The role of hornification in the deterioration mechanism of physical properties of unrefined eucalyptus fibers during paper recycling

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ABSTRACT: Physical properties of cellulosic paper deteriorate significantly during paper recycling, which hinders the sustainable development of the paper industry. This work investigates the property deterioration mechanism and the role of hornification in the recycling process of unrefined eucalyptus fibers.

The results showed that during the recycling process, the hornification gradually deepened, the fiber width gradually decreased, and the physical properties of the paper also gradually decreased. After five cycles of reuse, the relative bonding area decreased by 17.6%, while the relative bonding force decreased by 1.8%. Further results indicated that the physical property deterioration of the paper was closely related to the decrease of fiber bonding area. The fiber bonding area decreased linearly with the reduction of re-swollen fiber width during paper recycling. Re-swollen fiber width was closely related to the hornification. Hornification mainly reduces the bonding area of unrefined eucalyptus fiber rather than the bonding force. The work elucidates the role of hornification in the recycling process of unrefined eucalyptus fibers and the deterioration mechanism of paper physical properties, which will be helpful to control the property deterioration of paper and achieve a longer life cycle.

Application: In this work, the authors demonstrated that the deterioration of the paper physical properties of unrefined eucalyptus fibers was due to the decrease in fiber bonding area caused by hornification. In addition, the authors also found that the re-swollen fiber width can be used as a predictive indicator of physical properties.

Paper made of cellulose fiber is an essential daily necessity for human beings. The global annual consumption of paper and paperboard is up to 400 million tons [1]. Such a large amount of consumption requires massive forest resources as raw materials. However, the growth cycle of trees is too long to meet the growth of paper consumption. The data show that a total of 386 million hectares of forest were lost worldwide in all forest types combined from 2001 to 2019, and this loss represents an almost 10% decrease in tree cover since 2000 [1]. Therefore, waste paper is recycled for papermaking, and the recycling rate of global waste paper was up to 57.8% in 2020. Recycling waste paper has several advantages, including meeting production requirements; reducing costs; saving resources and energy; protecting forest resources; and reducing carbon emissions [2-4]. For example, recycling 1 ton of paper saves around 1400 L of oil, 26500 L of water, and 17 trees [5]. However, waste paper cannot be recycled indefinitely due to the property deterioration caused by fiber hornification [6]. Therefore, it is important to study hornification and property deterioration in paper recycling, which is conducive to the sustainable development of human beings.

Hornification is a technical term used in the literature on cellulosic materials, which refers to the stiffening of the polymer structure of cellulosic materials upon drying or water removal [7-9]. At present, it is believed that hornification is the main reason for the deterioration of the physical properties of cellulose paper. The hornification phenomenon includes the reduction in swelling capacity, conformability, wet flexibility, and bonding potential of cellulosic fibers, especially cellulosic fibers with high cellulose content [9,10]. Among these characteristics, the change in the fiber's swelling capacity is particularly obvious [11]. Even after being resuspended in water, the hornified fiber does not return to its initial water-swollen state [12,13]. Therefore, Jayme describes hornification as a decrease in water retention value (WRV) that is expressed as a percentage of the initial value [14]. For decades, irreversible hydrogen bonding and cocrystallization have also been widely accepted as hornification mechanisms [15-17]. In our recent work [18], it has been further clarified that the hornification mechanism includes cocrystallization and crystallization that occur in different drying stages.

Cellulose is the dominating component for the strength properties of wood and pulp fibers [19]. Cellulose supramolecular structure affects the strength properties of cellulosic paper [20]. For example, the increase of cellulose microfibril

aggregation resulted in the reduction of physical properties [20]. Therefore, fiber hornification (i.e., cellulose recrystallization) also leads to the degradation of physical properties during paper recycling [7,18]. However, the effects of hornification on the paper's physical properties also depend on the specific pulp source, chemical composition, and paper properties [10,21-24]. Repeated water absorption and drying of chemical softwood pulp decreases tensile strength, bursting strength, tearing strength, break length, and density, but increases the light scattering coefficient and bulkiness [22]. The degree of fine fibrillation on the surface and inside of dried fibers is reduced compared to never-dried fibers for both mechanical and chemical pulp [21]. Therefore, the cellulosic fiber in each reuse requires refining [25]. However, the fiber cell wall is severely damaged after repeated refining and can no longer be used for papermaking [6,25]. This is not the case with high-yield softwood pulp, where the effects of pulping and refining make repeatedly used fibers shorter and more broken, but the original inter-fiber bonding force does not decrease and even sometimes increases [22,26]. After five times of repeated use, the paper density and breaking length increased by 10%, the bursting strength and tearing strength remained unchanged, and the scattering coefficient decreased slightly [22]. Chemical composition affects the hornification of fibers, thereby affecting paper performance. During paper recycling, kraft softwood or hardwood pulp exhibits a higher tendency to hornify and lose strength after removing hemicellulose [24]. Research on the deterioration mechanism of waste paper occurred decades ago, and there have been no relevant research reports recently. The changes in chemical composition, degree of polymerization of cellulose, and fiber strength are relatively small in recycling [21]. The property deterioration of recycled fibers is mainly caused by the loss of fiber bonding strength [27]. However, researchers have different views on the loss of bonding strength of recycled fibers [21]. One view is that the loss is mainly due to the fiber surface inactivation caused by certain reasons, such as the reorientation of fiber surface molecules, migration of extractives and sizing agents (fatty acids, rosin size, and resin acids), and the loss of fiber components [28,29]; that is, the decrease of the bonding force. The other view is the reduction of the fiber bonding area [27,30,31]. However, the impact of hornification on these two aspects is still not clear enough due to the interference of other factors.

Chemical eucalyptus pulp is a typical cellulose fiber with severe hornification and property deterioration in paper recycling. Therefore, paper recycling in this study is carried out using unrefined chemical eucalyptus pulp as raw material and without the addition of sizing agents and fillers. In this case, the interference of fines and additives is minimized to highlight the role of hornification. In this study, the effect of fiber hornification on the morphology and ultrastructure of recycled fibers was clarified. Then, the physical property deterioration of paper during paper recycling was explored. Next, the fiber hornification and physical properties were correlated and an appropriate indicator was found to represent the changes in physical properties. Finally, the deterioration mechanism of physical properties under ideal conditions was clarified.

MATERIALS AND METHODS

Materials

In this work, never-dried unrefined eucalyptus chemical bleached pulp containing 80.1% moisture content was selected as the raw material, which was supplied by the paper mill in Guangning, China. The pulping process for this cellulosic fiber was as follows: eucalyptus chips were first alkaline cooked, then bleached in three stages (chlorine dioxide and chlorine gas; sodium hydroxide and oxygen; chlorine dioxide), and finally beaten. The fiber freeness of the raw material was 16°SR. According to the NRELP method [32], this fiber consisted of 85.1% cellulose, 13.6% hemicellulose, 0.53% lignin, and 0.34% ash.

Recycling procedure

The paper recycling procedure mainly included swelling, paper forming, and drying. The raw material was soaked with deionized water for 12 h to obtain the swollen pulp. The pulp slurry with a consistency of 1.2% was disintegrated by an L&W 991509 disintegrator (Lorentzen & Wettre; Kista, Sweden) for 30000 revolutions, then diluted to a concentration of 0.3%, and finally made into a handsheet by a Kaiser automatic handsheet machine (RK3AKWT, Paper Testing Instruments; Laakirchen, Austria). The basis weight was 60 g/m^2. The prepared wet handsheet was dried at 90°C for 10 min on the same machine to obtain the dried paper [33]. The moisture content of the paper was about 5%. The recycling procedure was repeated for a total of five cycles. Choosing to recycle five times is because cellulose fibers can only be recycled 5–6 times before the fibers become too short and weak to make paper [6,30]. To avoid thermal shock, the paper had a rest time of 12 h before starting the next drying cycle.

Fiber characterizations

Scanning electron microscopy

Scanning electron microscopy (SEM) from Merlin (Zeiss, Germany) was used to characterize morphological changes of the cellulosic papers. The samples were sputter-coated with a layer of gold before SEM observation.

Fiber quality analysis

A MorFi Compact fiber quality analyzer (Techpap; Gières, France) was used to detect the morphology of cellulosic fiber after full swelling, including arithmetic average length, width, kink angle, and fines content. The paper was first swollen and then dispersed into the single fiber by using a matching tool. The test concentration of fiber was 30 mg/L. The experiments were conducted in triplicate.

Fourier transform infrared spectroscopy

About 3 mg of dried sample and 300 mg of dried potassium bromide (KBr) were put into an agate mortar and carefully ground and mixed. Then, they were poured into the tablet press to obtain a transparent tablet. The Fourier transform infrared (FTIR) spectrum was measured on the TENSOR 27 FTIR spectrometer (Bruker; Billerica, MA, USA) with a range of 4000–500 cm^{-1} at 4 cm^{-1} resolution and 32 scans. The spectrum was first normalized to the peak at 1160 cm^{-1} and then further normalized to the interval [0, 1].

X-ray diffraction

The samples were equilibrated in a constant temperature and humidity laboratory according to ISO 187-1990 "Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples" (23 ± 1°C, 50 ± 2% relative humidity [RH]) for 24 h. The crystallinity was analyzed by an X-ray diffraction (XRD) measurement with X'pert Powder (Malvern Panalytical; Almelo, Netherlands) with nickel (Ni)-filtered and copper (Cu) radiation (k_α=0.15418 nm). The scattering angles (2θ) ranged from 4° to 60°. The Segal method [34] was used to determine the crystallinity index (*CrI*) of different samples:

$$\mathrm{CrI} = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad (1)$$

where I_{200} is the scattered intensity at the main peak around 22.7°, and I_{am} is the intensity of the amorphous portion at 18.7° [35].

The Scherrer equation was used to calculate the size of cellulose crystal as follows:

$$L(200) = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where $L(200)$ is the crystal size (nm) in the direction normal to (200) plane; K is the Scherrer constant (0.9); λ is the incident X-ray wavelength (0.15418 nm); β is full width at half maximum of (200) plane diffraction peak obtained after peak deconvolution, in radians; and θ is the Bragg angle (°) for (200) plane [11].

Water retention value

The WRV was measured by a centrifugation method according to Chinese standard GB/T 29286-2012 (modified from ISO 23714-2017 "Determination of water retention value (WRV)"). The sample (3 g, ovendry weight) was added to 1 L of distilled water, followed by overnight stirring at 250 rpm with an IKA stirrer (IKA Co.; Staufen im Breisgau, Germany). The fully swollen sample with a concentration of 3 g/L was filtered by a vacuum pump to obtain the pulp pad. The pad was then dewatered with a centrifugal force of 3000 g for 30 min. Finally, the centrifuged sample was divided into three portions and dried in an oven at 105 ± 0.5°C to a constant weight. The WRV is calculated by:

$$WRV = \frac{W_{wet} - W_{dried}}{W_{dried}} \times 100\% \quad (3)$$

where W_{wet} and W_{dried} are the weights of the wet centrifuged substrate and the dried substrate, respectively. The hornification degree (HD) is calculated by Eq. 4:

$$HD = \frac{WRV_0 - WRV_n}{WRV_0} \times 100\% \quad (4)$$

where *HD* is the hornification degree, WRV_0 is the *WRV* of the virgin fiber, and WRV_n is the *WRV* of the dried substrate. The experiments were conducted in triplicate at least.

Paper physical properties

The moisture of handsheets was equilibrated in an ISO standard constant temperature and humidity laboratory with temperature at 23 ± 1°C and relative humidity of 50 ± 2% for 24 h before testing physical properties. The properties of the handsheets were measured with the equipment and test methods described in **Table I**.

The relative bonding area was calculated by the following equation:

$$RBA = 1 - \frac{S}{S_0} \quad (5)$$

where *RBA* is the relative bonding area; *S* is the light scattering coefficient of cellulosic paper (m^2/kg); and S_0 is the light scattering value when the fiber is completely unbound (m^2/kg). The value of S_0 is obtained by linear extrapolation of the light scattering coefficient when the tensile strength is zero.

The fiber bonding strength was calculated by the Page equation [36]:

$$\frac{1}{T} = \frac{1}{Z} + \frac{1}{B} \quad (6)$$

where *T* is the tensile strength (N/m); *Z* is the zero-span tensile strength (N/m); and *B* is the fiber bonding strength (N/m).

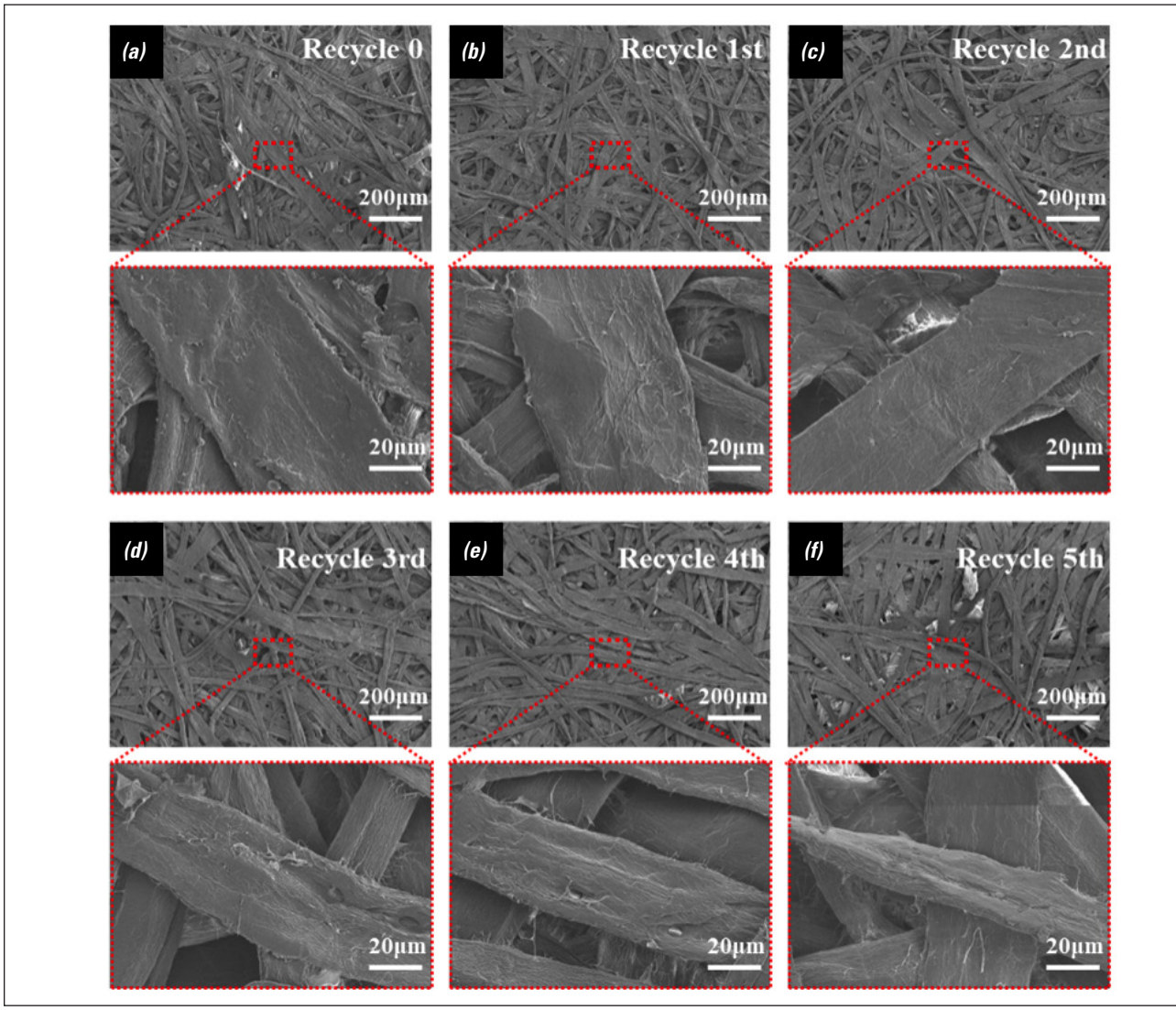
The relative bonding force was calculated according to the following equation:

$$RBF = \frac{B}{RBA} \quad (7)$$

where *RBF* is the relative bonding force (N/m); *RBA* is the relative bonding area; and *B* is the fiber bonding strength (N/m).

Physical Property	Measurement Method
Tensile index and stretch at break	L&W CE062 tensile tester (Lorentzen & Wettre; Kista, Sweden) according to ISO 1924-2008 "Paper and board — Determination of tensile properties — Part 2: Constant rate of elongation method (20 mm/min)."
Burst index	L&W CE180 burst testing apparatus according to ISO 2758-2001 "Paper — Determination of bursting strength."
Tear index	L&W 009 according ISO 1974-1990 "Paper — Determination of tearing resistance (Elmendorf method)."
Folding endurance	S13505 double collet folding endurance tester (Frank-PTI; Birkenau, Germany) according to ISO 5626-1993 "Paper — Determination of folding endurance."
Zero-span tensile index	Z-span 2400 zero-span tensile strength tester (Pulmac International; Williston, VT, USA) according to ISO 15361-2000 "Pulps — Determination of zero-span tensile strength, wet or dry."
Light scattering coefficient	ColorTouch PC CTP-ISO whiteness meter (Technidyne; New Albany, IN, USA) according to ISO 9416-2017 "Paper — Determination of light scattering and absorption coefficients (using Kubelka-Munk theory)."

I. Equipment and methods for measuring physical properties of handsheets.



1. Scanning electron microscopy (SEM) images of unrefined eucalyptus fibers during paper recycling.

RESULTS AND DISCUSSION

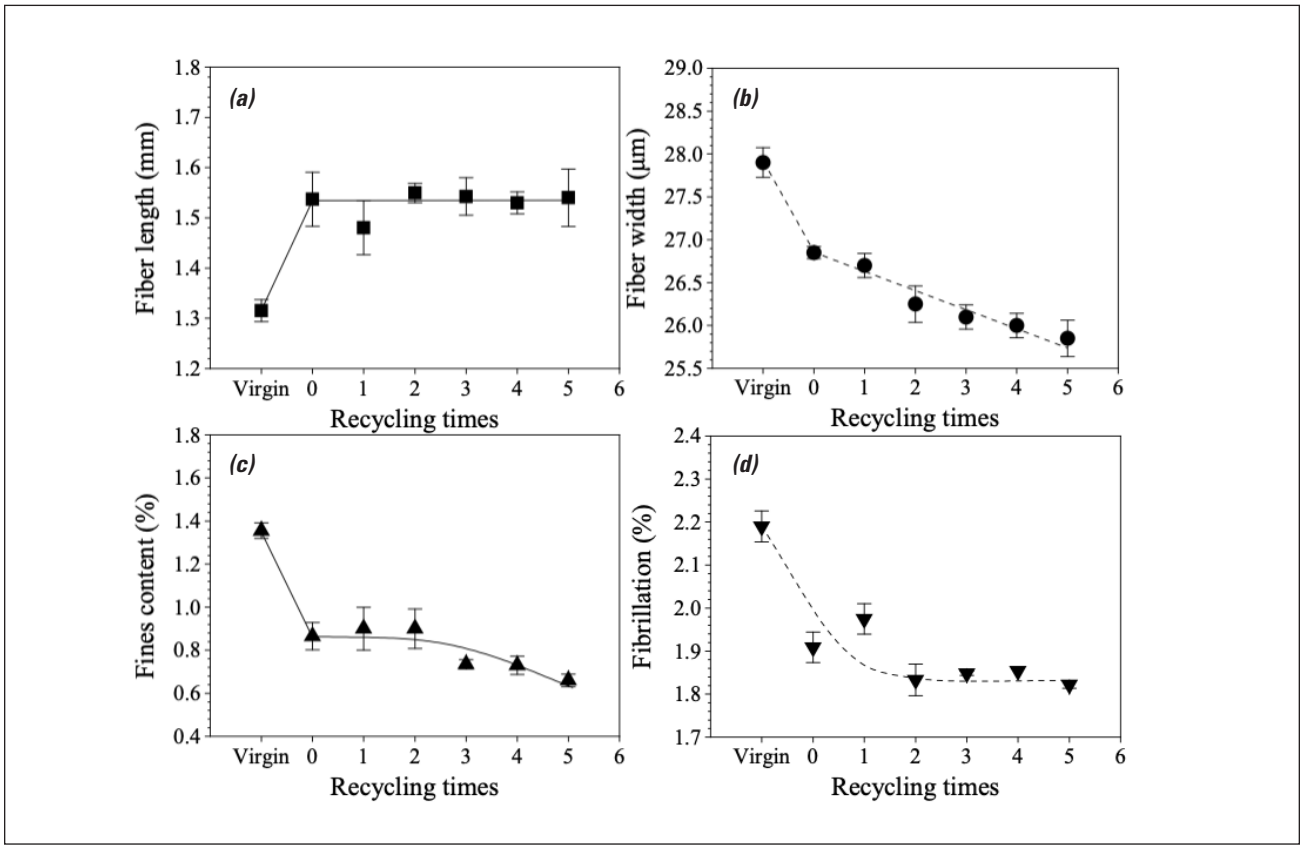
Morphology, ultrastructure, and hornification changes of fibers

Figure 1 shows SEM images of cellulosic paper during paper recycling. The flat eucalyptus fibers are clearly shown in the SEM images. The magnified images showed that the cellulose fiber shrank and thickened gradually during paper recycling. **Figure 2** shows the specific numerical changes in fiber morphology during paper recycling. The results showed that the first drying resulted in a change in fiber morphology, but the next few rounds of drying did not play a significant role in some morphological characteristics. The arithmetic mean length of the fiber increased after the first drying and remained stable during paper recycling (Fig. 2a). The increase in length may be due to the loss of fines (Fig. 2c). Although the raw material was the unrefined fiber, there is some level of fines in it. The fiber width and fines content decreased greatly after the first drying and continued to decline in the paper recycling process (Fig. 2b and Fig. 2c). The fibrillation of fibers also decreased sharply after the first drying but then stabilized.

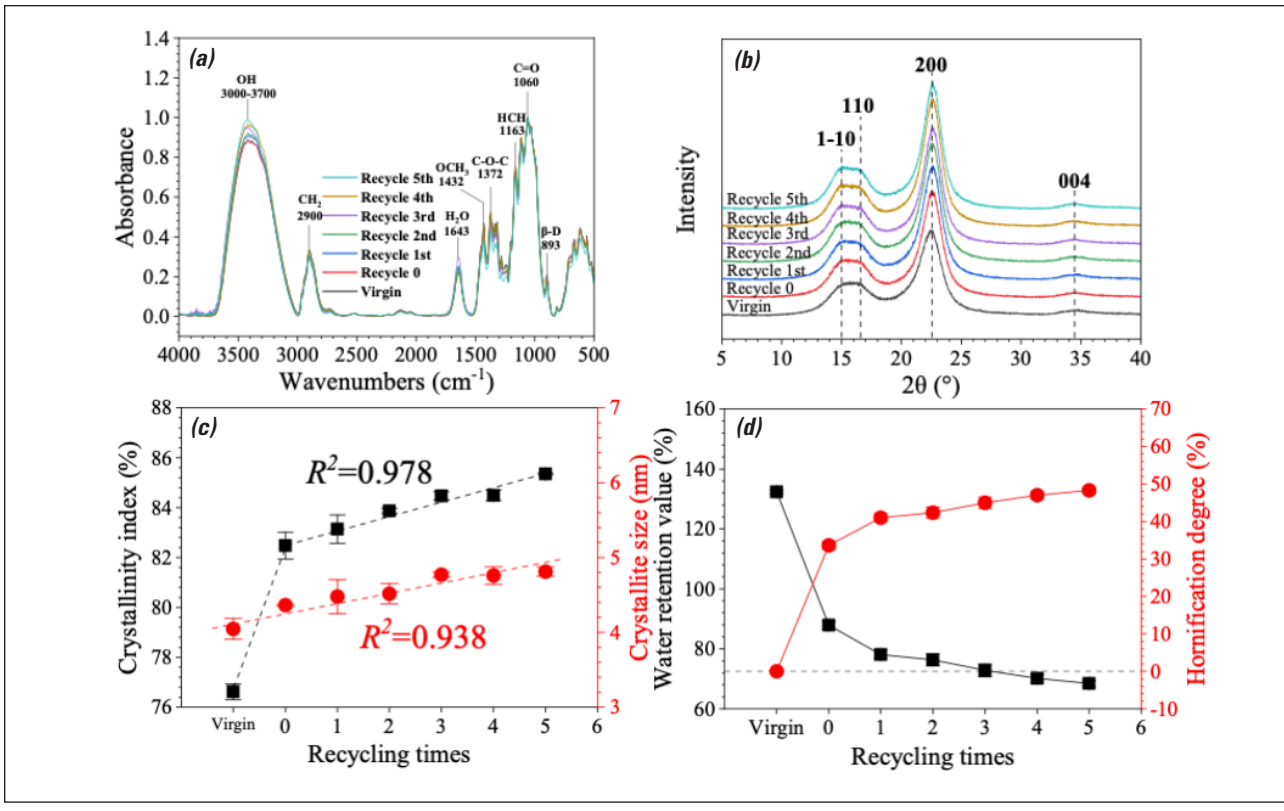
Figure 3 shows the changes in fiber ultrastructure and hornification during paper recycling. The FTIR spectrum was used to show the changes in hydrogen bonds in fibers. As shown in Fig. 3a, the content of hydrogen bonds (30005–3700 cm^{-1}) of fibers increased with recycling. The trends (Fig. 3b and Fig. 3c) of crystallinity index and crystal size during paper recycling were consistent with previous reports [37]. The crystallinity index increased significantly in the first drying and then increased linearly. The crystal size increases linearly in the recycling process. The WRV decreased significantly during the first drying and continued to decrease at a slower and slower rate during the recycling process. The hornification degree increased significantly during the first drying and continued to increase at a slower and slower rate during paper recycling. Here, the relationship between the changes in fiber ultrastructure and fiber characteristics was further studied (**Fig. 4**). The results showed that there was an excellent linear correlation between the crystallinity index and water retention value (Fig. 4a). The hornification degree also showed an excellent linear positive correlation with the crystallinity index (Fig. 4b). This once again confirms that cellulose recrystallization is the mechanism of hornification.

Physical property deterioration of cellulosic paper

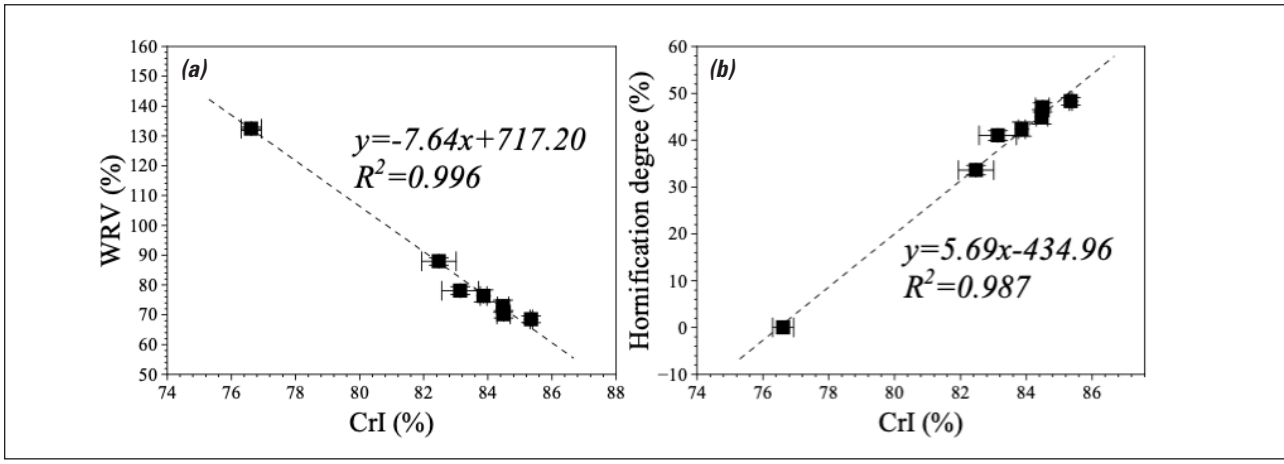
Unrefined eucalyptus fibers are used for papermaking to reduce other influence factors, such as fines. The results showed that different physical properties showed different trends (**Fig. 5**). The zero-span tensile index, which reflects the fiber strength, first increased and then stabilized with the increase of recycling times (Fig. 5a). Other physical properties that mainly depend on the bonding force showed



2. Morphological changes of eucalyptus fibers during paper recycling.

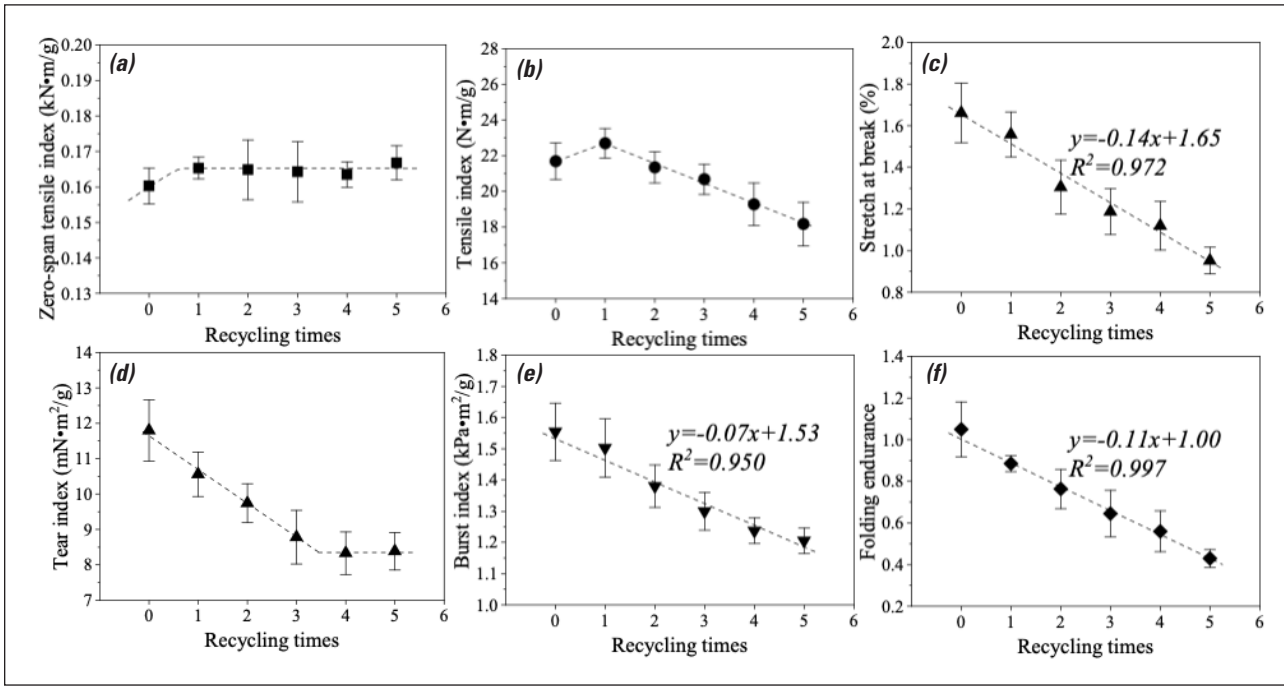


3. Ultrastructure changes and hornification of unrefined eucalyptus fibers during paper recycling.

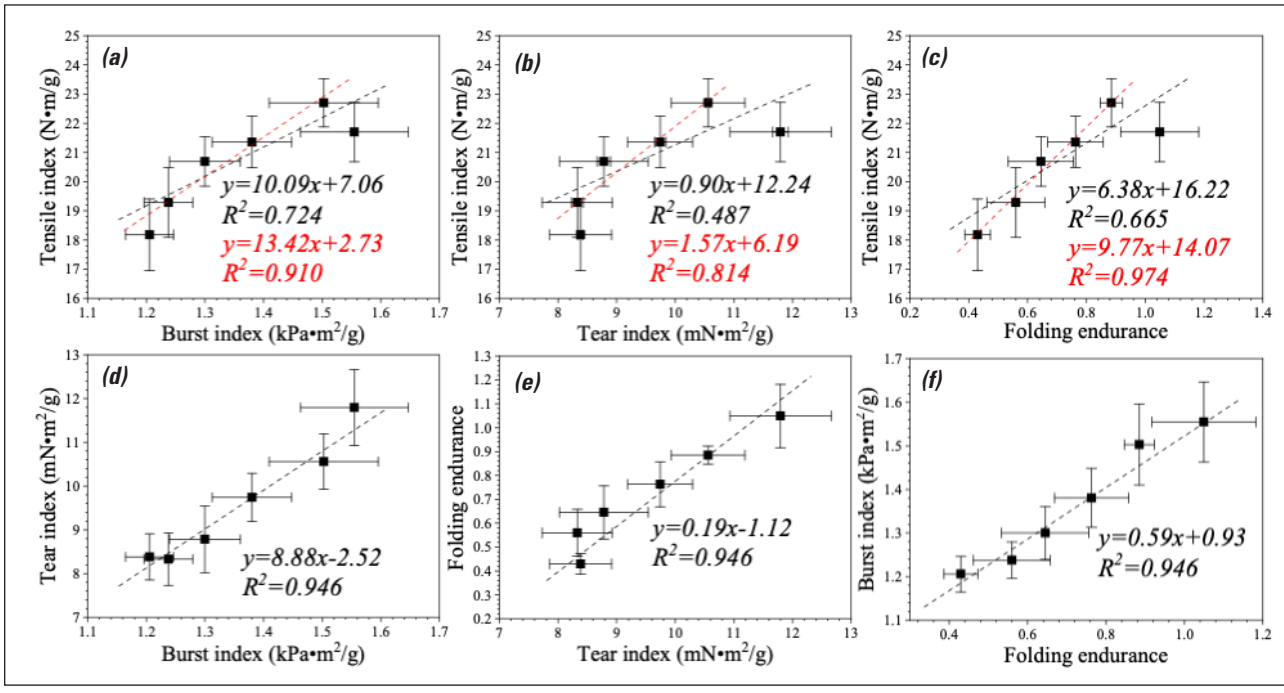


4. Relationship between the crystallinity index and hornification of unrefined eucalyptus fibers during paper recycling.

different results from the zero-span tensile index. The tensile index first increased and then decreased linearly (Fig. 5b). The tear index decreased linearly first and then stabilized after four cycles of reuse (Fig. 5d). Other physical properties, including stretch at break, burst index and folding index, decreased linearly during paper recycling (Fig. 5c, Fig. 5e, and Fig. 5f). After five cycles of reuse, the physical properties of cellulose paper decreased by 16.2% (tensile index), 42.8% (elongation at break), 21.9% (burst index), 29.0% (tear index), and 59.0% (folding index), respectively. The tensile index is affected by fiber strength and bond strength, while other physical properties are mainly affected by bond strength. The recycling process includes swelling and drying, so these changes reflect the role of drying-induced hornification. The increase in fiber strength indicates that drying-induced fiber shrinkage and cellulose recrystallization were beneficial to fiber strength. The decline in the physical properties of cellulosic paper shows that drying-induced hornification harmed the fiber bonding properties. When the fiber strength was constant, the tensile index and other physical properties showed a good linear positive correlation (**Fig. 6**). In addition, there is a



5. Physical property deterioration of unrefined eucalyptus fibers during paper recycling.

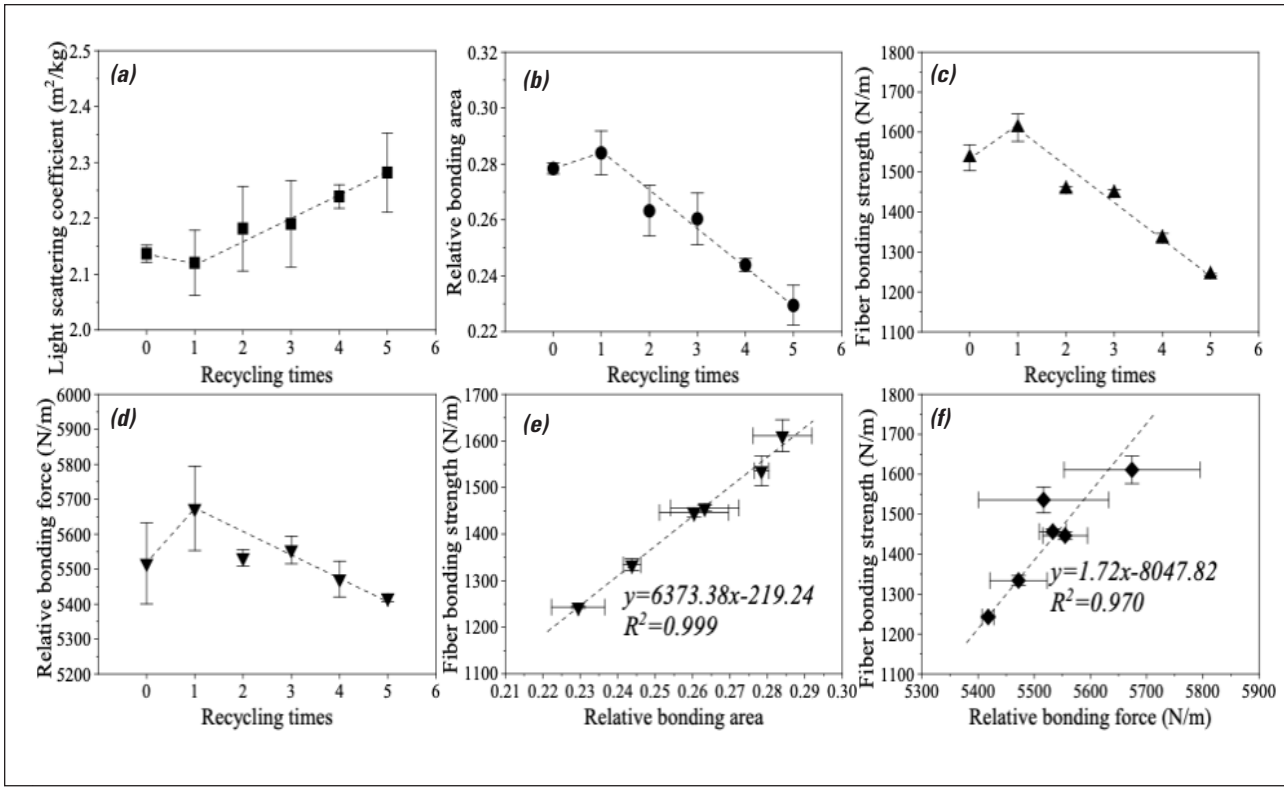


6. Relationship between physical properties of cellulosic paper produced by unrefined eucalyptus fibers. Tensile index is affected by its own strength and bonding strength, while other physical properties are mainly affected by bonding strength.

good linear positive correlation between the physical properties affected by the fiber bonding properties (Fig. 6). This shows that the physical property deterioration of cellulose paper during paper recycling is mainly affected by the bonding properties. The tensile index is also affected by the strength of the fiber itself, which is also an important factor [36].

Fiber bonding properties of cellulosic paper

The physical properties of paper made of the same fiber are mainly related to the fiber bonding strength, which is related to the fiber bonding area and the bonding force. The light scattering coefficient is an indicator of fiber bonding area. The results showed that the light scattering coefficient decreased first and then increased linearly (**Fig. 7a**)



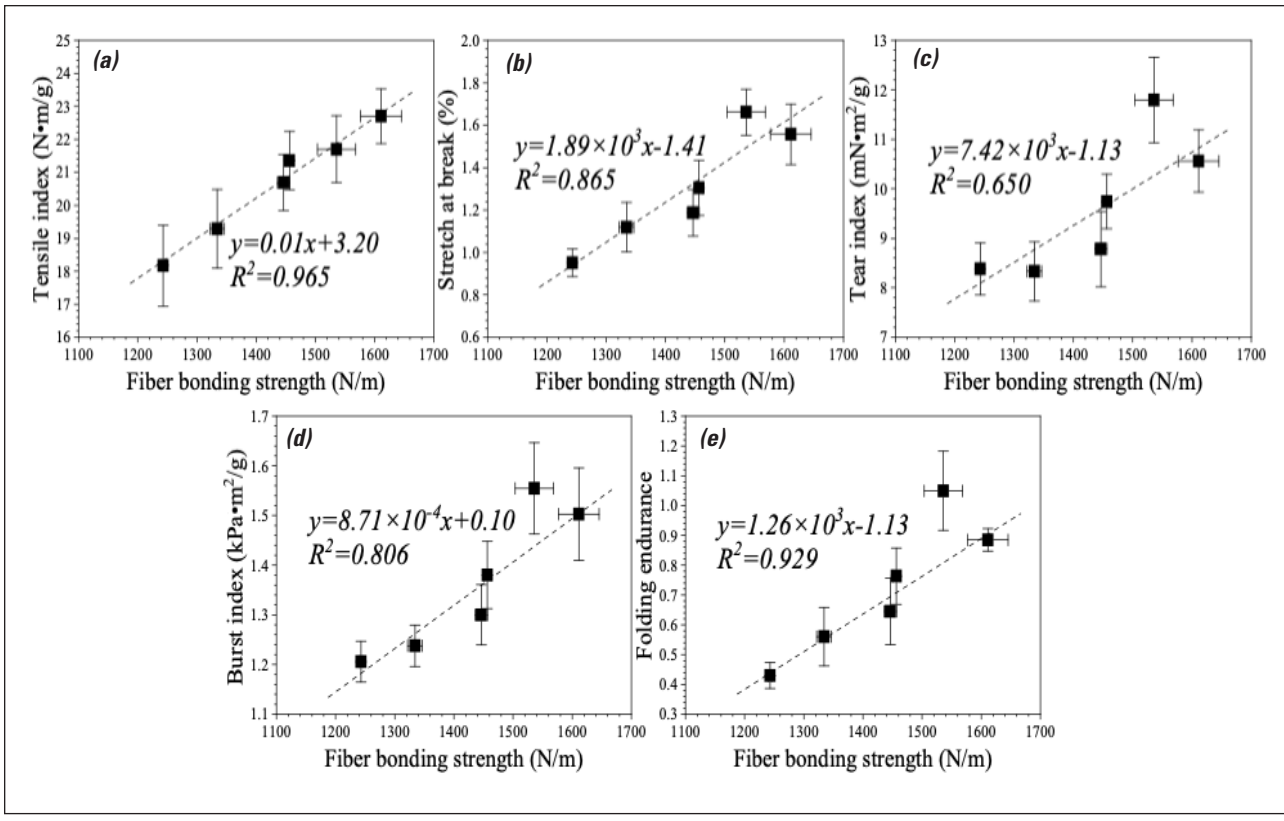
7. The changes in (a) light scattering coefficient, (b) relative bonding area, (c) fiber bonding strength, and (d) relative bonding force of the paper during paper recycling. (e) Correlation between relative bonding area and fiber bonding strength; and (f) relative bonding force and fiber bonding strength during paper recycling.

with paper recycling. This indicated that the fiber bond strength of the paper first increased and then decreased linearly (Fig. 7b). Similarly, the relative bonding area and relative bonding force also increased first and then decreased linearly (Fig. 7c and Fig. 7d). Figure 7e shows a perfect linear positive correlation between the relative bonding area and the fiber bonding strength, while the fiber bonding strength had a weaker correlation coefficient with the relative bonding force (Fig. 7f). In addition, after five cycles of reuse, the relative bonding area decreased by 19.08% and the relative bonding force decreased by 1.79%. Therefore, the fiber bonding area decreased significantly while the fiber bonding capacity remained basically unchanged during paper recycling. These results indicate that the fiber bonding strength was mainly controlled by the fiber bonding area during paper recycling.

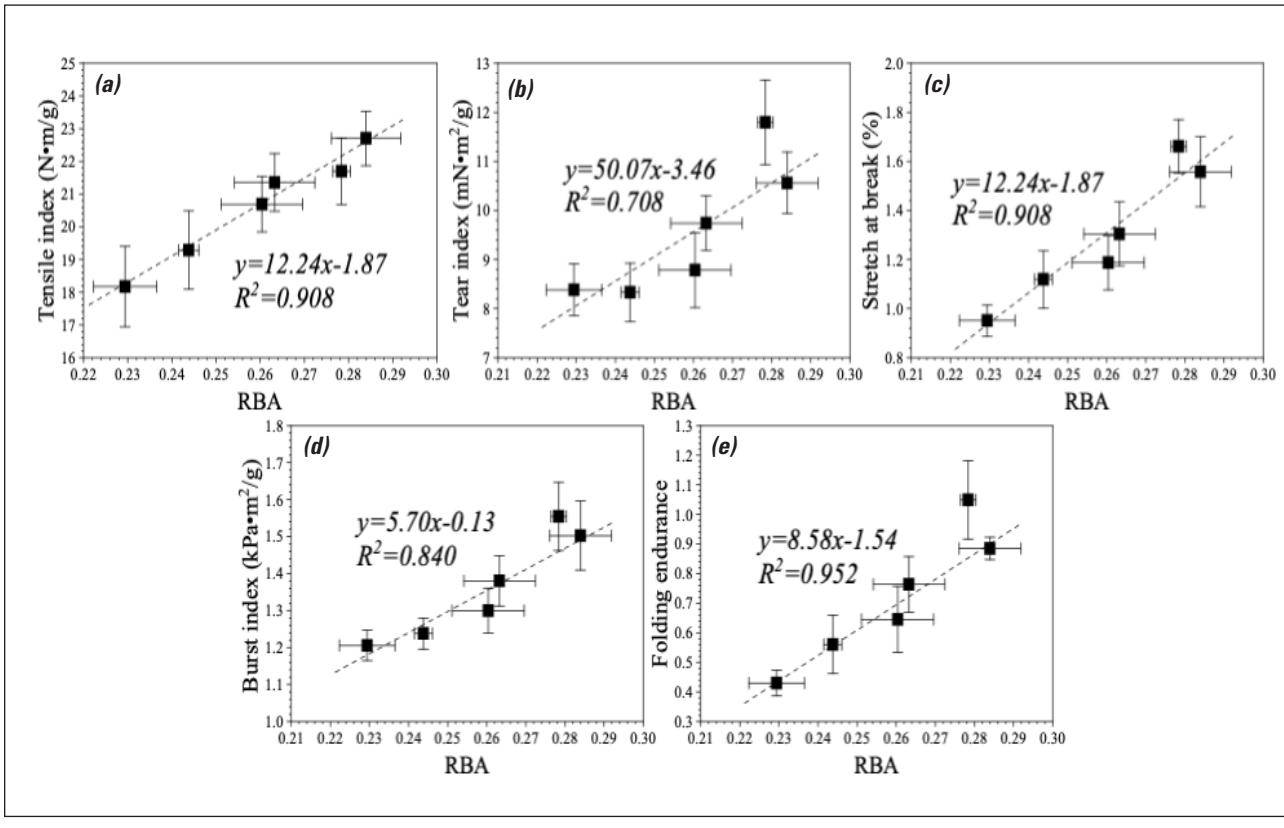
Correlation between fiber properties and physical properties

Here, the relationship between fiber bonding strength and paper's physical properties was explored. Physical properties are closely related to the fiber bonding strength (**Fig. 8**). At the same time, there was a stronger correlation between the relative bonding area and the paper's physical properties (**Fig. 9**). The relative bonding area was linearly related to the light scattering coefficient of the paper according to Eq. 5 and **Fig. 10a**. Therefore, the relationship between the light scattering coefficient and the paper's physical properties was investigated. As shown in Fig. 10b–10f, there was a good linear negative correlation between the light scattering coefficient and the paper's physical properties, especially the tensile index.

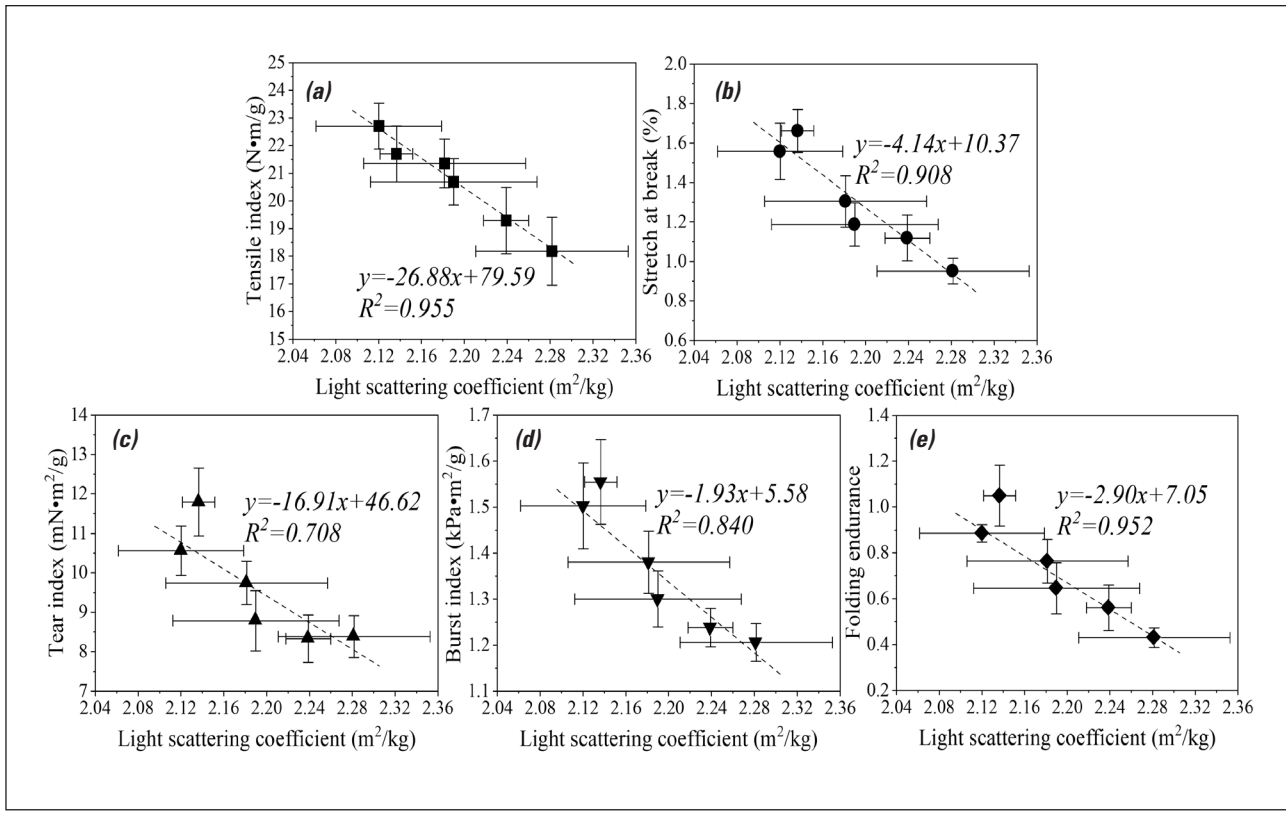
Based on the previously noted results, it is considered that the main reason for the decline of the paper's physical properties is the decrease of fiber bonding strength caused by the reduction of fiber bonding area. The fines content also affects the bonding area and bonding force, but its value was too small and had no good correlation with physical properties, bonding area, or bonding force. Therefore, according to the results of fiber morphology, the fiber bonding area was mainly affected by the fiber lateral variation because the fiber length kept stable. However, the linear correlation coefficient between fiber width and fiber bonding strength was not great enough (**Fig. 11a**). At the same time, the correlation between fiber width and the paper's physical properties was not strong enough (Fig. 11b–11f). Surprisingly, the re-swollen fiber width showed a good linear positive correlation with fiber bonding strength (**Fig. 12a**). Furthermore, there was a good linear positive correlation between the re-swollen fiber width and most of the paper's physical properties (Fig. 12b–12f). These results show that the fiber width before paper forming cannot reflect the fiber width when paper forming, while the fiber width after re-swelling can better reflect the fiber width



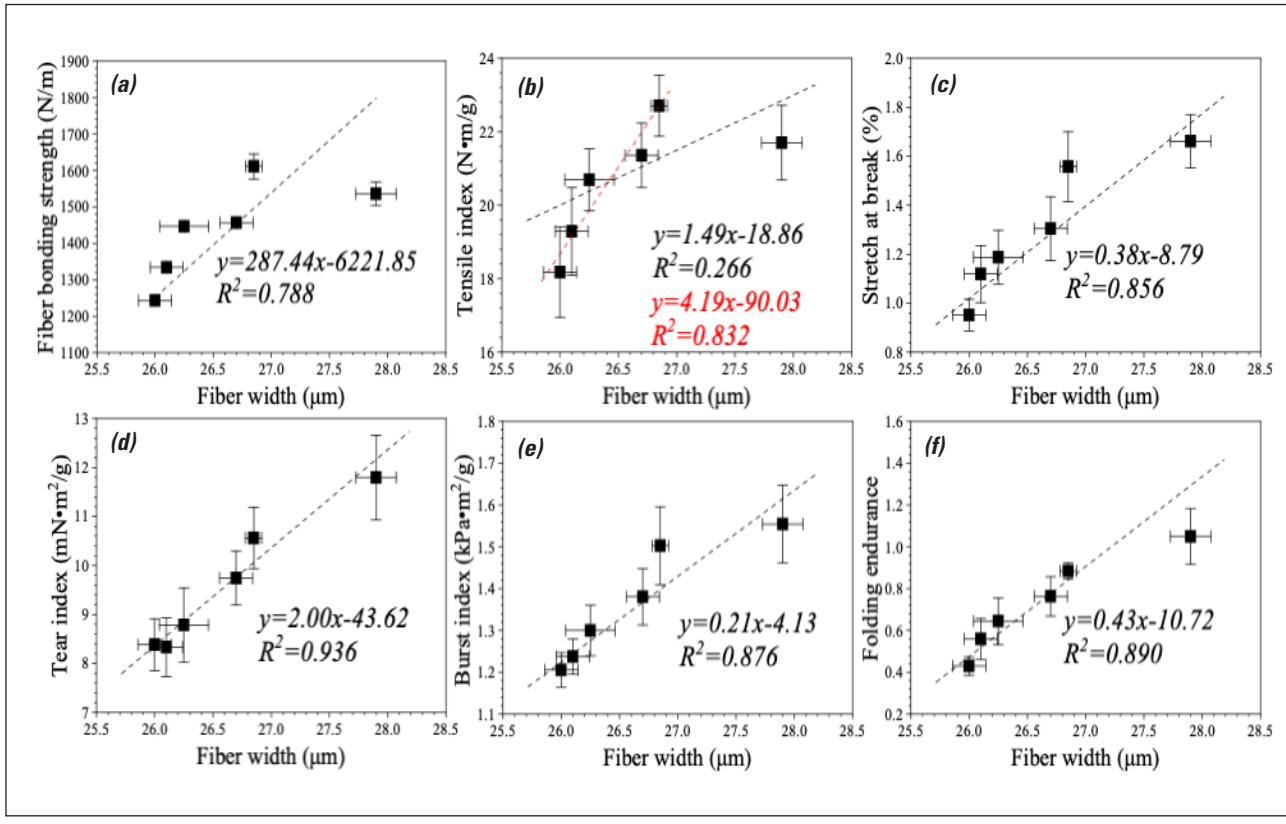
8. Correlation between fiber bonding strength and physical properties during paper recycling.



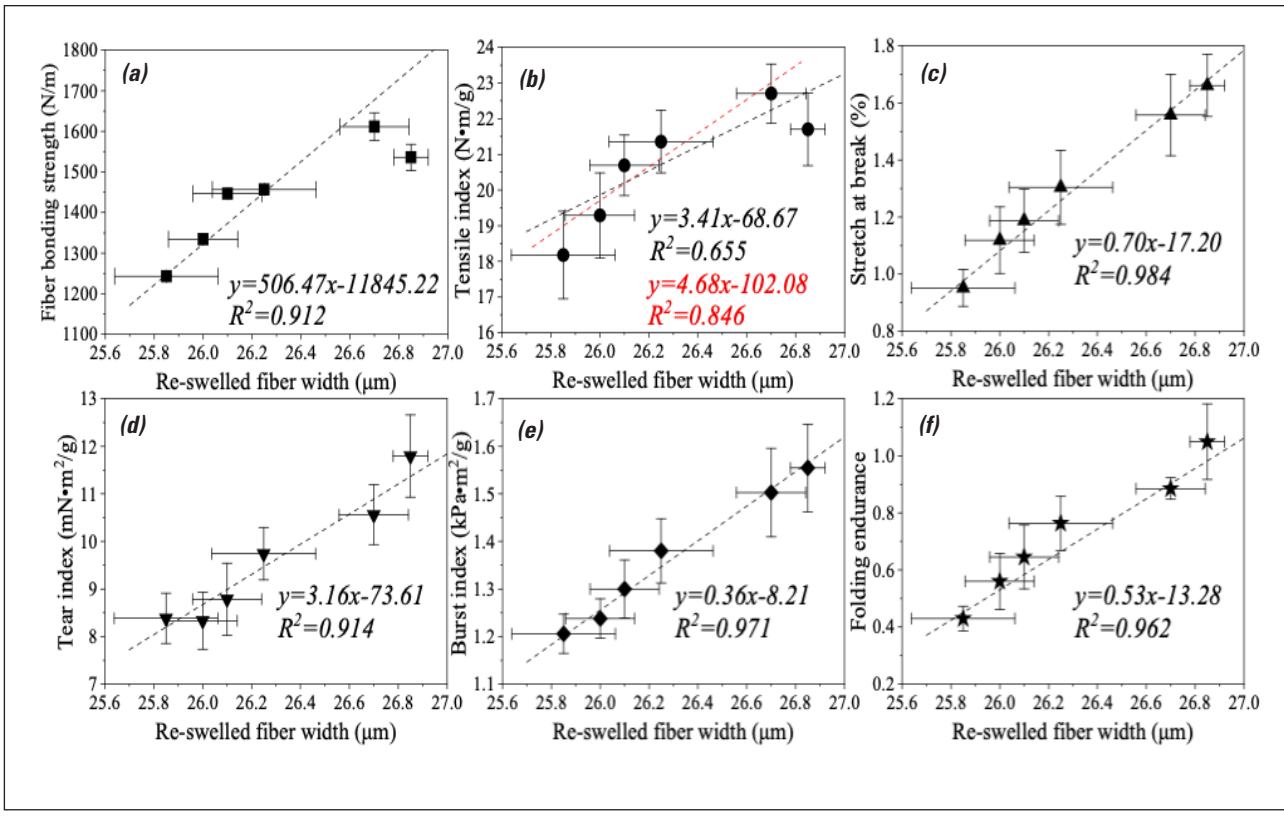
9. Correlation between relative bonding area (RBA) and physical properties during paper recycling.



10. Correlation between light scattering coefficient and (a) relative bonding area, (b-f) physical properties during paper recycling.



11. Relationship between fiber width and physical properties during paper recycling.



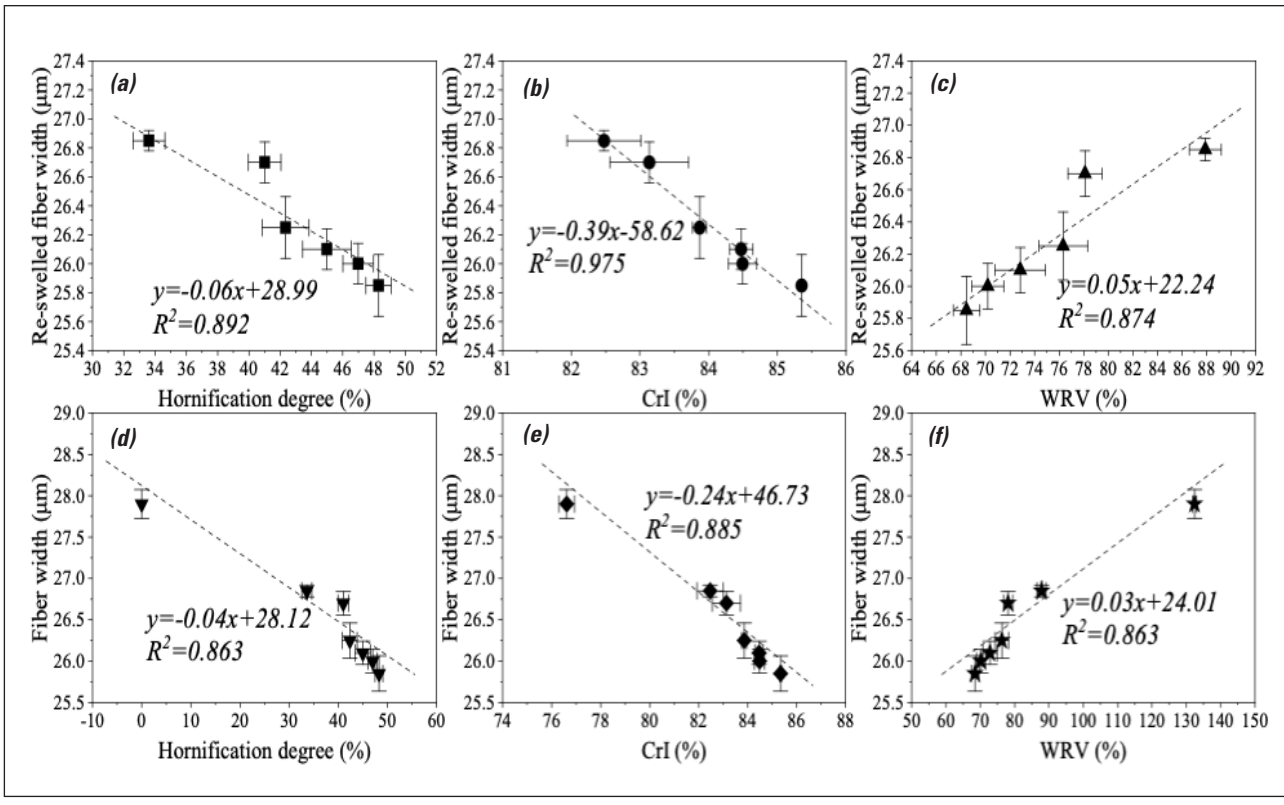
12. Correlation between re-swollen fiber width and (a) fiber bonding strength, and (b-f) physical properties during paper recycling.

when paper forming the last time. In our previous work, the cross-section of the never dried fiber was square, but it became smaller and rectangular after drying due to the collapse of the cell lumen and fiber shrinkage [18]. A significant reduction in WRV (Fig. 3d) indicates this deformation could not be recovered when re-swelling with water [37]. Based on the results of the WRV and fiber width, it is considered that after the first drying, the cross-section shape of the fiber remained unchanged (i.e., irreversible cell lumen collapse) [38] and only shrank in the subsequent recycling. It is worth noting that there is a poor correlation between the tensile index of the first paper-forming (drying) and the re-swollen fiber width. This is because the strength of the fiber itself was stable after the first cycle (i.e., the second drying). In summary, the width of re-swollen fibers can be used to reflect paper's physical properties and the papermaking potential of the fiber during paper recycling.

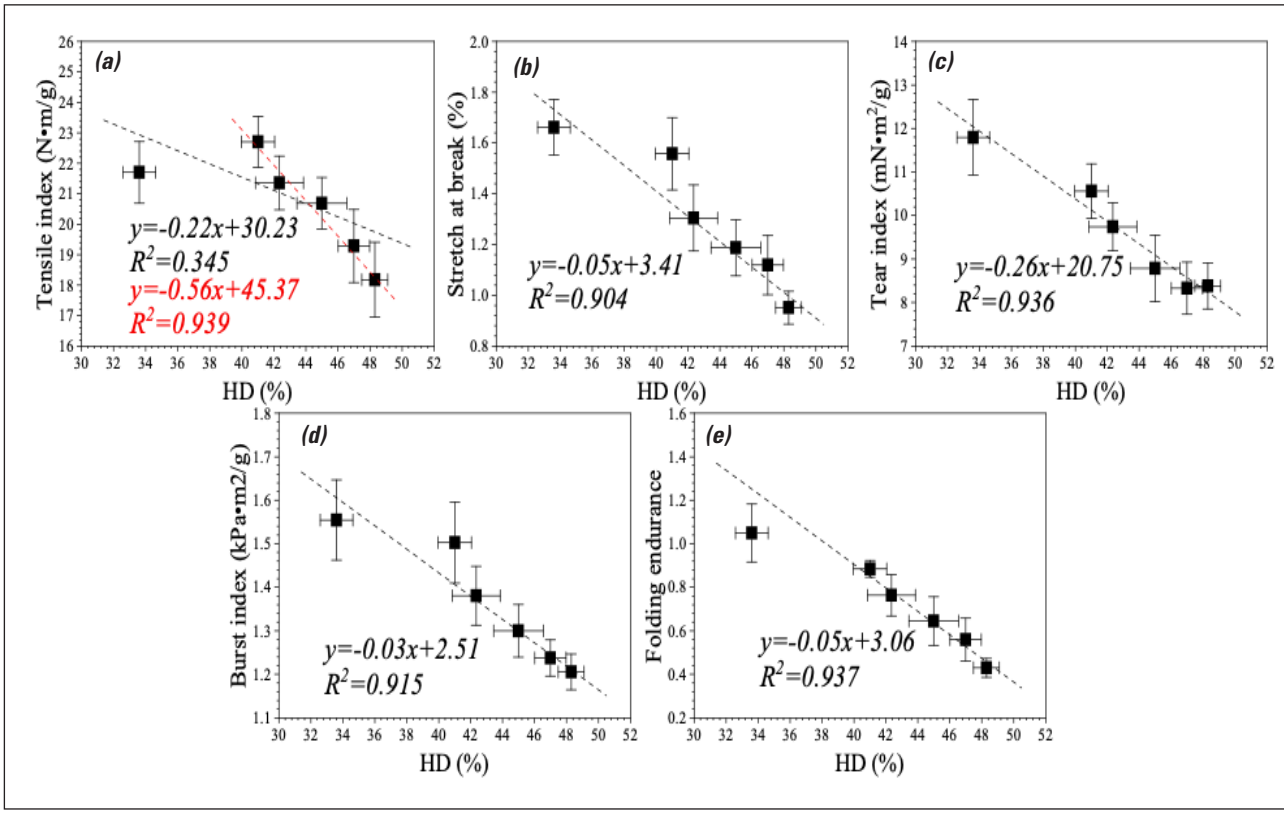
Hornification is the main reason for the change in cellulose fiber morphology and properties during paper recycling [18,39]. Re-swollen fiber width is a morphological index of the fiber and is affected by hornification. Therefore, the relationship between fiber hornification and fiber width was investigated. Whether re-swollen fiber width or fiber width, the index of fiber hornification had a good linear correlation with it (**Fig. 13**). However, the correlation between hornification index and re-swollen fiber width was better. In particular, the crystallinity index showed an excellent linear negative correlation with the re-swollen fiber width. Therefore, we also investigated the correlation between the indicators of fiber hornification (the hornification degree, the crystallinity, and the WRV) and the physical properties of paper. The results showed that except for the tensile index, other physical properties were closely related to the hornification indicators (**Figs. 14–16**). The weak correlation of the first tensile index was also due to the influence of fiber strength. Through the discussion of the previously noted results, it can be concluded that the re-swollen fiber width and the crystallinity index were closely related to the deterioration of the paper's physical properties and can predict the physical properties of the paper.

Deterioration mechanism of unrefined cellulosic paper

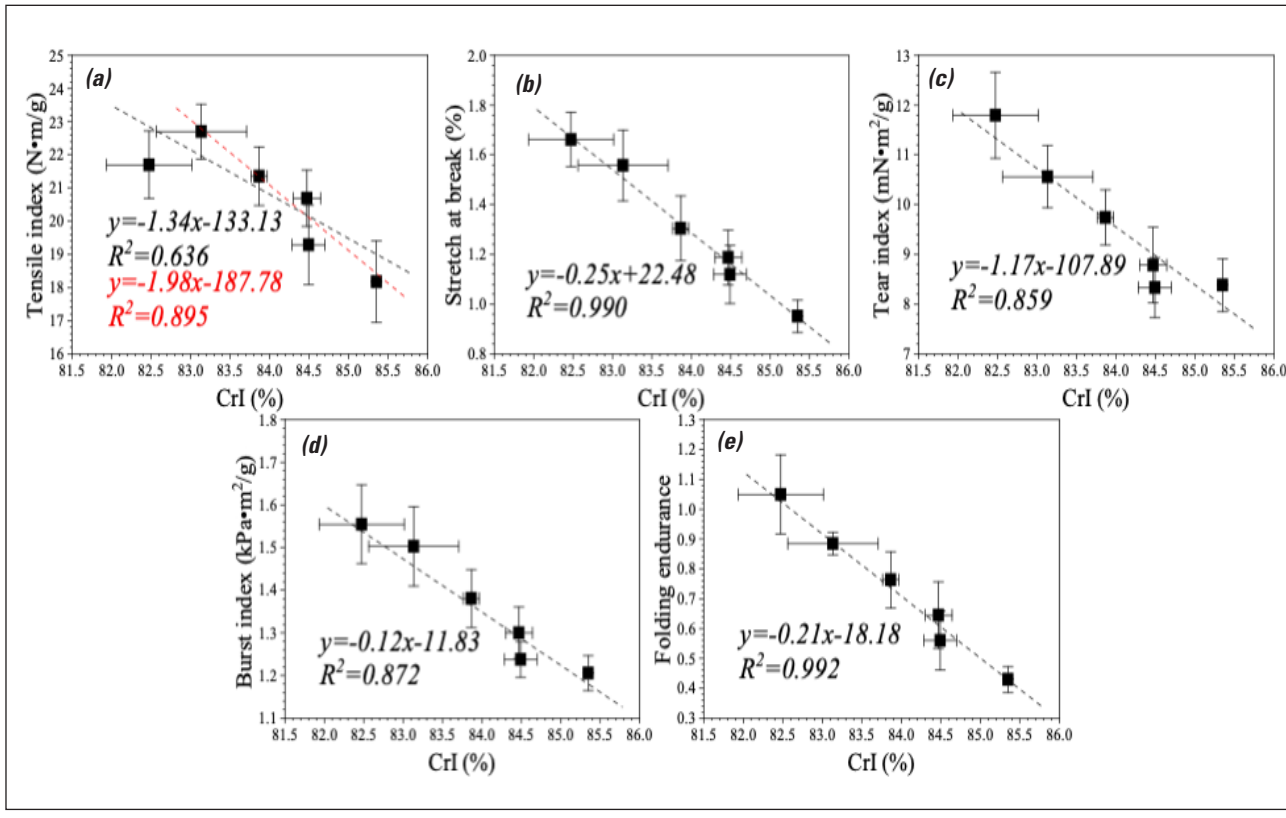
As shown in **Fig. 17**, the mechanism for physical property deterioration of unrefined eucalyptus fibers during paper recycling was discussed based on the previously noted results. The virgin cellulose fiber has a square cross-section. In addition, it has high flexibility, since the fiber never dries. On the first drying, the square cross-section becomes rectangular. At the same time, water removal leads to fiber shrinkage, mainly a change in width. The shape of the cross-section is semi-fixed because of cellulose recrystal-



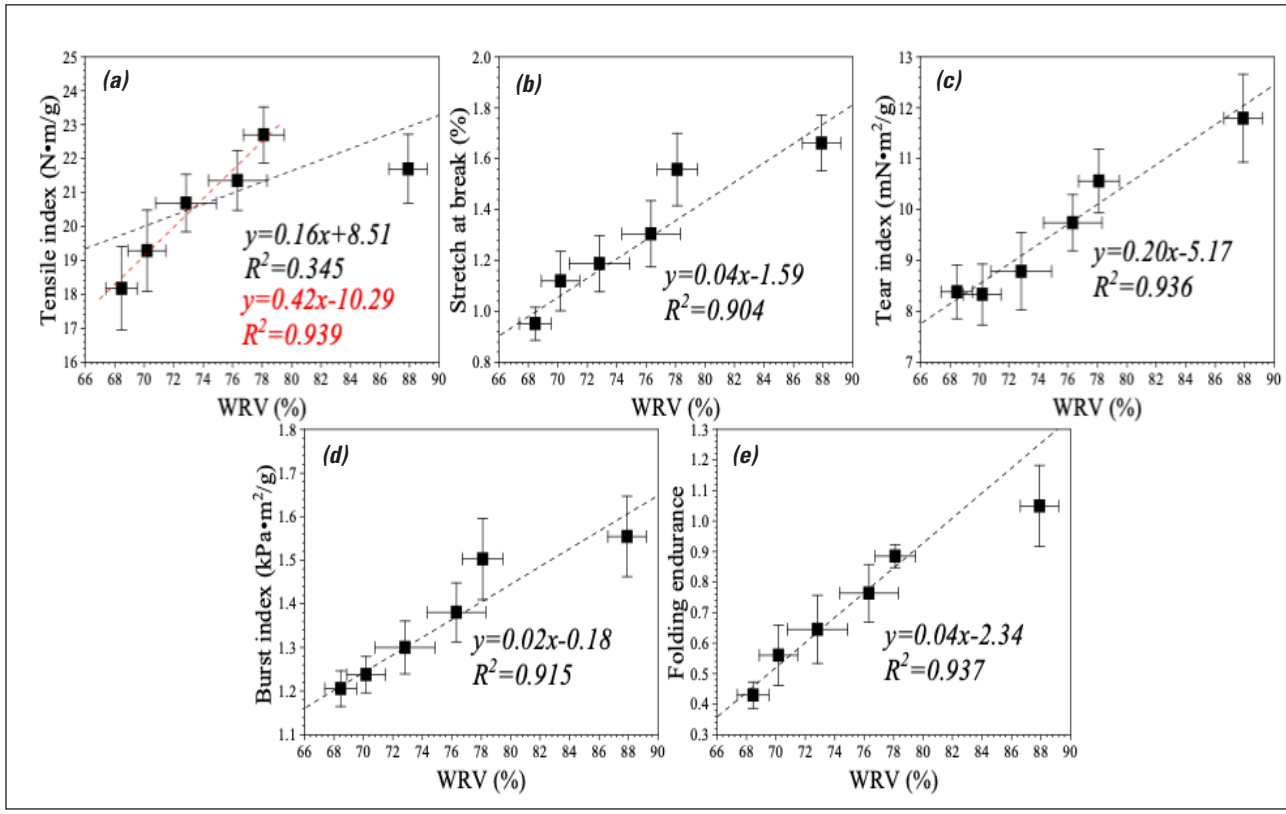
13. Correlation between fiber hornification and fiber width, including (a-c) re-swollen fiber width and (d-f) fiber width before drying, during paper recycling.



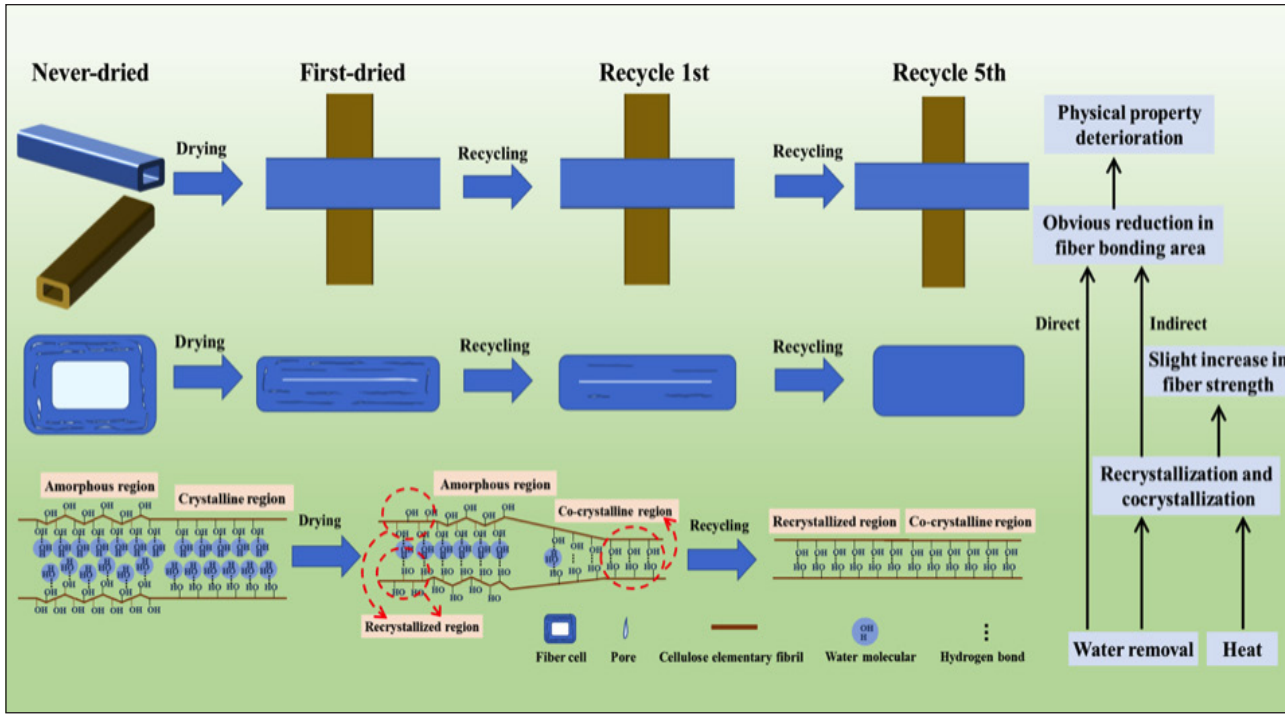
14. Relationship between the hornification degree (HD) and physical properties during paper recycling.



15. Relationship between the crystallinity index and physical properties during paper recycling.



16. Relationship between water retention value (WRV) and physical properties during paper recycling.



17. Deterioration mechanism for physical properties of cellulosic paper produced by unrefined eucalyptus fibers during paper recycling.

lization. Recrystallization here is a broader concept, including amorphous cellulose recrystallization and crystalline cellulose cocrystallization. The change of ultrastructure is reflected in the decrease of water accessibility and flexibility, as well as the increase in fiber strength. The fiber shrinkage and ultrastructure changes during the first drying determined the initial bonding area and fiber strength of the cellulose fiber. Our results indicated that the strength, bonding force, and length of the fiber itself had little change in the first drying, and the physical properties of the unrefined fiber were mainly determined by the bonding area (i.e., fiber bonding width). Our results indicate that re-swollen fiber width is an effective indicator of fiber bonding width. Therefore, the paper's physical properties can be improved by controlling the drying procedure to maximize the re-swollen fiber width (i.e., minimize fiber recrystallization) in the final bonding stage. According to others and our research, the fiber width is the largest when the cell lumen collapses during the initial drying [13,18,40,41]. At this time, the water content is about 30%, i.e., the fiber saturation point [42]. Then, the fiber width decreases until the drying is completed. Therefore, the final fiber property is controlled by the re-swollen fiber width at the end of this stage. Therefore, adopting some methods to make the process of fiber shrinkage more relaxed and the fiber recrystallization less can effectively improve the fiber bonding area. For example, the Chinese patent CN 101654895B reports that the physical properties of the paper using high-low temperature combined drying are higher than those of the paper using a traditional drying procedure [43]. This shows that the drastic drying method can be used before the fiber shrinkage where the dehydration rate needs to be controlled during the fiber bonding to form the largest bonding area possible. In addition, in our previous works [33,44], we used the pore expansion effect to increase the porosity and weaken the fiber shrinkage, thus achieving the increase of some paper properties, such as bursting strength.

Since the first drying, the initial value of the fiber width that affects the strength of the fiber has been fixed. Paper recycling is based on further fiber shrinkage and recrystallization. The cross-section shape of the fiber changes greatly during the first drying. Therefore, the physical properties of the paper decreased linearly with the decrease of the re-swollen fiber width rather than the fiber width before drying. During paper recycling, water removal leads to fiber shrinkage; that is, width reduction. Drying-induced hornification (i.e., cellulose recrystallization) hardens the shrunk fiber so that the original state cannot be restored when the fiber is re-swollen. The decrease in fiber width caused by fiber shrinkage reduces the fiber bonding strength. The decrease of fiber bonding strength leads to the physical property deterioration of paper. Our previous work [18] has proved that the fiber shrinkage ends at about 11% moisture content, while the moisture content of the paper in the paper mill is about 8%. Therefore, increasing the final moisture content of the paper (about 10%) can ensure the fiber bonding area and reduce the fiber shrinkage (for the paper property this time) and recrystallization (for the paper property next time). The results of this work represent the

most ideal situation, because the fiber used in this work was unrefined fiber. The deterioration of paper's physical properties in actual production is more complex and needs further exploration.

CONCLUSIONS

This work investigates the property deterioration mechanism of unrefined eucalyptus fibers and the role of hornification in the paper recycling process. The results showed that the bonding strength and bonding area of the fiber decreased continuously, while the fiber bonding force slightly decreased during the paper recycling process. Hornification mainly caused a decrease in fiber bonding area rather than fiber bonding force. The fiber structure hardening caused by cellulose recrystallization resulted in the irreversibility of fiber lateral shrinkage induced by dehydration, thus reducing the fiber bonding area and finally leading to the physical property deterioration of unrefined eucalyptus fibers during paper recycling. The work elucidates the mechanism of physical property deterioration of unrefined eucalyptus fibers during paper recycling, which will be helpful to control the property deterioration of paper to achieve a longer life cycle. **TJ**

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About this journal

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Although we know that the deterioration of paper performance with repeated recyling is caused by hornification, it is still unclear how this process operates. Research has shown that performance degradation is caused by a decrease in fiber bonding strength, but researchers have different views on the loss of bonding strength of recycled fibers. One view is that the loss is mainly due to the fiber surface inactivation; that is, the decrease of the bonding force. The other view is that it is due to reduced fiber bonding area. However, the impact of hornification on these two aspects is still not entirely clear due to the interference of other factors. Another important problem is the lack of more reasonable indicators to represent the papermaking potential of recycled fibers.

The most challenging aspect of this study was how to control for other factors to highlight the role of hornification. For this reason, we chose unbeaten chemical pulp as the raw material and did not add sizing agents and fillers during the paper recycling process. The interference of fine fibers was controlled without beating. The hornification of the chemical pulp was very significant, and there was no extract in chemical pulp. There was also no deactivation of the fiber surface caused by other substances, as there were no extracts, sizing agents, and fillers. These conditions ensured that the deterioration of performance was entirely due to hornification.

We found that the fiber structure hardening caused by cellulose recrystallization (also known as fiber hornification) during paper recycling resulted in the irreversibility of fiber lateral shrinkage induced by dehydration, thus reducing the fiber bonding area and finally leading to the physical property deterioration of the paper. Hornification mainly caused a decrease in fiber bonding area rather than fiber bonding force. The re-swelled fiber width was linearly related to the physical properties of paper, which could be used as a prediction index of paper properties during paper recycling. This was an interesting finding.

Our research indicates that fiber width is an important indicator of paper performance. For mills, increasing the final water content of the paper (about 10%) might ensure the fiber bonding area and reduce the fiber shrinkage (for the paper property this time) and recrystallization (for the paper property next time).

In the next phase of our research, we will introduce continuous beating to study how the physical structure of fibers affects the deterioration of paper performance.

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