

# Preparation and Properties of Cellulose–Olefinic Thermoplastic Elastomer Composites

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**ABSTRACT:** Fibrous cellulose (fibrous W400) was substantially dried and mechanically milled with stearic acid under several conditions. Milled with 2 wt% stearic acid at a rotational speed of 200 rpm for 24 h, fibrous W400 were pulverized into fine flake-shaped particles (flake-shaped W400) with an average particle size of ca. 10  $\mu\text{m}$ . Composites of the flake-shaped W400 and olefinic thermoplastic elastomer (TPV) were prepared under melt mixing and passed through an open roll to orient the particles. The tensile properties of the composites without any compatibilizer were deteriorated with increasing content of the particles.

However, the tensile modulus and hardness of the composites prepared by the addition of a compatibilizer (CA-60) were increased with increasing content of particles, because of the strong adhesion between flake-shaped W400 and TPV. The damping properties of the composites were improved in comparison with TPV. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 144–148, 2005

**Key words:** olefinic elastomer; composites; cellulose; orientation; compatibility

## INTRODUCTION

Thermoplastic elastomer (TPE) has the unique characteristics of rubber elasticity at ambient temperature and plasticity at high temperature. The manufacturing process of TPE can be simplified in comparison with that of vulcanized rubber since the vulcanization process is not necessary. Thus, its productivity is better and the total production cost is lower than for vulcanized rubber. In addition, it has attracted a lot of attention as an environmentally conscious material since TPE is suitable for material recycle. However, TPE has some disadvantages of poor heat resistance and compression set, because its crosslinking is not chemical but physical. Therefore, the field of application of TPE as a substitute for vulcanized rubbers is limited.

Cellulose is one of the most abundant and valuable natural resources on earth. It has very high specific strength, good thermal stability, etc. However, its application has been limited, as cellulose exhibits no thermoplasticity due to strong inter- and intramolecular hydrogen bonding. Therefore, the effective use

and high functionalization of cellulose have been investigated in recent years.

Studies on polymer composites with cellulose utilizing this advantage<sup>1–7</sup> were reported. Many studies have been carried out on elastomer composites reinforced with short fibers,<sup>8–32</sup> in which short fibers are oriented to exhibit an anisotropy. The composites with the anisotropy have been widely used in V-belts (transmission belt), hoses, rollers, etc. It is reported that the final properties of the composites are determined by many factors such as the aspect ratio, content and dispersion of short fibers, and the compatibility and interfacial adhesion between the elastomer and short fibers.<sup>22</sup> Pretreatment of short fibers and chemical modification of the matrix elastomer have been reported in order to increase the interfacial adhesion between the elastomer and short fibers.<sup>13,19,21</sup>

In this study, we studied the mechanical ball milling of fibrous cellulose under several conditions and prepared the cellulose particles–olefinic TPE composites with isotropy, unlike the elastomer composites reinforced with short fibers. The composites were synthesized by compounding the cellulose particles with olefinic TPE under melt mixing. The effect of the shape and content of cellulose particles and the interfacial adhesion between the matrix elastomer and cellulose particles on the mechanical and damping properties of the composites were discussed.

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## EXPERIMENTAL

### Materials

Fibrous cellulose was made from wood pulp (W400, Nippon Paper Chemicals Co., Ltd., Japan). Olefinic TPE was dynamically crosslinked (Santoprene 8201-60, Advanced Elastomer Systems Japan, Ltd., abbreviated TPV). Polypropylene modified with maleic anhydride (Umex CA-60, Sanyo Chemical Industries, Japan, abbreviated CA-60) was used as a compatibilizer to improve the compatibility and interfacial adhesion between TPV and W400. Stearic acid as a inhibitor of aggregation of fine W400 particles was a commercially available grade (Sakura, NOF Co., Japan).

### Methods

#### Preparation of flake-shaped W400

Fibrous W400 were dried in a vacuum dryer at 60°C for 48 h and mechanically milled in a planetary ball mill (P-5, Fritsch, internal volume, 500 cm<sup>3</sup>) with 25 balls of zirconia 20 mm in diameter, using stearic acid of several wt% for the cellulose aggregation inhibitor. The 50-g cellulose sample was usually milled at room temperature and a rotational speed of 200 rpm for 4–96 h. The free space in the sample cell other than the cellulose and balls was about 200 cm<sup>3</sup>.

#### Preparation of flake-shaped W400-TPV composites

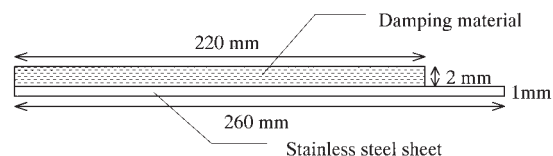
Flake-shaped W400 and TPV were mixed with CA-60 in a melt mixer (30C150 Labo Plastomill, Toyo Seiki Seisaku-sho, Ltd., Japan; chamber volume, 60 cm<sup>3</sup>). First, a mixture (45 g) of flake-shaped W400, TPV, and CA-60 was preheated at 180°C for 2 min in the mixer, and then it was compounded at 180°C and 60 rpm for 20 min. After compounding, the composites were passed through an open roll (Laboratory Mill, Kansai Roll Co., Ltd., Japan; roll diameter, 6 inch) at 180°C in order to orient the flake-shaped W400 along the rolling direction.

#### Preparation of the sheet of composites

Sheets of composites were prepared by a compression molding method. The thickness was adjusted by using middle flame of 1- or 2-mm thickness. The composites were heat pressed at 180°C and 10 MPa for 5 min using a compression molding machine (SFA-37 Automatic Molding Press, Shinto Metal Ind., Ltd., Japan) into sheets of 1- or 2-mm thickness.

#### Tensile test

Tensile properties were measured using an Instron-typed tensile tester (Autograph AGS-5kNG, Shimadzu



**Figure 1** The specimen used in the damping test.

Co., Japan) according to JIS K 6251 (tensile testing methods for vulcanized rubber). The specimens were conditioned at 20°C and 65% relative humidity for 24 h in a climate-controlled room before the tests. The tests were carried out at 20°C with a crosshead speed of 500 mm/min.

#### Hardness test

Hardness tests were carried out according to JIS K 6253 (hardness testing methods for vulcanized rubber) with a durometer-type tester (type A) at 20°C. The specimens were conditioned as described above before the tests. For measurement of hardnesses, three sheets of 2-mm thickness were stacked to attain a total of 6-mm thickness.

#### Damping test

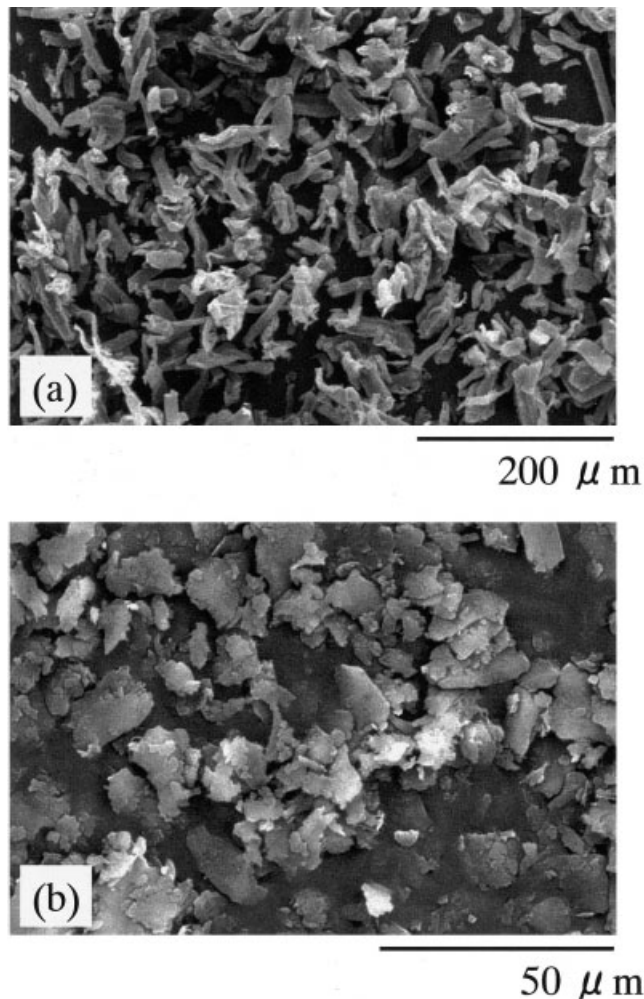
Damping properties were evaluated by use of the loss factor ( $\eta$ ) measured using a damping tester (cantilever-beam-damping test device, B&K) according to JIS G 0602 (test methods for vibration-damping property in laminated damping steel sheets) with cantilever-beam-type laminated steel sheets at 20°C. Each specimen was laminated on a steel sheet with double-sided tapes. The specimens were 220 mm in length, 10 mm in width, and 2 mm in thickness and the steel sheets were 260, 10, and 1 mm (Figure 1). The specimens were conditioned as described above before the tests.

#### Measurement of particle size distribution

After the sample (fibrous W400 or flake-shaped W400) was dispersed in water using an ultrasonic water bath for several minutes, the size distribution of the sample was measured by a laser diffraction and scattering method using a particle size distribution measuring device (LMS-24, Seishin Enterprize Co., Ltd., Japan) with a flow cell.

#### Observation of the shape of W400 and the fractured surface

The shape of W400 and the tensile fractured surface of the composites were observed with a scanning electron microscope (SEM, S-2460N, Hitachi, Ltd., Japan) after being coated with a thin gold-palladium layer.



**Figure 2** SEM pictures of (a) nonmilled W400 and (b) W400 mechanically milled in a planetary ball mill with 2 wt% stearic acid under suitable conditions.

**RESULTS AND DISCUSSION**

**Preparation of flake-shaped W400**

Natural cellulose fibers are biosynthesized in plants as follows: first, some molecules of cellulose are united regularly into a microfibril, which is a microscopic molecular bundle. The microfibrils are united regularly into a fibril and finally the fibrils are united into fibrous cellulose (several millimeters).<sup>33,34</sup>

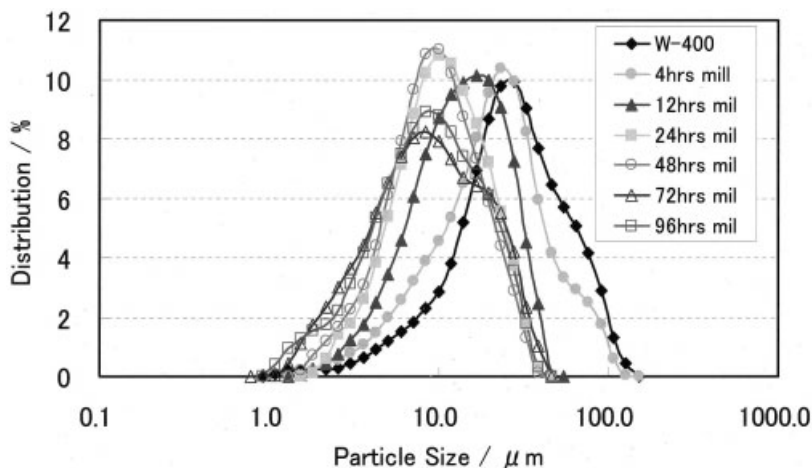
It was supposed that cellulose fibers are mechanically milled into flake-shaped particles, because they may be exfoliated into the unit of microfibril or fibril with water, organic solvents, fatty acids, etc., under suitable conditions.

Figure 2a shows an SEM picture of nonmilled W400. The shape of nonmilled W400 was fibrous and the average of the aspect ratio was about 5. On the other hand, Figure 2b shows W400 (fine W400 particles) mechanically milled in the planetary ball mill with 2 wt% stearic acid under suitable conditions: a rotational speed of 200 rpm for 24 h. As seen in the image, W400 was milled into fine flake shape, similar to talc, mica, etc., and the average particle size was ca. 10 μm.

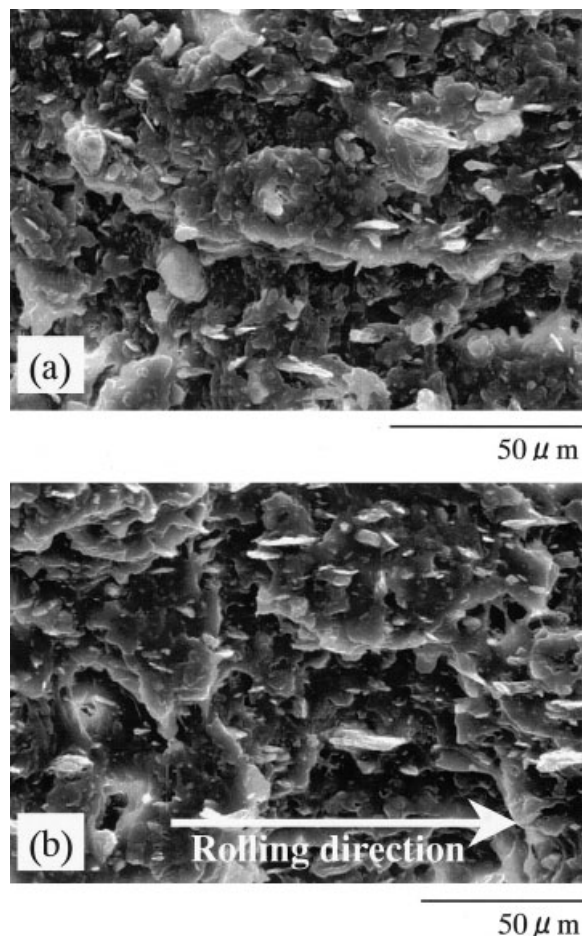
Figure 3 shows the dependence of particle size distribution on the milling time. The average particle size of nonmilled W400 was more than 20 μm and that of fine W400 particles decreased to about 7 μm with an increase in milling time. However, the size distribution in the range of ca. 20 μm did not disappear, since the fine W400 particles easily aggregate due to hydrogen bonding despite the addition of stearic acid.

**Preparation of flake-shaped W400-TPV composites**

Figure 4 shows SEM pictures of the tensile fractured surface of the composite of TPV with flake-shaped W400 mechanically milled in the planetary ball mill



**Figure 3** Relationships between the particle size distribution and milling time; (◆) nonmilled or milled for (●) 4, (▲) 12, (■) 24, (○) 48, (△) 72, and (□) 96 h.

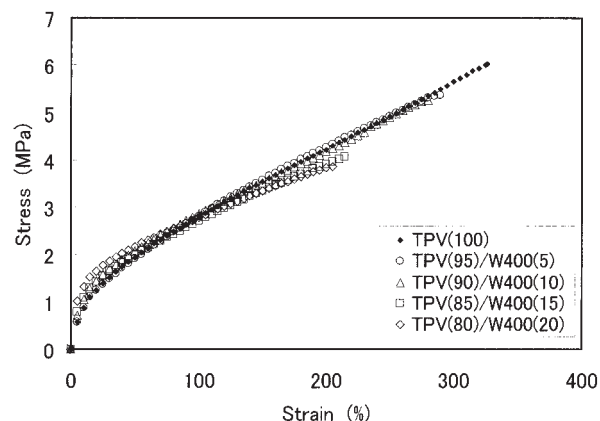


**Figure 4** SEM pictures of the tensile fractured surface of the flake-shaped W400-TPV composites; (a) not passed through an open roll and (b) passed through an open roll.

with 2 wt% stearic acid under the suitable conditions described above. In the case of the composite, which was not passed through an open roll after compounding (Figure 4a), it can be seen that the flake-shaped W400 are dispersed randomly. In the case of the composite that was passed through the open roll after compounding (Figure 4b), the fine flake-shaped W400 particles are oriented along the rolling direction. The composite passed through an open roll after compounding was used for evaluating the mechanical and damping properties.

### Tensile properties of the composites

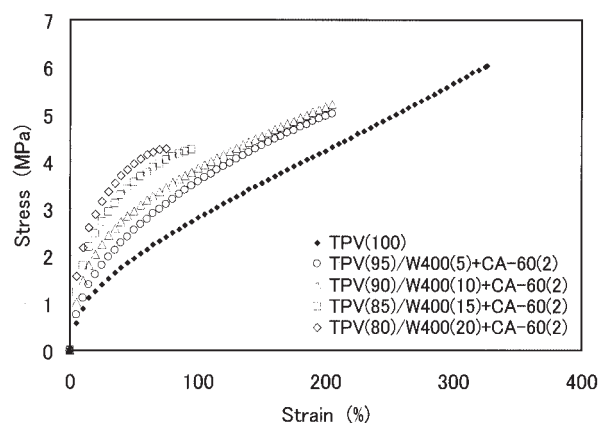
Cellulose, flake-shaped W400, with high specific strength and good thermal stability, were used as a reinforcing agent. However, the interfacial compatibility between hydrophobic TPV and hydrophilic W400 was poor. CA-60 was used as a compatibilizer to improve the compatibility and interfacial adhesion between TPV and W400. Figure 5 shows stress-strain curves of TPV as a reference and of flake-



**Figure 5** Stress-strain curves of (◆) TPV and flake-shaped W400-TPV composites containing (○) 5, (△) 10, (□) 15, and (◇) 20 wt % W400 without CA-60, respectively.

shaped W400-TPV composites containing 5, 10, 15, and 20 wt% W400 without CA-60, respectively. The tensile properties of the composites without CA-60 were deteriorated with increasing content of W400 particles.

In order to improve these properties, CA-60 was added by the amount of 1–3 wt% to the composites. Figure 6 shows stress-strain curves of TPV and of flake-shaped W400-TPV composites containing 5, 10, 15, and 20 wt% W400 with 2 wt% CA-60, respectively. The tensile modulus at low elongation was increased in comparison with that of TPV. The results suggest that the compatibility and the interfacial adhesion between TPV and W400 particles are improved because of esterification between the hydroxyl groups of W400 and the maleic anhydride groups of CA-60. It is expected that more fine milling of the particles is required to increase tensile properties, in particular, tensile strength and elongation of the composites.



**Figure 6** Stress-strain curves of (◆) TPV and flake-shaped W400-TPV composites containing (○) 5, (△) 10, (□) 15, and (◇) 20 wt % W400 with 2 wt% CA-60, respectively.

### Hardness of the composites

Hardnesses of TPV and flake-shaped W400-TPV composites containing 5, 10, 15, and 20 wt% W400 with or without 2 wt% CA-60 are shown in Table I. The hardness of TPV was slightly increased by the addition of CA-60. That of the composites was significantly increased in comparison with that of TPV and with increasing content of W400 particles.

### Damping properties of the composites

The damping properties of TPV and flake-shaped W400-TPV composites containing 10 and 20 wt%, W400 with 2 wt% CA-60 were evaluated using the loss factor,  $\eta$ . As shown in Table II, the magnitude of  $\eta$  was increased with increasing content of W400 particles. This indicates that the damping properties were improved with increasing content of the particles acting as damping fillers due to the flake shape and orientation along the rolling direction, since the energy loss caused by the interfacial friction between the particles and TPV increased.

### CONCLUSION

Fibrous cellulose, W400, were mechanically milled into fine flake-shaped particles with stearic acid under suitable conditions. Composites of TPV and fine flake-shaped W400 particles, in which the cellulose particles were well oriented, were obtained by melt mixing and passage through an open roll. The tensile properties of the composites were decreased with increasing content of the particles, but tensile modulus was improved by the addition of polypropylene modified with maleic anhydride. The hardness of the composites was increased in comparison with that of TPV and with increasing content of the particles. The damping properties were improved with increasing content of the particles.

TABLE I  
Hardnesses of TPV and Flake-Shaped  
W400-TPV Composites

	Type A durometer hardness	
	Without CA-60	With 2 wt% CA-60
TPV	60	62
TPV(95)-W400(5) composite	61	63
TPV(90)-W400(10) composite	64	67
TPV(85)-W400(15) composite	67	71
TPV(80)-W400(20) composite	70	77

TABLE II  
Damping Properties of TPV and Flake-Shaped  
W400-TPV Composites

	$\eta$
TPV	0.00249
TPV(90)-W400(10) composite	0.0039
TPV(80)-W400(20) composite	0.00668

### References

- Collier, J. R.; Lu, M.; Fahrurrozi, M.; Collier, B. J. *J Appl Polym Sci* 1996, 61, 1423.
- Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. *J Appl Polym Sci* 1997, 65, 1227.
- Karnani, R.; Krishnan, M.; Narayan, R. *Polym Eng Sci* 1997, 37, 476.
- Hedenberg, P.; Gatenholm, P. *J Appl Polym Sci* 1996, 60, 2377.
- Vieira, A.; Nunes, R. C. R.; Visconti, L. L. Y. *Polym Bull* 1996, 36, 759.
- Endo, T.; Kitagawa, R.; Hirotsu, T.; Hosokawa, J. *Kobunshi Ronbunshu* 1999, 56, 166.
- Zhang, F.; Endo, T.; Qiu, W.; Yang, L.; Hirotsu, T. *J Appl Polym Sci* 2002, 84, 1971.
- Akhtar, S.; De, P. P.; De, S. K. *J Appl Polym Sci* 1986, 32, 5123.
- Boluk, M. Y.; Schreiber, H. P. *Polym Comp* 1986, 7, 295.
- Lewis, G. *Mater Eng* 1989, 5, 47.
- Richards, B. D.; Harding, J. A. *Soc Plast Eng. Annu. Tech. Conf.* 1990, 48, 1680.
- Ding, J.; Chem, C.; Xue, X. *J Appl Polym Sci* 1991, 42, 1459.
- Nagatani, A.; Ishihara, M.; Mori, M.; Okumura, J.; Yamaguchi, K. *Nippon Gomu Kyokaishi* 1993, 66, 741.
- Roy, D.; Bhowmick, A. K.; De, S. K. *Polym Eng Sci* 1992, 32, 971.
- Roy, D.; Bhowmick, A. K.; De, S. K. *J Appl Polym Sci* 1993, 49, 263.
- Kutty, S. K. N.; Nango, G. B. *Plast Rubber Compos Process Appl* 1993, 19, 105.
- Ashida, M.; Guo, W. *J Appl Polym Sci* 1993, 49, 573.
- Guo, W.; Ashida, M. *J Appl Polym Sci* 1993, 50, 1435.
- Chen, F.; Bazhenov, S.; Hiltner, A.; Baer, E. *Composites* 1994, 25, 11.
- Roy, D.; De, S. K.; Gupta, B. R. *J Mater Sci* 1994, 29, 4113.
- Ibarra, L.; Macias, A.; Palma, E. *J Appl Polym Sci* 1995, 57, 831.
- Nagatani, A.; Yamaguchi, K. *Nippon Gomu Kyokaishi* 1996, 69, 615.
- Ibarra, L.; Macias, A.; Palma, E. *J Appl Polym Sci* 1996, 61, 2447.
- Roy, D.; Jana, P. B.; De, S. K.; Gupta, B. R. *J Mater Sci* 1996, 31, 5313.
- Ibarra, L.; Panos, D. *J Appl Polym Sci* 1998, 67, 1819.
- Correa, R. A.; Nunes, R. C. R.; Franco, W. Z. F. *Polym Compos* 1998, 19, 152.
- Nagatani, A.; Yamaguchi, K. *Polifile* 1999, 36, 52.
- Amornsakchai, T.; Sinpatanapan, B.; Bualek-Limcharoen, S.; Meesiri, W. *Polymer* 1999, 40, 2993.
- Chantaratcharoen A.; Sirisinha, C. *Polym Compos* 1998, 19, 152.
- Saikrasun, S.; Amornsakchai, T.; Bualek-Limcharoen, S.; Meesiri, W. *Polymer* 1999, 40, 6437.
- Lopez-Manchado, M. A.; Biagiotti, J.; Kenny, J. M. *Polym Compos* 2002, 23, 779.
- Vajrasthira, C.; Amornsakchai, T.; Bualek-Limcharoen, S. *J Appl Polym Sci* 2003, 87, 1059.
- Preston, R. D.; Nicolai, E.; Reed, R.; Millard, A. *Nature* 1948, 162, 665.
- Frey-Wyssling, A. *Science*, 1954, 119, 80.