

Production of recycled cellulose fibers from waste paper via ultrasonic wave processing

Xiuyan Guo,^{1,2} Zhengwu Jiang,¹ Haoxin Li,¹ Wenting Li¹

¹Key Laboratory of Advanced Civil Engineering Materials, Ministry of Education, Tongji University, Shanghai 200092, China

²School of Mechanical & Electrical Engineering, Jinggangshan University, Ji'an Jiangxi 343009, China

Correspondence to: Z. Jiang (E-mail: jzhw@tongji.edu.cn)

ABSTRACT: Recycling waste paper can be considered as a means to displace the use of natural cellulose fibers applied in building materials, because it is composed mostly of cellulose. The water absorption and special surface area of cellulose fibers are the key properties for their use in building materials. The objective of this article was to study the production of recycled cellulose fibers from waste paper using ultrasonic wave processing. The physical and chemical properties of recycled cellulose fibers, such as water absorption, specific surface area and pore characteristics, etc., were investigated with various testing methods. The results indicated that the ultrasonic cavitation effect was feasible for the preparation of the secondary fibers. When the ultrasonic treatment time lasted for 10 min, the water absorptions of both newsprint fibers and kraft fibers increased significantly and reached the highest values of 12.5 g/g and 11.2 g/g, respectively, which were nearly two times than that of fibers without ultrasonic treatment. With a pretreatment of 20 min, the average length and fineness of recycled cellulose fibers decreased by 4% and 25%, respectively, and the length-diameter ratio of the recycled cellulose fibers was 1.28 times than that of the untreated fibers, which greatly increased the special surface area of the recycled cellulose fibers. This work also determined that NaOH was useful to improve the physical properties of the recycled cellulose fibers. Because the recycled cellulose fibers after processing, fulfilled several technical indexes, they can be considered as a filling material for used in cement-based materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41962.

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INTRODUCTION

With the incessant development of the economy, a large number of solid wastes from cities, industries, and constructions are produced, resulting in the depletion of materials resources. If such wastes are not properly treated, resources will be wasted and the environment will be polluted. Current resource shortages and ecological deterioration make the recycled uses of these wastes and the preparations of renewable materials imperative.

Cellulose is a polymer, and consists of unbranched β (1 \rightarrow 4) D-glucopyranosyl units, described by the molecular formula $(C_6H_{10}O_5)_n$.¹ The crystalline region and amorphous region coexist in the supermolecular structure of cellulose, crystalline region is constituted by a large amount of hydrogen bonds, causing the orderly molecular stacking, while the molecular structure of amorphous regions is irregular and loose, both of which make the most solvent molecular reach only amorphous region and the surface of crystalline region.² To improve the activity of cellulose, the hydrogen bonds have to be broken.³ Some simple processes, such as papermaking, textile degum-

ming, are operated to obtain cellulose fibers (CFs). In these processes, most of the hemicellulose and lignin are removed from the cell walls, leaving the cellulose microfibrils, which are the main raw material for CFs.^{4,5} These cellulose microfibrils can be randomly laid together during the CFs preparation process. This arranged pattern endows the CFs with a favorable hydrophilic property in addition to good flexibility.⁶ Accordingly, CFs are widely applied in polymer composites,⁷ pulp,⁸ and textiles.⁹ When used in the building industry, CFs can improve the durability and service life,¹⁰ stop crack formation, and delay crack growth,^{11,12} and provide reinforcement for cement-based materials.^{13,14} To ensure the implementation of the superior properties of CFs, good absorbency, larger specific surface, and amorphous structure must be maintained. The hydrogen bond is one of the significant influences on the water absorbency of CFs, which must be broken to change the absorbency and enable the CFs to use in cement-based materials, so a reasonable pretreatment is necessary. For now, the hemicellulose and lignin of wood must be removed in the pretreatment process to produce commercial CFs, which increases the production

cost and makes the cement-based materials containing CFs more expensive. Therefore, finding an alternative to substitute for CFs is worth studying.

Waste paper is mainly composed of CFs and can be used as raw materials to produce recycled paper and biomass materials,¹⁵ but many acids and bases must be added to enhance the deinking effect^{16,17} and the biodegradability of cellulose in these processes.^{18,19} Without a proper management system, black liquor would be discharged after performing these processes, thus causing serious water and soil pollution. In addition, sludges will also be produced, which must be buried in landfills, and bring tremendous threats to the atmospheric environment and human health. As a result, the development of an economic and environmental friendly waste paper disposal method involving the recycling of waste paper can protect the environment by addressing these potential forms of pollution. Theoretically speaking, waste paper can be used as a substitute for the CFs and applied in cement-based materials. Moreover, the waste paper used in cement-based materials does not require the use of the deinking and bleaching processes, thereby greatly reducing the emissions of hazardous substances in the wastewater. However, waste paper must be pretreated to improve the specific surface area and increase the water absorption, and ultrasonic provides a favorable tool for modifying fibers. Some studies indicated that the morphological structures of the fibers were changed and that fibrillations appeared on the surfaces of fibers when ultrasonic pretreatments were conducted.^{20,21} Other studies reported the improvement of the accessibility and reactive ability of fibers by a method for which the ultrasonic pretreatment had little impact on the fiber lengths, while the coarseness of the fibers was obviously decreased.^{22,23} However, the majority of studies on fibers pretreated with ultrasonic are mainly focused on virgin plant fibers,^{24,25} few literature studies regarding the application of ultrasonic pretreatments to waste paper fibers is found. As a result, the modification of the properties of waste paper via ultrasonic technology is worthy of study.

In this text, the effects of ultrasonic waves on the properties of CFs, such as water absorption, specific surface area, pore volume, average length, and fineness of the recycled cellulose fibers (RCFs), from waste paper are researched, and the feasibility of the RCFs obtained from waste paper via ultrasonic waves is analyzed. The results of this study are useful for the effective recycling of waste paper and the production of RCFs via ultrasonic waves.

EXPERIMENTAL

Materials

The newsprint and kraft paper were obtained from Shanghai, China. The glue contents and the amounts of impurity substances and junk in this research were controlled to within 1% and 0.25%, respectively. In addition, the content of cellulose in each paper was more than 75%. Kaoline (6000 mesh) and hexadecyl trimethyl-ammonium chloride were purchased from the sino-pharm chemical reagent Co., Ltd, China.

Preparation of Recycled Cellulose Fibers

RCFs from waste newsprint fiber (NF) and kraft pulp fiber (KF) were produced in our own lab using three steps: waste paper

crashing, ultrasonic pretreatment, and formation of composite specimens.

In the first step, the waste paper was firstly soaked in water for 12 h, and then ground in a PL2-00 high-thick hydropulper machine at 300 rpm for 30 min with a pulp consistency of 12% and temperature of 60 °C. After grinding, the pulp was rinsed with water, filtered using a vacuum pump to 80 mesh, and then dried in the thermostatic oven at 60 °C for 24 h. The waste paper was dissociated without deinking in this process, and the discharge quantity and organic concentration of the wastewater were far less than those of deinking pulp. After being treated using the flocculating method,²⁶ the wastewater could be recycled or applied into construction.

Two programs were performed in the second step, one is only using ultrasonic radiation, and another one is combing alkali treatment with ultrasonic radiation. For the first program, the dry pulp was dispersed in water and then pretreated by ultrasonic radiation in the JY92-II DN sonifier cell disrupter at 300 W with a pulp consistency of 2% and temperature 20 °C. These samples from NF were labeled as NF-5, NF-10, NF-15, NF-20 for the treatment times of 5 min, 10 min, 15 min, and 20 min, respectively, and those from KF were labeled as KF-5, KF-10, KF-15, and KF-20 for the treatment times of 5 min, 10 min, 15 min, and 20 min, respectively. For another program, the dry pulp was firstly soaked in the 1 to 3% (in mass) NaOH solution for 2 h, and then filtered with water to pH 7.0 and treated with the similar process as in the first program. The ultrasonic treating time was 10 min. The samples treated in this program were marked as 1-NF-10, 2-NF-10, 3-NF-10, 1-KF-10, 2-KF-10, and 3-KF-10. After these two programs, all the samples were dried under the same conditions as those in the first step.

In the last step, each sample was soaked in water and stirred in an electric mixer at 600 rpm for 30 min with a pulp consistency of 5%. Eighteen percent (in mass) kaoline and 0.5% (in mass) hexadecyl trimethyl-ammonium chloride were simultaneously added in this process. After being filtered and dried under the same condition as that in the first step, RCFs were finally produced.

Testing Methods

Water Absorption. Water absorption was measured following the Chinese National Standard (GB/T 461.3-2005) and the Chinese Enterprise Standard (Q/320683KDW01-2007). About 2.0 grams of RCFs was placed in a vacuum oven at 60 °C for 24 h and then weighed (W_0) after cooling in a desiccator. The RCF sample was placed into a nonwoven fabrics bag filter and then immersed in the water at room temperature for 30 min. Next, the bag filter was hung until no water dropped, and then the RCFs were taken out and weighted (W). The water absorption was tested according to the eq. (1).²⁷

$$WA = \frac{W - W_0}{W_0} \quad (1)$$

where WA is the water absorption; W is the total weight of the sample and the absorbed water; W_0 is the initial weight of the dried sample.

Pore Characteristics. The nitrogen adsorption static capacity method was performed using a 3H-2000PS2 instrument to

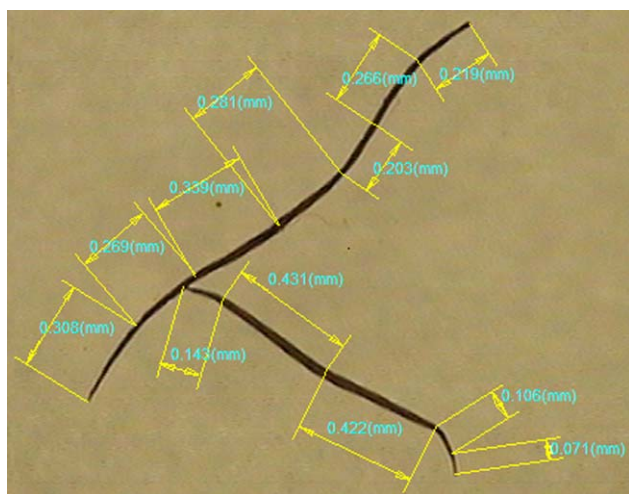


Figure 1. The measuring method of the fiber dimension. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

determine the specific surface area, pore diameter, and pore volume of the RCFs at 77.3 K. Each sample was degassed for 3 h to remove the adsorbed moisture from its surface and pores. The temperature was 105 °C, and the saturated vapor pressure was 1.05 bar. Then, the sample was weighted and moved to the measurement device.

Length and Fineness. Length and fineness of RCFs were measured by image analysis method, according to the Chinese National Standards (GB/T 28218-2011).

About 0.1 g of dry fibers was diluted with deionized water to become a pulp consistency of 0.01%, and three to five drops of suspensions were taken using a dropper to a glass slide. Removed the glass slide and did not take out it from the thermostatic oven at 60 °C until surface drying. Added two drops of I₂-ZnCl₂ (Herzberg) dyes to the glass slide and then covered it with a coverslip after 1 min. Each sample was placed on the VMS3020 image measuring instrument and the enlarged fiber image could be shown on the computer screen. The RCF was subdivided into segments and measured, respectively, as shown in Figure 1. There were differentiated from the fibers by their dimensions, considering fiber length values between 0.6 mm and 4 mm, width between 12 μm and 65 μm, three hundred fibers were employed in this study to obtain the average length and fineness of RCFs. Ran the program three times and took the average as the final fiber length and fineness and calculated errors.

Surface Morphology. A HITACHIS-2360N scanning electron microscope (SEM) was used to observe the surface morphology of fluffy RCFs produced from waste paper. All the samples were coated with a thin layer of gold. The accelerating voltage of the SEM was 15 kV, and the magnification was set to 500, 800, and 1000.

Crystal Characteristics. The crystal characteristics of the RCFs was analyzed using a D/MAX 2550VB3/PC* X-ray powder diffractometer. The patterns produced using Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 100 mA were recorded in the

range of 2θ from 8° to 40°, in 0.02° steps, counting by 4 s per step. In this study, C_r of RCFs was calculated using the following equation:²⁸

$$C_r = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

where C_r is the relative crystallinity; I₀₀₂ is the maximum intensity of the diffraction plane of (002) which locates at between 22 and 23 degrees; I_{am} is the intensity of diffraction of the amorphous part, which is taken at a 2θ angle between 18 and 19° where the intensity is at a minimum.²⁹

Fourier Transform-Infrared (FT-IR) Spectroscopy. RCFs were placed in the vacuum oven at 60 °C for 24 h, and their surface functional groups were analyzed using a EQUINOXSS/HYPER spectrophotometer with a resolution of 2 cm⁻¹. FT-IR spectral analysis was performed within the wave number range of 500 to 4000 cm⁻¹.

RESULTS AND DISCUSSION

Water Absorption

Cellulose fibers have an excellent hydrophilic and a cavity structure,³⁰ which enable cement hydration products to adhere to their surfaces, thereby reinforcing the bonds between the cements and fibers.³¹ The cement hydration process also can be accelerated.³² The microstructures of cement-based materials can be densified, and the durability of cement-based materials can be improved. However, obtaining these benefits rely on the water absorption of the cellulose fibers. Therefore, the water absorption of RCFs from waste paper was determined, as shown in Figure 2.

It was clear that the water absorption of RCFs was related to the ultrasonic treating time. In the early stage of ultrasonic treating, the mechanical force from ultrasonic vibration led to fibrillation on the surface of RCFs. These fibrils increased the specific surface area of RCFs and formed a large number of capillary pathways, which allowed more water to permeate or outflow. Therefore, the water absorption of RCFs was improved when they were treated via ultrasonic vibration for a suitable time. When the ultrasonic treatment was 10 min, the water absorptions of both newsprint fibers (NFs) and kraft fibers (KFs) increased significantly and reached the highest values of 12.5 g/g and 11.2 g/g, respectively. However, after continued processing, the surface of RCFs was seriously damaged and lost support strength to resist the impact. That was, with the ultrasonic treatment, the fiber structure degraded and thus decreased the water absorption caused by capillary effects. Therefore, the water absorption of RCFs was improved only when the ultrasonic treatment time was appropriate. In addition, at various stages of the ultrasonic treatment process, the water absorption of RCFs from the NFs was slightly higher than that of the KFs [Figure 2(a)].

The water absorption initially increased slowly, and then decreased sharply with the increase of alkali content [Figure 2(b)]. The water absorptions of 2-NF-10 and 2-KF-10 samples increased to 13.5 g/g and 12.7 g/g, respectively, which were twice of those without ultrasonic treatment. The function of alkali solution could remove hemicellulose in the fiber and much more easily penetrate into the layer gap of cellulose, which broke the hydrogen bonds between intramolecular and

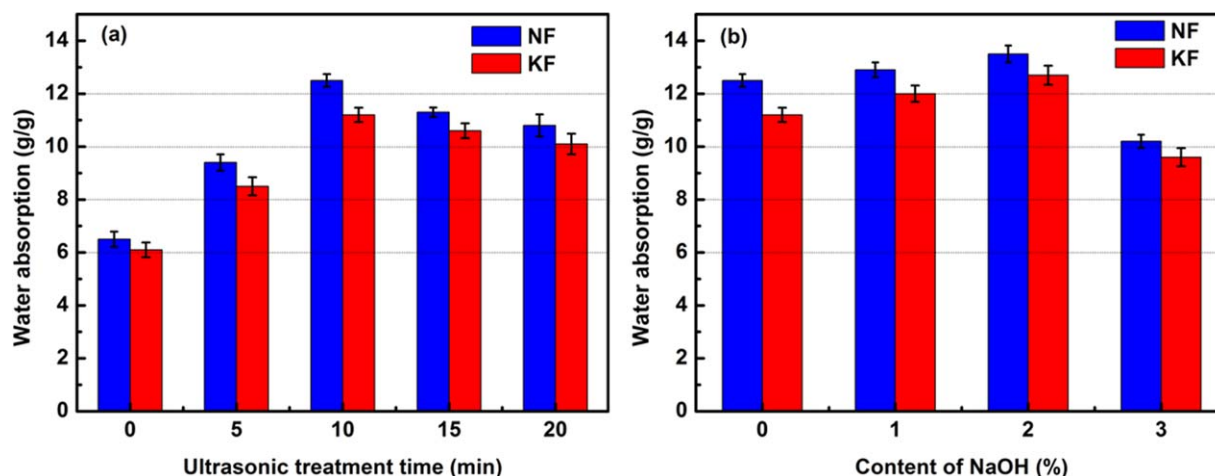


Figure 2. The changes of water absorption of recycled cellulose fibers with ultrasonic treatment time (a) and content of NaOH (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intermolecular chains and affected the rearrangement of cellulose chains.^{33,34} In addition, alkali solution made the surfaces of the fibers become looser and form more fibrillation, which improved the special surface area and water absorption. However, a higher concentration of alkali solution would destroy the surface morphology of RCFs. It was obvious that the water absorption of RCFs, to a certain degree, could be improved with these treatment methods.

Briefly, the water absorption of RCFs exceeded eight times their self-weight, meeting the water absorption of industry standard of six to eight times of the self-weight for the anti-cracking fibers used in cement-based materials.

Specific Surface Area and Pore Characteristics

Cellulose fibers with an amorphous cavity structure and small diameter had a larger specific surface area than those of the other compound fibers, such as polypropylene fibers. The amorphous cavity structure and small diameter also improved the water absorption of the cellulose fibers and increased the contact area between the fibers and the cement-based materials. The specific surface area and pore volume of the RCFs are shown in Figure 3.

From Figure 3, regardless of which waste paper the RCFs came from, the specific surface area and pore volume were significantly improved when they were pretreated. Ultrasonic vibration played a crucial role in improving the surface structure. In the condition without NaOH, the specific surface area of the RCFs from NF or KF reached the maximum in the 20th min, and the maximum pore volume of the RCFs appeared after 10 min of ultrasonic treatment. The impact of ultrasonic radiation on the newsprint fibers was higher than that on the kraft fibers [Figure 3(a)]. If waste paper was soaked in NaOH for 2 h and then treated with ultrasonic for 10 min, then the specific surface area and the pore volume of samples still displayed an increasing trend. However, it was noticeable that long time ultrasonic treatment [Figure 3(a)] or excessive NaOH [Figure 3(b)] would destroy the fiber morphology, collapse the inner pores, and affect the water absorption of the cellulose fibers.

The pore diameter and the volume of the RCFs from NF and KF were estimated using the Barrett-Joyner-Halenda (BJH) method,³⁵ these results are shown in Figure 4.

The results described the same changing trends of the pore diameter and the volume. The pore diameter distributions of all

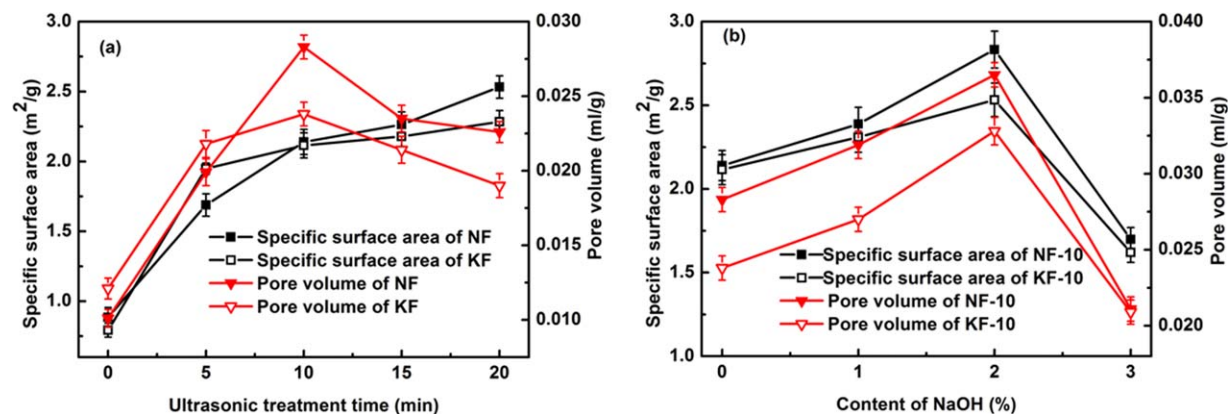


Figure 3. The changes of specific surface area and pore volume of recycled cellulose fibers with ultrasonic treatment time (a) and content of NaOH (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

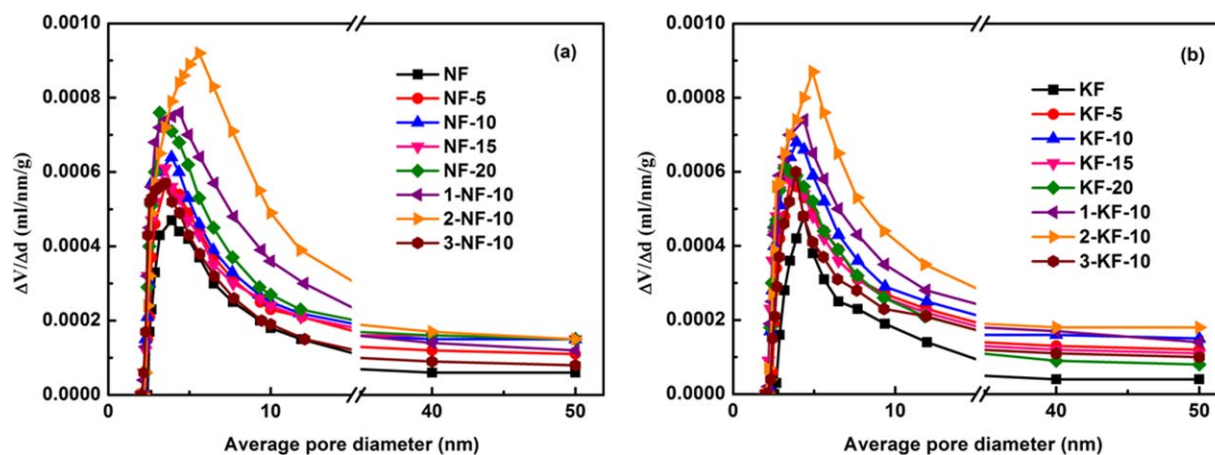


Figure 4. Distribution curves of pore diameter of recycled cellulose fibers from newsprint fibers (a) and kraft fibers (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

specimens were found to be concentrated in the range from 2 to 10 nm, and the sizes of the major pores were approximately 4 nm. These results are consistent with those reported by others.^{6,36} Both Figure 4(a,b) show that without being soaked in NaOH solution, the major pore diameter of the specimen treated with an ultrasonic vibration for 10 min is the largest. However, the pore diameters of specimens vary with the amount of NaOH solution, even if they undergo ultrasonic treatment at the same time. RCFs with larger pore diameters and higher pore volumes can be obtained when a 10 min ultrasonic treatment is performed after soaking for 2 h in a 2% NaOH solution. However, the inner pores of the cellulose fibers are destroyed by the mechanical force of the ultrasonic vibration, and small irregular pores appear after ultrasonic treatment is applied for an excessively long period of time. In addition, capillaries can also be cut off by these broken fibrils. Therefore, the pore diameter and volume of RCFs are decreased even when the RCFs have a higher specific surface area.

Length and Fineness

The size of RCFs is an important factor that influences the specific surface area, which is studied in this research to further explore the variables of the specific surface area.

The length and fineness of RCFs are shown in Figure 5. The length and fineness of all specimens were found to decrease when they were treated with both ultrasonic and NaOH solution. However, compared with the change of the fiber length, a more remarkable decline of the fiber fineness was observed. The values of the length and fineness of RCFs from NF were less than those from KF. From Figure 5(a), when waste paper fiber had been treated with ultrasonic for 20 min, its length and fineness decreased by 4% and 25%, respectively, while the length-diameter ratio of RCFs was 1.28 times than that of the untreated fibers, which greatly increased the special surface area of the RCFs.

We know that cellulosic fiber is composed of three layers including the primary wall, the middle lamellar, and the secondary wall. Some sticky substances existed in the middle lamellar and make the fibers glue together to form fiber bundle, which caused the fiber to be longer and thicker. However, the mechanical force produced by ultrasonic vibration impacted the surface of fiber and made it damage and loosen, the surface layers were stripped. These fiber bundles dispersed into single fibers, and each single fiber began to cellulose microfibrils with the extension of the treatment time, and thus causing a dramatic fall in the fineness of fiber.

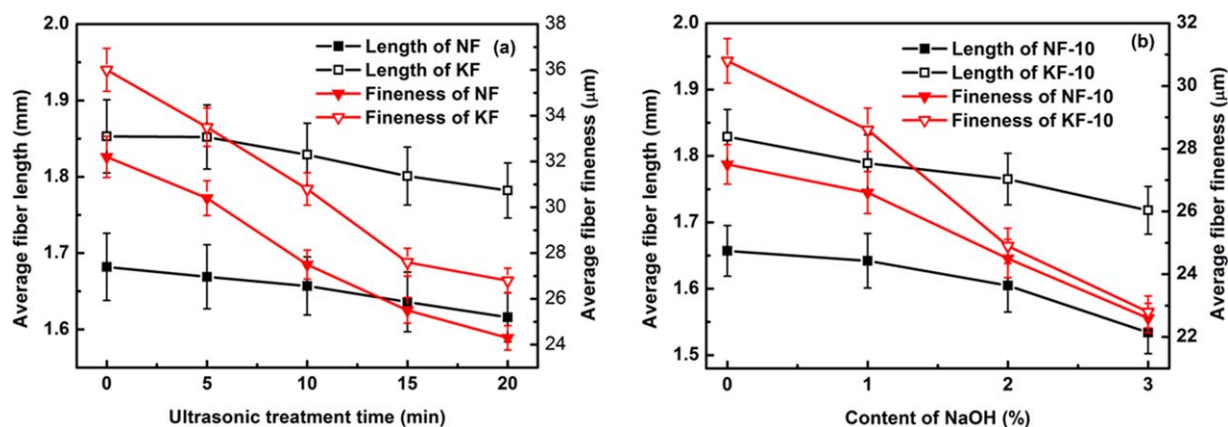


Figure 5. The changes of length and fineness of recycled cellulose fibers with ultrasonic treatment time (a) and content of NaOH (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

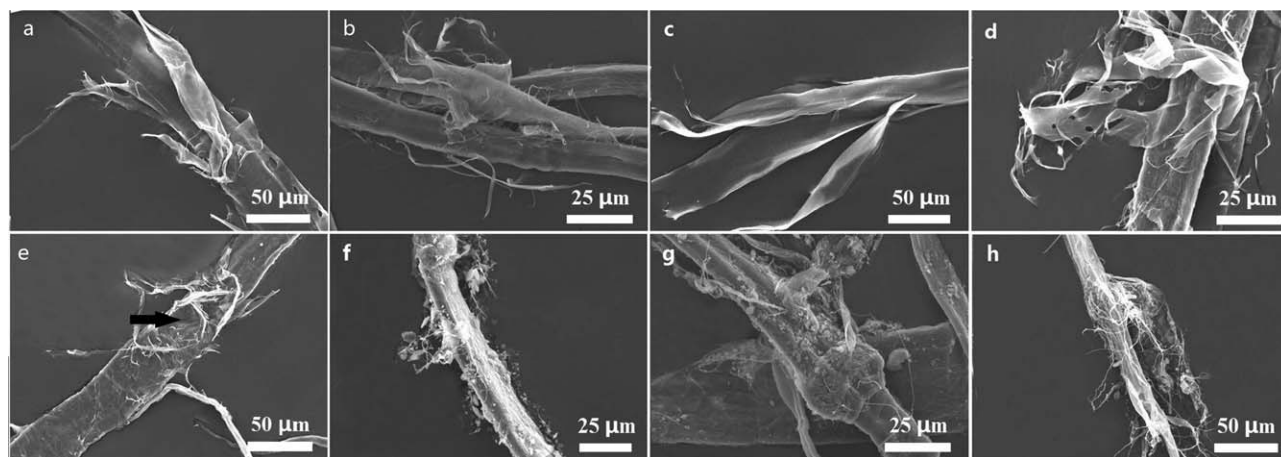


Figure 6. SEM micrograph with different magnifications of recycled cellulose fibers from waste newsprint fibers. (a) NF, (b) NF-5, (c) NF-10, (d) NF-15, (e) NF-20, (f) 1-NF-10, (g) 2-NF-10, (h) 3-NF-10.

It was obvious that NaOH was a beneficial factor to maintaining a suitable fiber length and fineness. The microfibrils of cellulose are oriented along the axial direction with a spiral angle and the hemicelluloses and lignin play as “matrix.” The alkali solution could dissolve hemicellulose and thus causing the separation of cellulose microfibrils. Once pretreated via ultrasonic, cellulose microfibrils could be formed as a single microfibril at a shorter ultrasonic time, and thus causing further decrease of fineness. From Figure 5(b), with only 10 min of ultrasonic treatment, the length and fineness of 2-NF-10 or 2-KF-10 decreased by 5% and 25%, respectively, which means that if NaOH was used, the same effect would be achieved even if the ultrasonic treating time was shortened. However, after being soaked in a 3% NaOH solution, the RCF length and fineness were shorter, and its pore volume and water absorption decreased. Thus, an appropriate range of content of NaOH would guarantee the superior performance of the RCFs.

Surface Morphology

Waste newsprint fibers and kraft fibers were both produced from wood fibers; because they had similar morphological characteristics, the waste newsprint fibers were used as an example in this part.

Figure 6 show the SEM images of RCFs from newsprint. The surface of the fiber bundle was smooth, with multiple layers observed [Figure 6(a)]. Such fibers are produced by mechanical pulping or chemical-mechanical pulping. However, when the thick fiber bundles were split, a thin layer of the fibers was formed. Additionally, the thick fiber bundles began to disperse into individual fibers for prolonged ultrasonic treatment [Figure 6(b)]. Little individual fiber bundles were found and split longitudinally and took the shape of the microfibrils when unceasingly treated with ultrasonic excitation for 10 min [Figure 6(c)]. Fibrillation was clearly observed in the fiber surfaces, and the microfibrils were stripped from the fibers after 15 min of ultrasonic treatment [Figure 6(d)]. With ultrasonic waves constantly impacting the fibers, the local region

was damaged and even broken into several parts, as shown in Figure 6(e).

Figure 6(f–h) shows that compound powders diffusely distributed onto the amorphous fiber surfaces and the dispersion of RCFs was accordingly improved. Morphology alternation proved the validity of using ultrasonic and a NaOH solution for the treatment of fibers. Either a long ultrasonic treatment time or a high concentration of NaOH solution would damage the surfaces of fibers, even causing fibers crack into several parts. An appropriate selection of ultrasonic treating time and NaOH solution concentration was crucial to maintain the fiber length and fineness.

Crystal Characteristics

The crystallinity of cellulose reflects the physical and chemical properties of fiber. In general, the relative density and size stability increase with an increase in crystallinity of cellulose, however, the softness and chemical reaction decrease.⁶ Therefore,

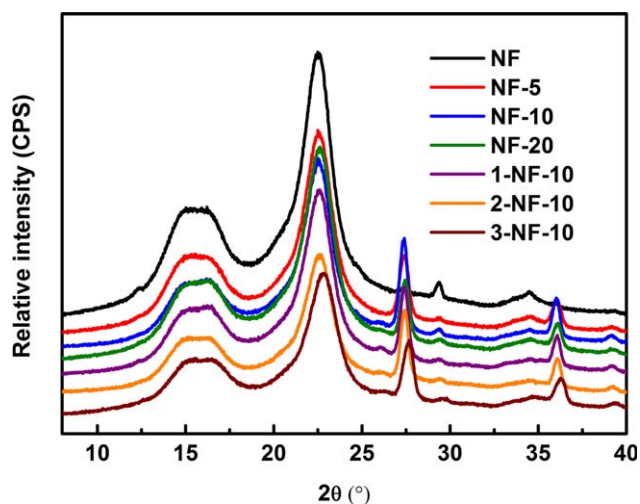


Figure 7. The X-ray diffraction curves of recycled cellulose fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

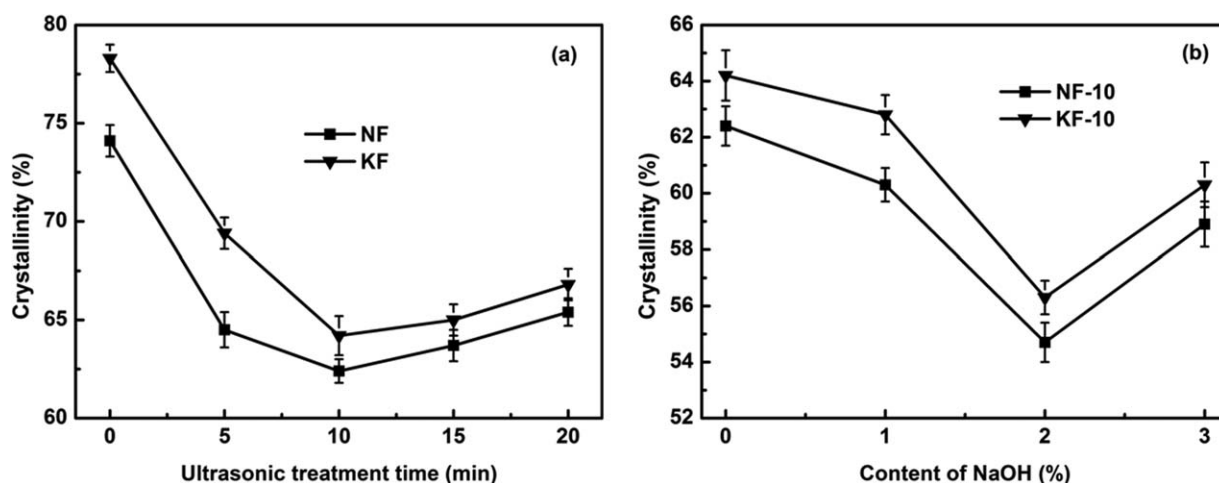


Figure 8. The changes of crystallinity of recycled cellulose fibers with ultrasonic treatment time (a) and content of NaOH (b).

the crystallinity of cellulose is an important parameter to understand fiber decay from structure.

RCFs from newsprint and kraft paper have remarkably similar structures, with RCFs from newsprint, for example, the X-ray diffraction curve is shown in Figure 7. The relative intensity for the diffraction peak of (002) was significantly reduced after the pretreatment. Without alkali solution, the relative intensity of fiber reached the lowest at the ultrasonic time for 10 min. However, if soaked in the alkali solution before the ultrasonic pretreatment, the relative intensity of fiber would continue to reduce even on the same ultrasonic time. In addition, the relative intensity of fiber reached the lowest under the content of 2% alkali solution and the ultrasonic time for 10 min.

According to the empirical formulae by Segal *et al.*,²⁸ the crystallinity of RCFs was estimated and shown in Figure 8. Figure 8(a) shows that the crystallinity of RCFs quickly decreased during the early period of ultrasonic treatment and then slowly decreased with time. The crystallinity values of NF and KF were reduced to 62.4% and 64.2%, respectively, after 10 min of ultrasonic treatment, which increased with further ultrasonic treat-

ment. The RCF characteristics were analyzed with soaking in a NaOH solution [Figure 8(b)]. With the same ultrasonic treatment time, the crystallinity of RCFs soaked in a 2% NaOH solution decreased by 7% compared with those that had not been soaked. Note that the crystallinity increased for RCFs treated with the content of 3% alkali solution.

The ultrasonic cavitation has two effects on cellulose, one is the mechanical effect from the bursting of acoustic cavitation bubbles, and the other is the damage of solid interfaces, both of which lead to the changes of cellulose in the morphological structure, the supermolecular structure and the accessibility aspects.^{37,38} The powerful impact induces an alternate vibration of particles in a uniform medium. This process involves a transfer of heat and an increase of the temperature of the circulation medium.³⁹ It could be suggested that the mechanical power removed the S1 layer with a high crystalline and broke the weak intramolecular or intermolecular hydrogen bonds, both decreasing the crystallinity of fiber. In addition, the mechanical impact damaged the surfaces of fiber and made the inside and outside surface expose, increased the ratio of the length and diameter of

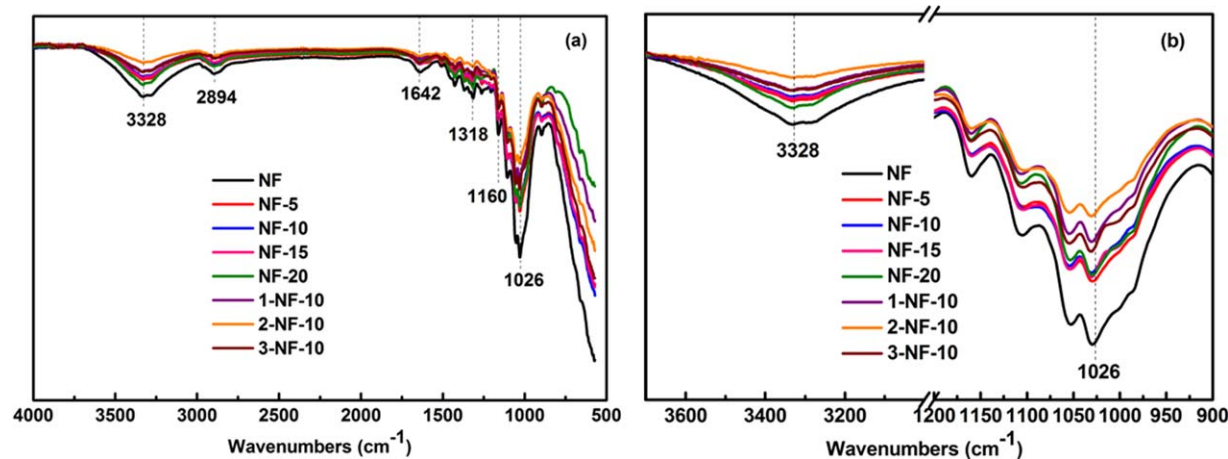


Figure 9. Infrared band assignments for recycled cellulose fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Infrared Band Assignments for Recycled Cellulose Fibers

Wavenumber (cm ⁻¹)	Assignment ^{16,42}
3328	O—H stretching
2894	C—H and CH ₂ stretching
1642	C=O stretching of hemicellulose and H—O—H bending of absorbed water
1318	CH ₂ rocking of cellulose
1160	C—O—C antisymmetric bridge stretching
1026	C—O stretching in cellulose and hemicellulose

fiber. More water was permitted to penetrate into the inside fiber and the amorphous region, and thus improving the water absorption of fiber. However, the thermo and mechanical effect coexisted in the medium as the ultrasonic treatment time increased. The increase of the temperature of the medium accelerated the diffusion of the solvents and made the defective cellulose molecular chain rearrange until the system reached equilibrium, and thus causing the increase of crystallinity at the later period of the ultrasonic pretreatment. At this point, the surface of fiber was severely damaged and broke by the mechanical force, more cellulose microfibril stripped from the fiber and blocked the pores, and thus leading to the decrease of pore volume and water absorption.

The alkali solution plays a supporting role in the pretreatment of RCFs. Alkali solution made the fiber swelling and penetrated into the amorphous regions and part of crystalline regions of cellulose, which removed the hemicellulose and lignin from the crystalline region of cellulose, thus enlarging the pore and weakening the binding force between the cellulose microfibril.⁴⁰ Some hydrogen bonds in the crystalline region were broken and the amorphous regions were increased, leading to the decrease of crystallinity of cellulosic fiber. In addition, the alkali treatment decreased the rotation angles of cellulose microfibrils and made the orderly hydroxyl transform free hydroxyl, which increased the accessibility of cellulose and permeability of water. Also, alkali solution enabled the internal and external surfaces of fibers to be exposed more easily,⁴¹ all of which causing the improvement of water absorption. However, the alkali treatment was an exothermic process, the temperature of system increased along with alkali concentration, which led to the rearrangement of cellulose chains and increase of crystalline.

FT-IR Analysis

To further study the ultrasonic radiation effect on fiber molecular structure, the functional groups of RCFs were investigated using FT-IR spectra. The FT-IR spectra of RCFs from newsprint are shown in Figure 9. The peaks of the RCFs were easily observed, while no new absorption peaks appeared.

Table I presents the FT-IR absorption peaks of RCFs. Chinese newsprint pulp often contains a small quantity of wheat straw pulp besides wood pulp. The wheat straw pulp commonly contains large hemicellulose. Therefore, the peaks of C=O stretching vibration and absorption peak of H₂O at 1642 cm⁻¹ could all be observed, and the intensity of these peaks gradually decreased

with the increase of the ultrasonic treatment time [Figure 9(a)]. The absorption bands at 3328 cm⁻¹ and 1026 cm⁻¹ were obviously reduced [Figure 9(b)]. It was proved that the molecular chain of cellulose was partially destroyed and the breakage of H-bonds occurred. This result was also found from the crystallinity analysis.

CONCLUSIONS

This study discussed the production of RCFs from waste paper and demonstrated their performances. The important conclusions are summarized below.

The water absorption of RCFs was found to be closely correlated with the ultrasonic time. Ultrasonic vibration led to fibrillation on the surface of fibers with prolonged ultrasonic treatment. When the ultrasonic treatment time had lasted for 10 min, the water absorptions of both NF and KF reached the highest values of 12.5 g/g and 11.2 g/g, respectively.

Ultrasonic radiation was found to play a crucial role on the surface structure of RCFs. The specific surface area increased with the increase of ultrasonic time, and the maximum pore diameter and pore volume appeared after ultrasonic treatment of 10 min.

The length and fineness of RCFs decreased with the change of ultrasonic treatment time. In this situation, the fineness had a rather pronounced decrease in particular. When waste paper was treated with ultrasonic for 20 min, the average length and fineness decreased by 4% and 25%, respectively, the length-diameter ratio of RCFs was 1.28 times than that of the untreated fibers, which greatly increased the special surface area of the RCFs.

Alkali solution was found to be a beneficial factor to the physical properties of RCFs. Alkali solution could be penetrated into the amorphous regions and part of crystalline regions of cellulose, and removed the hemicellulose and lignin, thus enlarging the pore and weakening the hydrogen bonds. To achieve the same RCF properties, the use of NaOH was able to shorten the required ultrasonic treatment time. With the same ultrasonic treatment time, using NaOH increased the length-diameter ratio of the RCFs while improving the pore structure and enhancing the water absorption; the water absorption exceeded eight times their own weight, meeting the water absorption standard of six to eight times of self-weight for the anti-cracking fibers used in cement-based materials.

APPENDIX

1. Paper and board-determination of water absorption, Chinese National Standard, GB/T 461.3-2005.
2. Method of testing water absorbency of super absorbent fiber, Chinese Enterprise Standard, Q/320683KDW01-2007.
3. Pulp-Determination of fiber length by automated optical analysis, Chinese National Standard, GB/T 28218-2011.

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REFERENCES

1. Watson, B. J.; Hammouda, B.; Briber, R. M.; Hutcheson, S. W. *J. Appl. Polym. Sci.* **2012**, *127*, 2620.
2. Gao, J.; Tang, L. G. *Cellulose Science*; Science Press: Beijing, **1999**; p 42.
3. Cai, J.; Zhang, L. N.; Liu, S. L.; Xi, X. J.; Chen, X. M. *Macromolecules* **2008**, *41*, 9345.
4. Maloney, T. C.; Paulapuro, H. *J. Pulp Paper Sci.* **1999**, *12*, 430.
5. Topgaard, D.; Soderman, O. *Cellulose* **2002**, *9*, 139.
6. Chen, Y. M.; Wan, J. Q.; Zhang, X. L.; Ma, Y. W.; Wang, Y. *Carbohydr. Polym.* **2012**, *87*, 730.
7. Wu, J. H.; Kuo, M. C.; Chen, C. W.; Kuan, P. H.; Wang, Y. J.; Jhang, S. Y. *J. Appl. Polym. Sci.* **2013**, *129*, 3007.
8. Rodríguez, A.; Sánchez, R.; Ana, R. A.; Ferrer, A. J. *Clean Prod.* **2010**, *18*, 1084.
9. Han, S. O.; Son, W. K.; Youk, J. H.; Park, W. H. *J. Appl. Polym. Sci.* **2008**, *107*, 1954.
10. Tonoli, G. H. D.; Belgacem, M. N.; Siqueira, G.; Bras, J.; Savastano, H. *Cem. Concr. Compos.* **2013**, *37*, 68.
11. Flores, M. N.; Barluenga, G.; Hernández-Olivares, F. *Compos. B* **2014**, *61*, 214.
12. Barluenga, G. *Cem. Concr. Res.* **2010**, *40*, 802.
13. Fisher, A. K.; Bullen, F.; Beal, D. *Cem. Concr. Res.* **2001**, *31*, 543.
14. Coutts, R. S. P. *Cem. Concr. Compos.* **2005**, *27*, 518.
15. Wang, L.; Sharifzadeh, M.; Templar, R.; Murphy, R. *J. Energy Environ. Sci.* **2012**, *5*, 5717.
16. Nedjma, S.; Djidjelli, H.; Boukerrou, A.; Benachour, D.; Chibani, N. *J. Appl. Polym. Sci.* **2013**, *127*, 4795.
17. Singh, A.; Yadav, R. D.; Kaur, A.; Mahajan, R. *Bioresour. Technol.* **2012**, *120*, 322.
18. Baba, Y.; Tada, C.; Fukuda, Y.; Nakai, Y. *Bioresour. Technol.* **2013**, *128*, 94.
19. Lin, Y.; Wang, D.; Wu, S.; Wang, C. *J. Hazard. Mater.* **2009**, *170*, 366.
20. Zhu, Z. F.; Qi, D. P.; Wang, J. H.; Han, Q. *J. Textile Res.* **2012**, *1*, 25.
21. Wei, J. R.; Tang, A. M.; Sun, Z. H. *J. Mater. Eng.* **2009**, *4*, 61.
22. Tang, A. M.; Liang, W. Z. *Tech. Acoust.* **2000**, *3*, 121.
23. Wang, L.; Jiang, Z. X.; Yan, J. *J. Textile Res.* **2006**, *10*, 77.
24. Renouard, S.; Hano, C.; Doussot, J.; Blondeau, J. P. *Mater. Lett.* **2014**, *129*, 137.
25. Iskalieva, A.; Yimmou, B. M.; Gogate, P. R.; Horvath, M.; Horvath, P. G. *Ultrasonic Sonochem.* **2012**, *19*, 984.
26. Liu, T. Z.; Duan, X. L.; Duan, W. J. *China Pulp Paper.* **2010**, *1*, 43.
27. Carrillo, F.; Martin, G.; Lopez-Mesas, M. *J. Compos. Mater.* **2011**, *8*, 1733.
28. Segal, L.; Creely, J.; Martin, A.; Conrad, C. *Textile Res. J.* **1959**, *29*, 786.
29. Nitta, Y.; Goda, K.; Noda, J.; Lee, W. *Compos. A* **2013**, *49*, 132.
30. Berthold, J.; Salmen, L. *Holdorsehun.* **1997**, *4*, 361.
31. Kawashima, S.; Shah, S. *Cem. Concr. Compos.* **2011**, *33*, 201.
32. He, J. L.; Jie, H. W.; Li, K. Y.; Chu, D. D. *J. Qinghai Univ. (Nat. Sci. Ed.)* **2014**, *4*, 29.
33. Awrwick, J. O.; Wright, A. C. *J. Appl. Polym. Sci.* **1967**, *11*, 659.
34. Okano, T.; Sarko, A. *J. Appl. Polym. Sci.* **1985**, *30*, 325.
35. Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.
36. Guo, W. J.; Wang, Y.; Wan, J. Q.; Ma, Y. W. *Carbohydr. Polym.* **2011**, *83*, 1.
37. Tang, A. M.; Liang, W. Z. *Tech. Acoust.* **2000**, *2*, 78.
38. Xiong, J.; Ye, J.; Liang, W. Z. *Tech. Acoust.* **1999**, *1*, 66.
39. Feng, R.; Li, H. M. *Anhui Sci Technol. Press* **1992**, *24*, 294.
40. Jackson, M. G. *Anim. Feed Sci. Technol.* **1997**, *2*, 105.
41. Li, L. J.; Hu, Y. T.; Liu, D. Z.; Chen, Z. X. *Chin Synth. Resin Plast.* **2005**, *6*, 53.
42. Singh, B.; Gupta, M.; Anchal, V. *Polym. Int.* **2000**, *49*, 1444.