Improvement of Moisture Sorption of Polyurethane Fiber by Blending Cellulose

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Abstract: An improvement of moisture sorption (MS) ability of polyurethane (PU) was attempted by blending cellulose (Cell). PU-Cell blend was prepared from PU-cellulose diacetate (CA) blend by saponification. CA was apparently miscible with PU in a wide range of blend ratio on the optically microscopic observations. However, the incompatible interaction between them in less than 70 % CA content was suggested by Δb from the viscosity measurement. Saponified CA formed cellulose II structure in PU at above 30 % CA content. Essentially, CA was, therefore, immiscible with PU. The MS of PU fibers blended with 5 % of CA was dramatically enhanced after 1 % NaOH treatment. In the case of films, the MS was increased by the increase in CA content without saponification. By saponification, the MS ability was further improved.

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1. Introduction

The development of novel functional polymer by the polymer blend method has been focused on with respect to reducing both of research cost and plant investment [1]. PU fibers are highly elastic as termed "Spandex", therefore they are applied to athletic wear. However, they have a big drawback that is little MS ability. On the other hand, cellulosic fibers have excellent MS ability next to wool [2], but an inferior elasticity. In this study, the MS ability of PU fibers was attempted to be improved by the blend of cellulose without spoiling the high elasticity.

It was reported that the MS ability of PU fibers could be improved by blending hydrophilic polymers or fine powders, such as silica gel, with high MS ability [3,4]. However, such methods required significant amount of additives, and concomitantly the increase in the additives deteriorated the spinnability. It was expected that the problem would be solved when the polymer blend was accomplished with the common solvent for the blended components to prepare a dope. Cellulose is dissolved in LiCl / dimethyl acetamide (DMAc). DMAc is a good solvent for PU, but a viscosity of PU in LiCl / DMAc was remarkably increased as compared with that in DMAc solution. The solvent system makes spinning of PU difficult. Hence, we first prepared PU-CA moldings such as fiber and film, and then PU-Cell blend was obtained by saponification of CA in the PU-CA

moldings.

In this paper, the miscibility between PU and CA was investigated to suppose a structure of PU-Cell blend, and the MS of PU-CA blends was also examined before and after saponification.

2. Experimental

2.1 Materials

PU pre-polymer was synthesized by the reaction of 4,4'-diphenylmethane diisocyanate (2870 parts) with polyoxytetramethylene glycol (630 parts; $M_n=1820$). The mixture of ethylene diamine (56 parts) as a chain extender and diethylamine (2 parts) as a chain terminator was added to the pre-polymer solution in DMAc. After the chain extending reaction, PU was obtained as a DMAc solution.

CA with the degree of substitution of 2.5 was purchased from Wako Pure Chemical Co. Ltd., Tokyo. CA and other agents were used without further purification.

The weight average molecular masses of PU and CA were 70 and 129 kDa, respectively, determined by size-exclusion chromatography referring to those of authentic polyethylene oxides.

2.2 Preparation of polymer blend and its molding

CA solution in DMAc was mixed well with PU solution to give a dope of PU-CA blend. PU-CA blend fibers were prepared by the dry spinning. The spinning conditions were as follows; solid content in the dope, 32 %; dope viscosity, 5000 P at 30 °C; spinneret, 0.2 mmφ x 3 holes; discharge, 6.94 g of dope/min; temperature of spinning head, 220 °C; temperature of spinning cylinder, 200 °C; hot air circulation, 100 m³/h; winding rate, 500 m/min; winding stretch, 10 %. Spinnability and fiber characteristics of PU-CA blend were evaluated in terms of the following items. Thread breakage was counted during the spinning and represented as times per 24-h spinning. Tensile strength was the force (gram / denier, g/d) at the breakage. Modulus was tensile strength at 300% elongation. Modulus recovery was measured at 20°C and relative humidity (RH) of 65 %, and calculated according to the following equation.

$$\text{Modulus recovery (\%)} = L_1 / L_0 \times 100$$

Where L_0 was fiber length (cm) when 40-mm fiber was elongated to 300 % at an elongation speed of 1000 %/min, and L_1 was the length at zero stress when the elongated fiber was returned.

Ten wt.% of PU-CA solutions with CA content of 0-100 % were cast on glass plates, and dried under reduced pressure until complete coagulation. The obtained films were washed with water and lyophilized.

The fibers and films were saponified with 0.1 and 1 % NaOH aqueous solution for 1 h at 80 °C without tension. The samples were washed with water thoroughly and lyophilized.

2.3 Fluorescence microscopic observation

PU-CA fibers before and after NaOH treatment were dyed with Calcoflour White ST[5]. A fluorescence image was observed on a confocal laser scanning microscope (LSM-310, Carl Zeiss, Oberkochen, Germany). The excitation was 364 nm, and the band pass filter (410-440 nm) was used.

2.4 MS measurement

First, the fibers (3 g) and films (5 sheets, 3 x 3 cm) in containers were placed in a chamber at 25 °C and RH 60 % until constant weight. The containers were placed at 35 °C and RH 90 % for 30 min, and then at 25 °C and RH 53 % for 30 min. The latter two conditions were repeated alternatively. The weight of the specimen was measured at certain intervals. The moisture content was represented as percent based on dry weight.

2.5 Other analyses

The reduced viscosity of PU-CA blend solution in DMAc was measured against the concentrations using an

Ubbelohde viscometer at 25 °C. FT-IR spectra were obtained using Bio-Rad FTS-50A spectrometer. The resolution was 0.5 cm⁻¹. X-ray diffraction was monitored on a Rigaku X-ray diffractometer with nickel filtered Cu-Kα radiation (40 kV and 30 mA). Scanning conditions were as follows: step-interval, 0.02°; scan speed, 2.00 °/min.

3. Results and Discussion

3.1 Miscibility between PU and CA

The miscibility and interaction between PU and CA were investigated to suppose the structure of PU-Cell blend that was regenerated by the saponification. A viscometric study is one of the easiest methods to evaluate the miscibility [6]. Fig. 1 shows the reduced viscosity (η_{sp}/c) against the concentration of PU-CA blend with CA content of 0-100 %. In whole blend ratio, η_{sp}/c indicated linear without cross-over, and the lines lay between PU and CA lines. Furthermore, the relative viscosity against the CA content also showed linearity ($R^2 = 0.989$, the graph not shown). Rao et al. [6] and Dondos et al. [7] reported that such viscometric relations apparently revealed the miscibility between PU and CA.

Fig. 1 Reduced viscosity of PU-CA blend. CA content: (○) 0%, (+) 10%, (×) 30%, (◆) 50%, (■) 70%, (▲) 90%, and (●) 100%.

An interaction parameter (Δb) was calculated from the intrinsic viscosities ($[\eta]$) of PU-CA blends in accordance with the theory of Kribaum and Wall [6,8]. When Δb is positive, the polymer blend system is miscible. When negative, the system is immiscible. From Table 1, at less than 70 % CA content, Δb was negative. Strictly, PU was, therefore, immiscible with CA in such range. The value increased with increasing in CA content. At 90 % CA, it reached 0.48. This suggested that CA was miscible well with PU at the high CA content.

Table 1 Interaction parameter (Δb) calculated from $[\eta]$

CA ¹	0	10	30	50	70	90	100
$[\eta]$	1.16	1.23	1.36	1.40	1.53	1.59	1.69
Δb		-0.20	-0.17	-0.11	-0.02	0.48	

¹ CA content (%).

3.2 Spinnability of PU-CA blends and their saponification

Table 2 shows the spinning results and the characteristics of the resultant fibers. Times of thread breakage were increased by the increase in the CA content under the same spinning conditions tested. Tensile strength and modulus recovery were reduced by more than 10 % of CA addition. Therefore, PU-CA blend fibers could be spun without spoiling the high elastic property of PU until the CA content of 5 %. The PU-CA fibers with 5 % CA (PU-5 % CA) were applied to the following experiments.

Fig. 2 Transmittance images (upper) and fluorescence images (lower) of PU-CA fibers before and after saponification.

The saponification of PU-5 % CA fibers was examined under two alkaline conditions, 0.1 and 1 % NaOH at 80 °C for 1 h. Fig. 2 shows transmittance images and their fluorescence images dyed with Calcoflour White ST before and after NaOH treatments. The fluorescent dye was well known to strongly interact with Cell so that it is used as optical whitening agent for cotton. In a fluorescence image of non-treated fiber, a little fluorescence was observed merely at a part of fiber edge. This observation seemed to be resulted from dyeing free hydroxyl group in CA with the agent. The fluorescent could be confirmed in the entire edge by 0.1 % NaOH treatment. By 1 % treatment, strong fluorescence was observed in whole fiber except for center where the laser light probably did not reach enough. These observations indicated that CA in the blend was completely saponified with 1 % NaOH. This indication was supported by FT-IR, because the carbonyl band assigned to acetyl group disappeared upon the saponification. Consequently, the regenerated Cell was distributed homogeneously in the fiber. Therefore, CA was also assumed to be distributed without phase separation in the optically microscopic level.

3.3 Preparation of the blend films, and their structure before and after saponification

Because of deteriorating the spinnability with the increase in CA content, it was difficult to get the fibers with a wide range of CA contents. Hence, the PU-CA blend films with various contents of CA were prepared by the dry method. Thin films with less than 1 mm in thickness were readily prepared in the whole CA contents. After 1 % NaOH saponification, homogeneous distribution of Cell was observed for all the films as similar to that of the fiber. However, thick films with the CA content of 30-70% could not be obtained, because a phase separation occurred for a long period standing to evaporate the solvent under the reduced pressure at

Table 2 Spinning results and properties of the resultant fibers.

CA content (%)	Thread breakage (Times)	Finess (d)	Tensile Strength (g/d)	Elongation (%)	Modulus (g/d)	Modulus recovery (%)
0	0	40.8	1.17	650	0.208	92.3
1	0	41.0	1.23	662	0.228	91.8
3	0	40.3	1.20	658	0.273	92.6
5	0	40.5	1.24	671	0.221	91.7
10	0	39.6	1.08	531	0.328	86.0
15	1	39.9	0.99	548	0.201	82.3
20	12	38.2	0.68	530	0.178	78.1

ambient temperature. This was probably due to the immiscibility suggested by Δb in the viscometric study. In the case of 10% CA content, the thick blend film could be prepared in spite of the higher immiscibility. The complete phase separation did not occur because of very low CA content.

Fig. 3 IR spectra of PU-CA blend films in 2500-4000 cm^{-1}

Table 3 Characteristic band in 3000-3500 cm^{-1}

CA (%)	Characteristic band (cm^{-1})
0	3323
10	3323
30	3323 3482
50	3323 3482
70	3323 3481
90	3492
100	3492

The interaction between PU and CA in the films was examined by FT-IR [9]. Fig. 3 shows IR spectra of thin blend films in the range of 2500-4000 cm^{-1} because no significant difference was observed for the fingerprint region. CA showed the band of the free hydroxyl group at 3492 cm^{-1} , while PU had a band at 3323 cm^{-1} , which was probably assigned to amide or amino groups, as listed in Table 3. In the spectra of the blend with CA content of 30-70 %, a new band at 3482 cm^{-1} instead of the hydroxyl band was observed in addition to the amide band. The hydroxyl band of CA might be shifted down by 10 cm^{-1} . Since the shift was very small, the shift would be caused by intra-molecular hydrogen bonding. Taking the negative Δb into the consideration, the free hydroxyl groups of CA in the 30-70 % CA blend films might form slightly stronger intra-hydrogen bonding each other than that of intact CA, as a result of micro-phase separation. Therefore, the interaction rendered the preparation of thick film difficult.

X-ray diffraction of the PU-CA films was examined to clarify the structure of PU-Cell blend. Before saponification, similar diffractograms of CA to those of authentic CA was observed. However, we did not further analyze the results, because any obvious peak could not be obtained without annealing. By the saponification, the diffractogram of PU-Cell blend even with 30 % CA indicated Cell-II structure. The 2θ degrees had a tendency to increase as increasing in CA content, as shown in Table 4. This means that the size of a unit cell decreases. These results might also reflect the phase separation of CA in the blend. Therefore, Cell-II structure was readily regenerated from the low CA content.

Table 4 Diffraction angle (2θ) and lattice constant calculated from the angles.

CA (%)	2θ (degree)				Lattice constant ($\text{\AA}$)		
	110	110	102	200	<i>a</i>	<i>b</i>	<i>c</i>
10			19.7		-	-	-
30	12.1	-	19.9	21.8	8.07	9.18	10.2
50	12.1	-	19.6	21.6	8.08	9.23	10.4
70	12.4	-	20.2	22.0	7.82	9.07	10.0
90	12.3	-	20.0	22.0	7.91	9.08	10.2
100	12.4	-	20.4	22.2	7.88	9.00	9.96
Cell-II	12.1	19.9	20.5	21.9	8.14	9.14	10.3
PU			20.0		-	-	-

Lattice constant was calculated as $\gamma = 117.2^\circ$. The parameters of Cell-II were cited from Andress [10].

3.4 MS ability of PU-CA blends before and after saponification

Fig. 4 shows changes in the moisture contents of the PU-5 % CA fiber upon the variation of temperature and RH. This experiment was conducted repeatedly under two conditions of moisture adsorption and desorption. An initial MS and a MS gain are defined as the moisture content at 25 °C and RH 60 % and the difference in the moisture content between the initial conditions and the adsorption conditions, respectively.

Fig. 4 MS profile of PU-CA fibers before and after saponification under alternative conditions of 35°C, RH 90% and 25°C, RH53%. (●) Non-treatment, (◇) 0.1% NaOH treatment, (□) 1.0% NaOH treatment, (▲) PU fibers.

The initial MS and MS gain of the blend fibers were similar level to those of PU fibers. Accordingly, MS ability of PU fibers was not influenced by the addition of CA. A slight improvement of MS ability was observed for the saponified fibers with 0.1 % NaOH. The MS ability was dramatically enhanced by 1 % NaOH saponification. Although the MS gain of cellulose was approximately 6% [11], the gain of the saponified fibers even with 5 % CA reached 3.5 %. As suggested by fluorescence microscopic observation, Cell was regenerated by such saponification. Therefore, Cell was found to contribute to improve the MS ability of PU even in a small content.

A relation between MS and CA content was further examined using the blend films. Fig. 5 and 6 show MS profiles before and after 1 % saponification, respectively. The initial MS of PU-CA film was increased with increasing in the CA content. The MS gain also showed a similar tendency. These results indicated that free hydroxyl groups in CA contributed to MS ability.

By saponification, both of initial MS and MS gain was obviously increased. The MS gain was enhanced

Fig. 5 MS profile PU-CA blend films before saponification. CA content: (○) 0%, (+) 10%, (×) 30%, (◆) 50%, (■) 70%, (▲) 90%, and (●) 100%.

Fig. 6 MS profile PU-CA blend films after 1.0% NaOH treatment. CA content: (○) 0%, (+) 10%, (×) 30%, (◆) 50%, (■) 70%, (▲) 90%, and (●) 100%.

Fig. 7 MS profile of PU-CA fibers and film under the conditions of 35°C and RH 90%. (●) blend fibers with 5% CA before saponification, (○) after saponification; (▲) blend film with 10% CA before saponification, (△) after saponification.

markedly in more than 50 % CA. The MS gain of such films was further improved after one cycle of adsorption and desorption. The maximum MS gain of the saponified PU-70 % CA film reached 13 %. The enhancement seems to be resulted from the immiscibility of CA in the PU blend. It is assumed that the moisture is adsorbed into gaps that were formed between the two blended components resulted from the phase separation by a capillary phenomenon.

The MS ability of the fibers with 5 % CA was compared with that of films with 10 % CA when both samples were stand for a long period at 35 °C and RH 90 %. Before saponification, the MS of the film was superior to that of fibers because of larger free hydroxyl groups (Fig. 7). In addition, the immiscibility would influence the MS as mentioned above. The MS abilities were almost the same after saponification. This result suggested that fibers were improved by Cell more efficiently probably due to the difference in surface area.

4. Conclusion

The PU-CA blend fibers could be prepared by dry spinning. The spinnability was deteriorated by the increase in CA content, since PU was essentially immiscible with CA. in less than 70% CA content. Judging from the strength, the maximal addition of CA was 5%. The MS ability of PU fibers was improved by the CA addition followed by the saponification. In the case of films, the ability was improved only by the CA addition. Upon the saponification, the blend effect became larger. Thus, the improvement of MS ability of PU in both forms of fibers and film was carried out by the blend with Cell. Since the unexpected improvement of MS ability is suggested to be related to the immiscibility, the relation must be further investigated to clarify the Cell contribution to MS ability.

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