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Starches modified with polyurethane microparticles: Effects of hydroxyl numbers of polyols in polyurethane

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ABSTRACT

In this work, three different types of polycaprolactone (PCL) polyols-PCL diol, PCL triol and PCL tertol were used to synthesize polyurethane prepolymers (PUPs) with 4, 4′-methylenedi-p-phenyl diisocyanate (MDI). The obtained PUPs then were used to modify thermoplastic starch (TPS) in an intensive mixer. Results showed that the grafting ratio of PUP used for modified starch was 99.6 ± 0.2%, and the hydrophobicity of the modified starches improved compared to that of pure starch. With the increasing —OH numbers of polyols in PUP, the compatibility between polyurethane and starch was improved. The toughness and thermal stability of modified starches were thus increased while the crystallinity of starch decreased. In addition, due to the existence of dense cross-linking, there was strong interaction between starch and PCL tertol based PUP, and the modified starch showed excellent toughness compared to pure starch. The superiorly formed, modified starch could have great potential applications.

1. Introduction

The past two decades have witnessed a growing public and scientific concern regarding the use of biodegradable plastic material as a solution for the growing problem of plastic waste (Dunja, Abou, Rolf, & Wolf, 2004). Among the many kinds of candidates including aliphatic polyesters, natural polymers, and their derivatives, starch is one of the most studied because of its biodegradation, low price and natural abundance (Kim, Cho, & Park, 2001). However, the moisture sensitivity and the brittleness of thermoplastic starch limit its potential applications. Therefore, starch has been blended, plasticized or chemically modified with other compounds by many researchers (Loubna, Thomas, Amar, & Mustapha, 2010).

In order to improve the properties of starch, hydrophobic and ductile polymers are used as modifiers. For example, PCL was directly mixed with starch to make a prepared blend, and the obtained blends acquired superior hydrophobicity and biodegradability as a result (Santayanon & Wootthikanokkhan, 2003). However, the mechanical properties of the blend become poorer with the increase of starch content in the blend due to the incompatibility between hydrophilic starch and hydrophobic PCL (Koenig & Haung, 1995). Improving compatibility between starch and polymers thus is the key problem as it directly affects the properties of starch based composites. In recent years, polyurethane prepolymer (PUP), a polymeric material with various chemical, mechanical, and degradation properties, has been widely used to modify starch (Elodie, Zheng, Michel, & Luc, 2008), and the NCO groups in PUP can form a covalent bond with OH groups in starch. In order to improve the compatibility between starch and polyurethane, PUP was prepared into waterborne polyurethane (WPU) (Wang & Zhang, 2008). WPU has a potential miscibility with starch because they both have hydrophilic groups (Wu & Zhang, 2001). Because the WPU interacted with starch through hydrogen bonds, the mechanical properties of the starch-PUP mixture was also limited.

In our previous work, 20% of castor oil based PUP was used to modify starch with water plasticizer in an intensive mixer (Wu, 2008; Wu, Wu, Tian, Zhang, & Cai, 2008). Compared with pure starch, the toughness of modified starch obviously improved. The SEM result demonstrated that the hydrophobic PUP had good compatibility with hydrophilic starch. The multi-functional PU micro-particles increased the reaction probability of the PU modifier and starch, resulting in high grafting efficiency of PUP (near to 100%). Therefore, the grafting ratio of PUP was almost independent of the given temperature (Wu, Chen, Zhang, Wu, & Huang, 2011), and the given residence time (Wei et al., 2011). It is thus an effective method to modify starch.

In our study, the properties of the modified starch were affected by the structure of the PU microparticles such as hard domains (Zhang, Fan, et al., 2011) and polyol softsegments (Zhang, Zhang, Chen, Wu, & Wu, 2011). During polyurethane synthesis, the reaction speed, crosslink density and properties of polyurethane are directly associated with hydroxyl numbers of the used polyol.

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However, the effect of hydroxyl numbers of the used polyol on the structure/properties of the modified starch has not been studied.

In this work, various polyurethane prepolymers were synthesized using PCL diol, PCL triol, PCL tetrol, and the polyurethane prepolymers were mixed reactively with starch–water mixture to prepare modified TPS. The effects of the polyols structure on the properties of modified starches were investigated. PCL was chosen due to its flexibility, biodegradability and its hydrophobic nature (Huneault et al., 2007).

2. Experimental

2.1. Materials

Polycaprolactone diol ($M_w = 1000\,\mathrm{g\,mol^{-1}}$, hydroxyl value =113 mg KOH/g), Polycaprolactone triol ($M_w = 900\,\mathrm{g\,mol^{-1}}$, hydroxyl value =184 mg KOH/g) and Polycaprolactone tetrol ($M_w = 1000\,\mathrm{g\,mol^{-1}}$, hydroxyl value = 218 mg KOH/g) were purchased from Perstorp UK Ltd. (Cheshire, UK). 4, 4′-methylenedi-p-phenyl diisocyanate (MDI, 98%) was purchased from Sigma–Aldrich Fine Chemicals (St. Louis, MO, USA). Corn starch (CS, amylose: 23–26 wt.%; moisture: 12 wt.%) was obtained from Wuhan Corn Starch CO. Ltd. (Wuhan, China) and used without any further pretreatments. Butyl acetate (analysis grade) was purchased from China National Pharmaceutical Group Corporation (Shanghai, China).

2.2. Synthesis of PUP

When excess isocyanate (MDI) was reacted with polyols, PU-polyols (PUP) with terminal NCO groups were created, and these terminal NCO groups could then crosslink the PUP and starch. The molar number ratio of isocyanate to hydroxyl group (NCO/OH) was 2.0. PCL diol (151.5 g) was charged into a 500 mL three-necked flask fitted with a stirrer operating at a speed of 300 rpm, an inlet and an outlet. The system was dried in vacuum (2 mmHg) at 110 °C to remove the moisture in the PCL diol. After 30 min, the temperature of PCL diol in the flask was decreased to 70 °C, and then MDI (109.2 g) was charged in the flask under a nitrogen atmosphere. The translucent mixture in the flask quickly became transparent. Fifteen minutes after the addition of MDI, the mixture was stirred vigorously and left to react at 80 °C for 1 h. A transparent white PUP was finally obtained. The PUP prepared with PCL diol was designated PU2. Under the same conditions, PCL triol was also used to synthesize PUP with MDI and designated PU3. PCL tetrol-based PUP could not be obtained with the above synthesis method because the polymerization reaction quickly reached its gel point. Therefore, PCL tetrol reacted with MDI at the temperature of 40 °C for 10 min, the obtained PUP was designated PU4.

2.3. Preparation of PU powder

The PU3 was poured into a mold and cured at ambient conditions for 30 days to prepare the PU3 sheet. In this case, the un-reacted terminal NCO groups of the PUP were consumed by moisture in the air. The PU3 sheet was milled into PU powder in a polymer grinder (GP-00001 model, Wuhan Qien Science & Technology Co., Ltd., Wuhan, China) with the use of liquid nitrogen. The PU3 powder was then filtered using a screen with 40 meshes.

2.4. Preparation of modified TPS

Corn starch (45.8 g), PU2 (11.5 g), and water (15.8 g, added water and the moisture content of starch) were charged into an intensive mixer (SU-70, Changzhou Suyan Science and Technology Co., Ltd., Changzhou city, China) and mixed reactively at 90 °C with a stirrer speed of 100 rpm. After 20 min, a white modified starch was obtained. The modified starch was equilibrated in a sealed plastic bag for 1 day before use. The starch modified with the PU2 was designated as CP2. The "CP" stood for corn starch modified with PCL-based polyurethane, the number of 2 represented for the —OH numbers of PCL groups in the PUP used for modifying corn starch. With the same procedure, PU3, PU4 and PU3 powder were used to prepare CP3, CP4 and TPS-PU3, respectively. The weight of PU to the total weight of dry starch and PUP in all modified starches was controlled to be 20 wt.%. Without addition of PUP, native corn starch was also processed and assigned as TPS.

2.5. Preparation of sample sheets by compression-molding

Modified starches were compression-molded in a hot press (R3202 model, Wuhan Qien Science & Technology Co., Ltd., Wuhan, China) equipped with a water cooling system. The molding time, temperature and pressure were 5 min, 90 °C and 20 MPa, respectively. The wet sheets were cut into a dumbbell-like sheet (5A type) according to GB/T1040-2006. The length of the dumbbell-like sheet was 75 mm, and width of the narrow section was 4 mm. The sheets were equilibrated at 60% RH for at least 2 weeks before testing.

2.6. Moisture content measurement

Small parts (about 1 g) were cut from the molded starch sheets, weighed and dried at 110 °C. After drying the sample until constant mass, the sample was weighed again to calculate the moisture content in the sample:

$$\text{Moisture content}\ \ (\%) = \frac{W_1 - W_2}{W_1} \times 100 \tag{1}$$

where W_1 and W_2 are the weight of starch sheets before drying and after drying, respectively.

2.7. NCO content

NCO content was measured using the 2-dibutylamine method reported by Cong and Yu (2003).

2.8. Tensile test

Mechanical properties were measured using a tensile tester (CMT6503, Shenzhen SANS Test Machine Co. Ltd.) according to ASTM D 882-81 with a strain rate of 5 mm min^{-1}. The distance between the two clamps was 40 mm. Strength at break (σ_b, MPa) and elongation at break (ε_b, %) of the sheets were recorded. Four duplications were made.

2.9. Grafting ratio

CP4 (5 g) and water (250 g) were heated in a beaker (500 mL) at 95 °C for 1 h to obtain a starch dispersion. Butyl acetate (20 g) was then added to separate the unreacted PU component in the CP4. After mixing for 30 min, the aqueous system was stood at 5 °C for 12 h to obtain a transparent butyl acetate layer and a water layer. The water layer was roughly taken out of the beaker using a pipette, and the residue in the beaker was washed 4 times with a large amount of water. The washed residue (containing unreacted PU) was concentrated, dried and weighed. As a control, dried unmodified starch (4 g) was extracted using the above water–butyl acetate solvent mixture. In order to discern the efficiency of this analysis method, polyurethane powder (1 g) and dried unmodified starch (4 g) were mixed and extracted using the same procedure as that for CP4. According to our previous work (Zhang, Fan, et al., 2011; Zhang, Zhang, et al., 2011), the weight of the solid residue in the butyl acetate layer (polyurethane powder) was 0.97 g. This was near to the weight of added PU powder (1 g), suggesting that unreacted PU could be almost completely separated and recycled. Therefore, the quantitative method for analyzing the grafting ratio of PU was efficient. The "CS-SR" and "CP4-SR" represent the solid residue (SR) in butyl acetate layer of the CS sample and CP4 sample, respectively.

The grafting ratio of modified starch was calculated as follows:

$$\text{Grafting ratio} \quad (\%) = \frac{100-(W_{\mathrm{L}}-W_1)}{W_2} \times 100 \qquad (2)$$

where W_{L} represented the weight of solid residue in butyl acetate layer for modified starches, W_1 was the weight of solid residue in butyl acetate layer for dried unmodified starches, W_2 was the weight of PU used to modify starch in theory (1 g). Three duplications were carried out.

2.10. Fourier transform infrared spectroscopy (FTIR)

A FTIR spectrometer (avator 360, Nicolet, MA, USA) at room temperature was used. Test samples were pulverized with KBr and pressed into transparent disks for analysis. All spectra of samples were recorded in transmission mode at a resolution of 4 $\mathrm{cm^{-1}}$ with accumulation of 8 scans.

2.11. Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC, Agilent 1100, USA). Mobile phase was tetrahydrofuran (THF) at a rate of 1.0 $\mathrm{mL\,min^{-1}}$ and the column temperature was maintained at 35 °C. Polystyrenes with ten different molecular weights from 2000 to 5,000,000 $\mathrm{g\,mol^{-1}}$ were used as standards. All samples (1 wt.%) were prepared in THF and used for GPC analysis.

2.12. Emission Scanning Electron Microscopy (ESEM)

An ESEM (FEI, Quanta 200 FEG, Netherlands) was used to observe the cross-sections of fractured samples. Each sample was frozen using liquid nitrogen, and then fractured using tweezers to produce cross-sections. The cross-sections were then coated with gold and used for ESEM observation.

2.13. Viscosity measurements

A rotary viscosimeter analyzer (DV-II + PRO LV, Brookfield, USA) was used to determine the viscosity properties of the starch suspension. Before the test, castor oil was used for the calibration of the instrument. Starch aqueous suspension (6%, w/w) was prepared, and the starch suspension was cooked at 60 °C with stirring. The Brookfield viscosity of the sample was measured with 100 rpm of spindle speed and a No. S61 spindle. The viscosity of dispersion samples was also tested at 70 °C, 80 °C, and 90 °C, respectively.

2.14. X-ray diffraction (XRD)

Sheets were measured with wide-angle X-ray diffraction (WAXRD) (Y-2000 Dandong radiative instrument group Ltd. Co., China). For irradiation, the Cu Kα line was applied (λ at 0.1542 nm, cathode at 30 kV and 20 mA), and scattering was recorded in the range of $2\theta = 5\text{–}40^{\circ}$.

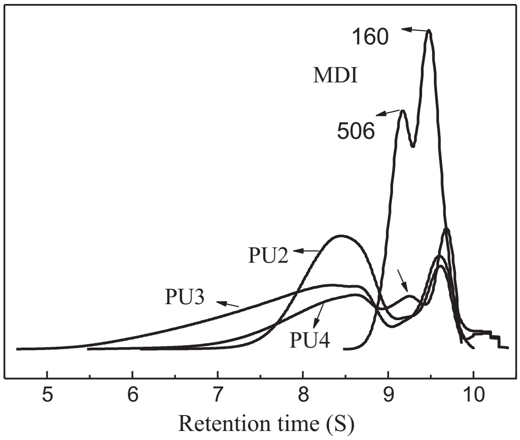


Fig. 1. GPC chromatogram of PU2, PU3, PU4 and MDI.

2.15. Thermal Gravimetric Analysis (TGA)

Testing was conducted using a thermal gravimetric analyzer (STA 449C, NETZSCH Instruments Inc., MA, USA). Approximately 10 mg of the sample cut from the sheet was equilibrated at ambient conditions and then subjected to heating from 30 to 500 °C at a rate of 20 °C $\mathrm{min^{-1}}$ in a nitrogen atmosphere. The weight loss with respect to temperature and the maximum degradation temperature (T_m) of samples were recorded.

3. Results and discussion

3.1. Structure

GPC chromatograms of PU2, PU3, PU4 and MDI are shown in Fig. 1. In MDI chromatogram, the peaks appeared at the retention times of 9.2 s and 9.4 s corresponded to components with the M_w of 506 $\mathrm{g\,mol^{-1}}$ and 160 $\mathrm{g\,mol^{-1}}$, respectively. The M_w of MDI monomer was 250 $\mathrm{g\,mol^{-1}}$, this result indicated that dimmer molecules of MDI formed. Theoretically, linear diols produces PU with linear chains, and branched polyols produces crosslinked PU, and gel may appear when the PU polymerization goes on to a point (Hepburn, 1982). In our experiment, when MDI reacted with PCL tetrol at the temperature of 80 °C, gel would rapidly form within 4 min. This indicated the gel could more easily form in highly branched polyols system. Finally, the reaction temperature of synthesis PU4 was decreased to 40 °C (melting temperature of MDI) and the reaction time was 10 min. The M_w of PU2, PU3 and PU4 obtained from GPC analysis were 5864, 18,770, 8902 $\mathrm{g\,mol^{-1}}$, respectively. PU4 could not be completely dissolved into THF solution in GPC experiment; consequently the result was lower than its actual value. In addition, PU4 was gel-like material while PU2 and PU3 were viscous flow materials, the M_w of PU4 should be higher than that of PU2 and PU3. Therefore, M_w of PUP increased with the increase of the —OH numbers in polyols.

FTIR spectra of TPS, CP2, CP3 and CP4 are shown in Fig. 2. As shown in Fig. 2, modified starches showed similar curves profile to that of TPS. Compared with the spectra of modified starches and TPS, the profiles of the band from 1730 to 1640 $\mathrm{cm^{-1}}$ were different, and three new peaks formed for modified starches in this range. The peak at 1710 $\mathrm{cm^{-1}}$ was attributed to the absorption of $\mathrm{C{=}O}$ in urea (—NH—CO—NH—) (Kishore, Chattopadhyay, & Raju, 2007), and the peaks at 1644 $\mathrm{cm^{-1}}$ and 1732 $\mathrm{cm^{-1}}$ were assigned to C—O and $\mathrm{C{=}O}$ absorption band of urethane (—NH—CO—O—) (Yang, Kwon, Kim, & Park, 2007), this confirmed that the starch OH groups had reacted with the NCO groups of PU. This result was in agreement

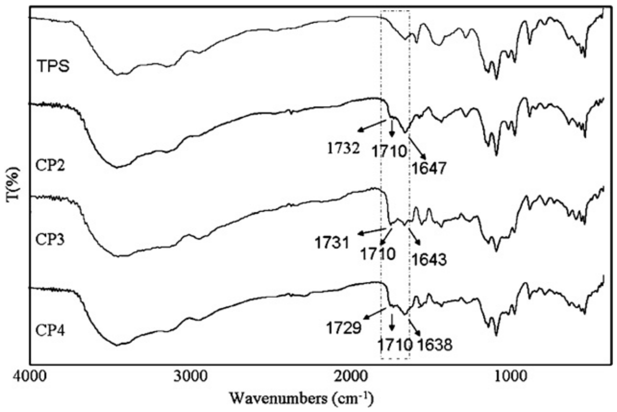


Fig. 2. FTIR spectra of TPS, CP2, CP3 and CP4.

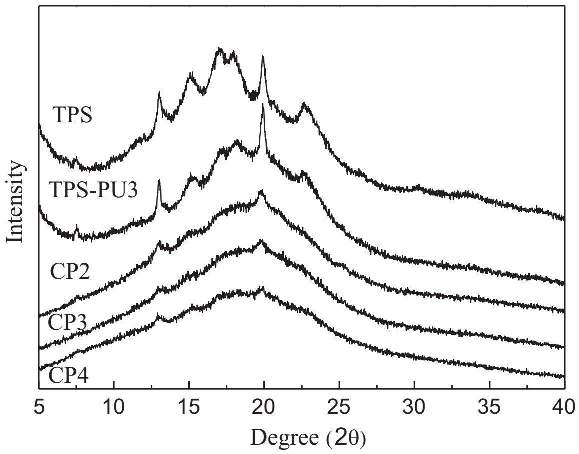


Fig. 4. WAXRD patterns of TPS, TPS-PU3, CP2, CP3 and CP4.

with the results obtained in other starch-PU system by our previous work (Wu et al., 2008). Moreover, the weight of CS-SR and CP4-SR were 0.020 ± 0.01 g and 0.024 ± 0.01 g, respectively, and the grafting ratio of PU4 used for modified starch (CP4) was 99.6 ± 0.2%. These indicated that PUP almost completely reacted with starch, suggesting that modification was efficient and successful.

The SEM images of fractured surfaces for the modified starches are shown in Fig. 3. It could be seen that the PUs existed as dispersed white dots in the starch matrix. Due to the low cross-linking density, the interface between starch and PU2 was not strong. The phase separation (Fig. 3a) and the holes in CP2 (Fig. 3b) could be clearly observed. The structure of PCL polyols and the preparation of the modified starches are shown in Scheme 1. Due to a locking stoichiometric ratio of MDI and polyol, the increasing —OH numbers of polyols in PUP resulted in an increase of the NCO groups on each polyurethane microparticle. As a result, the reaction probability between the microparticle and starch was enhanced. The cross-linking density between PU and starch would then increase, resulting in the improved compatibility between hydrophobic PU and hydrophilic starch. As shown in Fig. 3c and d, CP3 showed a better interface than CP2. What is more, the surface of the CP4 films exhibited the well-dispersed PU4 particles. The PU4 particles were embedded in starch matrix and the interface became unclear; suggesting a strong interaction between PU4 and starch. Therefore, the compatibility between starch and PU could be improved with increasing —OH numbers in polyols.

WAXRD patterns of TPS, TPS-PU3, CP2, CP3 and CP4 are shown in Fig. 4. As shown in the figure, there was no diffraction peaks observed for PUP, this was because the polyurethane prepared with PCL as soft-segments, when the M_n of PCL polyol was lower than a value of around 2000, usually showed no crystallinity because the PCL molecular chain length was not long enough for chain folding (Cao, Dong, & Li, 2007). The curve profile and the intensity of characteristic peaks of TPS-PU3 were similar to that of TPS, indicating the polyurethane powder had no effect on the crystallinity of starch. The crystallinity of corn starch was

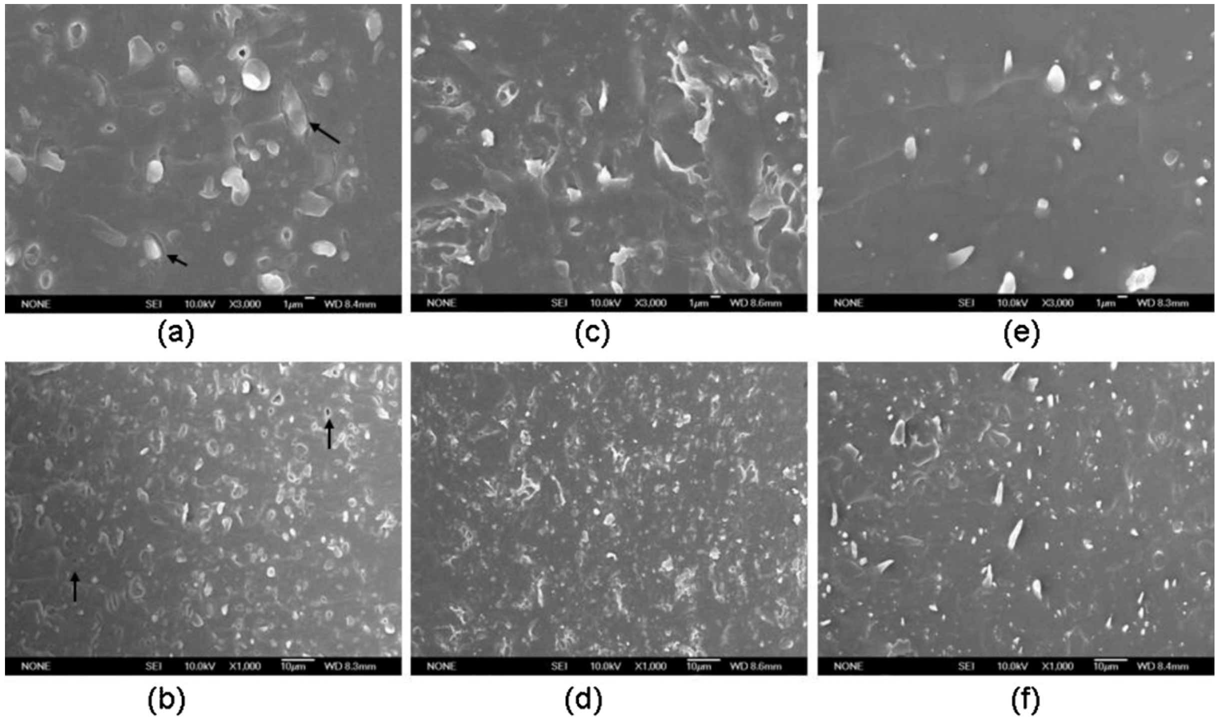
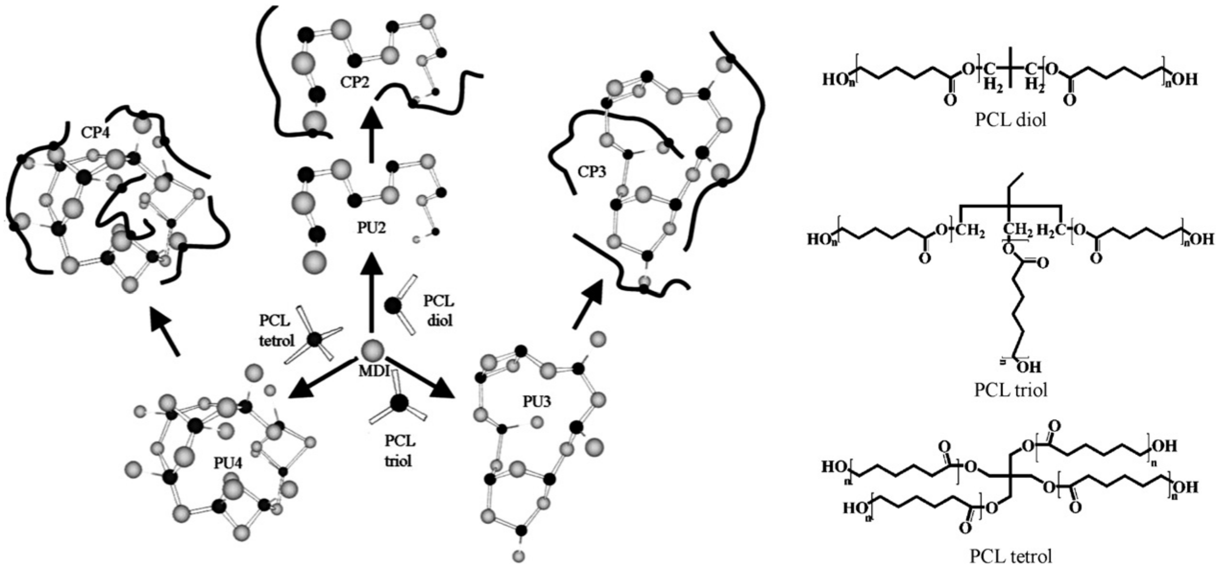


Fig. 3. SEM images of CP2, CP3 and CP4. SEM images of: (a) CP2 (10.0 kV, ×3000); (b) CP2 (10.0 kV, ×1000); (c) CP3 (10.0 kV, ×3000); (d) CP3 (10.0 kV, ×1000); (e) CP4 (10.0 kV, ×3000); and (f) CP4 (10.0 kV, ×1000).



Scheme 1. Structure of PCL polyols and preparation of CP2, CP3 and CP4. PU2, PU3 and PU4 represent PUP prepared by PCL diol, PCL triol and PCL tetrol, respectively; CP2, CP3 and CP4 represent starch modified by PU2, PU3 and PU4, respectively.

Table 1
Viscosity of TPS, CP2, CP3 and CP4 at different temperatures.

Samples	viscosity value (cp) at different temperatures			
	60 °C	70 °C	80 °C	90 °C
TPS	6.3 ± 1.3	10.8 ± 172.0	12.7 ± 1.8	27.5 ± 0.9
CP2	4.0 ± 0.6	3.6 ± 0.2	4.7 ± 0.1	5.2 ± 0.2
CP3	2.6 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	3.1 ± 0.1
CP4	4.7 ± 0.1	4.0 ± 0.1	4.1 ± 0.1	4.6 ± 0.1

ascribed to A-type, with peaks at 15.1, 17.71, 18.0 and 23.0 (Xie & Shao, 2009). However, the intensity of these characteristic peaks decreased or disappeared in the diffractogram obtained for modified starches. This was an indication that the interaction between starch and PUP changed the main crystalline form of modified starches. Due to the recrystallization of amylase of starch during cooling after processing (Van Soest & Vliegenthart, 1997), two V-type crystalline peaks at 13.0 and 19.7 formed, and the diffraction intensity decreased with the increase of the —OH numbers in polyols. The degree of crystallinity here depended on the ability of the chain to form crystals, as well as on the mobility of the chain (Cyras, Zenklusen, & Vazquez, 2006). The increase of cross-link between starch and PU decreased the interaction of the starch–starch chains. As a consequence, the crystallinity of starch in the blends decreased. The degree of cross-link between starch and PU increased with the increasing —OH numbers in PU, leading to the decreasing crystallinity of starch matrix in the modified TPS.

Viscosity values of TPS, CP2, CP3 and CP4 are shown in Table 1. Generally, the gelatinization temperature of pure starch was about 90 °C, the viscosity would sharply increase around this temperature. For TPS, the high temperatures and mechanical stresses during mixer processing destroyed the chains of amylose and amylopectin, the molecular weight of starch was reduced (Berzin, Tara, Tighzert, & Vergnes, 2010), leading to the disappearance of the gelatinization. The viscosity of TPS increased slightly as the temperature rose from 60 to 90 °C. Compared with TPS, the viscosity of modified starches obviously decreased and had no significant change as an increase of temperature. Therefore, the hydrophobic PU particles improved the hydrophobicity of modified starches. Moreover, the modified starches showed similar viscosity, this indicated that the —OH numbers of polyols had no effect on the hydrophobicity of modified starches.

The tensile properties of the molded starches are listed in Table 2. TPS is a quite brittle polymer, unable to undergo large deformation. The effect of PUs on the properties of modified starches could be clearly seen in the table. Linear PU2 had limited degree of crosslinking with starch, leading to partial compatible of two polymers in CP2. The elongation at break of CP2 was slightly increased compared to TPS. With increasing —OH numbers, the branched PU increased the degree of crosslinking with starch. The elongation at break of CP3 was consequently improved. However, large increases in the degree of crosslinking caused polymers to reduce elongation (Huneault & Li, 2007). The elongation at break of CP4 was thus smaller than that of CP3. Generally, the strength of modified starch sheets was affected by the balance of the increased molecular weight of starch and the content of PU (Wu et al., 2008). The PU microparticles with the highest number of available NCO groups were the most efficient cross-linkers, capable of increasing the molecular weight of the starch, resulting in the improvement of tensile strength of the modified TPS, while the PCL soft segments in PU decreased the strength. The effect of PU had dominance over the molecular weight in CP2 and CP3, leading to a decrease of strength. The large increase of the molecular weight also increased the strength of CP4. Therefore, PU4 was an effective additive for improving both the strength and elongation of starch sheets. Generally, toughness was a combination of strength and ductility; one

Table 2
Formulations and tensile properties of molded TPS sheets tested.

Sample	Formulations for modification			Properties of molded sheets			
	Starch (g)	PUP (g)	Water (g)	σ_b (MPa)	ε_b (%)	Toughness (J/m^3)	Moisture content (%)
TPS	60.0	–	24.0	43.7 ± 3.1	2.7 ± 0.4	41.3 ± 4.2	9.6 ± 0.7
CP2	45.8	11.5	22.7	33.8 ± 1.2	4.2 ± 0.1	53.3 ± 3.6	10.6 ± 0.5
CP3	45.8	11.5	22.7	34.8 ± 3.1	11.9 ± 0.9	138.8 ± 24.8	10.7 ± 0.3
CP4	45.8	11.5	22.7	47.8 ± 3.1	6.1 ± 0.5	246.8 ± 21.1	10.9 ± 0.1

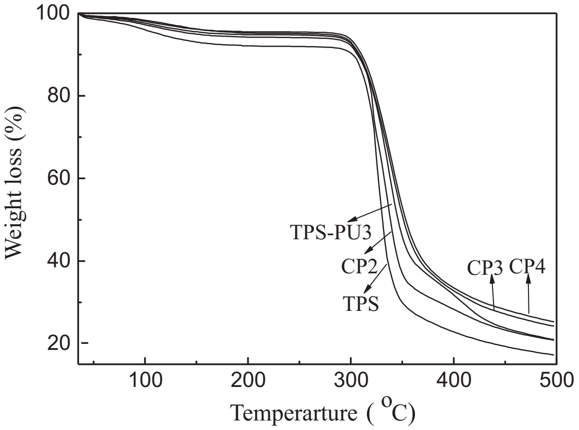


Fig. 5. TGA thermograms of CP2, CP3 and CP4.

of the most important properties of any material for virtually all design applications. As shown in Table 1, the toughness of modified starches increased with increasing —OH numbers and CP4 showed best toughness among the molded starches. Therefore, highly branched polyol based PUP could more effectively improve the performance of the materials.

TGA curves of CP2, CP3, TPS-PU3 and CP4 are shown in Fig. 5. In general, major weight losses were observed in the range of 280–350 °C for all samples, which correspond to the thermal decomposition of starch macromolecules (Liu, Yu, Liu, Chen, & Li, 2008). For TPS-PU3 and CP3, 63% and 49% mass loss respective occurred at 350 °C, and the maximum degradation temperature (T_m) of CP3 (340 °C) was higher than that of TPS-PU3 (322 °C). These indicated that CP3 exhibited better thermal stability compared to TPS-PU3. As analyzed in our previous work (Zhang, Fan, et al., 2011; Zhang, Zhang, et al., 2011), PU powder was incompatible with starch. There was no interaction between PU powder and starch in TPS-PU3. The improvement here was attributing to the urethane bond's interaction between starch and PU3. Therefore, chemical cross-link with PU could improve the thermal stability of modified starch.

As shown in Fig. 5, CP4 showed a slower degradation transition than CP3 and CP2. The T_m of CP2, CP3 and CP4 were 337 °C, 340 °C and 343 °C, respectively. This indicated that the thermal stability of modified starches was improved with the increasing —OH numbers of polyols. With the increasing —OH numbers of polyols, the compatibility between starch and PUP would be improved, and the improvement of compatibility was beneficial to improve the thermal stability of the modified starches. Hence, CP4 showed best thermal stability.

4. Conclusion

The modified starches were successfully prepared from corn starch and PUPs with different —OH numbers in polyols. The hydrophobicity of modified starches was enhanced by incorporation of PU. With an increase of the —OH numbers in polyols, the compatibility between the starch and polyurethane was improved. The toughness as well as the thermal stability of the modified starches were simultaneously increased whilst the crystallinity decreased. The resulting recommendation; that utilizing PUP synthesized with high branched polyols can enhance the compatibility of polymers in modified starch, so as to improve the performance of the materials. Starch-urethane formulations like CP4 demonstrate excellent mechanical properties, with many potential applications.

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