# The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites

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**ABSTRACT** Fibrillated kraft pulp impregnated with phenolic resin was compressed under an extremely high pressure of 100MPa to produce high strength cellulose nanocomposites. To evaluate how the degree of fibrillation of pulp fiber affects the mechanical properties of the final composites, kraft pulp subjected to various levels of refining and high pressure homogenization treatments was used as raw material with different phenolic resin contents. It was found that fibrillation solely of the surface of the fibers is not effective in improving composite strength, though there is a distinct point in the fibrillation stage at which an abrupt increase in the mechanical properties of composites occurs. In the range between 16 and 30 passes through refiner treatments, pulp fibers underwent a degree of fibrillation that resulted in a stepwise increment of mechanical properties, most strikingly in bending strength, which increase was

attributed to the complete fibrillation of the bulk of the fibers. For additional high pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose's exposed surface area, and reached maximum value at 14 passes through the homogenizer.

**PACS:** 81.05.Lg; 81.05Qk

## 1. Introduction

It is well known that the mechanical properties of composites rely on those of the individual components and on their interfacial adhesion. Despite the good mechanical properties of natural fibers[1, 2], their true potential has not yet been fully exploited, most likely due to deficiencies in stress transfer ability among the components of fibrous composites. As a means of enhancing these interactions, fibers can be modified by physical methods that change their structural and surface properties. For example, in the case of pulp fibers for paper production, the bonding capability of fibers depends primarily on their flexibility and degree of fibrillation[3].

In our previous study[4], a new kind of high-strength composite was produced using a

cellulose with a nano-order-unit web-like network structure, called microfibrillated cellulose (MFC), and this composite was compared with kraft pulp-based composites manufactured following the same procedure. The two types of composites presented similar Young's moduli, but differed in strength; the MFC-based composites revealed superior toughness and strength due to higher elongation. As a result of its unique morphology, characterized by a nano-scalar web-like structure of interconnected fibrils and microfibrils, MFC allowed the manufacture of composites with mechanical properties rivalling those of commercial magnesium alloy (AZ91, T6 treated).

MFC is obtained through a mechanical treatment of pulp fibers, consisting of refining and high pressure homogenizing processes. The refining process used is common in the paper industry, and is accomplished via a piece of equipment called a refiner. In a disk refiner, the dilute fiber suspension to be treated is forced through a gap between the rotor and stator disks, which have surfaces fitted with bars and grooves, against which the fibers are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in the fibers, increasing their bonding potential by modification of their morphology and size[5].

In the homogenization process, dilute slurries of cellulose fibers previously treated by refining are pumped at high pressure and fed through a spring-loaded valve assembly.

As this valve opens and closes in rapid succession, the fibers are subjected to a large pressure drop with shearing and impact forces. This combination of forces promotes a high degree of microfibrillation of the cellulose fibers, resulting in microfibrillated cellulose (MFC)[6]. Microfibrillated cellulose (MFC) is a form of cellulose morphology developed by Turbak et al.[7] in the early 1980s.

The refining process is carried out prior to homogenization due to the fact that refining produces external fibrillation of fibers by gradually peeling off the external cell wall layers (P and S1 layers) and exposing the S2 layer[8], and also causes internal fibrillation that loosens the fiber wall, preparing the pulp fibers for subsequent homogenization treatment.

This study aims to clarify how the degree of fibrillation of pulp fibers affects the mechanical properties of high strength cellulose composites. It was found that the modulus and strength of composites do not depend linearly on water retention values, which characterize the exposed surface area of cellulose, but rather are determined by fiber morphology. Fibrillation of the surface of fibers had no discernible influence on the mechanical properties of highly compressed, phenolic resin-impregnated composites; they did not differ from those based on non-fibrillated pulp. Nonetheless, the complete disintegration of fibers after 30 passes through the refiner led to a sudden

and large rise, of about 50% over that of untreated pulp-based composites, in bending strength. Further homogenization treatment caused a linear increase in composite strength against water retention, achieving a maximum at 14 passes through the homogenizer.

## 2. Experimental

The starting material consisted of kraft pulp from Lodgepole Pine (*Pinus contorta*) (50%), White Spruce (*Pinus glauca*) (40%), and Douglas-fir (*Pinus menziesii*) (10%). Various degrees of fibrillation were obtained via physical treatment of kraft pulp; by several passes solely through a refiner, and by passes through a refiner and subsequently through a high pressure homogenizer. A 3% concentration pulp fiber slurry was passed 2, 4, 8, 16, and 30 times through a refiner with a gap of 0.1mm, and the last portion (30 passes through the refiner) was subsequently passed through a high pressure homogenizer 2, 6, 14, 22, and 30 times.

The degree of fibrillation of kraft pulp was evaluated indirectly by water retention, which was measured as moisture content after centrifuging 2% fiber content of treated pulp slurry at 1,000G for 15 minutes.

Fibrillated pulp was dissolved in water at a fiber content of 0.2% weight and stirred for 48 hours. A liter of the water suspension of MFC was vacuum filtered, producing a thin mat 185mm in diameter. Mats were oven dried at 70°C for 48 hours, then, in order to assure complete drying, they were further vacuum dried at 70°C for 5 hours, after which the weight was measured.

The dried mats of MFC were immersed in PF resin diluted in methanol, at concentrations suitable to obtain resin contents below 5%, 5 to 10%, and above 15%, as shown in Table 1. Immersed mats were maintained in reduced pressure at 0.03MPa for 12 hours, and kept at an ambient pressure at 20°C over 96 hours. Impregnated mats were taken out of the solutions, air-dried for 48 hours, cut into smaller circles 50mm in diameter, put in an oven at 50°C for 6 hours, then weighed again.

PF resin contents were calculated from the oven-dried dry weights before and after impregnation.

Finally, the small circles were stacked in layers of about 25 sheets, put in a circular metal dye 50mm in diameter, and hot pressed at 160°C for 30 minutes under a compressing pressure of 100MPa.

The phenol-formaldehyde (PF) resin used was a PL-2340, Mn=3,351, produced by Gun Ei Chemical Industry Co., Ltd.

Specimens having dimensions about 1.5mm thick, 45mm long, and 8mm wide were manufactured and subjected to a three-point bending test using Instron 4411. The span was set to 30mm, the crosshead speed to 5mm/min. Young's modulus (E) and bending strength ($\sigma_b$) were thus determined.

## 3. Results and discussion

The results for Young's modulus (E) and bending strength ($\sigma_b$) of composites as a function of degree of fibrillation of kraft pulp, depicted as water retention values, are presented in Figures 1 and 2, respectively. Water retention, a physical characteristic related to the exposed surface area of cellulose[7], serves as an approximate estimate of fibrillation. Although empirically manifest, it appears to be related to fibril and microfibril surface and volumetric phenomena[6]. A common value of water retention for papermaking pulp after beating using a PFI mill (one of the laboratory beaters commonly used to fibrillate and soften pulp) is approximately 150%, which is equivalent to 400 to 500ml Canadian Standard Freeness.

Each figure shows three different PF resin content conditions, at 2.4~3.9%, 6.8~10.5%, and 14.4~27.9%, respectively, with all samples compressed under 100MPa. This

compressing pressure was established based on a previous study[4] in which 100MPa yielded the best strength values for both pulp- and MFC-based composites.

All samples exhibited similar densities, with values in the 1.40~1.51g/cm$^3$ range, regardless of the degree of fibrillation or phenolic resin content.

There was not a significant change in Young's modulus in composites with higher resin contents (6.8~10.5% and 14.4~27.9%); it increased just slightly at more than 16 passes through refiner-treated pulps. However, a small step, noticeable in the case of composites with lower resin contents (2.4~3.9%), occurred between 16 and 30 passes through refiner-treated pulps, and divided the plottings into two distinct plateaus. This is also shown in Figure 3a, where some of the corresponding stress-strain curves are separated into two groups, one with lower (P, R8, and R16) and the other with higher Young's modulus (R30, H2, H6, H14, and H30).

Meanwhile, the bending strength showed a clear and substantial increase at the same point, with the change being more pronounced for lower resin content (2.4~3.9%) composites, at which it achieved a strength shift of about 50%, from around 200MPa of 16 passes through a refiner (R16) to around 300MPa for 30 passes through a refiner (R30). The stress-strain curves of Figures 3a and 3b show that the lower strength is due to a brittle failure behavior (P, R8, and R16), whereas the higher strength is due to

higher elongation before fracture (R30, H2, H6, H14, and H30). Beyond this point (R16 to R30), there was a linear increase in bending strength against water retention towards the 14-passes homogenizer-treated pulp, which reached the maximum and subsequently decreased for higher degrees of fibrillation.

Scanning electron micrograph observations of fibrillated pulp fibers revealed some interesting details about their morphology pertaining to the mechanical properties of composites. Fig. 4a shows the untreated starting material kraft pulp as single elementary fibers. With treatment consisting of 8 passes through a refiner (Fig. 4b), there are some signs of fibrillation, though this fibrillation is mainly restricted to the surface of the fibers, given that the dimensions of the original single fibers remain roughly the same. Although surface fibrillation is recognized as being effective for increasing interface interactions in conventional fibrous composites and most predominantly in paper[3], in the case of highly compressed composites, as illustrated by the bending strength values, it seems not to be a dominant factor. However, at treatment consisting of 16 passes through a refiner (Fig. 4c), these fibers are split apart into smaller bundles, and after an additional 14 passes through the refiner (i.e., 30 passes) (Fig. 4d), these small bundles are additionally separated into thinner fibril bundles, even though the water retention values do not change appreciably. Because water retention is related to the exposed

surface area of the cellulose, it provides an approximate means by which to express cellulose fiber's morphology. Nonetheless, this morphological change (which occurs between 16 passes and 30 passes through a refiner) was responsible for the sudden increment in strength of the composites. These results clearly indicate that it is not the fibrillation of the fibers surface but the disintegration of the bulk of the fibers that leads to an increase in composite toughness.

Given that the lower strength of composites based on pulp treated by fewer than 16 passes through refiner is predominantly due to a brittle fracture (Fig. 3a, b), it might be related to the presence of fiber defects that act as crack initiators, and the cracking might be abruptly propagated throughout the composite.

After additional homogenizing treatment consisting of 2 passes through the homogenizer (Figs. 4e and 5a), the previously separated tiny fibril bundles are expanded, creating small fibril aggregates that are fibrillated into even smaller aggregates as the number of passes through the homogenizer is increased, as suggested by the increasing water retention values. Hence, this added microfibrillation (formation of nano-order-scale interconnected fibrils and microfibrils) contributes to the increase in strength of the final composites; the maximum value was achieved at treatment consisting of 14 passes through the homogenizer (Figs. 3 and 5b). The gain in strength

is basically due to higher elongation (strain at yield), which is achieved only after whole fibrillation of the bulk of the fibers; these findings suggest that this fibrillation removes crack initiators, and at the same time expands the number of interfibrillar contacts, which hinders crack propagation. This crack-stopping mechanism relies on the unique morphology of the interconnected web-like structure of fibrils and microfibrils that are formed after complete disintegration of fibers.

Further passes cause a reduction of composite strength, though the corresponding morphological changes that occur in the microfibrillated cellulose are not discernible by SEM observations (Fig. 5c).

## 4. Conclusions

Highly compressed composites based on pulp treated by up to 16 passes through a refiner showed no improvements in mechanical properties as compared to those of composites based on untreated pulp because of a brittle fracture, which might be caused by rapid crack propagation that is not restrained by fibrillation of the fibers' surface. With composites based on treatment consisting of 30 passes through the refiner and those receiving additional high pressure homogenizing treatment, complete fibrillation

of the bulk of the fibers eliminated the weaker parts of the original fiber, which would act as crack initiators and simultaneously increase bond densities, which play a role in effective crack stopping. In short, only through disintegration of the whole fibers it is possible to achieve high strength in such composites.

**ACKNOWLEDGEMENTS.** The authors would like to thank Dr. T. Nishiwaki, Mitsubishi Chemical Group Science and Technology Research Center, Inc. – Analytical Services Division, Yokkaichi Laboratory, for support in taking the SEM photographs, and Daicel Chemical Industries for support in the refining and homogenizing treatments of kraft pulp. First author is also indebted to the support by a grant-in-aid from the Ministry of Education, Science, and Culture of Japan.

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**List of figure and table captions**

**Table 1** Resin contents achieved by impregnated mats (R. C.) with corresponding phenolic resin solution concentrations (S. Conc.).

**Fig. 1** Young's modulus of composites vs. water retention of kraft pulp with resin contents of 2.4~3.9%, 6.8~10.5%, and 14.4~27.9%, respectively. Plots labeled R relate to kraft pulp treated by refiner only, and those labeled H refer to kraft pulp additionaly treated by homogenizer after 30 passes through the refiner. Numerals denote the number of passes through the refiner or homogenizer.

**Fig. 2** Bending strength of composites vs. water retention of kraft pulp with resin contents of 2.4~3.9%, 6.8~10.5%, and 14.4~27.9%, respectively. Plot labeling is the same as that described in Fig. 1.

**Fig. 3** Selected stress-strain curves of composites based on kraft pulp exposed to different degrees of fibrillation with resin contents of: **a** 2.4~3.9%, **b** 6.8~10.5%, and **c** 14.4~27.9%, respectively.

**Fig 4** Scanning electron micrographs of: **a** kraft pulp; **b** 8 passes through refiner pulp; **c** 16 passes through refiner pulp; **d** 30 passes through refiner pulp; **e** 30 passes through refiner + 2 passes through homogenizer pulp. All pictures were taken under x500

magnification.

**Fig 5** Scanning electron micrographs of: **a** 30 passes through refiner + 2 passes through homogenizer pulp; **b** 30 passes through refiner + 14 passes through homogenizer pulp; **c** 30 passes through refiner + 30 passes through homogenizer pulp. All pictures were taken under x5,000 magnification.

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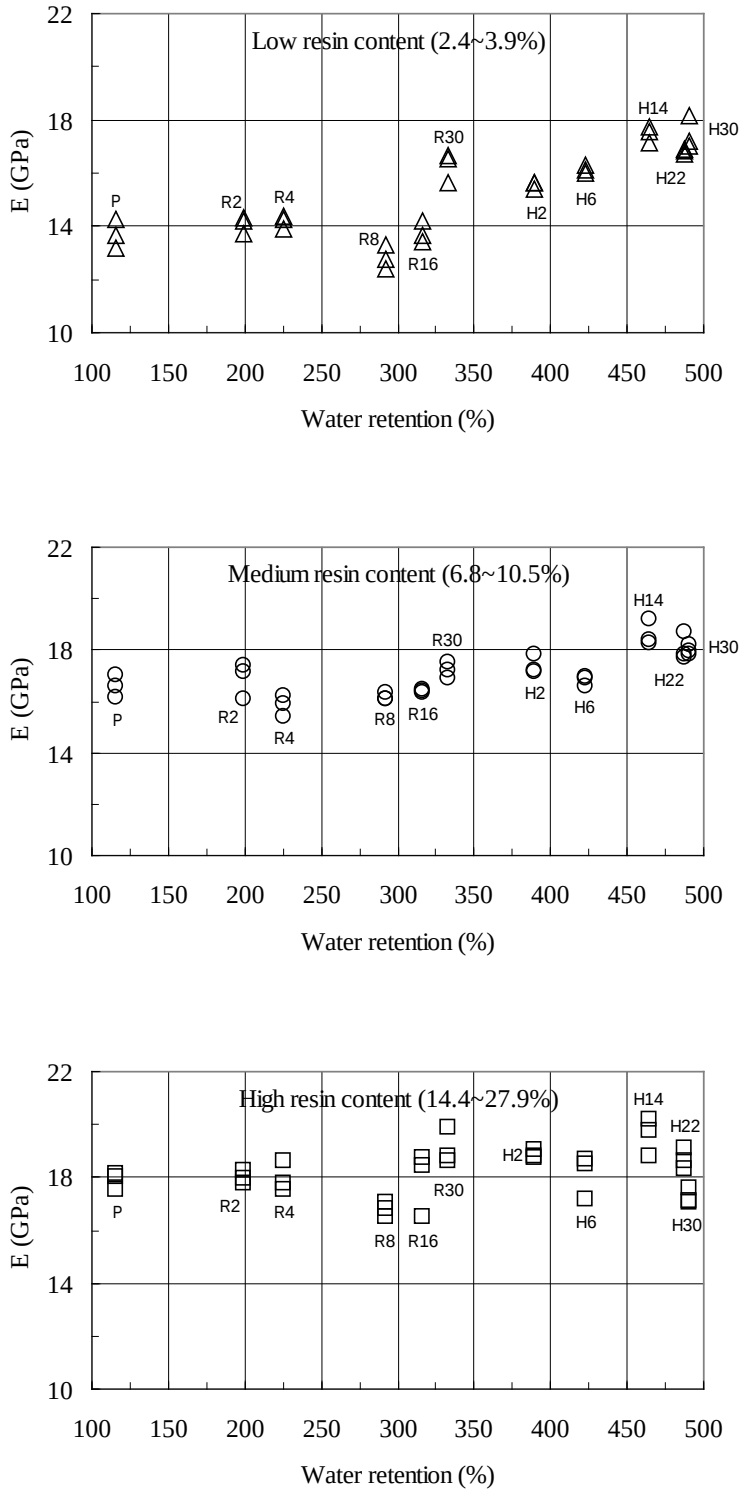
| Sample | Tratment | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Refiner** | **Homogenizer** | **S. Conc. (%)** | **R. C. (%)** | **S. Conc. (%)** | **R. C. (%)** | **S. Conc. (%)** | **R. C. (%)** |
| P | - | - | 0.7 | 3.9 | 2.6 | 10.5 | 7.4 | 23.2 |
| R2 | 2 passes | - | 0.7 | 3.5 | 2.6 | 9.8 | 7.4 | 22.2 |
| R4 | 4 passes | - | 0.7 | 3.2 | 2.6 | 8.4 | 7.4 | 19.7 |
| R8 | 8 passes | - | 1.2 | 3.4 | 5.5 | 8 | 17 | 20.1 |
| R16 | 16 passes | - | 1.2 | 3.1 | 5.5 | 7.2 | 17 | 14.4 |
| R30 | 30 passes | - | 2 | 2.9 | 10 | 9.4 | 25 | 26.5 |
| H2 | 30 passes | 2 passes | 2 | 2.5 | 10 | 8.9 | 25 | 22.2 |
| H6 | 30 passes | 6 passes | 2 | 2.6 | 10 | 8.3 | 25 | 23.5 |
| H14 | 30 passes | 14 passes | 2 | 3 | 10 | 10.2 | 25 | 27.9 |
| H22 | 30 passes | 22 passes | 2 | 2.8 | 10 | 7.4 | 25 | 24 |
| H30 | 30 passes | 30 passes | 2 | 2.4 | 10 | 6.8 | 25 | 18.9 |

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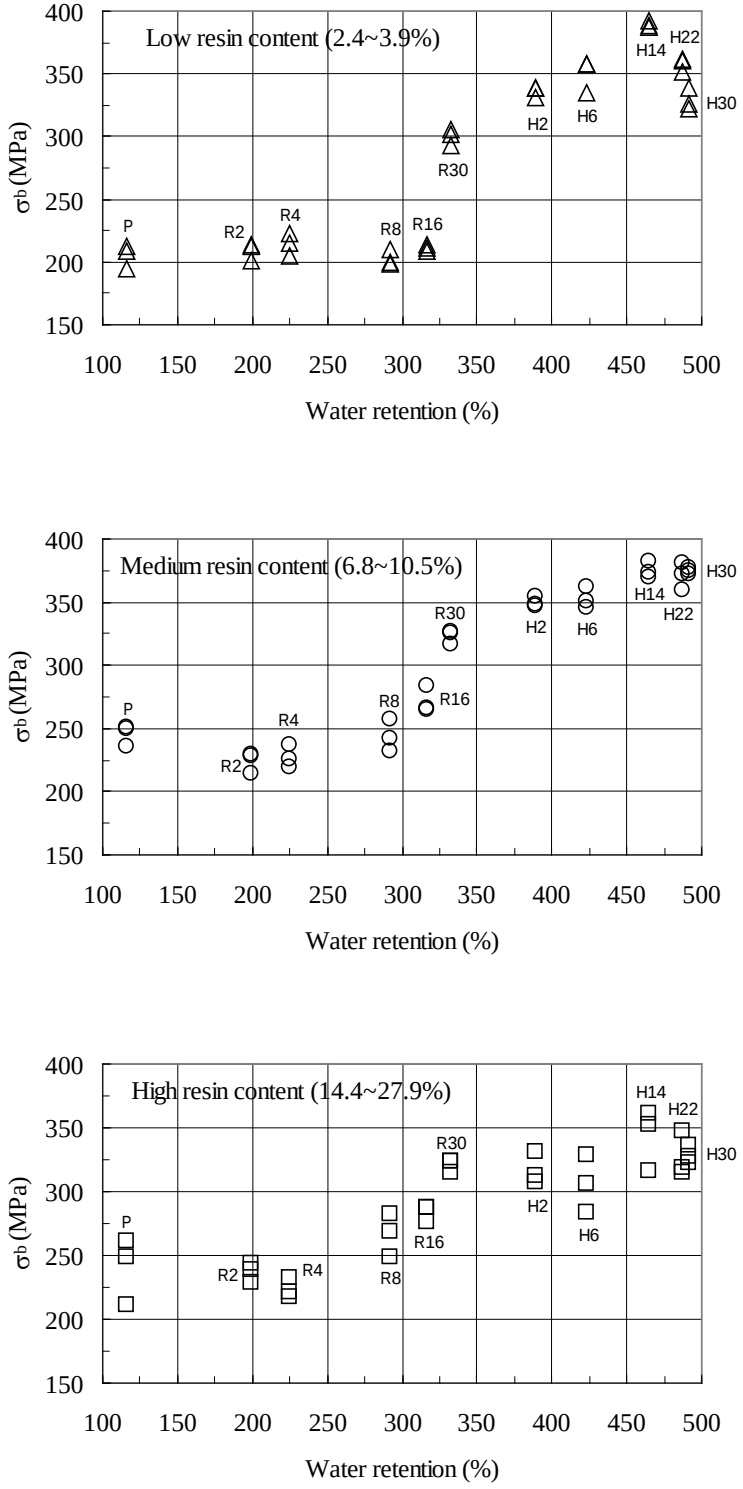


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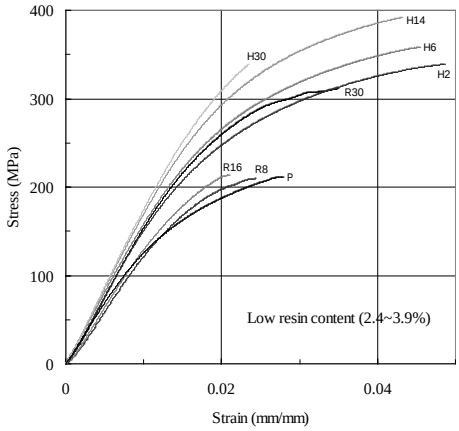


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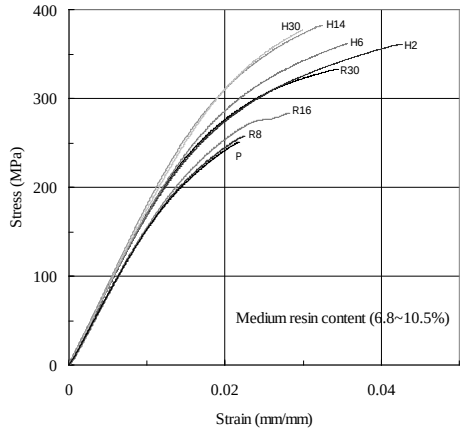


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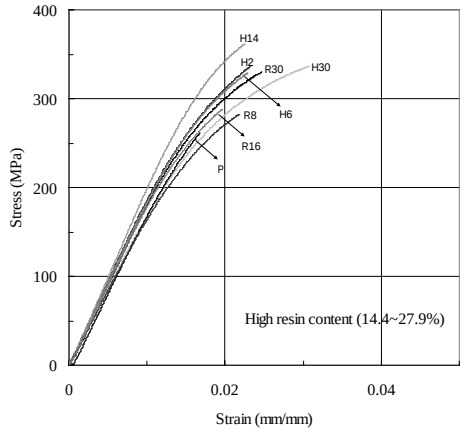


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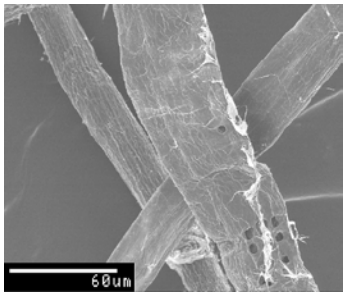


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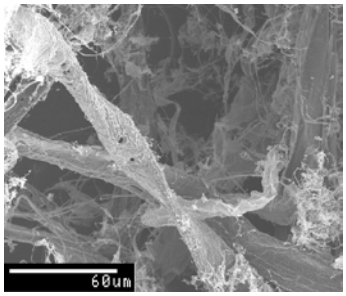


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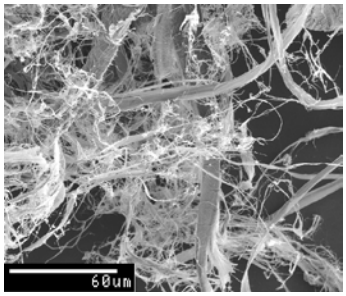


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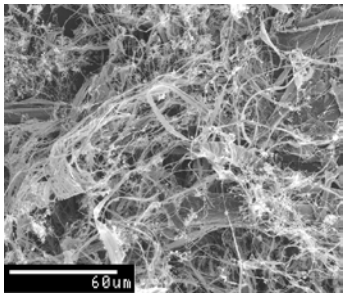

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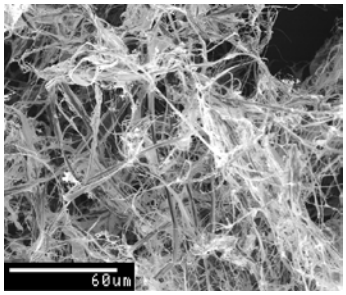


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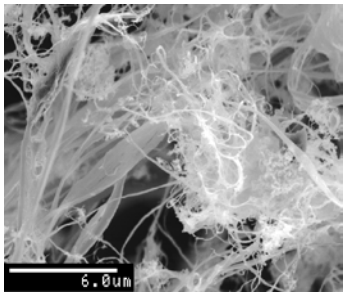


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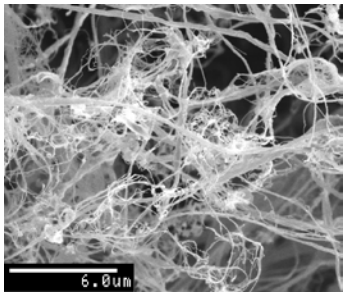


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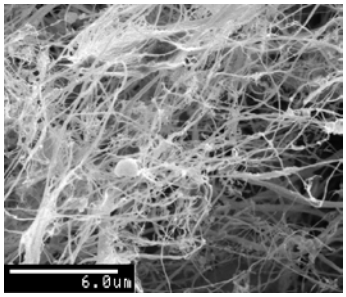


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