EFEECT OF CELLULOSE NANOFIBER (CENF) AND DISPERSING AGENT ON SCRATCH RESISTANCE AND TRANSPARENCY OF POLY(VINYL ALCOHOL)/CENF COMPOSITES

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Keywords: Cellulose nanofiber, Poly(vinyl alcohol), Composite, Scratch resistance, Transparency

ABSTRACT

The effect of the diameter of cellulose nanofiber (CeNF) and potassium phosphate (K_3PO_4) as a dispersing agent for CeNF on the pencil hardness (scratch resistance) and transparency of PVA/CeNF/cross-linking agent (CL) composites was studied. The pencil hardness of CeNF/PVA/CL composites was increased with the increase of the CeNF addition, but the diameter of CeNF gave little influence on the pencil hardness of CeNF/PVA/CL composites. On the other hand transparency of CeNF/PVA/CL composite increased with the decrease of CeNF diameter. In addition the addition of K_3PO_4 gave no influence on the pencil hardness of CeNF/PVA/CL, but had an effect on the improvement on its transparency. K_3PO_4 could suppress the aggregation of CeNFs resulting in the nano-size dispersion of CeNF to increase the transparency of CeNF/PVA/CL. It was made clear that the addition of thinner CeNF and K_3PO_4 as a dispersing agent was effective for the enhancement of transparency of PVA/CeNF/CL composites without lowering their pencil hardness (scratch resistance).

1 INTRODUCTION

Touch panels have been applied to the electronic devices such as a smart phone and personal computer in our daily life. The surface of touch panels, transparent conductive membrane, is required to have not only excellent transparency but also higher scratch resistance. The methods to improve the scratch resistance of plastic films, ①cross-linking of the film surface, ②filling nano-particles with high hardness such as silica (SiO_2), alumina (Al_2O_3) and carbon nanotube (CNT) in films, and ③forming nano peaks on the surface, have been studied and applied actually to the goods on the market now [1, 2]. Filling Nano particles with higher hardness into the surface of plastic films is effective for the improvement of scratch resistance and abrasion resistance. Cellulose nanofiber (CeNF) with the average diameter of less than 30 nm has high crystallinity and high modulus, which is produced from cellulose materials such as pulp, bamboo. Then CeNF is now a promising material for the improvement of mechanical properties such as tensile strength and modulus of the polymers. For example, CeNF filled poly(vinyl alcohol) (PVA) and CeNF filled poly(lactic acid) exhibit stronger tensile strength and higher modulus.

Since CeNF is nano particles like CNT with hardness based on high crystallinity, CeNF is expected to have an ability of improving scratch resistance of polymers without lowering their transparency. There was no study on the effect of CeNF on the scratch resistance of the polymer composites. The authors have been studying the effect of the addition of CeNF on the scratch resistance of poly(vinyl alcohol) (PVA). It was made clear that CeNF was effective for the improvement of the scratch resistance of PVA and the simultaneous use of the cross-linking agent (polycarbodiimide) [3-5] enhanced the scratch resistance more[6, 7]. However there was no reports on the effect of CeNF on the transparency of PVA.

In this paper the effect of the diameter of CeNF and its dispersing agent on the scratch resistance and transparency of PVA/CeNF/CL composites will be discussed.

2 EXPERIMENT

2.1 Materials

2% CeNF/water slurry (commercial name: BiNFi-s) was purchased from Suginomachine co. ltd. in Japan. Water-soluble polycarbodiimide as a CL (commercial name: Carbodilite V-02-L2) and PVA (commercial name: PVA505) was provided from Nisshinbo Chemical Inc. and Kuraray Co. Ltd. respectively. The chemical structure and characteristics of CeNF, PVA and CL are summarized in Figure 1. Potassium phosphate (K_3PO_4) as a dispersing agent for CeNF/H_2O slurry was purchased from Aldrich co. ltd.. 1%CeNF/water dispersion, 5% PVA/water solution and CL/water were prepared before their use and applied to the CeNF/PVA/CL composites.

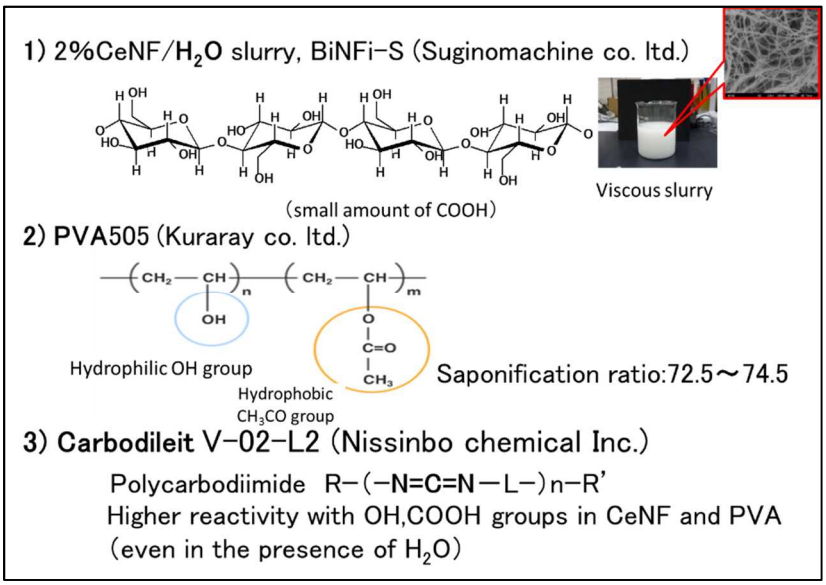

Figure 1 Chemical structure and characteristics of CeNF, PVA and CL

2.2 Preparation of thinner CeNF

CeNF with thinner diameters were prepared by crashing original CeNF in water with an ultrasonic generator GSD 600 CVP (Ginsen Company) for 1 and 2 hours respectively [8]. The diameter of the thinner CeNFs was estimated by the SEM photos.

2.3 Preparation of CeNF/PVA/CL composites

The mixture of CeNF/water slurry, PVA/water solution and CL was stirred well and defoamed with the mixing & defoaming equipment (AR100 by Thinky co. ltd.). The weight ratio of CL/ (CL+PVA) was kept 0.2. Mixing time and defoaming time were 1min and 1min respectively. The concentration of CeNF/PVA/CL slurry for coating was adjusted by the addition of pure water. The definite quantity of CeNF/PVA slurry was coated on the glass slide (25mm(length)×25mm(breadth)×2mm(thickness)) and dried at 60℃ for 10 min followed by the heat treatment at 120～130℃ for 1 hour. The thickness of the dried CeNF/PVA/CL solid layer was controlled to be around 10μm. Its actual thickness was determined from the difference in the weight between non-coat glass slides and coated one.

2.4 Evaluation

2.4.1 Spectroscopic analysis

ATR spectra of the CeNF/PVA/CL composites on the glass slide were measured with the FT-IR spectroscopy, FT/IR-4000 (JASCO Corporation). The quantity of unreacted CL in the composites was checked by the peak height of 2100 cm^{-1} attributable to the carbodiimide group (-N=C=N-) in CL.

2.4.2 Transparency measurement

Transparency of the CeNF/PVA/CL composite was evaluated from the transmittance of CeNF/PVA/CL laminated glass slide and a glass slide, which was measured at the wave length of 550 nm with UV-VIS spectroscopy V-650 (JASCO Corporation).

2.4.3 Pencil hardness measurement

Scratch resistance of the composite was evaluated from its pencil hardness. Its pencil hardness was measured according to the method based on JIS K5600-4. Pencil hardness is usually classified to the following order, 2B, B, HB, F, 1H, 2H, 3H, 4H, 5H, and 6H. 2B means softer surface, while 6H means the hardest surface among them.

3 RESULTS AND DISCUSSION

3.1 Diameter of ultrasonic treated CeNFs

Table 1 shows the diameter of original CeNF and CeNF crashed with the ultrasonic generator. The diameter of the crashed CeNF decreases with the increase of the crashing time. In conclusion three kinds of CeNF with the diameters of 16, 21 and 25 nm were used in the following study.

No	Ultrasonic treatment time (hour)	Average diameter (nm)
0	0	25
1	1	21
2	2	16

Table 1 Average diameter of CeNF treated with ultrasonic generator

3.2 Effect of CeNF on pencil hardness (scratch resistance) and transparency of CeNF/PVA/CL composites

Figure 2 shows the relationship between CeNFs amount and pencil hardness of CeNF/PVA/CL composite with CeNF/ (CeNF+PVA+CL) weight ratio of 0.4. Figure 3 shows the ATR spectra of CL, PVA/CL (PVA reacted with CL) and CeNF/PVA/CL composite. The pencil hardness of CeNF/PVA/CL composites was increased with the increase of the CeNF addition. There was little difference in the pencil hardness among CeNF/PVA/CL composites with different diameter. However the transparency of CeNF/PVA/CL composite increased with the decrease of CeNF diameter. ATR spectra showed that absorbance of 2100 cm^{-1} attributable to carbodiimide group of CL disappeared in the PVA and CeNF/PVA/CL, and that the absorbance of 1146cm^{-1} attributable to the crystallization band of PVA could not be observed[9, 10], which exhibited there was no increase of crystallinity of PVA by the addition of thinner CeNF. Therefore there was no change of pencil hardness among CeNF/PVA/CL composites. It was made clear that the use of narrower size of CeNF is effective for the improvement of the transparency of CeNF/PVA/CL composites without lowering pencil hardness (scratch resistance).

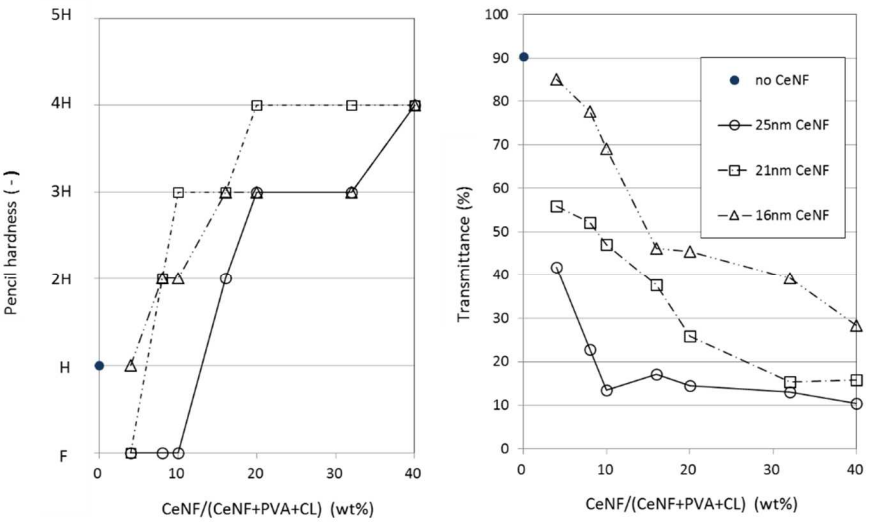

Figure 2 Effect of CeNF diameter on pencil hardness and transparency of CeNF/PVA/CL composites

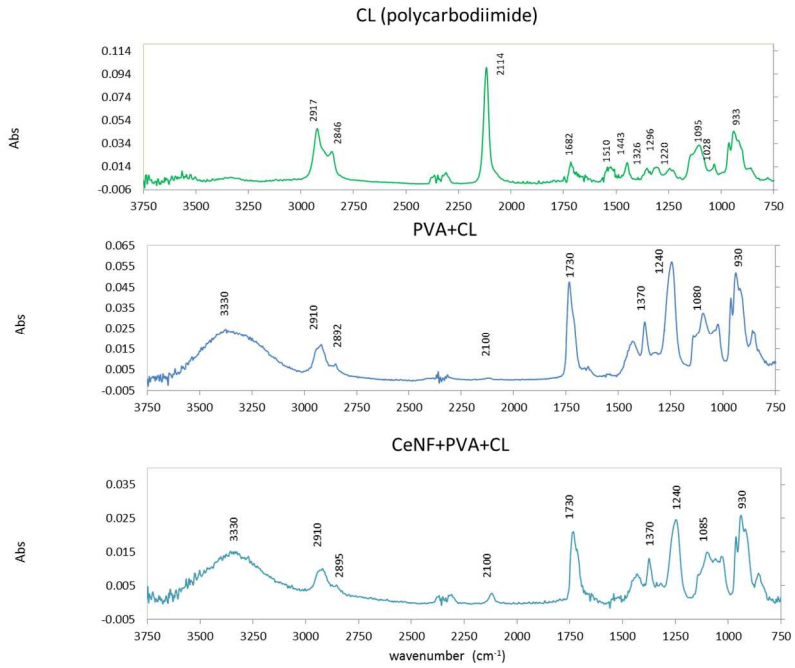

Figure 3 ATR spectra of CL, PVA/CL and CeNF/PVA/CL composites

3.3 Effect of K_3PO_4 on pencil hardness (scratch resistance) of CeNF/PVA/CL composites

The authors made it clear that K_3PO_4 was effective for the dispersion of CeNF in water and ethylene glycol. Its efficiency was the highest at the K_3PO_4/CeNF weight ratio of 0.1 [11]. Figure 4 shows the effect of K_3PO_4 on pencil hardness and transparency of CeNF/PVA/CL composites. The addition of K_3PO_4 gave no influence on the pencil hardness of CeNF/PVA/CL, but had an effect on the improvement

on its transparency. K_3PO_4 could suppress the aggregation of CeNFs, which resulted in the nano-size dispersion of CeNF to increase the transparency. It was made clear that the addition of K_3PO_4 as a dispersant was effective for the enhancement of transparency of CeNF/PVA/CL without lowering its pencil hardness.

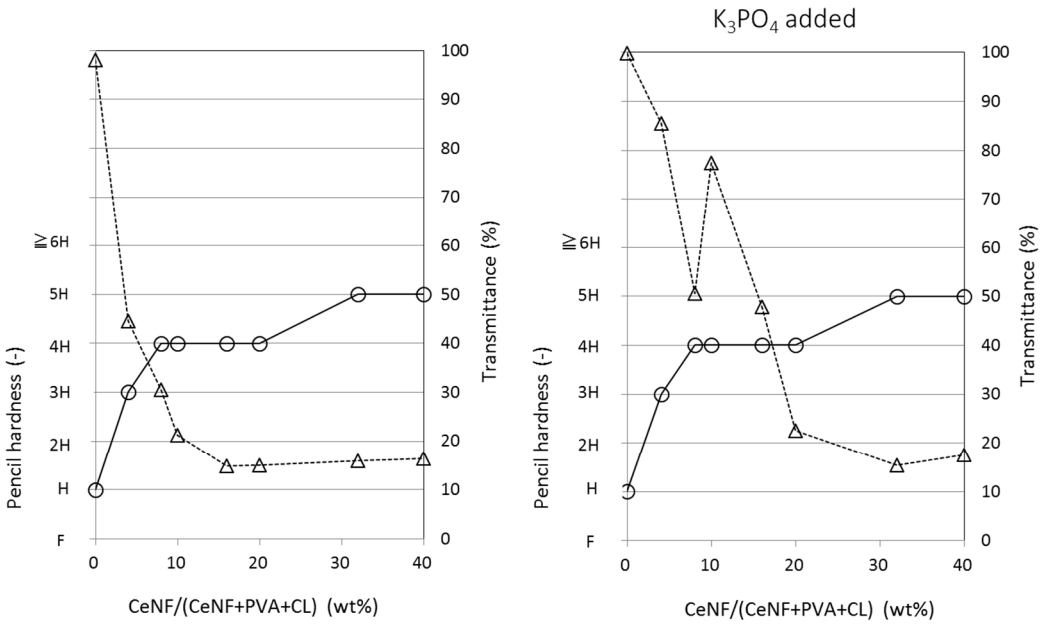

Figure 3 Effect of K_3PO_4 on pencil hardness and transparency of CeNF/PVA/CL

4 CONCLUSIONS

There was little difference in the pencil hardness among CeNF/PVA/CL composites with different diameter, but the transparency of CeNF/PVA/CL composite improved with the decrease of CeNF diameter.

The addition of K_3PO_4 gave no influence on the pencil hardness of CeNF/PVA/CL, but had an effect on the improvement on its transparency, which resulted from the suppression of CeNF aggregation, that is, better dispersion of CeNF in the composites.

It was made clear that the addition of thinner CeNF and K_3PO_4 as a dispersing agent was effective for the enhancement of transparency of PVA/CeNF/CL composites without lowering their pencil hardness (scratch resistance).

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Sanada in Toyama Prefectural University for the preparation of thinner CeNF/H_2O slurry, Nisshinbo Chemical for Carbodilite compound, Kuraray for PVA and Mr. Hayashi, Ms. Nishimura and Ms. Torii at the instrumental analysis laboratory in Nagoya University for SEM observation. This work was partly supported by JSPS KAKENHI (Grant Number 25420727) and Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Prof. Baba and Prof. Sakaguchi in Nagoya University).

REFERENCES

[1] A.Wakahara, The application of the nano particles to the coating industry, *J. Jpn. Soc. Colour Mater.*, 87 [9], 311-316(2014)

[2] Akihiko Nagasaka, Takashi Miyawaki, Tateo Machida, Kyoichi Oshida, Wataru Kawamura, Kenji Yanagisawa and Noritaka Momose, The effect of vapor-grown carbon fiber (VGCF) content on the mechanical properties and abrasion resistance of VGCF/PTFE composites, *Carbon (Tanso)* 2013[No.259], 255-260(2013)

[3] Khorana, H. G., The chemistry of carbodiimides, *Chem. Rev.* 1953, 53, 145– 166

[4] Kurzer, F., Douraghi-Zadeh, K., Advances in the chemistry of carbodiimides, *Chem. Rev.* 1967, 67 (2) 107– 152

[5] Williams, A. a. I.; Ibrahim, T.Carbodiimide chemistry: recent advances *Chem. Rev.* 1981, 81, 589– 636

[6] S. Konagaya, H. Furuhashi, T. Ohshio, K. Tada, T. Yamada and Noma, Effect of cellulose nanofiber (CeNF) on the enhancement of scratch resistance, *Proceedings of Seikei Kakou Symposia'15, Nov. 2-3, 2015, Fukuoka university (Fukuoka, Japan)*

[7] S. Konagaya, H. Furuhashi, T. Ohshio, K. Tada, T. Yamada and Noma, Effect of cellulose nanofiber (CeNF) on the enhancement of scratch resistance, *Proceedings of AWPP2015 (Asian-Australasian Workshop on Polymer Processing in Singapore 2015), December 1-4, 2015, National University of Singapore (Singapore)*

[8] S. Konagaya, K. Shimizu, M. Terada, T. Yamada, K. Sanada, O. Numata, G. Sugino, Effect of Diameter of Cellulosic Nano-Fiber on Conductivity of Poly(Aniline Sulfonic Acid) Composites, *Proceedings of PPS-29, July 15-19, 2013, Nuremberg, Germany*

[9] S. Murahashi, S. Nozakura, Synthesis of stereospecific poly(vinyl alcohol), *Kogyou Kagaku Zasshi* vol.70, No.11, 1869－1875（1967）

[10] Hiroyuki AOKI, Akihiro YOSHIDA, and Tsutomu SUZUKI, The Kinetic Evaluation for Photo-Oxidation of PVA (Polyvinyl Alcohol), *Zairyou,* vol.22, No.239, 776-784 (1973)

[11] S. Konagaya, T. Oshiro, M. Higashide, Cellulose nanofiber dispersion and its production, *Tokkai2012-5199 (P2012-51991A), 2012.3.15*