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Miscibility, free volume behavior and properties of blends from cellulose acetate and castor oil-based polyurethane

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Abstract

A series of blend films from cellulose acetate (CA) and castor oil-based polyurethane (PU) were prepared. Morphology, miscibility, free volume behavior and properties of such blend films were investigated by wide-angle X-ray diffraction (WXRD), infrared, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), positron annihilation lifetime spectroscopy (PALS), thermogravimetric analysis and tensile test. The results indicated that lager free volume cavities did not form at the interface of two polymers although a certain degree of phase separation was found by the studies of SEM and DSC. Strong intermolecular hydrogen bonding interactions at the interface, which was proved by Fourier transform infrared spectroscopy, favors even better molecular packing, that is, PU dispersed in CA continuous phase to form fine microphase separation domain in the CA-rich blends. Due to such special interactions in the fine microphase separation domain structure, optimized properties of tensile strength, breaking elongation and cold-resistivity were obtained in the blend film with 75 wt% CA. The toughness of all the blend films was significantly higher than that of the film CA, owing to the plasticizing of PU elastomer in the blends.

Keywords: Cellulose acetate; Polyurethane; Miscibility

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1. Introduction

In past decades, polymer blends continue to be a subject of intensive investigations in both industrial and academic domains because it has shown to be an excellent way for developing new materials often exhibiting combinations of properties superior to either of the pure components alone [1,2]. Miscibility and phase-separation phenomena of the polymer blends have received significant attention in the polymer applications [3]. Many experimental results have indicated that the presence of special interactions in a blend including hydrogen bonding, ion-ion pairing, etc. favors the enthalpy for mixing, and allows the components to mix completely. Among the entire interaction, hydrogen bonding quite efficiently improves the miscibility without accompanying much change of the component polymers [4], and the polymers containing proton donor groups are found to be miscible with those containing proton acceptor groups due to hydrogen bonding interactions [5].

Polymer blends from cellulose and its derivatives have been attracted much attention because it is a simple and effective way to achieve optimized properties. It is well known that polyurethane is a class of versatile materials because of its good flexibility and elasticity. The urethane linkages in homopolyurethane can serve as H-bond acceptor and donor [6]. Cellulose nitrate gave miscible blends with castor oil based polyurethane and poly(vinyl chloride-*co*-vinyl acetate), showing improved flame resistance [7]. In our previous works, grafted or semi-IPNs materials from castor oil-based polyurethane and natural polymers such as nitrocellulose [8], elaeostearin [9], and depolymerized chitosan [10] have been synthesized and coated onto regenerated cellulose (RC) films to improve mechanical properties and water-resistivity.

Cellulose acetate has been utilized as a membrane material for many years in reverse osmosis since it has a high salt rejection and is relatively inexpensive. Application of cellulose acetate membrane to processes with increasingly diversified macromolecular components requires the

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modification of cellulose acetate with balanced hydrophilic–hydrophobic moiety [11], and also requires better properties of mechanical strengths, toughness and cold-resistance. Recently, polyurethane has been successfully incorporated in cellulose acetate to introduce balanced hydrophilicity to achieve optimum membrane performance in terms of better rejection and flux [12–14]. However, in order to predict and enhance the physical and mechanical properties of such blends, it is important to understand the nature and the underlying factors of blending at the molecular level. One rational approach in this line of research is to investigate the correlation between free-volume and miscibility properties of blending [15]. In this work, the blend films were prepared by blending cellulose acetate (CA) with castor oil-based polyurethane (PU) in polar solvent. The interaction of hydrogen bonds and morphologies of the blend films were investigated by Fourier transform infrared spectroscopy (FT-IR), wide-angle X-ray diffraction (WXRD) and scanning electron microscopy (SEM). The thermal and mechanical properties of the blend films were evaluated by thermogravimetric analysis (TGA) and tensile test. To determine the miscibility, in addition to the standard technique of differential scanning calorimetry (DSC), a major work is to measure free volume of the blends by using positron annihilation lifetime spectroscopy (PALS) and to study the correlation between miscibility and free volume behavior of the blends.

2. Experimental

2.1. Materials

All the chemical reagents were obtained from commercial resources in China. 2,4-Toluene diisocyanate (2,4-TDI) was redistilled under reduced pressure at 110 °C. Castor oil, chemical grade with a 4.94 wt% content of hydroxyl groups and hydroxyl value of 163, was dehydrated at 100 °C under 20 mmHg for 1 h. Cellulose acetate (combined acetic acid, 54.5–56.0 wt%; viscosity, 300–500 Pa s) was supplied by Shanghai Chemical Reagent Company, and dried at 80 °C for 48 h. The other reagents were of analytical grade and used without further purification.

2.2. Preparation of CA–PU blend films

A three-necked flask was equipped with a nitrogen inlet tube, a mechanical stirrer and a pressure equalizing dropping funnel. 30 g of 2,4-TDI was poured into the flask. 59 g of caster oil were dropped into the flask under nitrogen atmosphere at 40 °C. The dropping was completed within 60 min, and then the stirring was maintained at 60 °C for 2 h to get the PU prepolymer.

The value of [NCO]/[OH] was predetermined theoretically to be 1.05. Thus, 3 g of PU prepolymer was mixed with 0.25 g of 1,4-butanediol as chain-extending agent in tetrahydrofuran (THF). At the same time, a stoichiometric amount of cellulose acetate (CA) was dissolved in a little amount of THF, and then the two solutions were mixed after fully dissolution. By adding THF, the resulting mixture was given a solid content of 15%, and then was cast on a glass plate after stirred at room temperature for 1 h. After slow solvent evaporation at room temperature in atmosphere, it was cured at 80 °C for 4 h. When the amount of cellulose acetate was lower than 40%, phase separation occurred in the mixture solution. Therefore, the blend films were prepared with cellulose acetate contents of 90, 80, 75, 70, 60 and 40 wt% coded as UCA90, UCA80, UCA75, UCA70, UCA60 and UCA40. The film of pure cellulose acetate was coded as CA. The film PU was obtained identically except the cellulose acetate addition but cured at 80 °C for 10 h. The curing time of film PU was much longer than that of the films UCA. The films were vacuum-dried at room temperature for 3 days and then were used for the measurements. The thickness of the dry films was measured to be about 80 μm.

2.3. Characterization of structure

Fourier transform infrared (FT-IR) spectra of the blend films were taken with KBr plate on a Nicolet 170SX FT-IR spectrometer in a wave number range of 4000–400 cm^{-1}. The films were cut to 1 mm length and 1 mm width, and then mixed with potassium bromide to laminate.

WXRD patterns of the films was carried out on an X-ray diffractometer (D/MAX-1200, Rigaku Denki, Japan). The X-ray diffraction patterns with Cu kα radiation ($\lambda = 1.5402$ Å) at 40 kV and 30 mA were recorded in the range of $2\theta = 6$–$40°$.

The free and fracture surface morphologies of the films were observed and photographed on a Hitachi model S-570 scanning electron microscope (SEM). As for the fracture surface morphologies, the samples were frozen in liquid nitrogen, snapped, vacuum-dried and coated with gold successively before observation.

2.4. Thermal and mechanical properties

DSC of the films was performed with DSC-2C thermal analyzer (Perkin–Elmer Co., USA) under nitrogen atmosphere (30 ml/min) at a rate of 10 °C/min from −60 to 200 °C. Thermal gravimetric analyses (TGA) of the films were performed on a thermal analyzer (DT-40, Shimadzu Co., Japan). The film was cut to pieces with 1 mm length and 1 mm width, then analyzed under nitrogen atmosphere with a flow capacity of 30 ml/min at a heating rate of 15 °C/min from room temperature to 550 °C.

The tensile strength (σ_b) and breaking elongation (ε_b) of the films were tested on a versatile tensile tester (CMT-6503, Shenzhen SANS Test Machine Co. Ltd, China) with the rate of 5 mm/min. The size of the samples was 70 mm length, 10 mm width, 50 mm distance between two clamps.

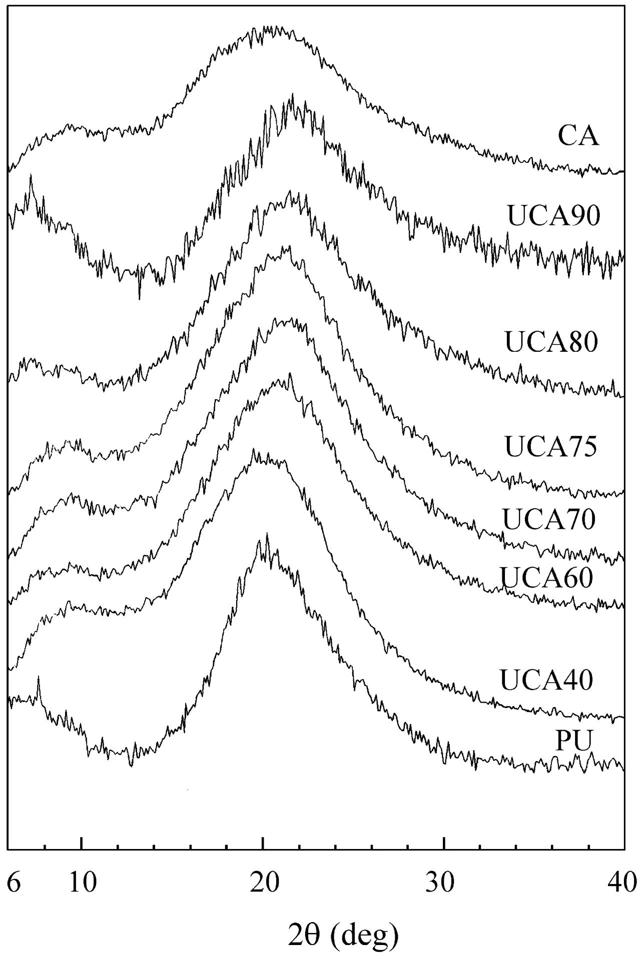

Fig. 1. WXRD patterns as a function of 2θ for the films CA, PU and the blend films.

Five films were tested for each sample, and their average value was given.

2.5. Positron annihilation lifetime measurement

A 20 μCi ^{22}Na positron source sealed between two sheets of aluminum foil (1 mg/cm^2) was sandwiched between two pieces of the same samples (1 cm width, 1 cm length and 1.5 mm thick), which were made by folding the films tightly together. PALS was carried out using a conventional fast-fast coincident spectrometer on the sample of the films PU, CA, UCA80, UCA75, UCA60 and UCA40 at ambient temperature. A million counts were collected for each spectrum in about 1.5 h.

3. Results and discussion

3.1. Miscibility of blends

The WXRD patterns of the films CA, PU and the blend films are shown in Fig. 1. A broad halo commencing from 13 to 32° in 2θ with lower magnitude is found for the films PU, CA and their blends, and the data in Fig. 1 also do not show clear Bragg diffraction peaks. This indicates the amorphous nature of polyurethane, cellulose acetate and their blend films, similar to our previous work [16]. Cellulose acetate can act as a proton accepting and donating polymer for its carbonyl group and unsubstituted hydroxyl group, while the urethane linkages in cast oil-based polyurethane can also serve as H-bond acceptor and donor. Fig. 2 shows the FT-IR spectra for the films CA, PU and the blend films in the hydroxyl group and N–H stretching regions. One large vibration band due to O–H stretches in pure cellulose acetate film (CA) is centered at 3491 cm^{-1}. This band is assigned to the contribution of self-associated hydrogen bonding hydroxyl groups within cellulose acetate [17]. Such band in the blend films shifts gradually to lower wavenumbers reaching 3483 cm^{-1} at the film UCA75, indicating self-associated O–H groups in cellulose acetate were decreasing to the benefit of formation of the intermolecular hydrogen bonding with the urethane linkages of polyurethane, similar to the peak changes in the binary blends of poly(ethylene oxide) and poly(methyl vinyl ether-maleic acid) [18]. The band centered at 3325 cm^{-1} with a small shoulder at 3440 cm^{-1} in pure polyurethane film (PU) is due to the self-associate bonded and free N–H

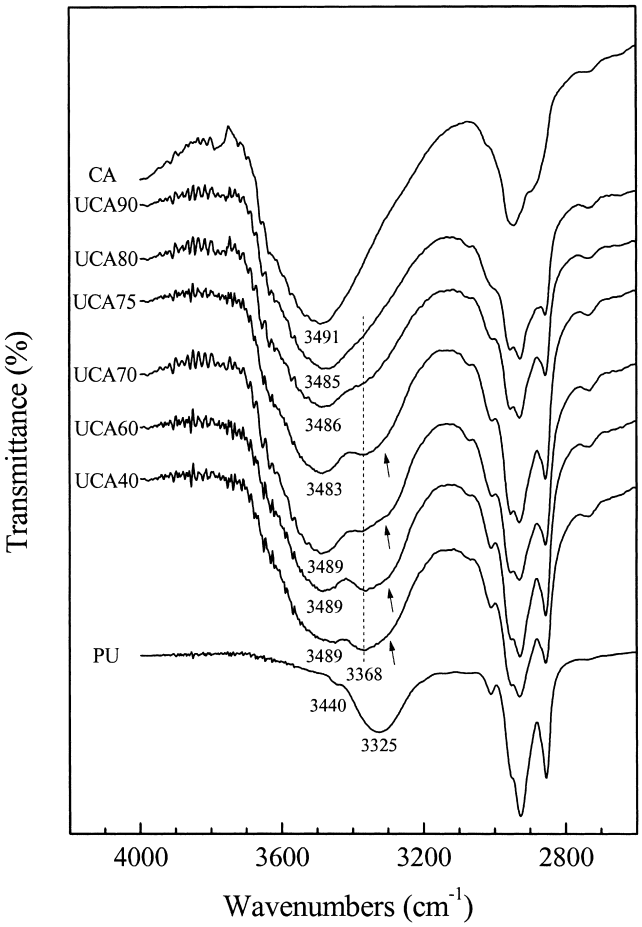

Fig. 2. FT-IR spectra in the hydroxyl group and N–H stretching regions for the films CA, PU and the blend films.

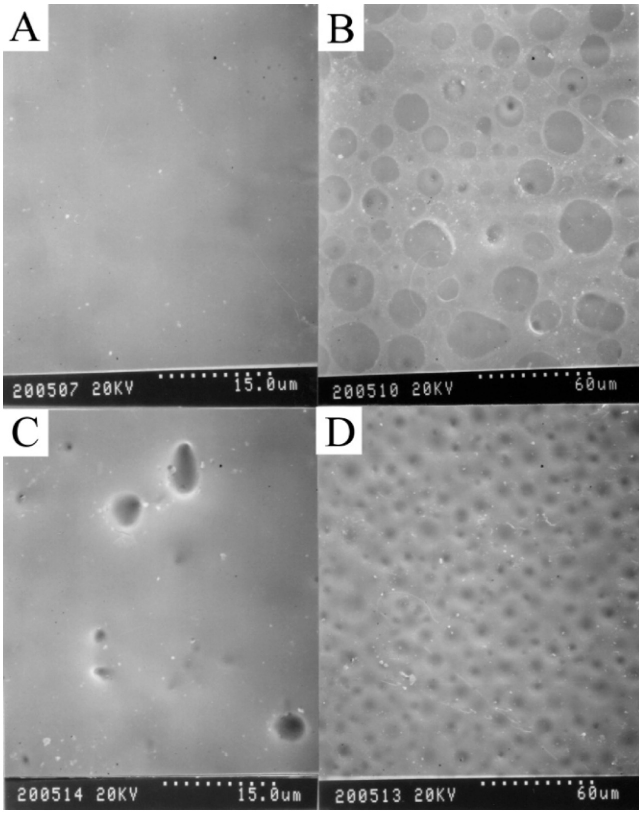

Fig. 3. SEM photographs of the surfaces of the films PU(A), CA(C), UCA40(B) and UCA75(D).

stretching. Interestingly, the center of N–H stretching absorption bands of all the blend films shift to 3368 cm^{-1}, indicating the formation of inter-hydrogen bonded N–H with the carbonyl group of cellulose acetate. The shoulder of N–H stretching band in the blends (pointed by arrows in Fig. 2) is assigned to the self-associate bonded N–H groups within polyurethane. However, the intensities of such shoulders increase with further decreasing of the CA content in the blends, and the center of O–H stretching vibration band shifts back to 3489 cm^{-1}. This suggests that the intermolecular hydrogen bonding interactions between the two polymers are weakened in the blends with lower CA content.

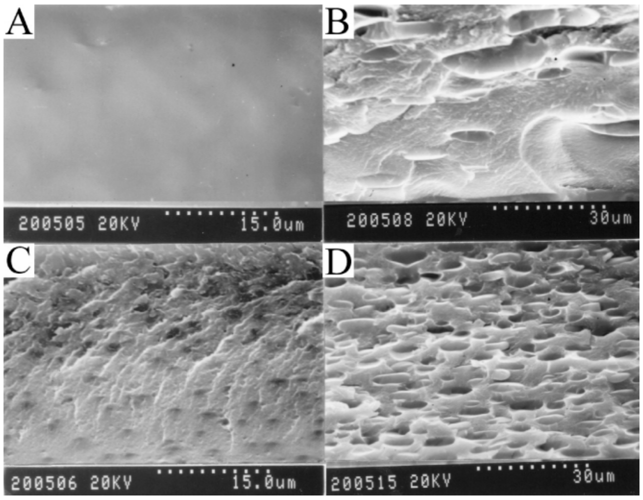

Fig. 4. SEM photographs of the fracture surfaces of the films PU(A), CA(C), UCA40(B) and UCA75(D).

The SEM photographs of the free surfaces of the films PU, CA, UCA75 and UCA40 are shown in Fig. 3. The films PU and CA display a smooth surface being consistent with a homogenous component. However, the blend films UCA75 and UCA40 exhibit basally homogenous morphology including CA as a continuous phase and PU as a dispersed phase, in which the circular concave is attributed to the polyurethane particle contraction due to the surface-driving forces, indicating a certain degree of phase separation between PU and CA occurred in the blend films. The dispersed PU domain size of the film UCA75 is much smaller than that of UCA40, showing stronger intermolecular interaction in the CA-rich blend than the blends with lower CA content, consistent with the results of FT-IR. The fracture surface morphologies of the films are shown in Fig. 4. Relatively larger phase separation appeared in the film UCA40. But microphase separation with fine domain structure appeared in the film UCA75, indicating enhancement of miscibility and increased interface area between the two polymers comparing to UCA40, which benefit the formation of intermolecular hydrogen bonding and increase the molecular interaction.

Fig. 5 shows the DSC curves for the films PU, CA, UCA75 and UCA40. Two glass transitions were detected in the blend films UCA75 and UCA40, revealing that the two polymers exhibited a certain degree of phase separation. However, the T_g temperature associated with the glass transition of PU for the blend films UCA40 was found to be 12 °C, which was lower than that of the pure PU film (21 °C), and the T_g for UCA75 was even lower (−7 °C). This indicated a better cold-resistivity for the CA-rich blend film. In explanation, there is a plasticizing effect [19] and an

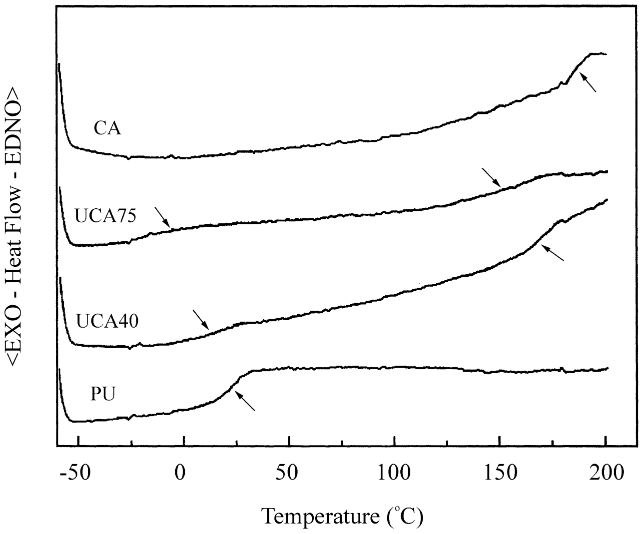

Fig. 5. DSC curves as a function of temperature for the films PU, CA, UCA75 and UCA40.

incompetently formed PU network caused by the molecular interaction between CA and PU, that is, a lower crosslinking density of the castor oil-based polyurethane similar to our previous work [16]. Meanwhile, the T_g temperature associated with the glass transition of cellulose acetate for the blend films UCA75 and UCA40 were also found to decrease from 184 to 150 °C and 166 °C, respectively. This can be explained that the strong interaction between polyurethane and cellulose acetate destroyed the self-associated inter- and intra-molecular hydrogen bonds in the cellulose acetate, which affected the chain rigidity of CA. Therefore, the strong interactions have taken place on the interface of the blends, especially for the CA-rich blends with fine microphase separation domain, resulting a homogenous structure composed of the dispersed PU spheric domain and CA continuous phase. Moreover, the blend films were basally THF-soluble, suggesting that the PU and CA formed blend rather than interpenetrating polymer networks (IPNs), which were organic solvent-insoluble [20,21].

3.2. Free volume behavior

PALS has emerged as a unique and potent probe for detecting the free volume properties of polymers in recent years [22–24]. In this work, all the lifetime spectra were best resolved into three components using PATFIT [25] after the background and the positron source correction were subtracted. The variations of the fit (χ^2) were smaller than 1.2. The shortest-lived component (τ_1) and the intermediate component (τ_2) are attributed to the self-annihilation of para-positronium (*p*-Ps) and the positron annihilation, respectively. The longest-lived component (τ_3) results from the pick-off annihilation of ortho-positronium (*o*-Ps) in the free volume sites. The *o*-Ps lifetime (τ_3) is a measure of size of free volume site in polymers (the greater τ_3, the larger size), and intensities (I_3) is indicative of the number concentration of free volume sites in polymers (the higher I_3, the greater concentration of free volume sites) [23]. The results for PALS free volume parameters *o*-Ps lifetime (τ_3) and intensities (I_3) as a function of cellulose acetate content (W_{CA}) in the blends are shown in Fig. 6. Although the *o*-Ps lifetime shows a monotonic increase with decrease of CA content, the *o*-Ps lifetime changes between pure PU and CA is only 165 ps. This fact means that the size of the free volume site does not vary with respect to the composition of the blends. However, major change (non monotonic) has been exhibited in the associated intensities. The intensities (I_3) values of blends with W_{CA} lower than 60% was almost equivalent to the weighted average, whilst I_3 values of the blends with W_{CA} higher than 75% shows a distinct, negative deviation from rule of mixture (ROM) behavior. Such a negative deviation of the free volume concentration in the CA-rich blends perhaps results from the strong intermolecular hydrogen bonding interactions between PU and CA, which can suppress the movements of the chains and result in blends of less free volume sites. These results suggest that lager free volume cavities did not form at the interface although a certain degree of phase separation was found by the studies of SEM and DSC, and the strong molecular interactions at the interface favors even better molecular packing in the CA-rich blends.

3.3. Mechanical and thermal behavior of blends

The mechanical properties as a function of cellulose acetate content (W_{CA}) for the blend films were shown in Fig. 7. The tensile strength σ_b of the blend films decreased with decreasing cellulose acetate content, which consistent with the extent of the phase separation and the decrease of hydrogen bonding interaction between the two phase. The breaking elongation ε_b of the blend films increased with decreasing cellulose acetate content, and showed a maximum value of 23% for 75% W_{CA}. Fig. 8 shows the strain-stress curves of the films PU, CA and the blends measured at room

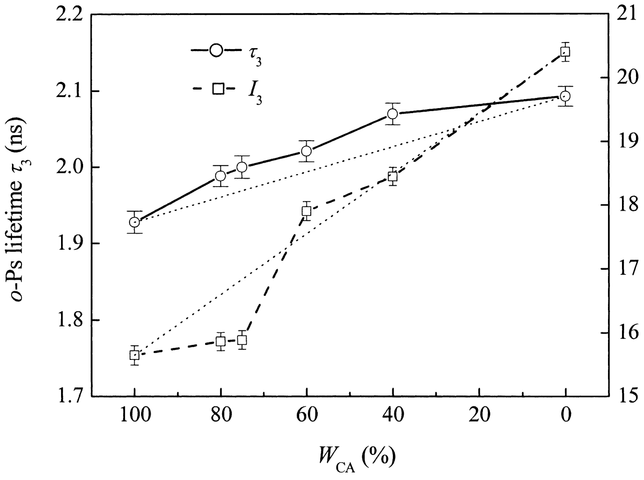

Fig. 6. PALS free volume parameters *o*-Ps lifetime (τ_3) and intensities (I_3) as a function of cellulose acetate content (W_{CA}) for the films.

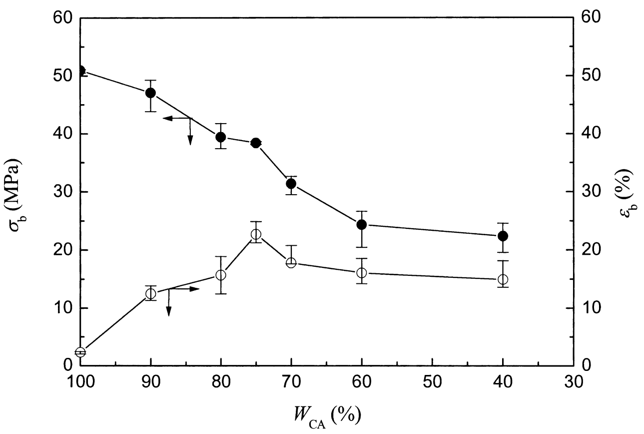

Fig. 7. The mechanical properties as a function of cellulose acetate content (W_{CA}) for the films at 25 °C.

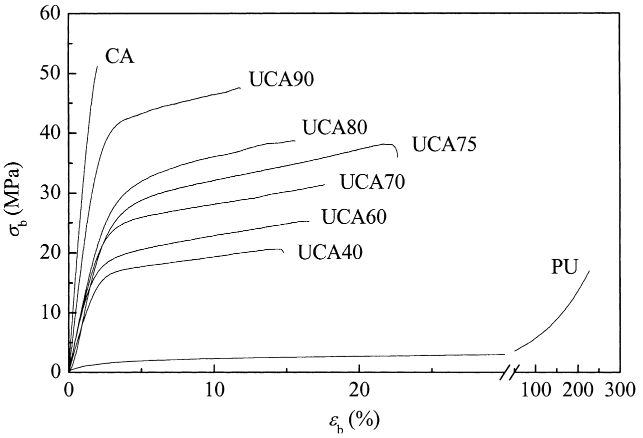

Fig. 8. The strain–stress curves for the films CA, PU and the films measured at 25 °C.

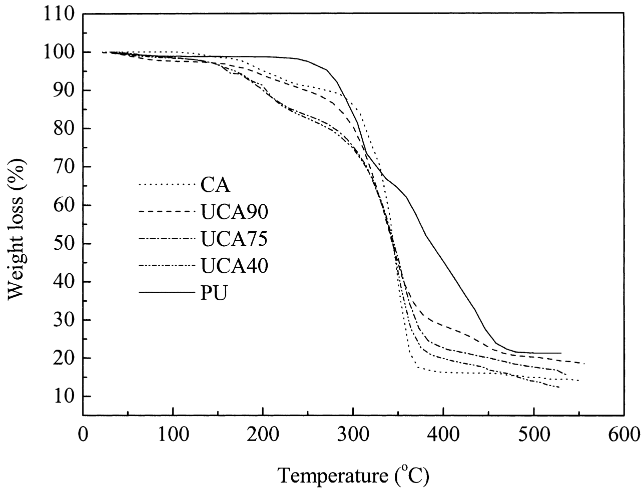

Fig. 9. TGA curves of the films CA, UCA90, UCA75, UCA40 and PU.

temperature. The area under the stress–strain curve can be used as a measurement of the polymer toughness. The relatively large area of the blend films exhibited a character of toughened plastic in the CA-rich blends. This indicated a brittle for CA to ductile transition, similar to that observed for cellulose acetate at different temperatures [26]. Young's modulus calculated from the stress–strain data shows that the moduli of CA, UCA75 and UCA40 are 2.64×10^9, 1.94×10^9 and 1.46×10^9 Pa, respectively. These values are much higher than 1.3×10^7 Pa for pure PU, a crosslinked rubber. Thus, such blends are consistent with plasticizing CA plastic by PU elastomer to achieve optimized toughness. It is worth noting that UCA75 has relatively better mechanical properties σ_b and ε_b, indicating relatively stronger intermolecular hydrogen bonds interactions in CA-PU blends with W_{CA} of 75% although microphase separation occurred.

TGA curves of the films CA, UCA90, UCA75, UCA40 and PU are shown in Fig. 9. The film PU can be stable up to 217 °C, and then decomposed in two distinct stages. Polyurethane was decrosslinked between 217 and 336 °C, which may mainly be caused by the breaking of urethane bond. The second decomposition stage of polyurethane lies in the range from 336 to 480 °C, due to castor oil molecules resulted in a faster rate of weight loss [27]. The weight of cellulose acetate decreased slowly from 170 to 264 °C, then decreased sharply with an increase of temperature from 264 to 395 °C. The decomposition process of the blend films was almost similar to that of CA. This suggests that polyurethane dispersed in the cellulose acetate continuous phase rather than form a network structure as PU. Thermal properties of the films CA, UCA90, UCA75, UCA45 and PU by TGA are summarized in Table 1. The 10, 50% mass loss temperature ($T_{10\%}$, $T_{50\%}$) of the blend films decreased with decreasing the cellulose acetate content, and are lower than those of the film CA. However, the maximum decomposition temperature (T_{max}) and mass residues at 500 °C of the blend films, especially in the CA-rich blend, are much higher than that of CA, which is attributed to the intermolecular hydrogen bonding between CA and PU.

Table 1
Thermal properties of the films CA, UCA90, UCA75, UCA45 and PU by TGA

Film No.	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	Residue at 500 °C (%)
CA	260	345	367	14.9
UCA90	242	343	401	20.3
UCA75	213	345	382	17.6
UCA40	203	344	376	14.0
PU	286	386	467	21.4

4. Conclusions

A series of blend films from CA and castor oil-based PU was successfully prepared. FT-IR results indicated that strong intermolecular hydrogen bonds occurred between the hydroxyl and carbonyl group of CA and the urethane linkages of PU, especially in the CA-rich blend films. SEM and DSC studies found that cellulose acetate and polyurethane exhibited a certain degree of phase separation in the blends, that is, the PU spherical particles dispersed in the CA continuous phase. However, Free volume size of the blend films probed by PALS did not change much and the concentrations of free volume sites even exhibited a distinct, negative deviation in the blend films with W_{CA} higher than 75%, indicating lager free volume cavities did not form at the interface and even better molecular packing in the blends, owing to the molecular interaction by hydrogen bonding. Thus, optimized properties of tensile strength, breaking elongation and cold-resistivity were obtained in the blend film with 75 wt% cellulose acetate, superior to those of the film CA. Moreover, the toughness of all the blend films was higher than that of the film CA, owing to the plasticzing of PU elastomer in the CA-rich blends.

Acknowledgements

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