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ORIGINAL PAPER

Preparation of fine fiber sheets from recycled pulp fibers using aqueous counter collision

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Abstract The utilization of waste paper is very important for saving wood resources and reducing waste generation. Various techniques for preparing cellulose nanofibers, which is a material recently proposed for potential applications in the paper industry, have been investigated. In the present study, fine fibers were prepared using recycled pulp and a nanoengineering aqueous counter collision treatment, and sheets composed of these fine fibers were prepared by filtration under reduced pressure conditions. Measurement of specific surface area and optical microscopic observation of fine fibers showed the recycled pulp was not readily miniaturized by the treatment compared with virgin pulp. The tensile strength of sheets produced from recycled pulp by 5 times of the treatment was higher than of those prepared from recycled pulp by 60 times and from virgin pulp regardless of the number of the treatment. Furthermore, the density of the sheet produced from recycled pulp by 5 times was lower than other sheets.

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Introduction

Paper remains an essential material in modern society, and 403 million tons of paper and paperboard (Japan Paper Association 2016) was produced all over the world at 2013. Post-consumer's paper and paperboard are collected as waste paper, at a utilization rate of 58 % (corresponding to 232 million tons) (Japan Paper Association 2016). The utilization of waste paper is very important for use in protecting wood resources and reducing issues associated with waste generation and final disposal.

The utilization of waste paper as recycled material presents the problem that the quality of pulp is reduced during recycling. Therefore, its utilization in the production of higher grades of paper such as printing and communication papers has been restricted by demands for high quality. One of the factors that decreases the quality of waste paper is the hornification of pulp (Garg and Singh 2006; Gurnagul et al. 2001; Minor 1994), which is a phenomenon that occurs when a chemical pulp repeatedly undergoes wetting and drying. Hornification reduces the pore volume in the wet pulp fibers, leading to a decrease in its water retention ability. If a new material can be produced using pulp that exhibits hornification, then the utilization of waste paper will increase in the future.

Recently, cellulose nanofiber has attracted attention as a potential new material for use in the paper industry. There are several methods used to produce cellulose nanofibers that fall into two categories: mechanical and chemical. In the case of the mechanical methods, high levels of external energy, greater than typical beating energies, can be used to miniaturize pulp in order to produce cellulose nanofibers (Iwamoto et al. 2007; Kondo et al. 2014). Moreover, it has been reported that once-dried pulp was not uniformly nanofibrillated; in other words, submicrofibers remained after the mechanical treatment used to produce cellulose nanofibers. However, never-dried pulp has been uniformly nanofibrillated (Iwamoto et al. 2008). It might therefore be possible to obtain fine fibers that contain micro- and submicro-fibers with a different fiber length from pulp that exhibits hornification, by using the mechanical method for producing cellulose nanofibers.

The fiber length of fine fibers significantly affects sheet properties such as density and tensile strength (Seo et al. 2002). In the present study, fine fibers were prepared from pulp that exhibited hornification (recycled pulp) using the mechanical method. The properties of sheets composed of these fibers were then compared with those made from virgin pulp.

Materials and methods

Preparation of recycled pulp

Softwood bleached kraft pulp (SBKP, commercially available wet pulp) was used as the raw material. The SBKP was first beaten using a Valley beater at a 2 % consistency to 300 mL Canadian Standard Freeness (CSF). The beaten SBKP was used as a control, and is referred to as "virgin pulp" in this work. 120 g/m^2 handsheets were subsequently prepared from each pulp sample using an approach based on ISO 5269-1, and dried at 80 °C for 24 h in a forced air circulation oven, after pressing. The dried handsheets were then immersed in water and defibrated using a standard disintegrator under the 1 % pulp consistency. This cycle was repeated for up to three times. Water retention value of pulp before and after recycled treatment was evaluated according to ISO 23714.

Preparation of fine fibers and sheets

An aqueous counter collision (ACC) machine (Star Burst Labo, SUGINO MACHINE LTD., Japan) (Kondo et al. 2014) was used in order to miniaturize the pulp in the water. Through this process, either virgin pulp or recycled pulp was diluted using pure water until the pulp consistency is 0.05 %. These diluted suspensions were processed using the ACC system at an injection pressure of 200 MPa, and using either 5 or 60 collision passes in order to obtain fine fibers.

In order to prepare the sheets using these fibers, fibers were obtained to target the basis weights of 60 g/m^2, and the fine fiber suspension was filtered under a reduced pressure through a membrane filter with a pore size of 0.45 μm, resulting in a wet sheet including in all fibers. During filtration under reduced pressure, the suspension was agitated using bladed stirring rod to make uniform sheet. This wet sheet was pressed a few times to dewater by using press machine, which is described in ISO 5269-1, at pressure of 410 kPa for 5 min between filter papers and then, held between filter paper and metal plate in the heated metal plates of a hot press (AH-1T, AS ONE Co., Japan) under at a temperature of 105 °C for more than 24 h and pressure of 18 kPa, in order to obtain a dried sheet that was composed of fine fibers. Sheet thickness was measured using micrometer described in ISO 534.

For testing, two types of handsheets were prepared using virgin pulp and recycled pulp to target the basis weight to 60 g/m^2. The handsheets were prepared based on the ISO 5269-1 method. The handsheet of type I used virgin pulp and set 80 °C of drying temperature (samples V 80 °C), and type II used recycled pulp and set 80 °C of drying temperature (samples R 80 °C).

Characterization of the sheets

Tensile and zero-span tests on the fine fiber sheets were conducted using approaches based on the ISO 1924-2 and ISO 15361 methods, respectively, with the sheet having 10 (width) and 30 mm (effective length). Each test was repeated using more than 15 specimens. Physical evaluations of the prepared handsheets were also conducted. In each case, more than nine specimens were tested.

Opaqueness of sheet was analyzed using software "Image-Pro 9.1". At first, the sheets were scanned on a black paper using scanner and to get digital images of the sheets. Then the images were quantified each pixel using the software based on 256 tones, where white is 255 and black is 0. Then the opaqueness per 60 g/m^2 of the sheet was calculated by following equations.

$$\mathrm{Op} = \frac{(S - BG)}{(255 - BG)} \times 100 \times \frac{60}{BW}$$

Op: Opaqueness ratio (%), *S*: Average tone of sheet, *BG*: Tone of back ground, *BW*: Basis weight (g/m^2).

Fine fibers produced using the ACC treatment were sandwiched between glass slide and cover glass, and dried prior to optical microscopy (Axio Imager. A1, Carl Zeiss Ltd., Germany) observations. Furthermore, for each fiber samples, 0.2 % fiber dispersions were prepared and 50 μL of the dispersions were put on the slide glass. Then the slide glass was covered by cover glass, the number of fibers having the length of more than 0.5 mm was counted per 24 × 24 mm^2 using optical microscopy.

For measurement of specific surface area of fine fibers, fine fiber suspensions prepared by ACC treatment were rapidly frozen using liquid nitrogen and then freeze-dried. The specific surface area of each dried fine fibers was calculated using its N_2 adsorption isotherm. These fine fibers were kept at 100 °C for 6 h, in order to remove any water remaining in the fine fibers. A surface area analyzer (BELSORP-mini, MicrotracBEL Corp., Japan) was used to measure N_2 sorption on the fine fibers at 77 K. The surface areas were estimated by fitting the adsorption data to the Brunauer, Emmett and Teller equation (Brunauer et al. 1938). The specific surface areas of the fine fibers were obtained by dividing the surface areas by the total mass of the fine fibers.

Results and discussion

Minimization behavior of the recycled pulp

Figure 1 shows optical microscopic images obtained for the fine fibers after ACC treatment in which various collision passes were applied. It is evident that in the increase from 3 to 5 collision passes (Fig. 1b, c and f, g), more long fibers were obtained from the recycled pulp than from the virgin pulp. This result indicates that the recycled pulp was not readily miniaturized by the ACC treatment. After the application of more collision passes, it was no longer possible to observe the fibers of either pulp using optical microscopy. This result demonstrated that the fine fibers had reached dimensions below the resolution limit of optical microscopy (approximately 1 μm) after 60 collision passes (Fig. 1d, h). In further experiment about BET surface area and physical properties, samples with 5 and 60 collision passes were chose among samples with 1, 3, 5 and 60 collision passes due to investigate the effect depending on collision times.

Figure 2 presents the BET surface areas of freeze-dried pulp and fine fibers. Both before and after ACC treatment, the surface area of the recycled pulp and fine fibers was less than that of the virgin pulp and fine fibers. The differences in the surface areas of the virgin and recycled pulp and fine fibers after 0, 5, and 60 passes were 18, 48, and 13 m^2/g, respectively. On the other hand, the water retention values of the virgin and recycled pulp were 210 and 115, respectively, prior to ACC treatment; the water retention of the recycled pulp was lower because of hornification. As noted previously, hornification refers to the shrinkage of pulp as it dries. The difference in the specific surface areas between the two pulps increased as the number of passes increased from 0 to 5, but then decreased between 5 and 60 collision passes. The significant difference between the two pulps observed at 5 passes occurred because the recycled pulp that exhibited hornification was more difficult to miniaturize. At 60 collision passes, this difference was minimized because both pulps had been reduced to fine fibers with less than 1 μm of width, which couldn't observed by optical microscopy.

Physical properties of the sheets

Figure 3 shows opaqueness of the sheets composed of fine fibers that were prepared using ACC treatment. The opaqueness of the sheet made from fibers prepared using 5 collision passes was higher than that of the material prepared using 60 passes. In addition, an increased number of collision passes evidently generated more fine fibers, and denser sheets could be prepared using these finer fibers. Thus, the densities of the two sheets prepared using 5 collision passes were

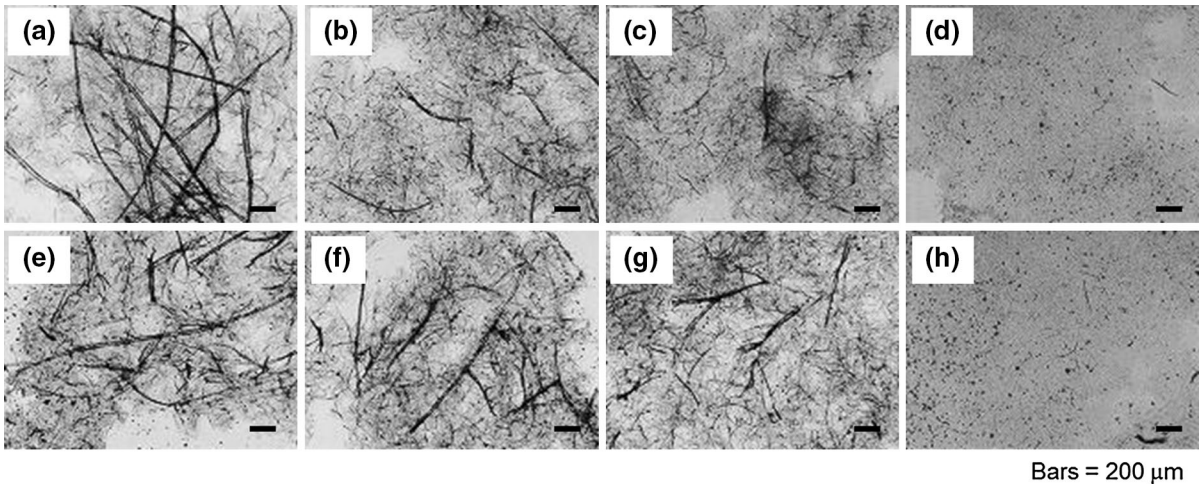

Fig. 1 Optical microscopic images of fine fibers after ACC treatment. Raw material/treatment condition, **a** virgin pulp/200 MPa, 1 pass, **b** virgin pulp/200 MPa, 3 passes, **c** virgin pulp/200 MPa, 5 passes, **d** virgin pulp/200 MPa, 60 passes, **e** recycled pulp/200 MPa, 1 pass, **f** recycled pulp/200 MPa, 3 passes, **g** recycled pulp/200 MPa, 5 passes, and **h** recycled pulp/200 MPa, 60 passes

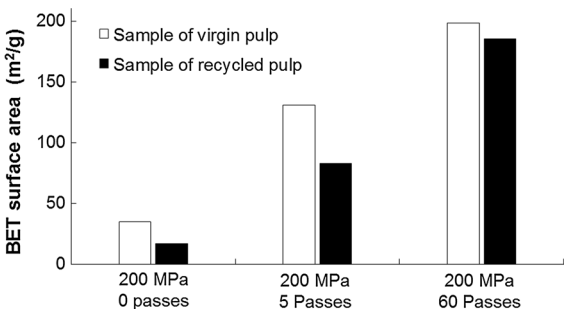

Fig. 2 Specific surface area of samples prepared from virgin pulp and recycled pulp

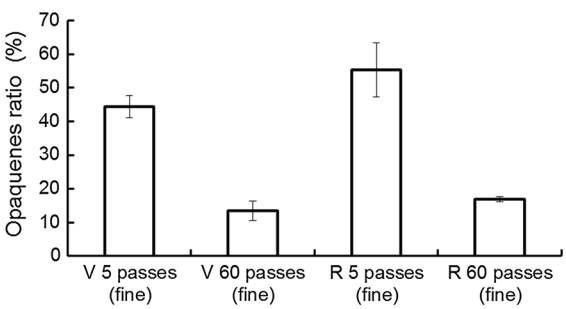

Fig. 3 Opaqueness ratio of sheets prepared using fine fibers

lower than those of both sheets prepared using 60 passes. Because the denser sheets exhibited a smaller surface area, reflection of light by the surface was reduced.

Figure 4 summarizes the tensile index values of fine fiber sheets and handsheets. When the virgin pulp sheets dried at 80 °C (samples V 80 °C) were compared with the recycled pulp sheet (sample R 80 °C), it was observed that the tensile indices of the virgin pulp sheets were higher than that of the recycled pulp sheet. It is usual that the tensile index and density of a recycled pulp sheet are lower than those of virgin pulp sheets, due to decreasing interfiber bonding areas attributed to the hornification of the pulp during recycling. In this study, the tensile indices of all the fine fiber sheets were higher than that of the recycled pulp sheet. In particular, it is of note that the tensile index of the fine fiber sheet composed of the recycled pulp that was obtained after 5 passes (sample R 5 pass) was the highest among all the specimens. There might be two reasons why V 60 passes (fine) and R 60 passes (fine) show lower tensile strength than R 5 passes (fine). One is the following things. Many times of mechanical treatment seem to cause shortening of the fine fibers, leading to lower tensile strength. Actually hard mechanical treatment having ability to produce nanofiber decreases tensile strength of sheet composed of the fine fibers including nanofibers (Iwamoto et al. 2007). Another reason is that uniformity of V 60 passes (fine) and R 60 passes (fine) decreases the tensile strength. Because the standard deviations of tensile strength of sheets after 60 passes are higher than those of pulp sheet and sheet after 5 passes. This

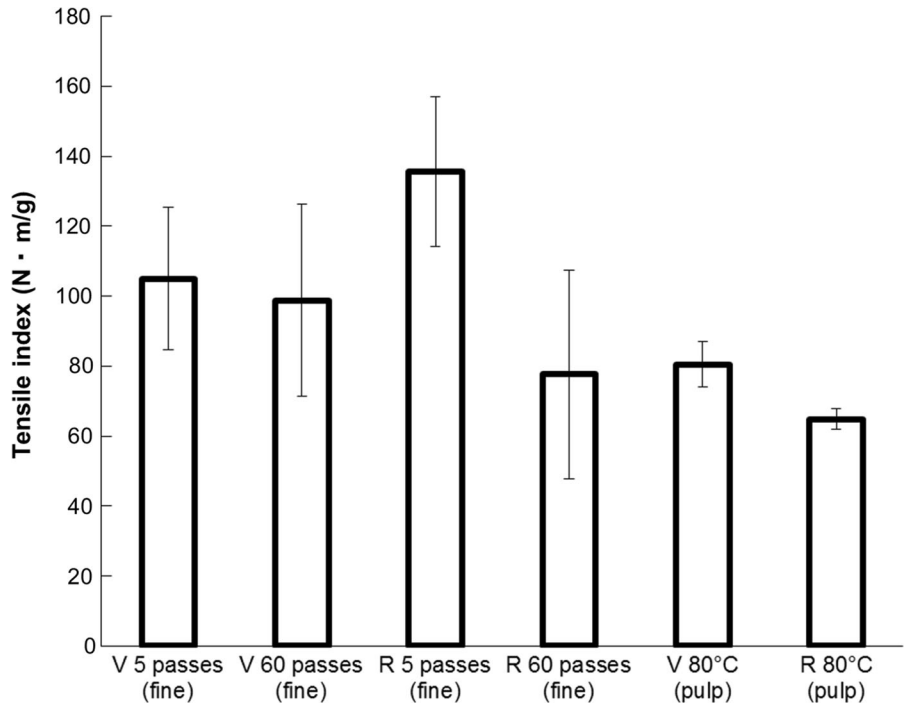

Fig. 4 Tensile indices of the sheets. *Error bars* give the SD

large value could be come from uniformity of the fine fiber sheets, thus is easy to receive stress concentration effect (Sakaemura and Yamauchi 2014).

Figure 5 presents the relationship between the density and the tensile indices of the sheets. Considering only the density values, the densities of the fine fiber sheets were higher than those of the pulp sheets, and the densities of samples V 60 passes (fine) and R 60 passes (fine) were higher than those of samples V 5 passes (fine) and R 5 passes (fine). This is to be expected, since increasing the number of collision passes generates finer fibers that tend to form denser sheets. Interestingly, there was a significant difference in density between samples V 5 passes (fine) and R 5 passes (fine). As shown in Fig. 1, compared to the virgin pulp, the recycled pulp was not easy to miniaturize using the ACC treatment, especially when employing a few collision passes, for example only 5 passes. It is likely therefore that the presence of long fibers in sample R 5 passes (fine) exhibited a reduced density.

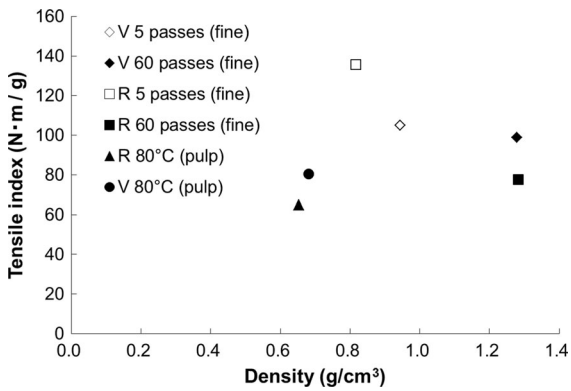

Fig. 5 Tensile indices and densities of the sheets

In general, the density of a sheet is positively correlated with its tensile index. In this study, the relationships between the densities and tensile indices of the virgin pulp sheets [V 80 °C (pulp)] and the recycled pulp sheet [sample R 80 °C (pulp)] agree with this principle. However, in the case of sheets composed of fine fibers prepared by the ACC treatment, the relationship between density and tensile index was significantly different. The densities of samples V 60 passes (fine) and R 60 passes (fine) were higher than those of samples V 5 passes (fine) and R 5 passes (fine); however, since amount of finer fibers increased with increasing in numbers of passes in the sheets, the tensile indices of samples V 60 passes (fine) and R 60 passes (fine) were lower than those of samples V 5 passes (fine) and R 5 passes (fine).

Furthermore, it is noteworthy that the tensile index of sample R 5 passes (fine), which exhibited a lower density, was significantly higher than those of samples V 5 passes (fine) and R 60 passes (fine), both of which exhibited higher densities. One of the possibilities to increase tensile strength of sample R 5 passes (fine) with low density is the following things. The length of fiber in sample R 5 passes (fine) is longer than that of sample from virgin pulp. Generally, longer fiber can make strong fiber network in sheet. Figure 6 shows distribution of fiber length having more than 0.5 mm per unit area under same fiber concentration. Actually the total number of fibers, which have more than 0.5 mm length, in sample V1 passes (fine) is more than that in R5 passes (fine). Further investigations are needed to clear whether the sample R 5 passes can be produced from only recycled pulp or both virgin pulp and recycled pulp. The tensile index of sample R 5 passes (fine) was almost twice that of the recycled pulp sheet [sample R 80 °C (pulp)]. The major reason is fiber bonding area increases by miniaturization of pulp. And as another reason, it is possible that higher temperature (105 °C) of press-drying for R 5 passes (fine) increase the index, since it is reported that a tensile index of sheet prepared by press-drying at 120 °C is higher than at 80 °C, although density don't change (Kimura et al. 1985). In this study, we used the standard micrometer described in ISO 534 to measure their thickness. Density depends on thickness value and the method (Yamauchi 1987). This method indicates larger thickness than other methods such as mercury method (Wasser 1974) and rubber platen method (Yamauchi 1989). This tendency is stronger if long fibers are present. Further investigation using the other methods is needed to analysis the relationship between density and tensile strength of sheet in detail and exactly.

Figure 7 shows the zero-span tensile indices of the sheets used in testing. This parameter is normally used as a measure of the strength index of a single pulp fiber. Here, the index of sample R 5 passes (fine) was not significantly higher than those of the other sheets. During recycling treatment, the zero-span tensile index of chemical pulp shows a constant value (Howard and Bichard 1992), which means that the strength of the chemical pulp does not increase after wetting and drying. These results indicate that the interfiber bonding strength of sample R 5 passes (fine) was reasonably high because tensile strength of sample R 5 passes (fine) is high without changing the strength index of the single pulp fiber. In order to better understand the mechanism by which sample R 5 passes (fine) exhibited low density and high tensile strength, further investigation of the relationship between the strength of fine fibers such as nanofibers and the zero-span tensile index of sheets composed of fine fibers is required.

Conclusions

The tensile strength of sheets composed of fine fibers that originated from ACC-treated recycled pulp while applying a few collision passes was approximately twice that of non-ACC treated recycled pulp sheets. This level of strength could not be achieved either by increasing the number of collision passes or by using virgin pulp under same treatment condition.

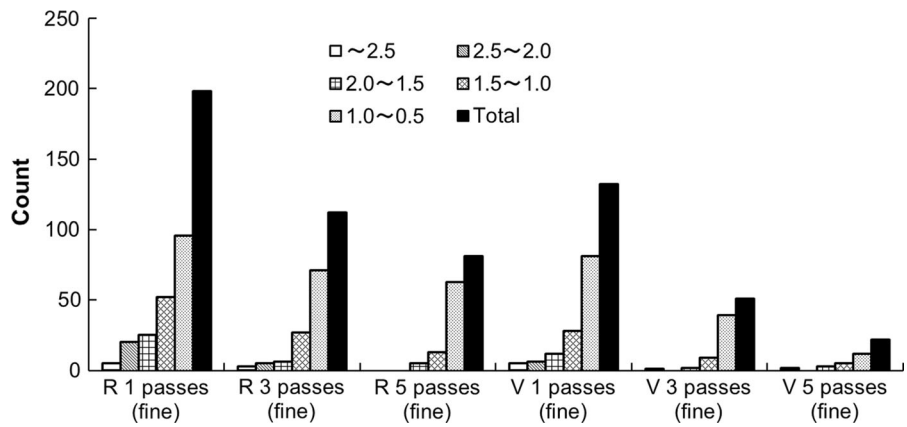

Fig. 6 Distribution of fiber length having more than 0.5 mm per 24 × 24 mm^2 under same concentration

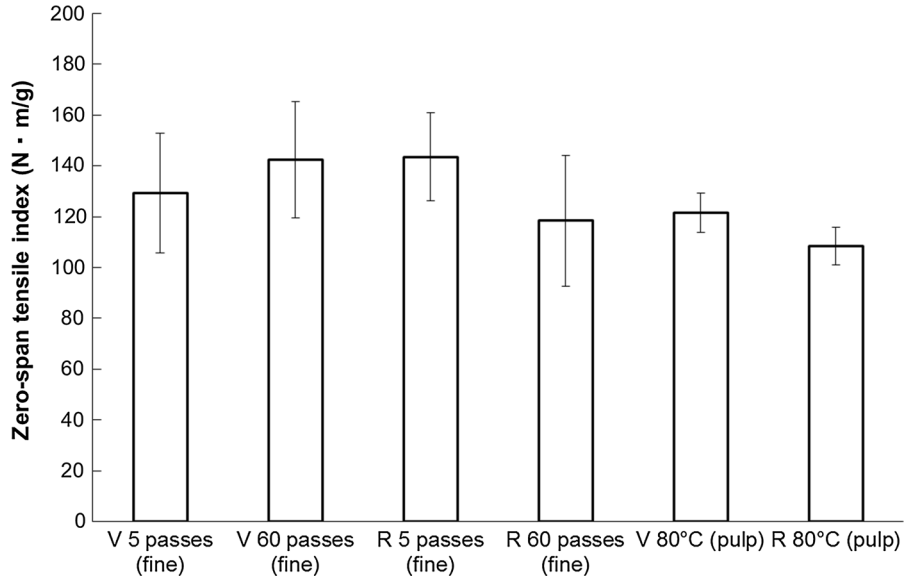

Fig. 7 Zero-span tensile index of the sheets

Furthermore, the densities of these sheets were lower than those of sheets composed of fine fibers prepared from virgin pulp using the ACC system and employing many collision passes. These results indicate that the high tensile strength sheets can be obtained from recycled pulp with little increase of the density.

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