

Toughening of Poly(propylene carbonate) by Carbon Dioxide Copolymer Poly(urethane-amine) *via* Hydrogen Bonding Interaction

Lin Gu^{a*}, Qing-yun Wu^b and Hai-bin Yu^{a*}

^a Key Laboratory of Marine New Materials and Application Technology, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

^b Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

Abstract A carbon dioxide copolymer poly(urethane-amine) (PUA) was blended with poly(propylene carbonate) (PPC) in order to improve the toughness and flexibility of PPC without sacrificing other mechanical properties. Compared with pure PPC, the PPC/PUA blend with 5 wt% PUA loading showed a 400% increase in elongation at break, whilst the corresponding yielding strength remained as high as 33.5 MPa and Young's modulus showed slightly decrease. The intermolecular hydrogen bonding interaction in PPC/PUA blends was confirmed by FTIR, 2D IR and XPS spectra analysis, and finely dispersed particulate structure of PUA in PPC was observed in the SEM images, which provided good evidence for the toughening mechanism of PPC.

Keywords: Carbon dioxide copolymer; Blend; Toughening; Poly(propylene carbonate); Poly(urethane-amine).

INTRODUCTION

Chemical fixation of CO₂ has attracted extensive attention due to environmental concerns and utilization of this potential carbon resource^[1, 2]. As a kind of promising approach, carbon dioxide utilization may supply materials for polymer synthesis, among which, poly(propylene carbonate) (PPC) have been given the most attention from the alternating copolymerization of carbon dioxide and propylene oxide (PO)^[3–5]. PPC is a biodegradable, amorphous and aliphatic polycarbonate, which can be used as binder resins and biodegradable packaging products because of low gas permeability of PPC films^[3–5]. However, the poor thermal and mechanical properties limit the practical applications of PPC. It is because PPC is a weak polar hydrophobic polymer with weak inter-molecular interaction, causing cold flow and dimensional changes in PPC films. In addition, PPC is easily decomposed over 170 °C, leading to a narrow processing window.

In the last two decades, copolymerization and blending have been done to improve the mechanical and thermal properties of PPC^[6–11]. As blending is simpler and more economic than copolymer synthesis, PPC has been attractively blended with other biodegradable polymers, such as poly(butylene succinate) (PBS)^[9], poly(lactic acid) (PLA)^[8], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)^[10] and so on. Nevertheless, their relatively weak inter-molecular interactions lead to low miscibility and phase segregation, and desired properties cannot be obtained easily. In contrast, hydrogen bonding is known to be satisfactory to enhance the miscibility and interfacial interaction in polymer blends^[11–14]. For example, the blends of PPC and starch have

* Corresponding authors: Lin Gu (顾林), E-mail: gulin@nimte.ac.cn

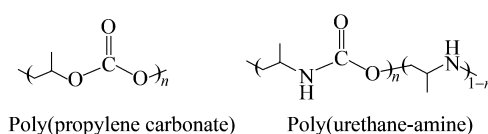
Hai-bin Yu (余海斌), E-mail: haibinyu@nimte.ac.cn

Received September 28, 2014; Revised October 11, 2014; Accepted October 12, 2014

doi: 10.1007/s10118-015-1633-z

hydrogen bonding, improving their interfacial interaction and tensile properties, but no toughening effect has been reported in the blends^[11]. Furthermore, introducing hydrogen bonding has been proven to be an effective way to toughen the polymer. Toughness of PLA was enhanced by blending with biodegradable hyperbranched poly(ester amide) (HBP) without sacrificing comprehensive performance, depending on the hydrogen bonding interaction between the OH end groups of HBP and C=O groups of PLA^[15].

A carbon dioxide copolymer poly(urethane-amine) (PUA) can be easily synthesized by the copolymerization of CO₂ and 2-methylaziridine (MAZ) without any catalyst^[16–18] and its structure is listed in Scheme 1. PUA can be produced in industrial quantities at low cost, because MAZ and CO₂ are inexpensive commercial available monomers. Thus, PUA has great potential for a wide range of applications in materials, especially for industrial use. Since PUA possesses many N–H groups, it should potentially interact with PPC *via* hydrogen bonding. Therefore, it is expectable that PUA could either improve the toughness or tensile strength of PPC. In this work, PUA was used as a modifying agent for PPC. FTIR, 2D IR and XPS analysis were first performed to prove the hydrogen bonding between PPC and PUA. Then, we detailedly evaluated the mechanical and thermal properties of the PPC/PUA blends.



Scheme 1 Chemical structure of PPC and PUA investigated

EXPERIMENTAL

Materials

PPC copolymer was supplied by Inner Mongolia Mengxi High-tech Materials Co. (China) and was prepared from CO₂ and propylene oxide with a ternary rare-earth metal catalyst system^[19]. The copolymer was purified by a repeated dissolution/precipitation procedure with acetone as a solvent and ethanol as a nonsolvent. The number-average molecular weight (M_n) and the polydispersity index (PDI) of the purified PPC were determined by gel permeation chromatography (GPC) as 9.9×10^4 g/mol and 3.05, respectively. The carbonate unit content of the purified copolymer was 98%, being estimated from the ¹H-NMR spectrum according to the formula described in the literature^[19]. PUA copolymer was synthesized by the copolymerization of CO₂ and 2-methylaziridine according to the previous literature^[16–18]. The PUA exhibited a M_n of 3814 g/mol, and PDI of 1.82. The urethane content of the PUA copolymer was 63%, being calculated from the elemental analyses according to the formula described in the literature^[18]. The chemical structure of PPC and PUA was presented in Scheme 1.

Sample Preparation

PPC and PUA were separately dissolved in dichloromethane at a concentration of 5% (*W/V*). The resultant solutions were mixed in desired weight proportions of PUA/PPC (1/99, 2.5/95, 10/90, 15/85, and 20/80), stirred at room temperature for 4 h, and then cast onto Teflon containers. Most solvent was allowed to evaporate at room temperature for 24 h. To further remove residual solvent, all the blends were dried under vacuum at 45 °C until constant weight. The final blends were stored in a desiccator before use.

Characterizations

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 instrument under a N₂ atmosphere. The samples were first heated from –30 °C to 100 °C at a rate of 10 K/min and then rapidly quenched to –30 °C, followed by a second heating process same as the first. The glass transition temperature (T_g) was taken from the second heating curve to minimize thermal history effects.

FTIR spectra were recorded on a Bruker TENSOR-27 spectrophotometer by collecting 64 scans at a spectral resolution of 2 cm^{–1}. The dichloromethane solutions of the blend samples were cast onto a KBr disk and

allowed to evaporate at room temperature, and then vacuum dried at 45 °C for 24 h. The films used here were sufficiently thin to obey the Beer-Lambert law.

2D IR correlation analysis was conducted using a software program (2Dshige (c) Shigeaki Morita, Kwansei-Gakuin University, 2004-2005) for the content-dependent FTIR spectra of the PUA/PPC blends. In the 2D correlation maps, the unshaded regions indicate positive correlation intensities, whereas the shaded ones are negative.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 spectrometer equipped with an Al K α radiation (1486.6 eV) and a hemispherical energy analyzer. The pressure in the analysis chamber was maintained at 10⁻¹³ MPa or lower during measurements, and a pass energy of 20 eV was applied in the analyzer. All core-level spectra were referenced to the C 1s neutral carbon peak at a binding energy (BE) of 284.6 eV. Each spectrum was curve-fitted using the XPSPEAK41 Version 4.0 software. In the curve fitting the widths (fwhm) of Gaussian peaks were maintained constant for all components in a particular spectrum.

Thermo gravimetry analysis (TGA) was tested on a Perkin-Elmer Pyris 1 TGA thermal analyzer under a N₂ atmosphere at a heating rate of 10 K/min from 40 °C to 500 °C.

Tensile tests were measured by a screw-driven universal testing machine (Z010, Zwick. Co., Germany) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at 20 °C using a cross-head rate of 10 mm/min according to the ASTM standard, and the data reported were the mean of the parallel values in five determinations.

Scanning electron microscopy (SEM) was observed on a JEOL JSM 6700F and a XL30 ESEM FEG (FEI Co.). To obtain a better observation of the phase morphology, the microtomed surfaces were etched in methanol for 4 h at room temperature to selectively remove the PUA phase, and then rinsed with MeOH and water, followed by vacuum drying at 45 °C for 24 h. Fracture surfaces from tensile test samples were also examined with SEM, but without any etching. All samples were gold coated by ion sputtering before observation.

RESULTS AND DISCUSSION

Miscibility and Hydrogen Bonding

DSC analysis

DSC is always employed to evaluate the miscibility of polymer blends by measuring the glass transition temperature (T_g) of the components. Figure 1 displays the second heating scans of DSC thermograms for PPC, PUA, and PPC/PUA blends with various compositions. All blends exhibit a monotonic T_g behavior, which suggested that PUA was miscible with PPC at all compositions we chose. Various equations have been designed to predict variations of T_g for miscible polymer blends as a function of composition. The most popular equation is the Kwei equation as follows^[20]:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \quad (1)$$

where W denotes the weight fraction of the composition, whose subscripts “1” and “2” indicated polymers 1 and 2, respectively, and k and q are fitting constants. The Kwei equation is applicable to miscible polymer blends with a specific interaction. Figure 2 shows the dependence of the T_g value on the composition of the PPC/PUA blends. The Gordon-Taylor^[21] and Fox equations^[22] do not fit well the experimental data. However, the Kwei equation can correlate well with the experimental data. $k = 39$ and $q = -29$ are obtained by a nonlinear least squares “best fit” analysis of the equation. Here q is a parameter corresponding to the strength of hydrogen bonding in the blend, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. The q value of the blend should depend on the entropy change corresponding to the change in the number of the hydrogen bonding interaction. A negative q of “-29” obtained in this study indicates that the inter-molecular hydrogen bonding is weaker than the intra-molecular ones, which

might tend to decrease the miscibility of the PPC/PUA blends^[13, 23]. SEM images presented later also show that PUA is only partially miscible with PPC, especially at relatively high contents of PUA. Furthermore, in the high content of PUA (> 10 wt%), there is a large deviation between the experimental data and Kwei equation, which suggests that PUA is not completely miscible with PPC.

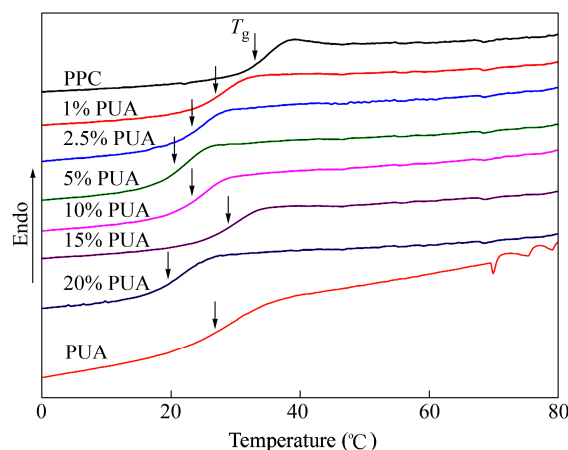


Fig. 1 DSC traces of PPC blended with various PUA contents

As seen from Fig. 2, all T_g s of the blends are lower than those of pure PPC and PUA, which is due to the partial removal of the self-association of the intra-molecular hydrogen bonding^[24]. As a result, a special interaction (*i.e.*, hydrogen bonding) must exist between PPC and PUA to reduce the PUA intra-molecular hydrogen bonding from DSC analysis.

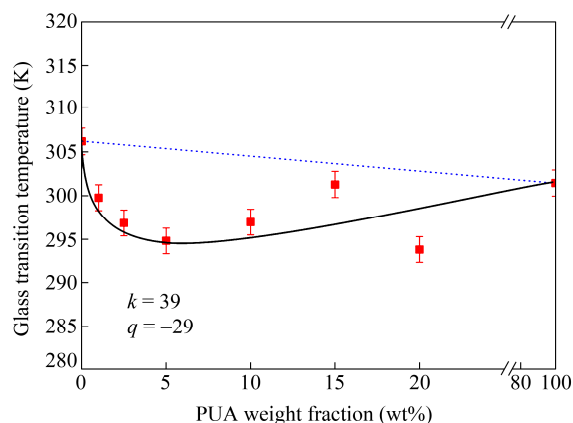


Fig. 2 Plots of glass transition temperature (T_g) versus composition based on the experimental data (■), the linear rule (---), and the Kwei equation (—)

FTIR analysis

Infrared spectroscopy is a highly effective means to investigate the specific interactions between polymers. Figure 3 shows the FTIR spectra of pure PPC and various PPC/PUA blends. For convenience of analysis, all the spectra had been normalized using the area of the C=O stretching region (1700–1800 cm^{-1}) of the samples. In the FTIR spectra of pure PPC, two strong absorption peaks can be observed at 1745 and 1233 cm^{-1} , assigned to the stretching vibrations of the C=O group and C—O—C bands of the carbonate group, respectively^[19]. The intensity of the amine groups (in the 3200–3400 cm^{-1} region) increased gradually with the increase of PUA content (Fig. 3). Meanwhile, two new absorption bands centered at 1706 and 1532 cm^{-1} , corresponding to the C=O stretching and N—H bending modes for urethane groups in PUA^[18], appeared upon adding PUA, and the

intensity increased with increasing the PUA content. The change of C=O absorption peak with various PUA contents is given in Fig. 4 and summarized in Table 1. According to the literatures^[25], the formation of hydrogen bonding between the components would result in shifting, broadening of the C=O absorption peak in the infrared spectra. Upon adding 1 wt% PUA, the C=O absorption peak became broader with the increase of half height width ($w_{1/2}$) from 29.8 cm^{-1} to 34.3 cm^{-1} , and blue shifted from 1745.4 cm^{-1} to 1747.4 cm^{-1} . With the increase of PUA, the C=O absorption peak shifted to a higher wavenumber, and its half height width increased in varying degrees. In addition, the N—H bending vibration peak in PUA shifted to a lower wavenumber compared with pure PUA, as shown in Fig. 3. Consequently, such significant change for the carbonyl group of PPC indicates the occurrence of hydrogen bonding interactions between PPC and PUA, in which the C=O group of PPC acts as hydrogen bonding acceptor and the N—H group of PUA is regarded as hydrogen bonding donor.

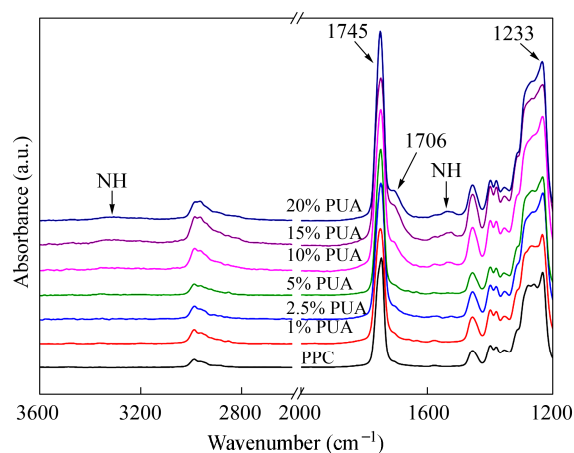


Fig. 3 FTIR spectra for PPC/PUA blends with various PUA contents

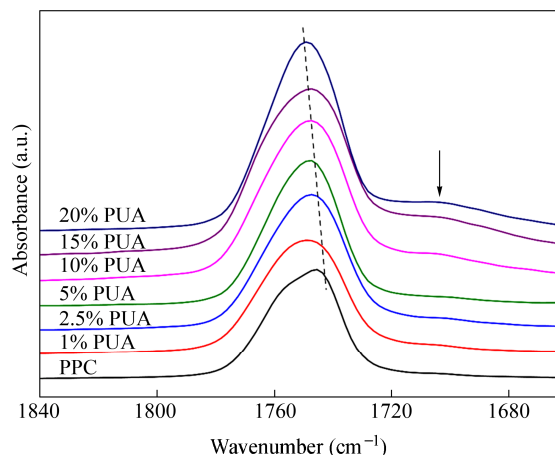


Fig. 4 FTIR spectra at carbonyl region for PPC/PUA blends

Table 1. The change of absorption peaks for C=O group in FTIR spectra of PPC/PUA blends with various PUA contents

PUA content (wt%)	C=O group of PPC	
	ν^a (cm^{-1})	$w_{1/2}^b$ (cm^{-1})
0	1745.4	29.8
1.0	1747.4	34.3
2.5	1747.7	33.4
5.0	1748.0	31.3
10	1748.4	34.5
15	1748.7	34.1
20	1749.1	31.2

^a The peak position of C=O group; ^b The half height width of the corresponding peak

2D IR analysis

Two-dimensional infrared correlation spectra were obtained to confirm the existence of inter-molecular interaction between PPC and PUA. Generalized 2D IR correlation spectroscopy^[26], which is an extension of the original 2D IR correlation spectroscopy^[27], is generated from a set of sequential 1D IR spectra under the external perturbation that is not only the time but also any other physical variables, such as temperature^[28], concentration^[29] and composition^[30]. In our study, the PUA content was used as the external perturbation. Figure 5 displays synchronous (a) and asynchronous (b) 2D IR correlation spectra in the 1800–1600 cm^{-1} region constructed by the content-dependent FTIR spectra. In Fig. 5(a), the obvious autopeak at 1745 cm^{-1} , which is assigned to the stretching vibrations of the C=O group in PPC, suggests that the carbonyl group changed significantly with the increase of PUA content due to the formation of hydrogen bond. As can be seen from

Fig. 5(b), the broad band in the C=O stretching region can be further split into five distinct peaks located at 1770, 1745, 1733, 1700 and 1660 cm^{-1} . The bands at 1745 and 1700 cm^{-1} can be assigned to free C=O stretching vibrations in PPC and PUA, respectively, while the bands at 1770, 1733 and 1660 cm^{-1} could be assigned to hydrogen-bonded C=O stretching vibrations. According to the Noda's rule^[26], the positive cross peaks (1770/1745 and 1770/1700 cm^{-1}) indicate that the intensity variation at 1770 cm^{-1} occurs predominantly before that at 1745 and 1700 cm^{-1} with the increase of PUA content. Meanwhile, the positive cross peaks (1733/1700 and 1745/1733 cm^{-1}) suggest that the intensity variation at 1733 cm^{-1} occurs predominantly before that at 1700 and 1745 cm^{-1} , whereas the evident negative cross peak (1745/1660 cm^{-1}) suggests that the intensity variation at 1745 cm^{-1} occurs after that at 1660 cm^{-1} . All the above information indicates the intensity variation of the hydrogen-bonded carbonyl group occurs predominantly before that of free carbonyl group with increasing the PUA content. Hence, the number of hydrogen bond increases with the increase of PUA content because the free carbonyl group changes into the hydrogen-bonded one.

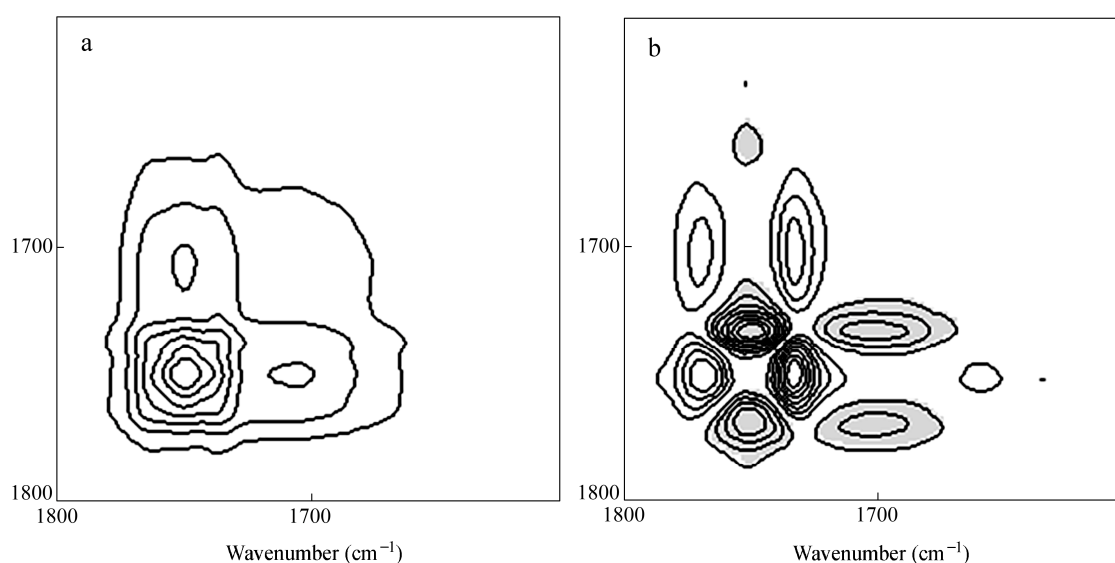


Fig. 5 (a) Synchronous and (b) asynchronous 2D correlation contour maps of content-dependent FTIR spectra at the spectral range between 1800 and 1600 cm^{-1} (Shaded area indicates negative correlation.)

XPS analysis

X-ray photoelectron spectroscopy (XPS) is useful to reveal specific interactions in polymer blends^[31, 32]. The development of a new peak or a shoulder can be observed in the XPS spectrum when the chemical environment of an atom in a polymer blend is perturbed as a result of a specific interaction. Hydrogen bond is electron transfer from proton acceptor to proton donor^[12], leading to increase the electron density in N—H bond, therefore, the binding energy (BE) of N_{1s} in N—H bond should shift to a lower band in XPS spectrum. Figure 6 exhibits the N_{1s} spectrum of pure PUA. For pure PUA, the N_{1s} peak can be deconvoluted into two component peaks. The peak at 399.1 eV is assigned to the amine nitrogen and the peak at 399.9 eV is assigned to the urethane nitrogen^[33]. Figure 7 shows the N_{1s} spectra of the PPC/PUA blends with various PUA contents. The N_{1s} peaks of the blends are broader and asymmetric, and each peak can be deconvoluted into four component peaks, with two remaining at 399.1 and 399.9 eV. Two new low-BE N_{1s} peaks appear in the spectra of all the blends indicating that both types of N—H bond in PUA interact with PPC. The two low-BE N_{1s} peaks are located at 398.1 and 399.3 eV, respectively. The former peak is 1.0 eV lower than 399.1 eV, which is attributed to the interaction between the amine N—H bond and the C=O group of PPC. The latter peak, with a BE value 0.6 eV lower than 399.9 eV, is attributed to the interaction involving the urethane N—H bond. It is suggested from Fig. 7 that the amine N—H bond interacts more strongly with the C=O group of PPC than the urethane N—H

bond does, since the amine nitrogen exhibits a larger BE shift. The different BE shifts of the two nitrogen atoms result from their different electronic environments.

The fractions of the amine nitrogen and urethane nitrogen of PUA involved in hydrogen bonding interaction can be calculated from the area of the low-BE N_{1s} peaks. As list in Table 2, only a moderate fraction of the amine nitrogen and urethane nitrogen atoms undergo hydrogen bonding interaction with PPC.

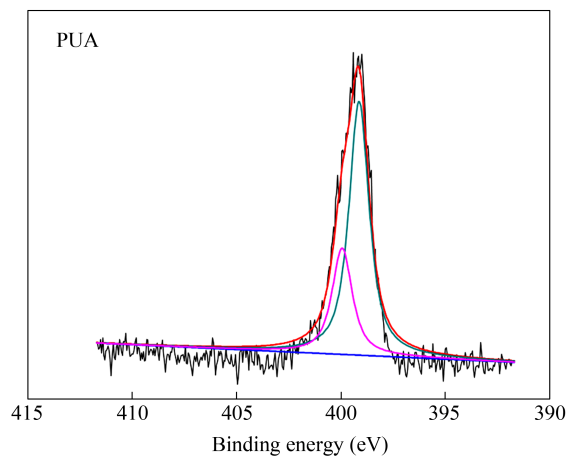
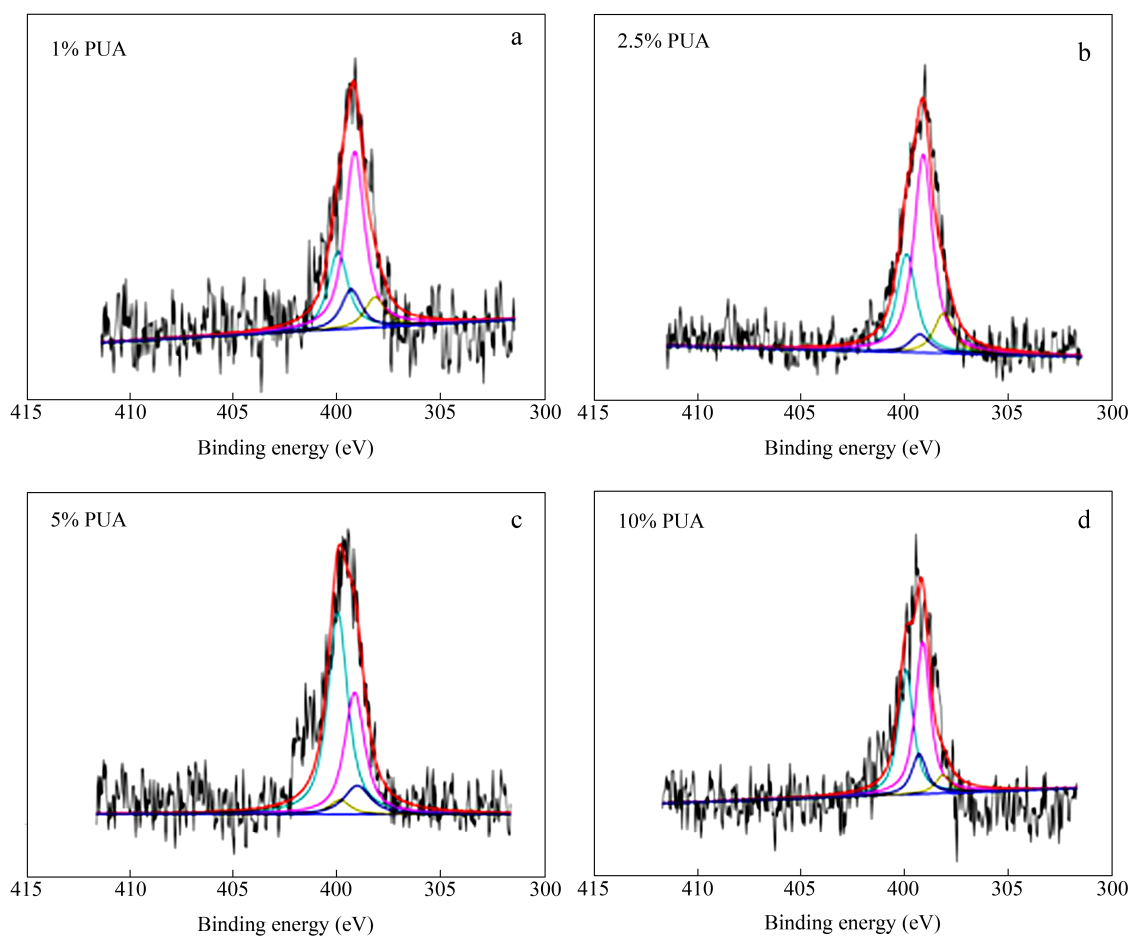


Fig. 6 N_{1s} XPS spectrum of pure PUA



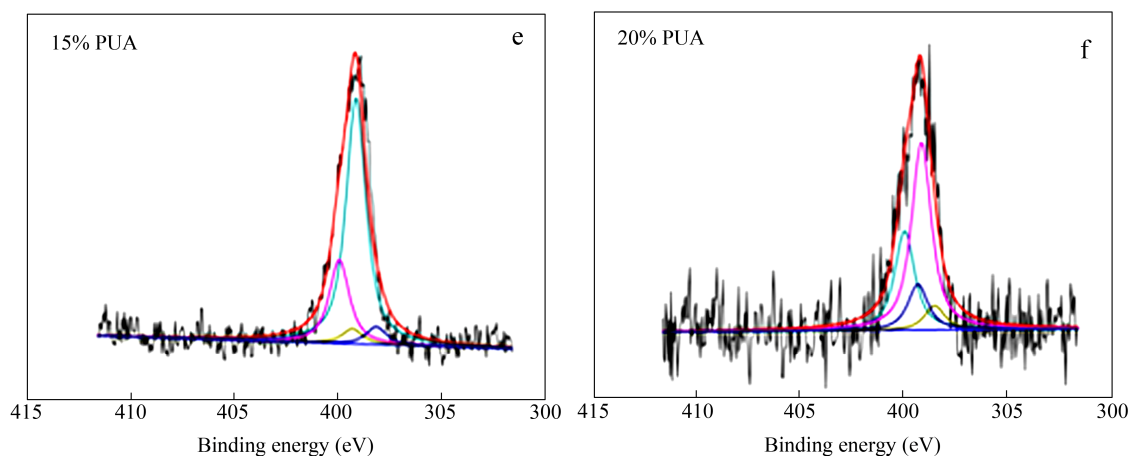


Fig. 7 N_{1s} XPS spectra of PPC/PUA blends with different PUA contents

Table 2. XPS analysis of the PPC/PUA blends

PPC/PUA	99/1	97.5/2.5	95/5	90/10	85/15	80/20	0/100
N_{1s} BE peak (eV)	399.1	399.1	399.1	399.1	399.1	399.1	399.1
	398.1	398.1	399.0	398.1	398.1	398.5	
	399.9	399.9	399.9	399.9	399.9	399.9	399.9
	399.3	399.3	399.8	399.3	399.3	399.3	
Position (and fraction) of the low-BE peak of N_{1s} (urethane) (eV)	399.3 (0.122)	399.3 (0.052)	399.8 (0.038)	399.3 (0.119)	399.3 (0.044)	399.3 (0.128)	
Position (and fraction) of the low-BE peak of N_{1s} (amine) (eV)	398.1 (0.094)	398.1 (0.113)	399.0 (0.098)	398.1 (0.058)	398.1 (0.049)	398.5 (0.068)	

Phase Morphology

The mechanical properties of a polymer blend will be determined not only by the properties of its components, but also by the phase morphology and the interfacial adhesion. In addition, phase morphology studies can provide the relationship between the microstructure and mechanical properties^[34]. Therefore, the phase morphology of the PPC/PUA blends was observed using SEM. To increase contrast, the blend was submerged into the methanol to remove the PUA phase. Figure 8 represents the SEM images of the microtomed surface of PPC/PUA blends with various PUA contents. Pure PPC was one uniform phase, while cavities were observed on adding 1 wt% PUA, indicating that the blend was heterogeneous. Thus, PPC formed a continuous phase and PUA formed a dispersed phase. It suggests that PPC was not miscible at the molecular level with PUA. When the PUA content was increased to 2.5 wt%, a few small and uniform spherical cavities (diameter 2–3 μm) are clearly visible in Fig. 8(b). The size of cavities shows narrow distribution, indicating that PUA phase finely dispersed in the blend. Figure 8(c) also displays narrow distribution of cavity sizes, but the number of spheres was more than that in Fig. 8(b). Continuing to increase the PUA content, the size of the cavities would increase to 3–5 μm as shown in Fig. 8(d) and 8(e), but the PUA phase still displayed good dispersion in the PPC matrix. When the PUA content reached 20 wt%, PUA domains happened to agglomerate and the size of cavities varied from 7 to 10 μm (Fig. 8f).

As is well-known, the hydrogen bonding can enhance interfacial adhesion of polymer blends and then increase their miscibility^[11, 13]. However, phase separation occurred in the blends especially for those with high PUA contents, as shown from the SEM images. The reason can be explained by two factors. First, the results from XPS analysis indicated that not all the N–H bonds in PUA undergo hydrogen bonding interaction with C=O group of PPC. Secondly, the intra-molecular hydrogen bonding is stronger than the inter-molecular ones, which was corresponded to the DSC analysis. Therefore, the increase of PUA incorporation in the blend leads to the aggregation of PUA, and the particle diameter of PUA in blends increased.

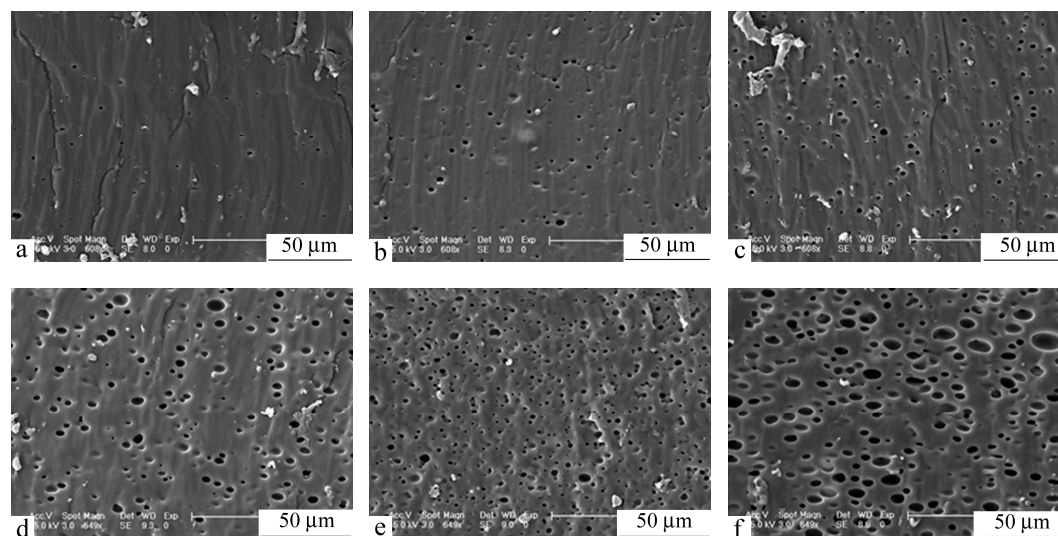


Fig. 8 SEM images of microtomed surface of PPC/PUA blends with various PUA contents: (a) 1 wt%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt% and (f) 20 wt%

Thermal Properties

The thermal properties of pure PPC, PUA and their blends are summarized in Table 3. The 5% weight-loss temperature ($T_{5\%}$) of PPC was 214.0 °C, while the blends with 1 wt%–5 wt% PUA showed a much higher $T_{5\%}$ in the range of 230–238 °C. This increase in $T_{5\%}$ is believed to be associated with the interaction between PPC and PUA *via* hydrogen bonding, which hindered the chain unzipping reaction of PPC under the thermal decomposition^[35]. The hydrogen bonding effect will be suppressed as PUA content increases due to the aggregation of PUA. Correspondingly, the $T_{5\%}$ of the blend decreased. It is evident from Table 3 that the incorporation of PUA into PPC can improve its thermal properties.

Table 3. Thermal properties for PPC, PUA and the PPC/PUA blends

PUA content (wt%)	0	1.0	2.5	5.0	10	15	20	100
$T_{5\%}$ (°C)	214.0	238.2	236.1	230.0	220.5	215.5	202.5	190.5
$T_{\max}^a$ (°C)	228.9	236.5	236.1	233.2	232.1	232.2	232.4	219.9
$T_{95\%}$ (°C)	259.1	249.0	244.1	242.4	259.8	303.3	313.2	325.2
T_g (°C)	33.07	26.61	23.70	21.64	23.81	28.13	20.64	28.30

^a $T_{\max}$ is the temperature of the maximum rate of weight-loss of the samples

Mechanical Properties and Toughening Effect

Figure 9 shows the dependence of the yielding strength and elongation at break on PUA contents of the blends. Table 4 summarizes the specific data for the mechanical properties of the PPC/PUA blends. With increasing the PUA content, elongation at break increased first and decreased after experiencing an optimal value. When PUA content was increased to 5 wt%, the elongation at break reached the maximum value of 51.48%, increasing by 4 times over that of pure PPC, but the yielding strength (33.5 MPa) was slightly lower than that of neat PPC. It is because that hydrogen bonding interactions between PUA and PPC enhance the interfacial adhesion and improve the mechanical properties of the blends. On the other hand, PUA has lower modulus and tensile strength than PPC. When the PUA content increased, the stereo hindrance and dilution effects of heterogeneous component PUA became dominant and suppressed hydrogen bonding effect, and at last tensile strength deteriorated (Fig. 9).

Toughness reflects the degree of energy absorption and can be achieved by adding a second phase in the form of particles, which induces large stress concentrations and leads to extensive shear deformation as a high-energy-absorbing process^[34, 36]. The toughening effect of particles depends on their size, distribution and particle/matrix interaction^[37, 38]. When the PUA was added in 1 wt%, phase separation of the blend was not

obvious. Continuing to increase its content, PUA phase finely dispersed in the PPC matrix and resulted in toughening effect. When PUA content was increased to 5 wt%, the dispersion of PUA phase in the blend became better and the size of particles was relatively small; consequently, the elongation at break reached the maximum value. The size of PUA dispersed phase became large as increasing the PUA content, but it was still in the range of the most efficient particle diameters for dispersed phase toughened composites, which was reported to range from 500 nm to 10 μm ^[39].

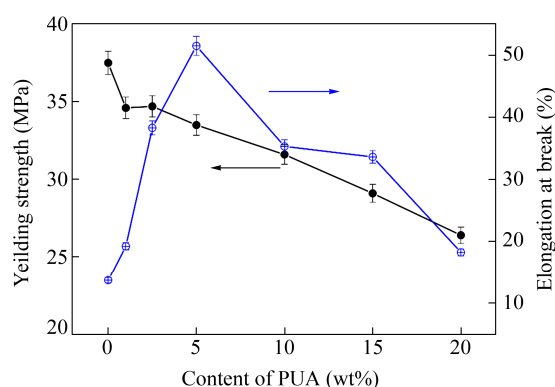


Fig. 9 Yielding strength and elongation at break of PPC with various PUA contents

Table 4. Mechanical properties of PPC with various PUA contents

PUA content (wt%)	Young's modulus (MPa)	Yielding strength (MPa)	Elongation at break (%)
0	1516	37.5	13.63
1.0	1318	34.6	19.21
2.5	1014	34.7	38.29
5.0	1078	33.5	51.48
10	952	31.6	35.30
15	1154	29.1	33.62
20	934	26.4	18.23

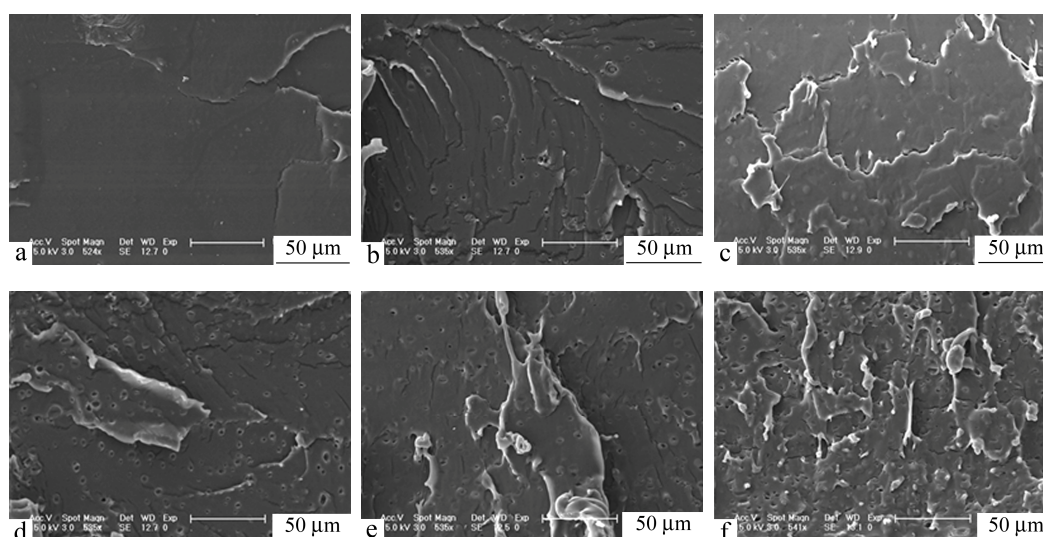


Fig. 10 SEM images of fracture surface of PPC/PUA blends with various PUA contents: (a) 0 wt%, (b) 1 wt%, (c) 2.5 wt%, (d) 5 wt%, (e) 10 wt% and (f) 15 wt%

To further investigate the toughening mechanism of PPC/PUA blends, the tensile fracture surface was studied using SEM. Figure 10 displays SEM images of fracture surface of PPC/PUA blends with various PUA contents. Pure PPC showed a smooth surface, indicating a typical brittle fracture behavior (Fig. 10a). Some fibrils appeared on the fracture surface of the blend with 1 wt% PUA (Fig. 10b). The toughening effect was moderated in this case. On the fracture surface of the blend with 2.5 wt% PUA, multiple fracture surfaces replaced the single surface and became very rough (Fig. 10c). With increasing the PUA content, many cavities appeared and the matrix around the cavities underwent some deformation, inducing a favorable toughening effect (Figs. 10d, 10e and 10f). These cavities are formed when the loading stress was higher than the bonding strength at the interface of the blend components. With the debonding progress, PPC matrix between the PUA particles deformed easily to achieve shear yielding and toughen. In summary, PUA, forming a finely dispersed particulate structure in PPC matrix, functioned as stress concentrations resulting in cavitations *via* debonding.

CONCLUSIONS

The PPC/PUA blends with various compositions have been successfully prepared by solution casting. The results from DSC analysis and SEM images indicated partial miscibility of the blends, which was due to the hydrogen bonding interaction between the N—H bond of PUA and the C=O group of PPC. The hydrogen bonding was confirmed by FTIR, 2D IR and XPS analysis. It is found that the addition of PUA significantly enhanced the toughness of PPC. The elongation at break of the blend was improved by 4 times compared to the pure PPC using 5 wt% PUA, without severely loss in tensile strength. It is because of the moderate interfacial bonding and finely dispersed particulate structure of PUA in PPC. We believe that the toughening strategy exhibits good prospects in expanding the application of the carbon dioxide copolymer PPC and fixing of carbon dioxide into polymers.

REFERENCES

- 1 Mikkelsen, M., Jorgensen, M. and Krebs, F.C., *Energy Environ. Sci.*, 2010, 3(1): 43
- 2 Yu, K.M.K., Curcic, I., Gabriel, J. and Tsang, S.C.E., *ChemSusChem*, 2008, 1(11): 893
- 3 Wu, D.D., Li, W., Liang, H.Y., Liu, S.R., Fang, J.Y. Zhang, H.L., Zhang, H.X. and Dong, L.S., *Chinese J. Polym. Sci.*, 2014, 32(7): 914
- 4 Gu, L., Gao, Y.G., Qin, Y.S., Chen X.S., Wang, X.H. and Wang, F.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2013, 51: 282
- 5 Gu, L., Qin, Y.S., Gao, Y.G., Wang, X.H. and Wang, F.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2013, 51: 2834
- 6 Khan, S.B., Akhtar, K., Seo, J., Han, H. and Rub, M.A., *Chinese J. Polym. Sci.*, 2012, 30(5): 735
- 7 Gu, L., Qin, Y.S., Gao, Y.G., Wang, X.H. and Wang, F.S., *Chin. J. Chem.*, 2012, 30(9): 2121
- 8 Ma, X.F., Yu, J.G. and Wang, N., *J. Polym. Sci., Part B: Polym. Phys.*, 2006, 44(1): 94
- 9 Pang, M.Z., Qiao, J.J., Jiao, J., Wang, S.J., Xiao, M. and Meng, Y.Z., *J. Appl. Polym. Sci.*, 2008, 107(5): 2854
- 10 Peng, S.W., An, Y.X., Chen, C., Fei, B., Zhuang, Y.G. and Dong, L.S., *J. Appl. Polym. Sci.*, 2003, 90(14): 4054
- 11 Peng, S.W., Wang, X.Y. and Dong, L.S., *Polym. Compos.*, 2005, 26(1): 37
- 12 He, Y., Zhu, B. and Inoue, Y., *Prog. Polym. Sci.*, 2004, 29(10): 1021
- 13 Kuo, S.W., *J. Polym. Res.*, 2008, 15(6): 459
- 14 Chen, X., Wang, S.J., Xiao, M., Han, D.M. and Meng, Y., *J. Polym. Res.*, 2011, 18(4): 715
- 15 Lin, Y., Zhang, K.Y., Dong, Z.M., Dong, L.S. and Li, Y.S., *Macromolecules*, 2007, 40(17): 6257
- 16 Soga, K., Chiang, W. and Ikeda, S., *J. Polym. Sci. Polym. Chem.*, 1974, 12(1): 121
- 17 Ihata, O., Kayaki, Y. and Ikariya, T., *Angew. Chem. Int. Ed.*, 2004, 43(6): 717
- 18 Gu, L., Wang, X.H., Chen X.S., Zhao, X.J. and Wang, F.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 5162
- 19 Liu, B.Y., Zhao, X.J., Wang, X.H. and Wang, F.S., *Polymer*, 2003, 44(6): 1803

- 20 Kwei, T.K., *J. Polym. Sci. Polym. Lett. Ed.*, 1984, 22(6): 307
- 21 Gordon, M. and Taylor, J.S., *J. Appl. Chem.*, 1952, 2(9): 493
- 22 Fox, T.G., *Bull. Am. Phys. Soc.*, 1956, 1: 123
- 23 Kuo, S.W. and Chang, F.C., *J. Polym. Sci., Part B: Polym. Phys.*, 2002, 40(15): 1661
- 24 Kuo, S.W. and Chang, F.C., *Macromol. Chem. Phys.*, 2002, 203(5–6): 868
- 25 Zhang, Z.H., Mo, Z.S., Zhang, H.F., Zhang, Y., Na, T.H., An, Y.X., Wang, X.H. and Zhao, X.J., *J. Polym. Sci., Part B: Polym. Phys.*, 2002, 40(17): 1957
- 26 Noda, I., *Appl. Spectrosc.*, 1993, 47: 1329
- 27 Noda, I., *J. Am. Chem. Soc.*, 1989, 111: 8116
- 28 Czarnecki, M.A., Maeda, H., Ozaki, Y., Suzuki, M. and Iwahashi, M., *J. Phys. Chem. A*, 1998, 102(46): 9117
- 29 Wu, Q.Y., Chen, X.N., Wan, L.S. and Xu, Z.K., *J. Phys. Chem. B*, 2012, 116: 8321
- 30 Nakashima, K., Ren, Y., Nishioka, T., Tsubahara, N., Noda, I. and Ozaki, Y., *J. Phys. Chem. B*, 1999, 103(32): 6704
- 31 Goh, S.H., Lee, S.Y., Zhou, X. and Tan, K.L., *Macromolecules*, 1998, 31(13): 4260
- 32 Luo, X.F., Goh, S.H., Lee, S.Y. and Tan, K.L., *Macromolecules*, 1998, 31(10): 3251
- 33 Beamson, G. and Briggs, D., "High resolution XPS of organic polymers". Chichester: John Wiley & Sons, 1992
- 34 Kim, G.M. and Michler, G.H., *Polymer*, 1998, 39(23): 5689
- 35 Peng, S.W., An, Y.X., Chen, C., Fei, B., Zhuang, Y.G. and Dong, L.S., *Polym. Degrad. Stab.*, 2003, 80(1): 141
- 36 Wu, J.S., Mai, Y.W., Yee, A.F., *J. Mater. Sci.*, 1994, 29(17): 4510
- 37 Riew, C.K. and Kinloch, A.J., "Toughened plastics I. advances in chemistry series", 1992, 233
- 38 Riew, C.K. and Kinloch, A.J., "Toughened plastics II. advances in chemistry series", 1996, 252
- 39 Pascault, J.P., Sautereau, H., Verdu, J. and Williams, R.J.J., "Thermosetting polymers". Marcel Dekker: New York, 2002