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Preparation and Characterization of Silk and Mulberry/Silk Papers

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Papers were prepared from cut cocoons and mulberry branches, which are byproducts from sericulture industry. The long filament of silk should be cut into appropriate length in order to prepare paper and this was achieved by chemical method. By a mixture of sodium hydroxide and sodium carbonate solution, the silk filaments were cut into short fibers (less than 1 mm in length). Since the short silk fibers (sSf) could not bind each other by itself, starch and poly(ethylene oxide)(PEO) were added as a bonding agent. When starch and PEO were used in a ratio of 3:7, the silk papers had optimum mechanical properties for paper. Fibers from the skin of mulberry branches (MBF) were added to sSf to enhance the mechanical properties of pure silk paper. Bleaching of MBF was performed with a mixture of hydrogen peroxide and sodium silicate. The mechanical properties were greatly enhanced and the optimum blend ratio of MBF and sSf were 7:3. The mulberry/silk paper has good absorption property against formaldehyde, and therefore, the paper could be applied as a wall paper for preventing the sick house syndrome.

Key words: Silk, Mulberry, Paper, Formaldehyde removal, Sick house syndrome

Introduction

Korean sericulture farmers produce *Cordyceps* named as Dong-chung-ha-cho from silkworms. The fungi are inoculated to the silkworm during the 5th instar and fruit bodies are grown on the pupae of silkworm. The fruit bodies of *Cordyceps* have anti-tumor and immuno-stimulating activities, and therefore, it is a highly valuable health food (Shin *et al.*, 2003). In order to harvest the fruit bodies of *Cordyceps*, the cocoon should be cut to collect the infected pupae. However, once the cocoon had been cut, it could not be used as a textile material. Currently, the only use of these cut cocoons are as a raw material of silk fibroin powder. On the other hand, mulberry branches are also produced during the sericulture. For a successful sericulture, the branches of mulberry should be pruned in an appropriate way to maintain the quality of mulberry leaves. As a result, a lot of mulberry branches are pruned during sericulture but there are no any specific applications of these pruned branches. Finding more valuable application of these byproducts, cut cocoons and mulberry branches, may create new revenues to the sericultural farmers.

Many people are interested in well-being life and it has become one of the trends in our society (Godoy *et al.*, 2005). From this viewpoint, people are more interested in natural products than in synthetic products. Most of natural products are free from the problematic substances such as volatile organic compounds (VOCs), endocrine disruptor, carcinogenic substance etc. Therefore, substitution of synthetic materials to natural materials is on progress in many fields. For example, Han-ji, Korean traditional paper made from paper mulberry, is used as wall papers in many houses for the substitute of synthetic wall papers to reduce "sick house syndrome." Sick house syndrome is the result of synthetic materials that are used for the construction of building. Such materials have many VOCs that are emitted for a period after construction (Yu and Crump, 1998; Sundell, 2004). By substituting the synthetic wall papers with Han-ji, it is expected that the symptoms of sick house syndrome could be reduced.

Han-ji is made from paper mulberry, *Broussonetia kazinoki*. Both mulberry and paper mulberry are in the same family, *Moraceae*. This came to us for an idea to make

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papers with mulberry fibers, and add it to silk paper. Previously, Kang *et al.* (1999) had prepared a paper made from silk fiber and paper mulberry. However, they did not succeed to prepare pure silk paper due to harsh condition. The length of fiber was too short; it was more likely particle rather than fiber. In addition they did not use any bonding agent, and therefore, they failed to prepare a pure silk paper.

The objective of this study is to prepare silk and mulberry/silk paper with the byproducts from sericulture, cut cocoons and mulberry branches. Their mechanical properties were characterized and some useful functionality of these papers was investigated.

Materials and Methods

Materials

The cut cocoons are kindly provided from Hung Jin Co. (Yongin, Korea) and the mulberry branches are collected from mulberry field of Seoul National University in May, 2004. All chemicals are purchased from Sigma-Aldrich LTD. (Yongin, Korea).

Methods

Fabrication of Silk Filaments into Short Silk Fibers (sSf) The cut cocoons are previously degummed in order to remove sericin. The cocoons were immersed in distilled water and kept for an hour at 120°C. Fabrication of Silk Filaments into Short Silk Fibers (sSf) was done with 0.5 wt% of sodium hydroxide and 4 wt% of sodium carbonate solution. Twenty grams of degummed cut cocoons were immersed to the solution for 30 min, which previously adjusted to 80°C. Finally, it was filtered with nonwoven filter (Miracloth, USA) and washed at least 5 times with water. The collected sSf were dried in an oven for 2 days.

Preparation of mulberry fibers

The skins of mulberry branches were peeled off right after collection and stored at room temperature. The stored skins of mulberry branches were immersed in warm water for overnight before use. The brown outer skins were peeled off with knife and only the inner skins were collected.

The inner skins of mulberry branches (MB) were fibrillated and bleached with chemicals. Hydrogen peroxide and sodium silicate were used for this purpose. A predetermined amount of hydrogen peroxide and sodium silicate were added to 1 L of water containing 10 grams of MB and it was boiled for an hour. After several times of washing, the bleached mulberry fibers (MBF) were dried in an oven.

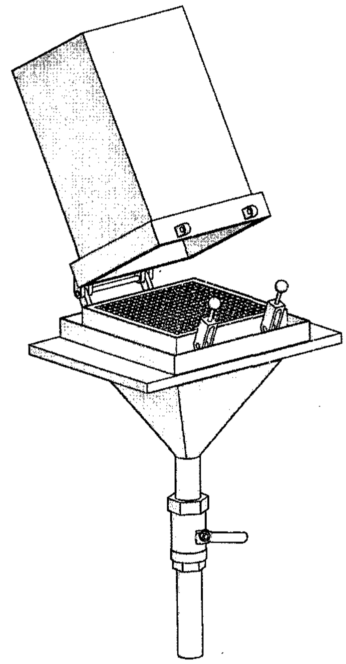


Fig. 1. Scheme of paper manufacturing machine.

Preparation of Paper

We have prepared a simple paper machine like in Fig. 1. The upper part of the machine contains fibers, sSf and/or MBF, that are suspended in water. A metal mesh is placed between the upper part and lower part. When the cock of lower part opens, the fibers will be collected on the metal mesh in a form of paper and dried under pressure. Each paper was prepared as follows.

Pure Silk Paper: In order to bond the sSf together, starch and polyethylene oxide (PEO, MW 200,000) were used as a bonding agent. The sSf were suspended in 5 L of water containing 5 wt% of bonding agent.

Mulberry/Silk Paper: Mulberry/Silk papers were prepared without any bonding agent. MBF were immersed in water for overnight and fibrillated further with a cutting mill. Appropriate amounts of sSf and MBF were added to 5 L of water. The mixed fibers in water were mixed thoroughly, until the fibers were dispersed evenly in water.

Measurement of Mechanical Properties

Tensile, tearing and bending properties were measured with Lorentzen & Wetter tester. The size of specimen for each measurement was different. For tensile, tearing, and bending, the size of each specimen was 3 × 1 cm, 7 × 6 cm, and 5 × 3.8 cm, respectively. All strengths are normalized to its grammage, grams per square meter.

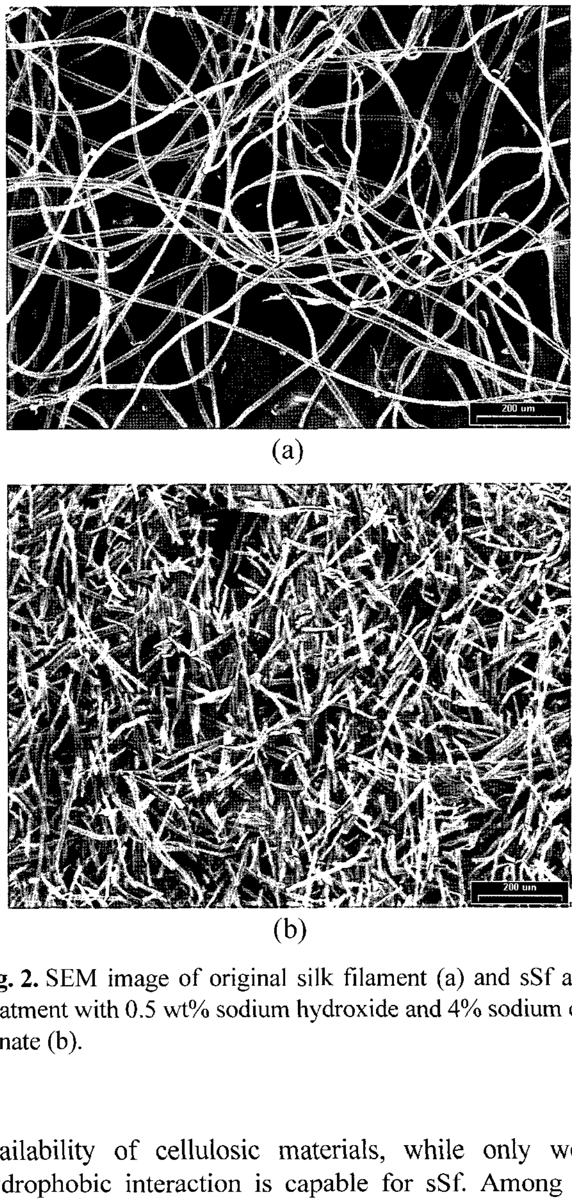
Removal Efficiency of Formaldehyde

The amount of absorbed formaldehyde was measured according to KS F3104 with slight modification. In a 50 ml conical tube, 10 ml of water were added and the paper was hung above the water with a thread. The weight of paper was 1g for each specimen. At the same time, an Eppendorf tube containing 500 μl of formaldehyde solution (36.5%) was also hung in the same conical tube. The conical tube was sealed and kept at room temperature for 12 hours. Finally, the water beneath were collected and the concentration of formaldehyde were measured as follows. At first, 150 g of ammonium acetate was dissolved in 800 ml of distilled water, and 3ml of glacial acetic acid and 2 ml of 2, 4-pentanedione were added. The solution was adjusted further with distilled water to 1 L and stored in amber bottle. Five hundred microliter of the collected water from the conical tube were mixed with the same amount of above solution and heated for 10 min at 60°C. The change of color was measured with UV-Vis spectrometer (Optizen 2120UV, Korea) at 415 nm.

Results and Discussion

Fabrication of Silk Filaments into Short Silk Fibers (sSf)

In order to prepare the silk paper, the long filament of silk should be cut into appropriate length, and at the same time, the short fibers should be dispersed evenly in water to get a paper of good quality. At first, we cut the degummed cocoon with scissors into 1 cm, but it could not be dispersed evenly. The fibers aggregated each other due to its hydrophobic nature. Therefore, we tried to use chemical method to cut the silk filaments into short silk fibers (sSf). Since silk are prone to alkaline solution, sodium hydroxide was chosen. Sodium carbonate was added to reduce the hydrolysis rate of silk filament. When the concentration of sodium hydroxide increased, the reaction time was reduced but the yield of sSf reduced. On the other hand, when the concentration of sodium carbonate was increased, the yield of sSf increased but it took too long time to accomplish the reaction or failed to get sSf (data not shown). The optimum concentrations of both chemicals were 0.5 wt% for sodium hydroxide and 4 wt% for sodium carbonate. Fig. 2 shows the SEM image of final sSf that are obtained after reaction with optimum condition. The average length of sSf was about 200 μm and the yield of sSf was 70%.

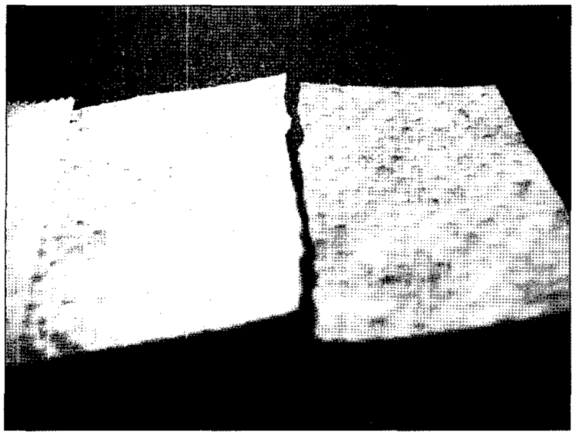


(a) (b)

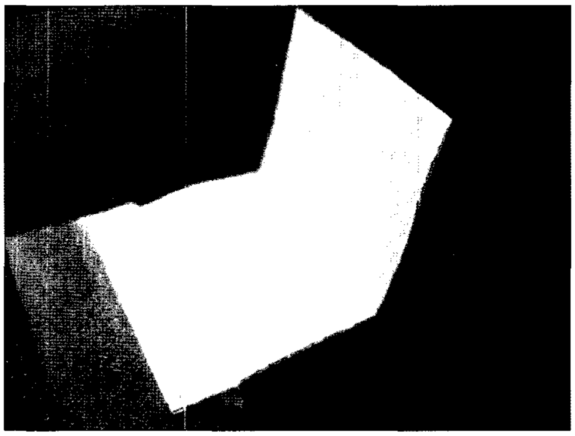
Fig. 2. SEM image of original silk filament (a) and sSf after treatment with 0.5 wt% sodium hydroxide and 4% sodium carbonate (b).

Preparation and Characterization of Silk Paper

The sSf could not bond each other without any bonding agent. By contrast, common papers made from cellulosic materials did not need any bonding agent unless specific properties are needed. This is due to hydrogen bonding availability of cellulosic materials, while only weak hydrophobic interaction is capable for sSf. Among the bonding agent, we utilized starch in order to bond sSf into paper. When pure starch (St100) was used, the paper was stiff but brittle. This brittleness made it unable to be folded (Fig. 3a). Starch is consisted of amylose and amylopectin. Amylose is a linear polymer where glucose units are linked through α-1, 4-glucoside linkage. On the other hand, amylopectin is a branched polymer where another polymer chain is linked to C6 position of glucose unit of main chain. When the content of amylopectin increases, the overall stiffness of starch also increases (Tester *et al.*, 2004). Therefore, the brittleness of St100 might be due to the amylopectin of starch. In order to reduce the brittleness of starch, some linear polymers were blended with starch (Wang *et al.*, 2003). We have chosen PEO as a linear polymer, since we found that PEO (MW 200,000) could be adopted as bonding agent of sSf (data not



(a)



(b)

Fig. 3. Photographs of folded silk paper prepared from different bonding agent; (a) St100 and (b) P70St30. St100: starch 100%; P70/St30: PEO 70% and starch 30%.

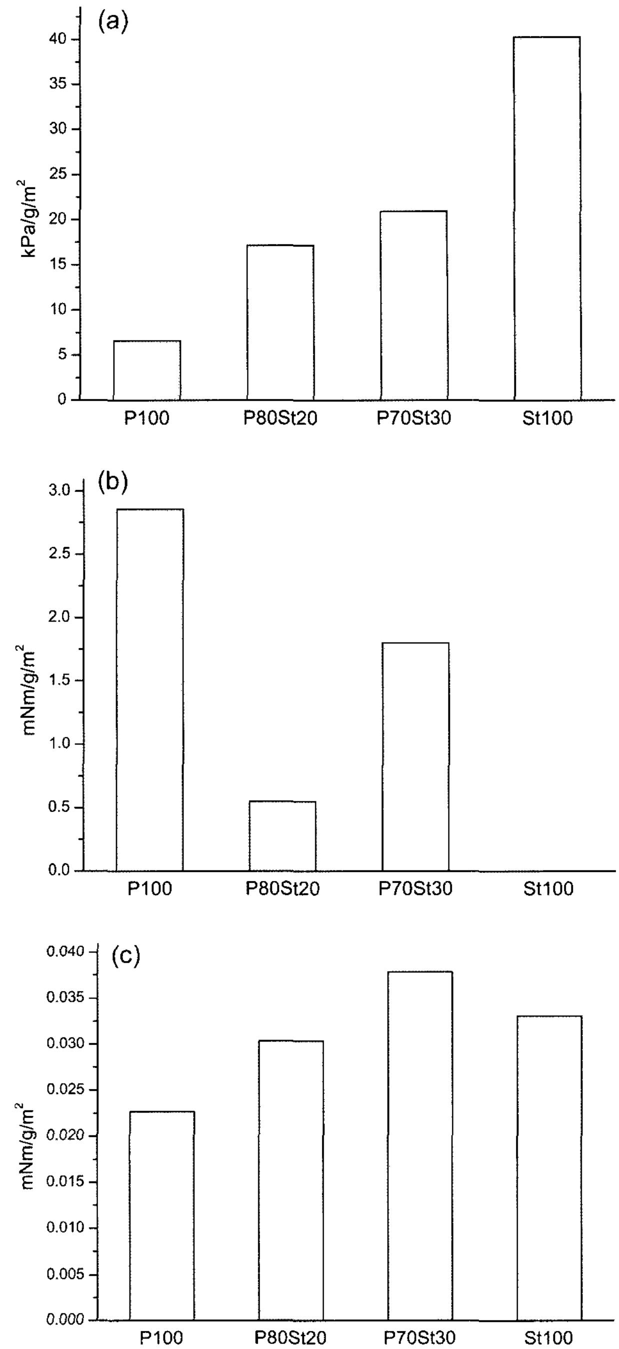
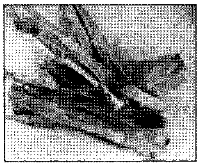
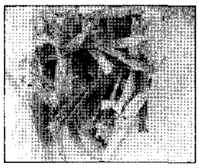
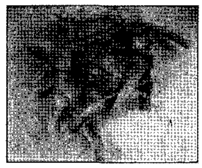
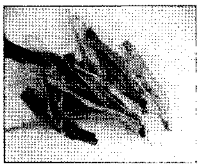
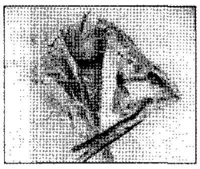
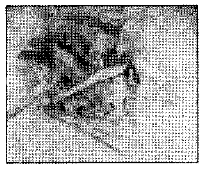
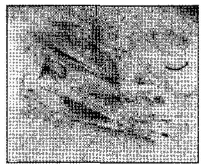


Fig. 4. Mechanical properties of silk paper prepared with different bonding agent; (a) tensile, (b) tearing, and (c) bending strength. P100: PEO 100%; P80/St20: PEO 80% and starch 20%; P70/St30: PEO 70% and starch 30%; St100: starch 100%.

shown). The addition of linear PEO relatively reduces the content of amylopectin in the bonding agent. When the PEO were added, the paper became flexible and could be folded (Fig. 3b).

The tensile, tearing, and bending strength of silk paper measured to characterize its properties (Fig. 4). When only starch (St100) was used as bonding agent, it had the highest tensile strength but the tearing strength could not be measured due to its brittleness. Meanwhile, when only PEO (P100) was used as bonding agent, it showed the highest tearing strength but the lowest tensile strength. By combination of these two polymers, we could obtain suitable mechanical properties for paper. As the content of starch increases, all mechanical strengths are increased due to the increase of amylopectin contents. In the case of bending strength (Fig. 4c), St100 showed high bending strength even though its brittleness. This is due to the definition of bending strength. The bending strength is determined as the resistance force of specimen when it is bended to only 5°. Although, the silk paper made from starch was brittle, it could bear a little distortion. From these results we found out that the optimum mixing ratio between PEO and starch is 7:3 for silk paper.

Table 1. Bleaching of mulberry inner skin fibers using hydrogen peroxide and sodium silicate.

Sodium Silicate (%)	0.1	0.2	0.4	0.8
Hydrogen Peroxide 10%				
Hydrogen Peroxide (%)	2.5	5.0	10.0	20.0
Sodium Silicate 0.4%				

Preparation and Characterization of Mulberry/Silk Paper

Even though pure silk paper was prepared successfully, the properties of paper needed to be improved in order to apply it as a wall paper. Therefore, mulberry fibers were added to silk paper. The collected inner skin of mulberry branches (MB) had brown color which should be bleached before use. We utilized two powerful bleaching agent, hydrogen peroxide and sodium silicate (Table 1). When each bleaching agent were used separately, neither was effective. However, by mixing these two bleaching agents, the brown color of MB changed to white color. Increasing the content of hydrogen peroxide was more effective than sodium silicate. For further experiments, a mixed solution of 10% of hydrogen peroxide and 0.4% of sodium silicate were used for bleaching the MB.

The mulberry/silk paper could be prepared without any bonding agent. Since the MBF is longer than the sSf, sufficient entanglement occurred between the MBF. The mechanical properties were shown in Fig. 5. The mechanical strength of mulberry paper (M100) was far greater than the silk paper (S100). As indicated previously, cellulosic fibers are able to form strong hydrogen bonding, and furthermore, it has longer fiber length compared to sSf. Therefore, there might be much stronger interactions between MBF than between silk fibers. By mixing sSf (S33M67 and S25M75), the mechanical strength decreases significantly but it was still better than silk paper. However, the mechanical strength was not proportional to the content of MBF. When the content of MBF was 67% (S33M67), it had better mechanical properties than S25M75, where the content of MBF was 75%. During the preparation procedure, we found that when the content of MBF increases to some extend, they agglomerated to each other rather than mixing homogenously with sSf. It means that a kind of phase separation had occurred between MBF and sSf. In such situation, each separated phase show their own properties, and in this case, the sSf phase

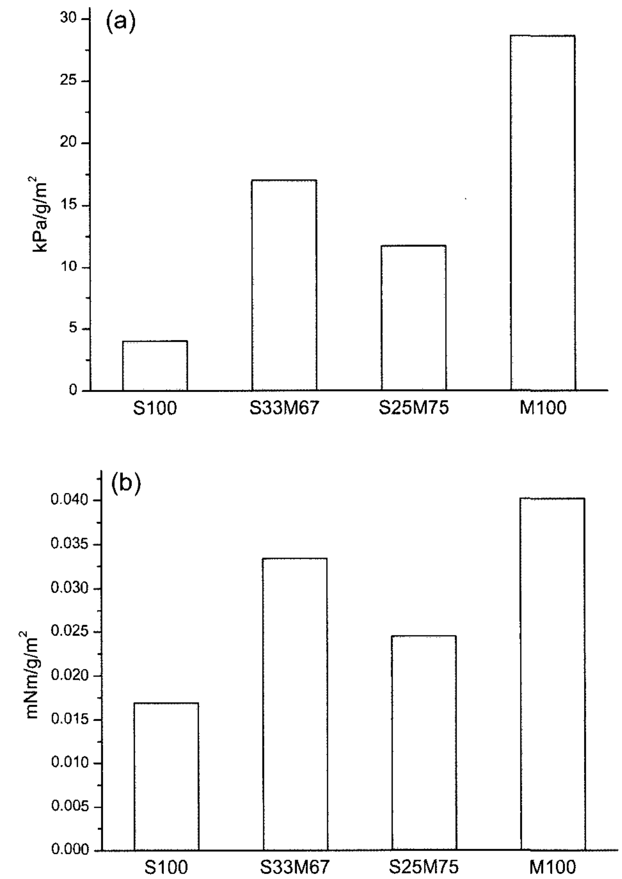


Fig. 5. Mechanical properties of mulberry/silk paper prepared with blending ratio; (a) tensile and (b) bending strength. S100: sSf 100%; S33M66: sSf 33% and MBF 67%; S25M75: sSf 25% and MBF 75%; M100: MBF 100%.

Table 2. Formaldehyde removal efficiency of silk and mulberry/silk papers

Sample[a]	A_{415}	Removal efficiency (%)	Specific removal efficiency[b]
Control	0.70	-	-
S100	0.28	65.3	3.60
S33M67	0.27	67.3	4.40
S25M75	0.33	58.1	2.83
M100	0.35	55.8	3.12
Commercial Paper	0.39	50.6	1.43

a: S100: sSf 100%; S33M66: sSf 33% and MBF 67%; S25M75: sSf 25% and MBF 75%; M100: MBF 100%.
b: Removal efficiency divided by the area of specimen.

breaks or tears earlier than the MBF phase. However, when the content of MBF reduced, the phase separation did not occur. Therefore, S33M67 shows better properties than S25M75 because they mix more homogeneously.

Removal of Formaldehyde by Mulberry/Silk Paper

Sick house syndrome is much related to VOCs from various substances that are used during the house manufacture (Yu and Crump, 1998). Formaldehyde is the major and serious substance among VOCs. Therefore the ability of formaldehyde absorption was measured with silk and mulberry/silk papers (Table 2). The removal efficiency of silk and mulberry/silk papers was far greater than common papers. The S33M67 absorbed 3 times greater than common papers. Silk paper showed better ability to absorb formaldehyde than mulberry paper. Since silk are protein, they have much more reactive site such as amino and hydroxyl groups than MBF, which has only hydroxyl groups. In the case of S25M75, however, it showed least absorbency than other specimen. This is because of there phase separation as mentioned previously. Since the fibers are entangled to each other with their own components, it has less specific area than the other samples, where the fibers were mixed more evenly.

In conclusion, the silk filaments from cut cocoons could be fabricated into sSf by chemical method. By using starch and PEO as a bonding agent, pure silk paper could be prepared with sSf. In order to increase the mechanical properties of silk paper, MBF were added to silk paper. Bleaching of MB was achieved with a mixture of hydrogen peroxide and sodium silicate. The mulberry/silk paper had good mechanical properties compared to silk paper and it could be used as wall papers, which has ability to absorb formaldehydes.

Acknowledgements

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