and POD Film

Properties Samples	POD handsheet	POD film
Relative dielectric constant (50 Hz)	2.04	2.5
Dielectric loss index (50 Hz)	7.3×10^{-3}	1.5×10^{-2}
Volume resistivity (Ω m)	5.1×10^{11}	3×10^{13}
Oxygen index (%)	28–30	27–29

It can be seen that surface components of POD fibers change after chemical–mechanical treatment and the absorption peak of the functional groups change by Comparing FTIR–ATR spectra with XPS spectra. The peak intensity of functional groups N—C=O, C=N increase.

The Structure and Properties of POD Handsheet

The strength of the POD paper is affected by the number and strength of the bond between POD fibers, the fiber strength, and the fracture initiation zones. The chemical–mechanical treatments will change not only the surface properties of the POD fibers but also the CSF and SSA of the POD fibers. The changes are conducive to the forming process of the paper in virtue of the increase of fiber polarity and strength of paper as a result of the increase of contact area, chemical bond, and physical bond of the fibers. The SEM of the surface of POD handsheet is shown in Figure 9. It can be seen from Figure 9(b) that the surface of POD fibers becomes swelling and the bonds between the fibers, which is determined by the chemical composition of the fibers, increase after chemical treatment. Figure 9(c) shows that the fibrils fill the gap of the sheet, so the sheet becomes dense after chemical–mechanical treatment. The effect of the chemical–mechanical treatment on the physical properties of the POD handsheet is shown in Table V. The increase of
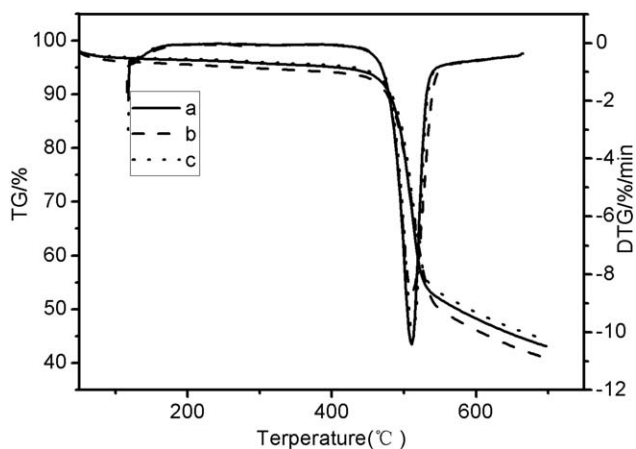

Figure 10. TG curve and DTG curve of the handsheet: (a) original fibers; (b) the fibers after treatment by 60% H_2SO_4 for 30 min; (c) the fibers after treatment by 60% H_2SO_4 together with refining.

the apparent density indicates that the fibers contact to each other strongly after chemical–mechanical treatment. The tensile strength, folding strength, and tear strength are predominantly affected by the adhesion between fibers, which is determined by the morphological structure and surface properties of the fibers. The morphological structure and surface properties of the treated fibers improve the apparent density, tensile strength, folding strength, and tear strength of the paper.

The special properties such as thermal stability, electrical properties, and flame retardant of POD paper were shown in Figure 10 and Table VI. As it can be seen from the results, the thermal stabilities of POD handsheets have little change after treatment by 60% H_2SO_4 for 30 min [Figure10(b)] and after treatment by 60% H_2SO_4 together with refining [Figure 10(c)]. When compared the electrical
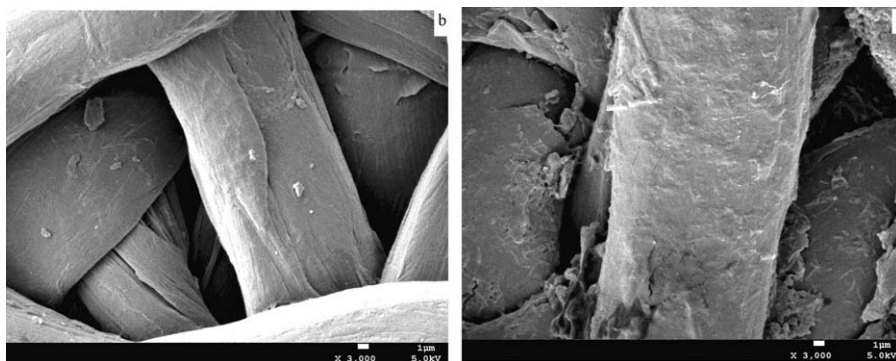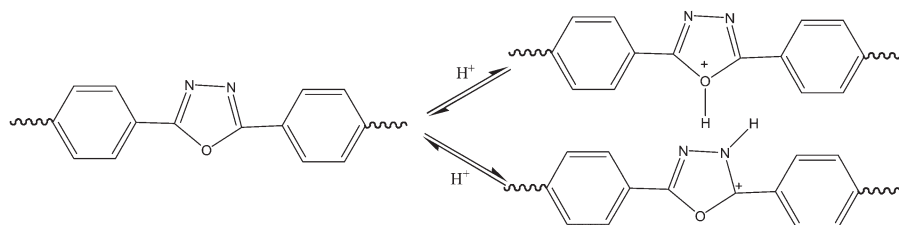

Figure 11. The SEM of the handsheet surface: (b) zoom of Figure 9(b), (c) zoom of Figure 9(b).

Scheme 1. The protonation mechanism of POD fibers in sulfuric acid solution.

properties of POD paper with those of clean POD film, dielectric loss index and volume resistivity of POD paper are less than those of POD film. LOI of POD paper is higher than that of POD film.

The Dependence of Interfacial Properties on Mechanical Properties of POD Handsheets

The joint among fibers affect on the mechanical properties of POD paper, and the interfacial properties of POD fibers affect on fiber–fiber joint. The rough surface with numerous grooves of POD fiber after treating by 60% H_2SO_4 with refining, and contact area increase, which contributed to improving fiber–fiber friction force and mechanical interlocking, as is shown in Figure 11. On the other hand, the results from FTIR–ATR and XPS showed that the content of N—H, O—H, N—C=O increased, which could contribute to the increase of hydrogen bond, ionic bond, coordination bond, and the Van der Waals forces and the improvement of fiber–fiber joint in a planar and interlayer.

CONCLUSIONS

POD pulps were prepared by the prechemical and mechanical treatment methods. The fibrillated degree of the POD fibers was found to be enhanced by testing the SSA and CSF. The surface morphology of the POD fibers changed largely after chemical–mechanic treatment. The fiber analyzer and SEM showed that the surface of the POD fibers became rough and the numerous grooves appeared on the surface of POD fibers after treatment. The irregularities of treated fiber surface improve the interlock of fiber, which improve paper properties. The WAXD confirmed that the crystallinity of the POD fibers increased after chemical and chemical–mechanical treatment. The surface free energy of the POD fibers increased by 8.41% and the polar part significantly increased by 32.10%.The spectra of the FTIR–ATR showed that the polar functional groups formed after chemical–mechanic treatments of POD fibers. It was proved by the XPS analysis that the oxygenic functional groups on the surface of POD fibers increased after chemical–mechanic treatments. Polar functional groups on the surface contribute to dispersion of POD fibers in the water, which improve the formation of paper. The improvement of dipole–dipole interaction, hydrogen bond as result of polar functional groups increase also has the contribution to improvement of paper properties.

ACKNOWLEDGMENTS

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