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The Improvement in Functional Characteristics of Eco-friendly Composites Made of Natural Rubber and Cellulose

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Abstract. We investigated the efficient use of cellulose to resolve the problem of the depletion of fossil resources. In this study, as the biomass material, the green composite based on natural rubber (NR) and the flake-shaped cellulose particles (FSCP) was produced. In order to further improvement of functional characteristics, epoxidized natural rubber (ENR) was also used instead of NR. The FSCP were produced by mechanical milling in a planetary ball mill with a grinding aid as a cellulose aggregation inhibitor. Moreover, talc and mica particles were used to compare with FSCP. NR and ENR was mixed with vulcanizing agents and then each filler was added to NR compound in an internal mixer. The vulcanizing agents are as follows: stearic acid, zinc oxide, sulfur, and vulcanization accelerator. The functionalities of the composites were evaluated by a vibration-damping experiment and a gas permeability experiment. As a result, we found that FSCP filler has effects similar to (or more than) inorganic filler in vibration-damping and O_2 barrier properties. And then, vibration-damping and O_2 barrier properties of the composite including FSCP was increased with use of ENR. In particular, we found that ENR-50 composite containing 50 phr FSCP has three times as high vibration-damping property as ENR-50 without FSCP.

Keywords: Natural Rubber, Cellulose, Composites, Vibrasion-damping, Gas Barrier
PACS: 81.05.Lg

INTRODUCTION

The depletion of fossil resources has become crucial problems. One important way to address this problem is through the replacement of fossil resources with “sustainable” biomass resources, which has been investigated in this research. Cellulose is one of the most abundant biomass resources on earth and it has lower density (1.5 g/m^3) than other inorganic filler [1]. Additionally, the cellulose as the wood-based biomass does not compete against food production. There is a large amount of biomass which is not yet used efficiently in Japan. For this reason, there is a great need to develop ways to effectively utilize and benefit from this enormous supply. So we developed to find effective use of cellulose: the FSCP. The FSCP were produced by mechanical milling in a planetary ball mill with a grinding aid as a cellulose aggregation inhibitor [2]. As a result, these have a platelet shape like talc and mica. There are some research that the composites including these fillers were improved vibration-damping and gas barrier properties because of having the large surface area [3], [4]. And then, it was reported that the gas barrier property of NR was improved by addition of cellulose whisker [5]. Therefore, the composite including the FSCP was expected to improve vibration-damping and gas barrier properties. In this study, as the biomass material, the green composite based on NR and FSCP was produced. Vulcanizing agents of the rubber composite are as follows: stearic acid, zinc oxide, sulfur, and vulcanization accelerator. NR was mixed with vulcanizing ingredients and then each filler in an internal mixer. The functionalities of the composites were evaluated by a vibration-damping experiment and a gas permeability experiment. And functionalities of the composite including the FSCP was compared to the composite with talc or mica particles. Moreover, in order to further improvement of vibration-damping property and gas barrier property, ENR was used instead of NR.

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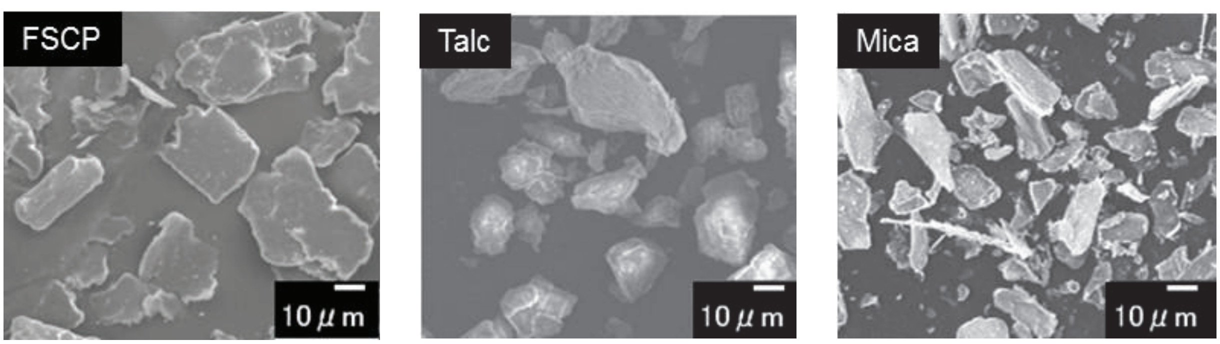
EXPERIMENTAL

Materials

Fibrous cellulose was made from wood pulp (W400, Nippon Paper Chemicals Co., Ltd., Japan). FSCP were obtained by mechanically milling the fibrous cellulose in a planetary ball mill with a grinding aid as a cellulose aggregation inhibitor. Talc particles were kindly offered by Nippon Talc Co., Ltd. (Japan). Mica particles were kindly offered by Shiraishi Kogyo Kaisha, Ltd. (Japan). **FIGURE 1** shows scanning electron microscope (SEM) pictures of each filler. As seen in this image, the FSCP were fine flake shape, similar to talc, mica, etc. Average particle sizes of the FSCP, talc, and mica were about 22 μm, 21 μm, and 24 μm respectively. The matrix rubbers were NR, and ENR. NR was Ribbed Smoked Sheet Grade 1. In addition, ENR with 50 mol% epoxidation (ENR-50) and 70:30 blend of NR/ENR-50 were used. Vulcanizing agents are as follows: stearic acid, zinc oxide, sulfur, and vulcanization accelerator (BBS; N-tert-butyl-2-benzothiazyl sulfenamide). The formulations used in this study are shown in **TABLE 1**.

TABLE 1. Compounding formulations

Agents	[phr]
NR	100.0
Zinc oxide	6.0
Stearic acid	0.5
Sulfur	3.5
Vulcanization accelerator	0.7
FSCP or Talc or Mica	20.0 or 50.0



(a) FSCP (b) Talc (c) Mica

FIGURE 1. Scanning electron microscopy (SEM) observation of (a)FSCP, (b)Talc, and (c)Mica

Preparation of the Composites

NR and each filler were mixed with the ingredients in an internal mixer (10C100 Labo Plastomill, Toyo Seiki Seisaku-sho, Ltd., Japan). The mixing parameters are as follows: fill factor is 0.7, mixing temperature is 60 ℃, and rotation speed is 30 rpm. The mixing time is decided by integrated energy and its value is 1600 MJ/m^3. First, NR was masticated until the value of integrated energy reached about 600 MJ/m^3. Second, it was mixed with the vulcanizing ingredient until the value reached about 700 MJ/m^3. Finally, they were mixed with each filler until the value reached 1600 MJ/m^3.

Preparation of the Sheet of Composites

Sheets of composites were prepared by a compression molding method. The size of sheets was adjusted by using molds. The composites were pressed using a compression molding machine (NF-50 Automatic Molding Press, Shinto

Metal Ind., Ltd., Japan) at 150 ℃ and 10 MPa. The respective cure times at 150 ℃ was determined using a rubber cure meter (curelastometer V, Orientec Co., Ltd., Japan).

Vibration-damping Experiment

Vibration-damping experiments were carried out by damping tester (cantilever-beam-damping test device, B&K) according to JIS K 7391 (test methods for vibration-damping property in damped composite beam of unconstrained type) with cantilever-beam-type test specimens at 20 ℃. Test specimens were made by bonding the composite sheet and a straight steel sheet with double-sided tapes (**FIGURE 2**); the composite sheet was 220 × 10 × 2 mm, and the steel sheet was 260 × 10 × 1 mm respectively. The experiment was carried out three specimens of each composite. Loss factor (η) was calculated from frequency response function by using the following Eq. 1:

$$\eta = \frac{f_2 - f_1}{f_0} \tag{1}$$

where f_0 is the resonance frequency, f_1 and f_2 are the frequencies that are three decibel smaller than the peak frequency response function value.

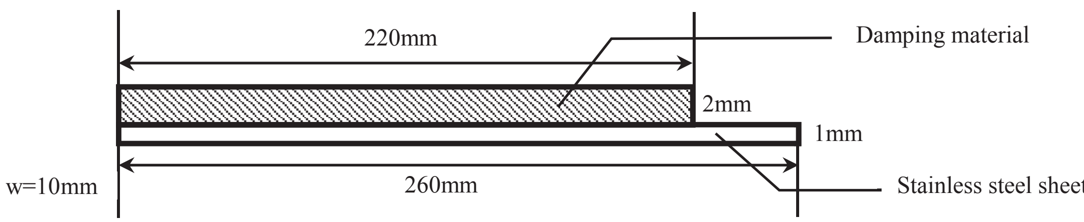


FIGURE 2. Unconstrained type test specimens used in the vibration-damping test.

Gas Permeation Experiment

Gas permeation experiments were carried out for O_2 at 20 ℃ with a gas permeation tester (GTR tester M-C3, Toyo Seiki Seisaku-sho, Ltd., Japan). The permeation cell was separated one above the other by the composite sheet. The upper was full of oxygen, and the under was vacuated. The Gas barrier properties of composites were evaluated by permeability coefficient expressed in [barrer] unit; 1[barrer] = 10^{-10} [cm^3 ・ cm/(cm^2 ・ s ・ cmHg)]. Then, we calculated the permeability coefficient from the measured gas permeability. The composite sheets were 100 mm in length, 100 mm in width, and 0.5 mm in thickness. To remove the volatile constituent of composite sheets, they were set in the vacuum dryer at 60 ℃ for 4 hours before the measurement.

RESULTS

Vibration-damping Properties of Composites

FIGURE 3 shows η value of pure NR and the composites containing 20 phr each filler (FSCP, talc, and mica). According to **FIGURE 3**, the composite including FSCP had the highest η value; that is, vibration-damping property of the composite including FSCP is superior to those including talc or mica. And **FIGURE 4** shows loss factor vs FSCP loading for FSCP reinforced each rubber matrix (NR, NR(70)/ENR-50(30), and ENR-50). As a result, vibration-damping properties of the composite including FSCP was increased with use of ENR. In particular, we found that ENR-50 composite containing 50 phr FSCP has three times as high vibration-damping property as ENR-50 without FSCP.

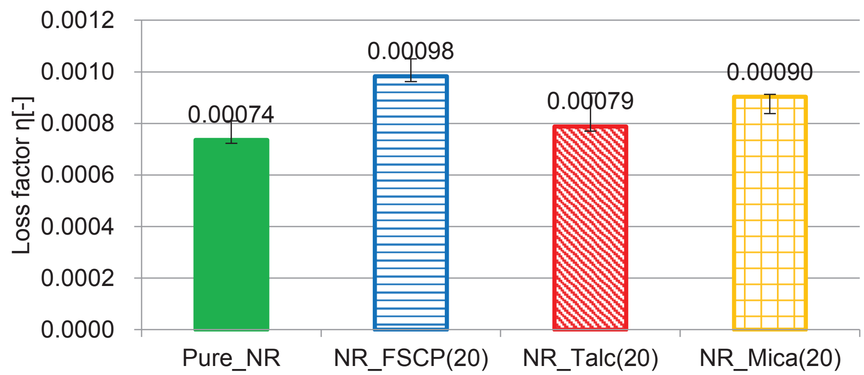


FIGURE 3. Comparison of loss factor between pure NR and the composites containing 20 phr each filler.(FSCP, Talc, or Mica)

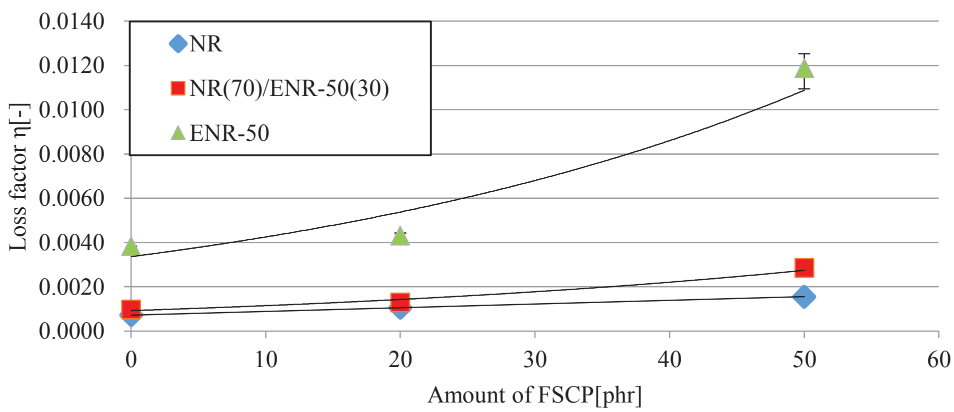


FIGURE 4. Loss factor vs FSCP loading for FSCP reinforced NR(◆), NR(70)/ENR-50(30)(■), or ENR-50(▲)

Gas Barrier Properties of Composites

FIGURE 5 shows O_2 permeability coefficient of pure NR and the composites containing 20 phr each filler (FSCP, talc, and mica). The gas barrier property is better when O_2 permeability coefficient shows lower value. According to **FIGURE 5**, the O_2 barrier property of the composite containing FSCP was comparable to the composites containing inorganic fillers. And **FIGURE 6** shows O_2 permeability coefficient vs FSCP loading for FSCP reinforced each rubber matrix (NR, NR(70)/ENR-50(30)). We found that the gas barrier property was improved by 70:30 blending of NR/ENR-50. Moreover, the property was further improved by adding FSCP to the blend rubber.

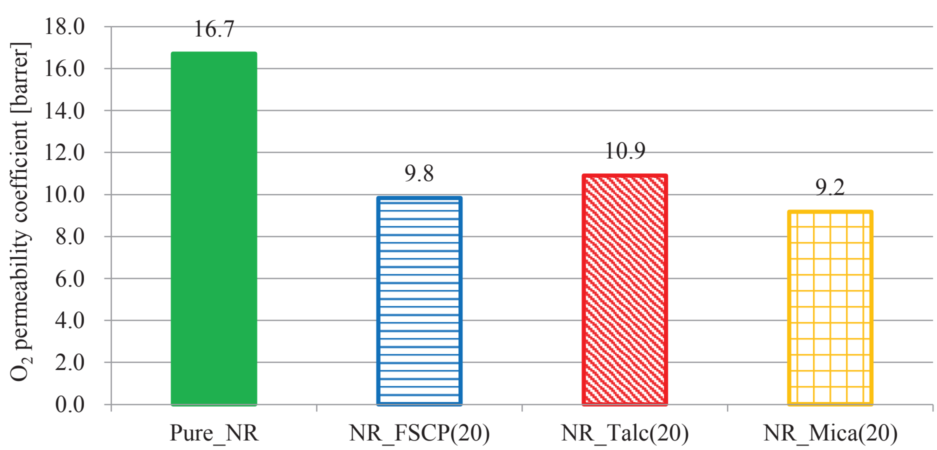


FIGURE 5. Comparison of O_2 permeability coefficient between pure NR and the composites containing 20 phr each filler (FSCP, Talc, or Mica)

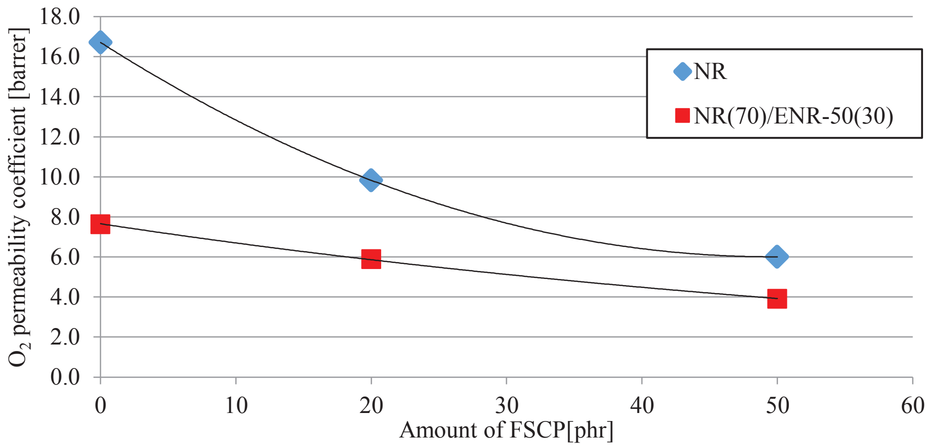


FIGURE 6. O_2 permeability coefficient vs FSCP loading for FSCP reinforced NR(◆), or NR(70)/ENR-50(30)(■)

CONCLUSIONS

The focus of our research was to find out functionalities of the "flat" cellulose filler (FSCP). To accomplish our objective we compared functionalities of the FSCP with inorganic fillers. Vibration-damping property and gas barrier property of the NR composites containing 20 phr each filler were evaluated. The result of vibration-damping experiments showed that the composite including FSCP has superior performance in comparison with talc or mica. And then, according to the result of gas permeation experiments, the O_2 barrier property of the composite containing FSCP was comparable to the composites containing inorganic fillers. Therefore, FSCP filler has effects similar to (or more than) inorganic filler in vibration-damping and O_2 barrier properties. It is thought that FSCP will be widely used in the rubber industry because of the advantages of cellulose: light, present in great quantity, "sustainable" biomass resource, and etc. Moreover, vibration-damping and O_2 barrier properties of the composite including FSCP was increased with use of ENR. In particular, we found that ENR-50 composite containing 50 phr FSCP has three times as high vibration-damping property as ENR-50 without FSCP.

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