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Studies on the toughness and water resistance of zein-based polymers by modification

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Abstract

To develop novel biodegradable materials, zein was modified using polycaprolactone (PCL)/hexamethylene diisocyanate (HDI) prepolymer. The modified zein polymers, containing various PCL–HDI components (PCLH) content and plasticized by Dibutyl L-tartrate (DBT), were compression-molded. Mechanical properties, water resistance, thermal properties and morphology of the molded zein-based sheets were investigated. The toughness was improved significantly by a small amount of PCLH due to the existence of micro-phase separation structure in the sheets. In particular, zein exhibited better mechanical properties when modified by 20–50 wt% PCLH, and when the corresponding sheets were immersed in water for 24 h than when stored in 75% relative humidity. This implies an excellent water resistance. Thermal analysis indicated that the formation of physical cross-linking from PCLH segment extension, and the plasticization of water to the zein matrix, improved the water resistance of modified zein sheets. DBT had a stronger interaction with zein than with PCLH, and was considered as a compatibilizer for zein matrix and PCLH component in modified zein sheets.

Keywords: Zein; Modification; Water resistance

1. Introduction

Reduction of greenhouse gas emissions is an effective solution to the present global warming problem [1,2]. A promising way to reduce greenhouse gas is to develop renewable raw materials to replace non-biodegradable plastics [3].

One important renewable raw material, protein, has attracted interest in the field of biodegradable polymers [4]. Zein, a protein derived from corn, can be used as a biodegradable material [5,6], and as early in 1909, it was used to prepare plastic [7]. Later, the related research was delayed due to the emergence of petroleum-based plastics. However, within the last two decades, zein has again attracted attention because of its biodegradability.

Zein film containing no plasticizer is fragile after it is equilibrated at low relative humidity (RH) [8]. Therefore, many attempts have been made to use plasticizers to improve the flexibility of zein. Lai et al. used oleic acid to plasticize zein, and found that it was more effective in molded film than in cast film, and that molded film had better toughness than cast film [9]. Lai also studied the effect of palmitic and stearic acid on the properties of the zein resin sheet [10]. Tillekeratne added poly(ethylene glycol) into zein film and concluded that 30% poly(ethylene glycol) substantially enhanced its tensile strength and resistance to water vapor transmission [11]. In these studies, however, the flexibility of zein material was improved at the price of the decrease of strength, and the problem of water resistance remained. Improvement of water resistance in this study is defined as ‘keeping stable or enhancement in mechanical properties of zein at wet state’.

In order to increase the toughness of a polymer, a scientific approach is to develop multiphase morphologies from partially miscible systems. In this approach, micro-phase separation is formed and the elastomeric domains serve to modify the stress distribution and modulus of the matrix polymer, enhancing of energy absorption. Polystyrene–polybutadiene–polystyrene resin and polyurethane are two typical examples. In such polymers, the minority component is usually more expensive than the majority phase, and the volume fraction of the minority phase is usually minimized for optimum performance. Therefore,

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this may be an effective way to develop a zein-based polymer with micro-phase separation structure to improve the mechanical properties of zein. α-zein has two fractionations with a similar cylinder-like structure within which nine helices are clustered. Hydrophilic residuals (Gln, Glu, Asn, Ser etc.) distribute along the cylinder surface, which contributes to the water sensitivity of zein [12]. The two fractionations with molecular weights of 24,000 and 22,000, respectively, possess several hundreds of amino acid residuals [6]. To improve the water resistance of zein, one method is to modify hydrophilic side groups such as $-NH_2$, $-OH$, $-COOH$ and $-SH$, by hydrophobic groups or polymer segments. Modified zein may show novel characters in both mechanical properties and water resistance. Thus, in our previous work, we prepared and characterized zein polymers modified by polycaprolactone (ZPs) [13]. We found that a small amount of polycaprolactone (PCL) significantly improved the toughness of the dried zein sheet, demonstrating the potential of implementing technique. However, there was insufficient data to describe the relationship between the structure and properties of the ZP sheets, so we studied this in this paper.

Dibutyl L-tartrate (DBT) contains ester and hydroxyl groups, which can potentially form hydrogen bonding with zein. Thus we considered it an efficient amphiphilic plasticizer to zein, and used in the following experiment. In this study, ZPs were plasticized by DBT, and then compression-molded into sheet. The mechanical properties, water resistance, thermal properties, and morphology of the sheets were investigated.

2. Experimental

2.1. Materials

α-zein (SHOWA ZEIN™) (Supplied by Showa Sangyo Co., Ltd, Japan) containing 96.3% protein, and 3.4% water, was vacuum-dried at 105 °C for 48 h prior to use. Other materials included PCL diol ($M_w = 2000$, CAPA® 2200) (supplied by Solvay Interox Ltd, Cheshire, UK) with a hydroxyl value of 56 mg KOH/g and less than 0.02% water content, hexamethylene diisocyanate (HDI, Wako first Grade) purchased from Wako Pure Chemical Ind., Ltd, and DBT (98%) from Aldrich (USA).

2.2. Preparation of ZPs

ZPs were prepared according to our previous report [13]. The main procedure is as follows. First, PCL prepolymer was prepared in bulk from PCL diol and HDI. Next, zein and prepolymer with various contents (10, 20, 30, 40 and 50 wt% in feed) were used to prepare ZPs in DMF solvent. Finally, ethanol was used to terminate possible residual isocyanate groups. Products were precipitated, vacuum-dried, milled and stored for using. These ZPs were coded as ZP10, ZP20, ZP30, ZP40, and ZP50. The PCL–HDI components (PCLH) contents determined by the method of Soxlet extraction [13] were 10, 19.7, 27.7, 39.0 and 47.8%, respectively. The unmodified zein content, determined by sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE) method [13], in ZP10, ZP20, ZP30, ZP40 and ZP50 were 9.3, 5.4, 2.9, 2.8 and 1.9%, respectively. For example, ZP30 was one of the ZPs with 30 wt% of PCLH in feed, or 27.7 wt% of PCLH in polymer and with 2.9 wt% of unmodified zein. Therefore, ZPs were a series of blends from unmodified and modified zein but this particular blend contained a much high content of the latter. As controls, samples with no PCL (coded as CZ) and with no zein (coded as PCLHE) were also prepared under the above synthesizing procedure, respectively. CZ means commercial zein, and PCLHE, shorten from PCL–HDI–Ethanol, is a derivative from prepolymer and ethanol.

2.3. Preparation of sheets by compression-molding

Powder samples were compression-molded according to our previous procedure [13]. CZ, ZP10, ZP20, ZP30, ZP40 and ZP50 were mixed with DBT at a constant ratio of 1:0.5 by weight, respectively. The mixture was stirred in a beaker using a glass bar for 10 min, then milled in a sample mill (WB-1, Osaka Chemical Co., Ltd, Japan) at 25,000 rpm for 30 s in order to obtain a homogeneous premix. Finally, the premix was sealed and equilibrated in an oven at 60 °C for 12 h. Each sheet was prepared according to the following procedure: 2.5 g of premix were placed into a mold ($110 \times 110 \times 0.20\ mm^3$) and covered with aluminum papers on both sides. The mold was then placed between two steel blocks of a hot press (Mini Test Press, Toyoseiki, Japan), whose temperature was maintained at 155 °C, and compression-molded at 17 kN for 1 min. After the premix was pre-heated, the pressure was quickly increased from 17 to 100 kN. 10 min later, the mold was cooled to 50 °C by a water-cooling system at a rate of 40 °C/min. A slight yellow and transparent sheet was released from the mold and stored in a desiccator. A series of sheets, coded as ZPS10, ZPS20, ZPS30, ZPS40, and ZPS50 from ZP10-50 was prepared and shortened into ZPS10-50. The sheet from CZ was coded as CZS. PCLHE is a wax-like material and impossible to compression-mold for tensile test.

2.4. Characterization

The mechanical properties and water resistance of the sheets were evaluated using an Instron tensile tester (Instron 5542, USA) according to ASTM D882-81 with some modification. A series of sheets with dimensions of $110 \times 10 \times (0.1–0.4)\ mm^3$ was immersed in water at a temperature of 25 °C for 24 h, and another series of sheets was equilibrated in a desiccator at 75% RH for 21 days. The testing temperature was 25.5 °C and 70% RH. Stress–strain curves, strength at break (σ_b) and breaking elongation (ϵ_b)

were recorded at 25 mm/min of tensile speed, and used to evaluate the mechanical properties and water resistance of the samples. For each treatment, at least five specimens were tested to calculate an average value and standard deviation.

DBT weight loss, residual DBT content, and water uptake of the sheets were measured by the following method. Each sheet was dried at 105 °C for 0.5 h, cooled in a desiccator containing P_2O_5, then weighted (W_0). The dried sheets were immersed in distilled water (1000 ml) at 30 °C. After 24 h, soft paper was used to absorb the surface water of each wet sheet, then the sheet was weighted (W_w). The wet sheets were dried at 70 °C for 4 h, and at 105 °C for 0.5 h. Finally, after being dried for a week in a desiccator containing P_2O_5, each sheet was weighted (W_d). The water uptake, DBT weigh loss and residual DBT content in sheets were calculated by use of the following equations

$$\text{Water uptake (wt\%)} = 100 \times (W_w - W_d)/W_0 \tag{1}$$

$$\text{DBT weight loss (wt\%)} = 100 \times (W_0 - W_d)/W_0 \tag{2}$$

$$\text{Residual DBT content (wt\%)} = 33.3 - \text{DBT weight loss} \tag{3}$$

Here, W_0, W_w, and W_d are the weights of the dried sheet before treatment, the wet sheet, and the dried sheet after treatment, respectively. The DBT percentage in untreated sheets with a weight ratio of polymers to DBT was 33.3.

A differential scanning calorimetry (DSC) experiment was performed with a thermal analyzer (DSC220C, Seiko Instrument, Japan) in a nitrogen atmosphere. Sample was packed into an aluminum pan and sealed with lid. Indium was used for temperature and heat capacity calibration of the instrument. Glass transition temperatures (T_g, the midpoint of glass transition), the change in heat capacity (ΔC_P), and melting temperature (T_m, melting peak temperature) were determined by heating samples (10 mg) from 32 to 140 °C at a rate of 10 °C/min, followed by cooling down to − 120 °C at a rate of 10 °C/min. The samples were then rescanned at a rate of 10 °C/min to 220 °C. All samples were analyzed in triplicates.

Viscoelastic properties of the sheets were tested by the use of a dynamic load thermomechanical analyzer (DTMA, TMA/SS150C, Seiko Instrument Inc., Japan). A block-like sheet ($10 \times 15 \times 3$ mm^3) was compression-molded in an aluminum mold (outer dimensions $90 \times 30 \times 3$ mm^3; inner dimensions $15 \times 10 \times 3$ mm^3) at 155 °C and 33 kN for 3 min. A punch was used to punch the block-like sample into cylindrical tablets (3 mm diameter and 3 mm height). Samples were stored in a desiccator containing P_2O_5 for 15 days prior to testing. Thermal properties of the sheet were analyzed in compression mode in a nitrogen atmosphere. Indium and Tin were used to calibrate the temperature scale of the furnace. A sinusoidal stress (offset, − 20 g; amplitude, 10 g; frequency, 0.1 Hz) was applied to the sample to produce a strain. Scanning was performed from − 95 to 220 °C at a scanning rate of 2 °C/min. Three duplications were made for each sample. Curves of loss tangent (tan δ) to temperature were plotted.

Thermal gravimetric analysis (TGA) was conducted using a thermal gravimetric analyzer (TGA, Exstar 6000, Seiko Instruments Inc., Japan). All of the sheets were stored in a desiccator containing P_2O_5 for 15 days prior to TGA. Approximately 15 mg of the sample cut from the sheet was dried to constant weight in a desiccator containing P_2O_5, then subjected to heating from 30 to 300 °C at 10 °C/min in a nitrogen atmosphere.

A scanning electron microscope (SEM) (SEM, JEOL, Technics Ltd, JSM-5600LV) was used to observe the sections of the sheets. Each sheet sample was frozen using liquid nitrogen, then fractured into at least three cross-sections using two tweezers. The cross-sections were coated with gold in an auto coater (JEOL JFC1500), and then used for SEM observation. Three duplications were made, and from these, a typical image was selected for analysis.

3. Results and discussion

3.1. Mechanical properties and water resistance

Fig. 1 shows the stress–strain curves of CZS and ZPS10-50, equilibrated at 75% RH for 21 days. All of the sheets were transparent. In order to analyze the macro-structure of the sheets, a control experiment as following was done. Equal amount of PCHE and zein were dissolved in acetone and acetone/water (4:1 v/v), respectively. Required DBT was added into zein solution, then PCLHE and zein solution were mixed to prepare PCLHE/zein blend film by casting method. The PCLHE/zein blend is the same composition as ZP50. We found that the blend showed serious phase separation in macro-structure, in which white strip-like material (PCLHE) separated with transparent zein area, showing an obvious heterogeneity. This control experiment and the transparent property of ZPs showed that ZPs were homogeneous in macro-structure. CZS was flexible with

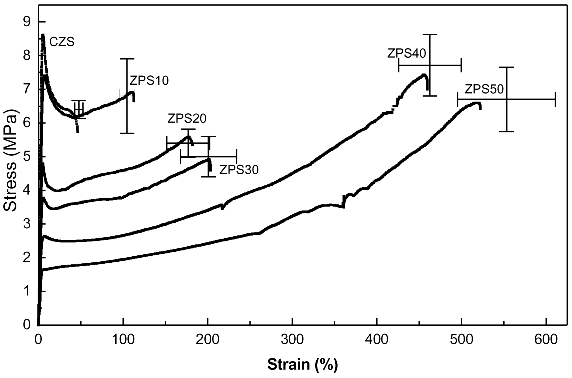

Fig. 1. Stress–strain curves of CZS and ZPS10-50. Samples were equilibrated at 75% RH for 21 days before test.

higher ϵ_b (47.7%) and lower σ_b (6.2 MPa) due to the plasticization of water and DBT. However, the CZS sheet without any water was stiff [13], indicating that water is an important plasticizer for zein. ZPS10-50 exhibited typical stress–strain behavior of plastic–rubber copolymers. This is attributed to the two phases in the ZPs, amphiphilic zein, which formed a hard matrix to determine the strength at yield point, and a hydrophobic PCL component to improve the elasticity of the sheets. Thus, the strength at yield point decreased with a decrease of zein content, and the ϵ_b values increased continuously with an increase of PCLH content in the ZPS10-50 (Fig. 1). After 10% of PCLH content was incorporated into zein, both σ_b and ϵ_b of ZPS10 (6.8 MPa and 104.7%, respectively) were enhanced, compared with that of CZS. ZPS40 and ZPS50 displayed good elasticity (462 and 543%, respectively), and a high strength at breaking (7.7 and 6.7 MPa, respectively), which suggests that the mechanical properties of zein material were significantly enhanced by modification. It was difficult to obtain a uniform sheet to cut elastic polymer, and also to test the thickness of the elastic sheet accurately. This leads to a large standard deviation for duplications as shown in Fig. 1.

Fig. 2 shows stress–strain curves of CZS and ZPS10-50 after being immersed in water for 24 h at room temperature. CZS and ZPS10 became white, but ZPS20-50 remained transparent, implying that ZPS20-50 had good water resistance. CZS exhibited medium mechanical properties in wet state with low σ_b (1.9 MPa) and medium ϵ_b (198%). ZPS10 also exhibited the same mechanical properties as CZS, which resulted from an unmodified zein in ZPS10 and lead to reduced water resistance. Interestingly, all ZPS20-50 samples possessed good mechanical properties with high strength and elasticity, and exhibited good mechanical properties in wet state.

Compared with the data in Fig. 1, the mechanical properties of ZPS20-50 were improved by the uptake of water. For example, the σ_b and ϵ_b values of ZPS20 immersed in water for 24 h were 11.9 MPa and 315%, which was higher than that of ZPS20 in Fig. 1 (5.4 MPa, 177%), equilibrated at 75% RH for 21 days. Unmodified starch soy protein isolate is known to exhibit weak mechanical properties after being immersed in water. Although some researches have been conducted to improve their mechanical properties in water [14,15], the improvement was limited. In this case, water did not reduce but improved the mechanical properties of ZPS20-50, displaying good potential in application. Besides that the hydrophobic property of PCLH components partially contributes to this improvement, the change in structure of ZPs is an important factor, which would be analyzed using more valuable data.

The above results indicate that 20% PCLH was 'critical' for improving the water resistance of this ZPs. We attributed the improvement of mechanical properties of ZPS20-50 to water. After zein-based sheets were immersed in water, water infiltrated the sheets while DBT passed out of the sheets, resulting in an increase of water content and a decrease of DBT content in the sheets. 24 h later, and before tensile testing, the sheets with different PCLH content contained different water and DBT content. Since water is the most efficient plasticizer for zein but not for PCLH, the sheets with higher zein content possessed lower strength at yield point, as shown in Fig. 2. After the yield point, zein blocks were easily mobilized due to the existence of sufficient water plasticizer. The mobilized zein component made the PCLH segments easier to recrystallize with extension, which caused high strength and elongation at the breaking point. Amphiphilic DBT was a plasticizer for both zein and PCLH. The decrease of DBT content also contributed to the improvement of strength in ZPS20-50. In order to support our analysis further, water uptake and DBT weight loss for wet sheets were measured.

The results are exhibited in Fig. 3. The water uptake reduced steadily with an increase of PCLH content, indicating improvement in water resistance due to the increase of hydrophobic PCLH content. The water uptake of ZPS50 was 8.5%, much lower than that of CZS (24.9%). The DBT weight loss of ZPS10-50 tended to rise with increasing PCLH content. Both DBT and zein are amphiphilic, but PCLH is hydrophobic. Therefore, the interaction between DBT and zein was stronger than that between DBT and PCLH. Sheets with more zein needed

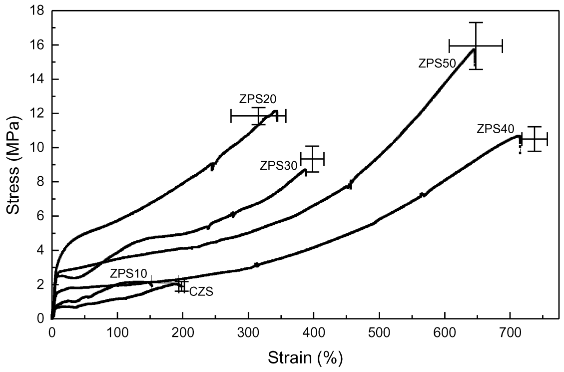

Fig. 2. Stress–strain curves of CZS and ZPS10-50, immersed in water for 24 h at room temperature before test.

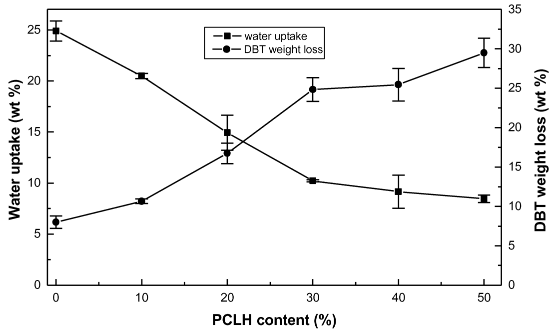

Fig. 3. Effect of PCLH content on the water uptake and DBT weight loss of CZS and ZPS10-50.

more DBT content, and sheets containing little zein content bonded little DBT. This resulted in that under the condition of same content in DBT for ZPS10-50, a part of DBT in the PCLH-rich sheets would be free from the matrix. As the PCLH content in ZPS10-50 increased, the amount of 'free' DBT increased, which contributed to the increased DBT weight loss since free DBT was easier to permeate into water than bound DBT. In order to support the above analysis, DSC experiments were conducted to test the content of free DBT and bound DBT.

3.2. Thermal properties

We conducted a control experiment in order to analyze DSC results clearly. White PCLHE was melted and blended with DBT to obtain a PCLHE/DBT mixture. The weight ratio of PCLHE to DBT was 2:1. DSC thermograms of PCLHE, DBT, PCLHE/DBT mixture, CZS, and ZPS10-50 at the second heating scan are shown in Fig. 4. DBT exhibited a crystallization peak at -19.6 ± 1 °C, a melting peak at 21.3 ± 0.3 °C, and a glass transition at -68.4 ± 0.2 °C. PCLHE exhibited a melting peak at 42.1 ± 0.4 °C and a glass transition at -53.4 ± 0.9 °C. However, in the PCLHE/DBT mixture, the two T_gs of PCLHE and DBT merged into one glass transition at -63.0 ± 0.8 °C, and the ΔC_P value (0.32 ± 0.04 J g^{-1} K^{-1}) was also between that of PCLHE (0.26 ± 0.03 J g^{-1} K^{-1}) and DBT (0.80 ± 0.04 J g^{-1} K^{-1}). In the mixture of PCLHE/DBT, the molecular chains of PCLHE and DBT bonded together by hydrogen bonding, which caused intermolecular forces of PCLHE macromolecules and the mobility of DBT molecules to decrease. This reduced the T_g of PCLHE to a low temperature and increased the T_g of DBT to a high temperature. Therefore, only one glass transition in their mixture (PCLHE/DBT) was observed. The crystallization peak at -19.6 °C for DBT in the mixture of PCLHE/DBT (Fig. 4, PCLHE/DBT) disappeared due to the interaction between PCLHE and DBT, implying that the crystallization of DBT molecules was completely destroyed. Therefore, the melting peak at 33.7 ± 0.7 °C should be only assigned to PCLHE due to the lack of DBT crystals in this mixture. The reduction of the melting peak of PCLHE in the PCLHE/DBT mixture indicated that an interaction existed between PCLHE and DBT. The glass transition, crystallization peak, and melting peak of DBT in CZS, the mixture from commercial zein and DBT by weight ratio of 2:1, were not observed in Fig. 4. This suggests a strong interaction between zein and DBT. There are two ester groups and two hydroxyl groups in every DBT molecule chain, which easily form hydrogen bonding with the carbonyl groups and hydroxyl groups in zein macromolecule. In particular, the glass transition of DBT for CZS disappeared but observed in the PCLHE/DBT mixture, indicating the interaction between zein and DBT was stronger than that between PCLHE and DBT. The exothermal peak at -19.6 °C and endothermal peak at 21.3 °C for ZPS50 were attributed to the crystallization and crystal melting of a part of DBT in the sheet. These two peaks occurred at the same temperatures as that of pure DBT, indicating this part of DBT had almost no interaction with zein or PCLH, and was free. The same occurred in ZPS40. However, CZS and ZPS10-30 did not show any peak of free DBT, implying that all DBT in these sheets was bonded with macromolecules. For the same DBT content, DBT in a PCLH-rich sheet became free more easily than in the zein-rich sheet because that PCLH and DBT had less ability to form hydrogen bonding than zein and DBT. While PCLH reached a critical content, the free DBT showed the same thermal behavior as pure DBT. The melting peaks of PCLH in ZP20-50 (modified zein materials without DBT plasticizer) were obvious in the results of our previous work [13]. However, these peaks in ZPS20-50 were not observed in Fig. 4, indicating DBT had destroyed the PCLH crystal in ZPS10-50. According to the above analysis, DBT plasticizer was, in fact, a compatibilizer to zein and PCLH components in modified zein sheets.

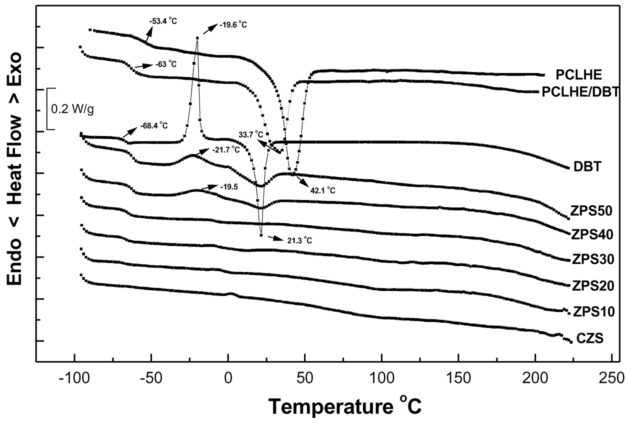

Fig. 4. DSC thermograms of PCLHE, DBT, PCLHE/DBT mixture, CZS, and ZPS10-50 at the second heating scan. The curve of DBT was compressed by 5 times along *Y* axle to plot the curve in this figure conveniently.

For ZPS10-50 (Fig. 4), the T_g and ΔC_P of the PCLH component changed with increasing PCLH content. To make a clear observation, we summarized and displayed

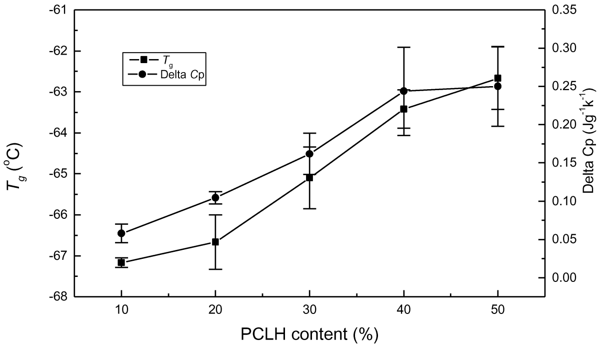

Fig. 5. Effects of PCLH content on the T_g and ΔC_P of PCLH component in modified zein sheets (ZPS10-50).

related data in Fig. 5. The mobility of the PCLH molecular chain decreased due to the existence of zein domains, resulting in the T_g of PCLH component increasing with an increase of PCLH content (Fig. 5). All change in ΔC_P is related to the weight fraction affected by glass transition [16], so the ΔC_P of the PCLH component also increased with an increase of PCLH content in Fig. 5. The glass transitions for zein for CZS and ZPS10-20 were broad and weak from 65 to 155 °C (Fig. 4), which made it difficult to obtain correct data from these transitions. Therefore, sensitive DTMA was used to analyze the glass transitions of the zein matrix.

The curves of loss tangent (tan δ) to temperature of CZS and ZPS10-50 are displayed in Fig. 6. A large tan δ peak for each sample, associated with the glass transition of the zein matrix, was clearly observed from 60 to 170 °C. This peak occurred at 180.4 °C for pure zein [13], but decreased down to 95.2 °C for CZS due to the plasticization of DBT. This indicates that DBT had a good efficiency on zein. Because all of the samples were dried before test, this peak was independent of moisture. According to our previous work [13], the peak of CZS at 95.2 °C, and its shoulder at 124.1 °C, maybe attributed to the two subfractions (22 and 24 kDa) of α-zein, respectively.

In order to study the important effects of water on the properties of modified zein, the residual samples after a DBT weight loss test (Fig. 3) were used for DSC analysis. The DSC thermograms of the samples are shown in Fig. 7, and the related data are summarized in Table 1. According to our calculation using the data in Fig. 3, the residual DBT contents by weight were 22.7% in ZPS10, 16.6% in ZPS20, 8.5% in ZPS30, 7.8% in ZPS40 and 3.8% in ZPS50. The residual DBT content in the sheets decreased with increasing PCLH content, which increased T_g of zein matrix from 110 °C for ZPS10 to 174.8 °C for ZPS50. Fig. 7 shows the clear melting peaks of PCLH component due to the weight loss of DBT. However, the corresponding melting peaks for the samples before DBT weight loss measurement, could not be observed on Fig. 4, which indicates the PCLH crystal was seriously retarded by DBT in the untreated sheets. The appearance of large crystal melting peaks of the PCLH component and obvious glass transitions of zein matrix (148 °C–175 °C) for ZPS30-50 (Fig. 7) implied that PCLH segments and zein matrix were in micro-phase separation. At 25.5 °C, all sheets subjected to a tensile test were nearly amorphous due to the fact that T_ms of ZPS20-50 were near or below 28 °C as shown in Table 1.

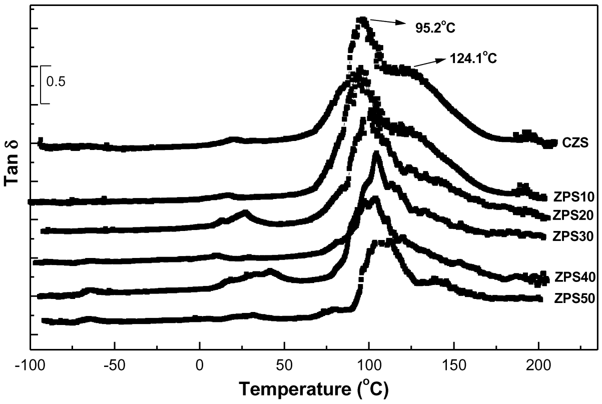

Fig. 6. Curves of the loss tangent (tan δ) to temperature of CZS and ZPS10-50.

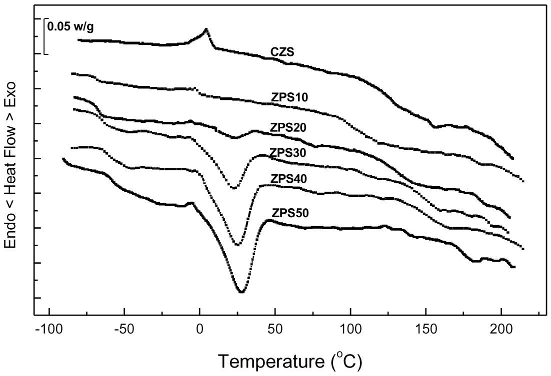

Fig. 7. DSC thermograms of CZS and ZPS10-50, which were immersed in water for 24 h, and dried for DBT weight loss analysis (Fig. 3), finally for this DSC test.

From Fig. 2, we can conclude that the mechanical properties of ZPS20-50 were improved after ZPS10-50 sheets were immersed in water for 24 h. Thus, according to the above thermal analysis, we propose the following detailed explanation for this phenomenon: A large amount of DBT was extracted from ZPS20-50 by water, and an obvious micro-phase separation formed in the sheets due to the loss of compatibilizer (DBT). During tensile testing, the well-separated PCLH component tended to aggregate together and extend easily, resulting in a formation of physical cross-link points, which in turn increased the breaking strength of the sheets. Alternatively, zein domains plasticized by water increased the elasticity of the sheets. Finally, the mechanical properties of the ZPS20-50 sheets immersed in water were improved. This is similar to the case of polyurethane elastomer, in which good micro-phase separation results in excellent mechanical properties and

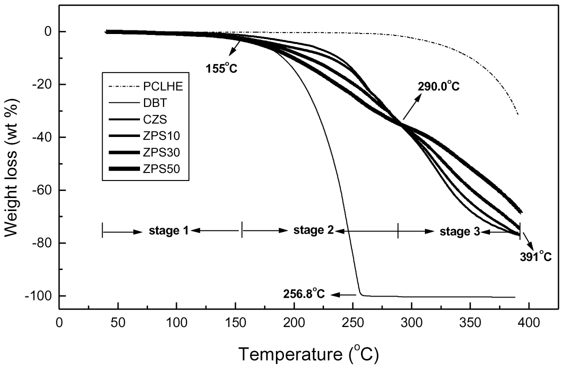

Fig. 8. TGA thermograms of DBT, CZS, ZPS10, ZPS30, ZPS50, and PCLHE.

Table 1
Results of DSC of CZS, and ZPS10-50, immersed in water for 24 h and dried before test

Material	Glass transition of zein matrix				Melting peak of PCL		Transition of PCLH	
	T_{g_o} [a] (°C)	T_{g_m} [b] (°C)	T_{g_e} [c] (°C)	ΔC_P (J g^{-1} K^{-1})	T_{m_m} (°C)	ΔH (J g^{-1})	T_g [d] (°C)	ΔC_P (J g^{-1} K^{-1})
CZS	119.9 ± 8.8	130.3 ± 5.1	139.0 ± 6.6	0.25 ± 0.03	–	–	–	–
ZPS10	102.5 ± 1.3	110.0 ± 2.4	121.7 ± 6.4	0.15 ± 0.05	–	–	−67.2 ± 2.2	0.04 ± 0.01
ZPS20	120.0 ± 6.3	132.6 ± 4.2	141.8 ± 6.6	0.18 ± 0.03	22.1	2.4 ± 0.4	−66.9 ± 0.4	0.06 ± 0.01
ZPS30	144.7 ± 0.2	148.1 ± 1.3	155.1 ± 4.4	0.13 ± 0.01	23.0 ± 0.7	7.30 ± 0.10	−62.3 ± 1.5	0.10 ± 0.02
ZPS40	141.0 ± 7.3	150.6 ± 4.0	162.2 ± 1.1	0.15 ± 0.02	26.0 ± 0.7	12.10 ± 0.62	−57.0 ± 1.0	0.16 ± 0.03
ZPS50	171.3 ± 0.4	174.8 ± 0.8	178.6 ± 1.6	0.09 ± 0.01	29.0 ± 2.4	14.17 ± 0.80	−57.0 ± 1.2	0.07 ± 0.02

[a] o, expresses as the onset temperature.
[b] m, the midpoint temperature.
[c] e, the end point temperature.
[d] T_g presents the temperature in the middle of transition.

complete miscibility leads to poor elastomeric properties [17].

The TGA thermograms of DBT, CZS, ZPS10, ZPS30, ZPS50 and PCLHE are shown in Fig. 8. Three stages were observed in these curves. During the first stage (30–155 °C), all samples exhibited an almost constant thermal stability, and according to the DTMA results, the storage modulus decreased sharply after 120 °C. Thus, the best processing temperature was from 120 to 155 °C. In this temperature range, modified zein-based materials were thermally stable and soft, and easily processed by used of hot press or extruder. The second stage is from 155 to 290 °C, in which DBT dissipated quickly, and lost 100% in weight at 256 °C. In CZS and ZPS10-50, however, the thermal resistance of DBT increased due to DBT in the matrix bonded with zein molecules by hydrogen bonding, resulting in that the DBT being exhausted by 290 °C, which was 33.2 °C higher than the temperature of complete dissipation of pure DBT (256.8 °C). According to the previous analysis (Figs. 3–5), some free DBT existed in ZPS50's matrix, and the amount of free DBT decreased with decreasing PCL content in ZPS10-50. This free DBT dissipates more easily than bonded DBT, so from 150 to 290 °C, the weight loss of ZPS50 decreased most quickly, followed by weight losses of ZPS30, ZPS10 and CZS. The third stage started at 290 °C and ended at 391 °C. The weight loss of ZPS50 was the lowest at a given temperature from 290 to 391 °C, and followed by those of ZPS30, ZP10S and CZS. All DBT was exhausted in this stage, but PCL showed more thermal stability then pure zein, which resulted from the thermal stability of ZPS10, ZPS30 and ZPS50 increased with an increase of PCLH content.

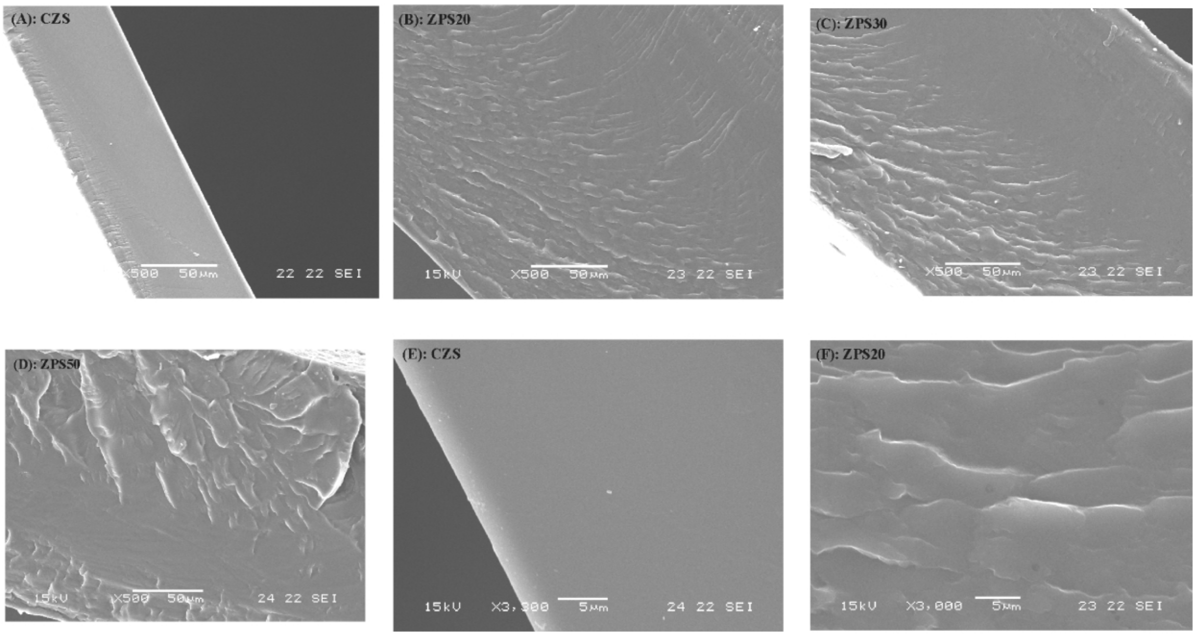

Fig. 9. SEM images of CZS, ZPS20, ZPS30 and ZPS50. (A) CZS × 500, (B) ZPS20 × 500, (C) ZPS30 × 500, (D) ZPS50 × 500, (E) CZS × 3300, (F) ZPS20 × 3000.

3.3. Morphology

SEM images of CZS, ZPS20, ZPS30 and ZPS50 are exhibited in Fig. 9. As shown in Fig. 9(A)–(D), CZS exhibited a smooth and continuously sharp fracture cross-section. However, the cross-sections of ZPS20, ZPS30 and ZPS50 were uneven and coarse and became more so with increasing PCLH content, demonstrating that the degree of phase separation increased with increasing PCLH content. In the amplified images (Fig. 9(E) and (F)), the section of ZPS20 exhibited a fluctuant structure resulting from the minor component (PCLH) being occluded into the matrix (zein), and there were no obvious holes, suggesting a good interface adhesion between two phases. SEM results provided direct evidence that modified zein-based materials had micro-phase separation structures.

4. Conclusion

Sheets from modified zein (ZPS10-50) were macro-homogeneous and micro-heterogeneous, which improved the toughness of ZPS10-50. Due to the aggregation of PCLH and the plasticization of water into the zein matrix, the mechanical properties of ZPS20-50 immersed in water for 24 h, were improved, suggesting good water resistance for ZPS20-50. DBT caused a stronger interaction with the zein matrix than with PCLH. Therefore, DBT is considered as a compatibilizer for the zein matrix and PCLH component. It is, however, expensive to modify zein in organic solution, so it is necessary to use reactive extrusion technology to solve this problem.

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