Effect of Prepolyurethane on the Performances of Poly(acrylates-*co*-urethane) Copolymer

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ABSTRACT: Poly(acrylates-*co*-urethane) copolymers were synthesized by the polymerization of acrylates and 2-hydroxyethyl acrylate terminated polyurethane (prepolyurethane) at room temperature. The polymerization was initiated by the radicals, which were produced by the oxidation of tri-*n*-butylborane (TBB) from the mixing of TBB/hexamethylene diamine complex and diisocyanate decomplexer. The effects of prepolyurethane on the performances of copolymers were discussed. The results indicated that the damping property and flexibility of copolymers were obviously higher than that of pure polyacrylates. Dynamic mechanical analysis and transmission electron microscope results showed that PU was dispersed in polyacrylates phase very well. The copolymers were found to bond well to low surface energy materials because of introduction of PU. The lap shearing strength of copolymer bonding polypropylene or polyethylene both had the trend of first increase followed by decrease with the prepolyurethane content increase. The copolymers as adhesives were also shown to have a long working life and be suitable for utilization at low temperature especially at room temperature. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3203–3210, 2010

Key words: poly(acrylates-*co*-urethane); prepolyurethane; adhesives; tri-*n*-butylborane (TBB); low surface energy materials

INTRODUCTION

Polyethylene (PE), polypropylene (PP) and their copolymers possessing a variety of attractive properties have been the most widely used commercial polymers in the fields of automobiles, toys, furniture, and so on. Because of the low energy surface of these materials, it is difficult to find adhesives to bond well to them.[1] In order to improve the adhesion of low surface energy materials, many kinds of surface treatments including physical and/or chemical methods have been utilized to promote interactions between the materials surface and adhesives. It is known that physical methods include plasma treatment, corona, electronic radiation, etc.,[2–7] and chemical methods include acid etching, grafting, etc.[8–11] Although most of these methods may be efficient for improving the surface adhesion of low surface energy materials, these methods generally have practical defects and are nonenvironmental friendly, which limits their widespread use.

According to the technology of organoborane initiated radical polymerization which was put forward since 1967,[12–15] Schoutchi, Zharov, Pocius, Sonnen-schein, and others reported series of acrylate adhesives for bonding low surface energy materials without surface pretreatment one after another from the early 1990s.[16–23] As is known, adhesives of polyacrylates with high cohesive strength exhibit brittle performance and are generally modified by acrylates with low glass transition temperature (T_g), but cohesive strength of the modified adhesives would be sacrificed. Thus, other modifying methods have also been used, for instance, cross-linking polyacrylates, copolymerizing acrylates with other monomers, blending polyacrylates with other polymers, and so on.[24–28]

Because of the excellent performances of polyurethane (PU), PU is very hopeful to be utilized to modify acrylate adhesives. Poly(acrylates-*co*-urethane) copolymers, initiated by high temperature initiator such as BPO, AIBN, and so on, were discussed in Refs. [29] and [30] and were proved not to be suitable for bonding of low surface energy materials. Trialkylborane, as a kind of radical initiators initiated at room temperature or low temperature, is hopeful to initiate the copolymerization of acrylates and PU in adhesives bonding low surface energy materials. For the kind of PU modified adhesives, introduction of PU is vital to the performances of adhesives. Deviny et al.[31,32] reported a kind of acrylate adhesives containing PU introduced by diamine of complex reacting with a class of compounds with NCO group on one terminal and unsaturated double bond on the

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other terminal. Almost at the same time, Pocius et al.[33] reported the use of extra polyols as components of adhesives to get a kind of acrylate adhesives containing PU, and they also reported another kind of acrylate adhesives containing PU by combining Deviny's and their methods.[34] PU introduced by their methods promoted the bonding of acrylate adhesives to low surface energy materials to a large extent, but introducing PU into acrylate adhesives by copolymerizing acrylates with unsaturated double bond terminated PU wasn't touched on. However, there is no report on such a study of copolymerizing acrylates with unsaturated double bond terminating PU with trialkylborane and oxygen as initiator.

In this article, we report a class of poly(acrylates-co-urethane) copolymer adhesives. PU terminated by unsaturated double bond (prepolyurethane) was introduced into copolymer adhesives system by us. The phase structures and adhesion properties of those copolymers were investigated using transmission electron microscope (TEM), dynamic mechanical analysis (DMA) and lap shearing strength (LSS) test, and then the effects of PU on the copolymer performances were mainly discussed.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) obtained from Mitsubish Chemical Holdings Corporation was used directly. Poly(tetramethylene glycol) (PTMG-1000, $M_n = 1000$ g/mol, Dupont) was dewatered for 2 hrs under vacuum at 120°C. Dibutyltin dilaurate (DBTDL) and hexamethylene diamine (Sinopharm Chemical Regent) were used as received. 2-hydroxyethyl acrylate (2-HEA) supplied kindly by Shanghai Huayi (Group) Company was distilled under vacuum after being treated by anhydrous Na$_2$SO$_4$. Methyl methacrylate (MMA) and butyl acrylate (BA) purchased from Sinopharm Chemical Reagent were firstly washed using sodium hydroxide solution and then treated by anhydrous Na$_2$SO$_4$, and finally distilled under vacuum. Tri-n-butylborane (TBB) synthesized according to the document[35] was used directly without characterization. PP plates ($d = 0.92$ g/cm^3, 4 mm thickness) purchased from Daqing Petrochemical Company and PE plates ($d = 0.96$ g/m^3, 2 mm thickness) purchased from BASF Company were used as received.

Synthesis and characterization of 2-HEA terminating PU (prepolyurethane)

The prepolyurethane based on TDI, PTMG-1000, and 2-HEA was synthesized through a two-step polymerization. In the first step, TDI (13.93 g) was added to a 100 mL three-neck round-bottom flask equipped

with a mechanical stirrer under nitrogen protection, and PTMG-1000 ([OH]/[NCO] = 1/2) was added dropwise into it over a period of 30–40 min at 70°C of water bath. The reaction was continued for an additional 3 hrs following the completion of addition of PTMG-1000 to get the isocynate-terminated PU prepolymer. The NCO content in the prepolymer was measured through standard di-n-butylamine back-titration method.[36] Then, the temperature of the system decreased to 60°C, 2-HEA ([OH]/[NCO] = 1.05/1) and 0.1 wt % DBTDL were added into prepolymer and the reaction was continued for 6 hrs. After that, the temperature of the system was heated to 80°C to react another 1 h. The products were dissolved with N, N-dimethylformamide, deposited with distilled water and settled by a centrifuge. The courses were carried out six times to get sediment. The sediment was washed three times with distilled water and dried under vacuum at 80°C for 24 h. The synthesis routes were shown in Scheme 1.

The synthesis of prepolyurethane and its structure were characterized by FTIR and ^{1}H-NMR respectively. FTIR experiment was conducted on a Perkin–Elmer 1000 FTIR spectrometer with a 4 cm^{-1} resolution from 400 to 4000 cm^{-1}. The scanning frequency was 64 times. The FTIR samples were prepared by coating film (N, N-dimethylformamide as solvent) on the KBr wafer and dried in vacuum. ^{1}H-NMR spectroscopy was carried out by Varian MERCURY plus 400 and 500 MHz spectrometers using Dimethylsulfoxide-d6 (DMSO-d6) as solvent.

Preparation of TBB/hexamethylene diamine complex

TBB was stabilized through complexing with diamine. After the 50 mL flask containing the quantitative hexamethylene diamine was extracted to be vacuum, the corresponding TBB ([N]/[B] = 1/1) was added into the flask by a syringe over a period of 20–30 min under N$_2$ protection, and the temperature of system was kept below 60°C by water bath. Magnetic stirring was applied during the course of the addition. After the completion of addition of TBB, the system was heated to 60°C to get a homogeneous complex, and then cooled to room temperature to get the complex powder.

Preparation of the copolymer adhesives

The two-part copolymer adhesives were formulated as shown in Table I. For the components of adhesives, the weight ratio of MMA/BA was 7/3, the concentration of boron was 0.3 wt % (percent in the total adhesives weight), and the mol ratio of TDI (decomplexer) and hexamethylene diamine in the complex was 1/1.
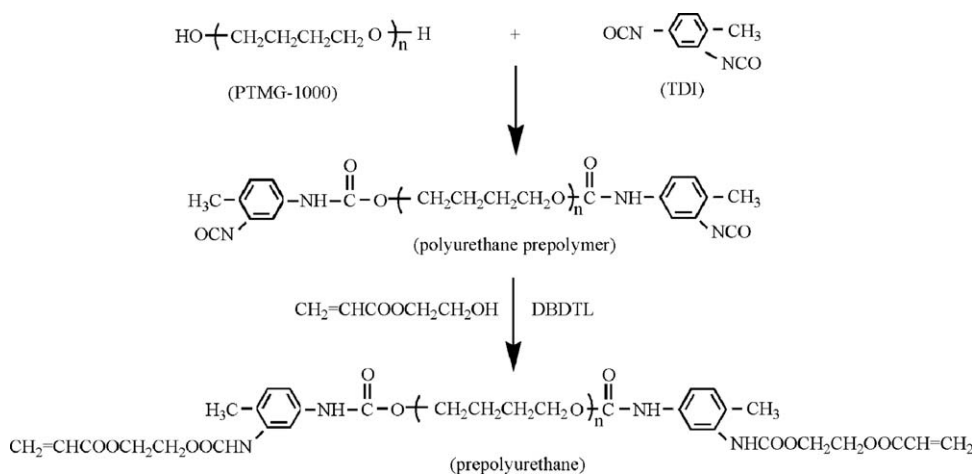
Scheme 1 Synthesis of polyurethane terminated by 2-HEA (prepolyurethane).

For samples preparation of LSS test, the two parts of copolymer adhesives were mixed in a plastic cup and were manually dispensed quickly by a glass bar, and the mixed adhesives were applied to the surface of low surface energy materials. The lapped area was 25 × 12.7 mm, and the adhesive thickness was controlled to about 0.2 mm with piano string (diameter 0.2 mm). After the copolymer adhesives were cured for 48 hrs, LSS of the lapped samples were tested on INSTRON 4465 universal electromechanical tester (with high-temperature cabinet) according to ASTM D-1002. The crosshead speed was 10 mm/min, and the test temperature and relative environment humidity were controlled to 23°C ± 1°C and about 50% respectively. The error of LSS for all lapped samples didn't exceed 0.4 MPa.

Working life of adhesives was tested according to GB/T 7213.1. The time for the two parts of adhesives beginning to mix was recorded as the initial time, and the lapped samples according to the method described in the LSS test were prepared at a time interval. After the adhesives were cured completely, LSS of the lapped samples were tested. Working life of adhesives was defined as the time that the service performance (LSS) of the adhesive could be maintained.

Dynamic mechanical analysis (DMA)

DMA of copolymers was performed on Perkin Elmer DMA 7e Dynamic Mechanical Analyzer. The frequency was 1 Hz, the rate of temperature ramping

TABLE I
Formulations of Copolymer Adhesives for Low Surface Energy Materials Bonding

Part A	Part B
TBB/hexamethylene diamine complex	Methyl methacrylate (MMA) prepolyurethane
Butyl acrylate (BA)	TDI (decomplexer)

was ∼ 3°C/min, and the test was carried out from −80 to 150°C. The dynamic mechanical properties of samples were studied in tensile mode.

Characterization of phases of copolymers

Microscopy samples of copolymers, ∼ 100 nm thick, were obtained at −80°C with a Leica ULTRACUT UC6 cryoultramicrotome. The thin sections were collected on a copper support grid. The electron micrographs of the prepared sections were observed by a JEM-2100 TEM running at an accelerating voltage of 200 kV.
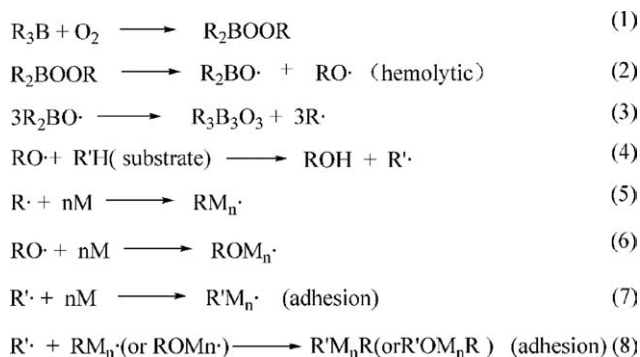
RESULTS AND DISCUSSION

With trialkylborane and oxygen as initiator system, acrylates polymerization could promote the bonding of low surface energy materials and the promoting mechanism was put forward by Sonnenschein et al as Scheme 2.[37,38] When trialkylborane is exposed to oxygen, it can be oxidized to create oxygen- and carbon-centered radicals. Then, the oxygen-centered radicals attract H atoms from the surface of low surface energy materials to create the carbon-centered radicals that can initiate acrylates to polymerize, which leads to the grafting of acrylates on the surface of low surface energy materials. Thus, the grafting of acrylates results in a strong chemical interaction between acrylate adhesives and low surface energy materials.

Because of the intrinsic pyropholicity of trialkylborane, it is necessary to control oxidation process of trialkylborane in adhesives system in order to realize the safety and controllability of acrylates polymerization. Generally, electron-rich compounds (for instance, amine, etc.) are utilized to complex and stabilize trialkylborane.[16–26] Sonnenschein et al. reported some works on the study.[39] Because small

$$R_3B + O_2 \longrightarrow R_2BOOR \tag{1}$$

$$R_2BOOR \longrightarrow R_2BO\cdot + RO\cdot \quad (\text{hemolytic}) \tag{2}$$

$$3R_2BO\cdot \longrightarrow R_3B_3O_3 + 3R\cdot \tag{3}$$

$$RO\cdot + R'H(\text{substrate}) \longrightarrow ROH + R'\cdot \tag{4}$$

$$R\cdot + nM \longrightarrow RM_n\cdot \tag{5}$$

$$RO\cdot + nM \longrightarrow ROM_n\cdot \tag{6}$$

$$R'\cdot + nM \longrightarrow R'M_n\cdot \quad (\text{adhesion}) \tag{7}$$

$$R'\cdot + RM_n\cdot(\text{or ROMn}\cdot) \longrightarrow R'M_nR(\text{or}R'OM_nR) \quad (\text{adhesion}) \tag{8}$$

Scheme 2 Mechanism of trialkylborane promoting the adhesion to low surface energy materials.

molecule existing in adhesives would immigrate to the interface to weaken the interaction between adhesives and substrates, hexamethylene diamine that can react with decomplexer diisocyanate to create polyurea was adopted to complex with trialkylborane by us.

Characterization of prepolyurethane

Figure 1 shows the FTIR spectra of the reaction products with reaction time. The characteristic absorption of —NCO at about 2273 cm^{-1} and that of —OH at about 3451 cm^{-1} still exist in the spectrum at 5 hrs but disappears at 7 hrs for the second step. The result indicates that the reaction was completed after 7 hrs.[40]

The chemical structure of the synthesized product was confirmed by ^{1}H-NMR. Figure 2 shows the ^{1}H-NMR spectrum of the product in DMSO-d6. The peaks in the range of 5.95–6.36 and 4.28–4.32 ppm are attributed to the ethenyl and the ethylene group of 2-HEA respectively. The peaks at 8.92 and 9.49 ppm are ascribed to the protons of —NH— groups in urethane unit. The peaks at 7.02–7.46 and 2.08 ppm are assigned to the protons of benzene ring and methyl group in TDI unit. The peak at 4.02 is assigned to the methylene group of PTMG unit attached to the urethane, and the peaks in the range of 3.24–3.36 ppm are attributed to the methylene group of PTMG unit attached to the O of ether. The peak at 1.47 ppm is assigned to the ethylene group in the middle position of PTMG unit. On the other hand, the ratio of the protons is in agreement with the structures shown on the top of Figure 2. The results suggest that the synthesized product is prepolyurethane as shown in the Scheme 1.

To utilize the synthesized prepolyurethane, poly(acrylates-*co*-urethane) copolymers were synthesized by polymerization of acrylates and the prepolyurethane initiated by TBB/hexamethylene diamine complex and oxygen. The copolymer performances with prepolyurethane were discussed as follows:
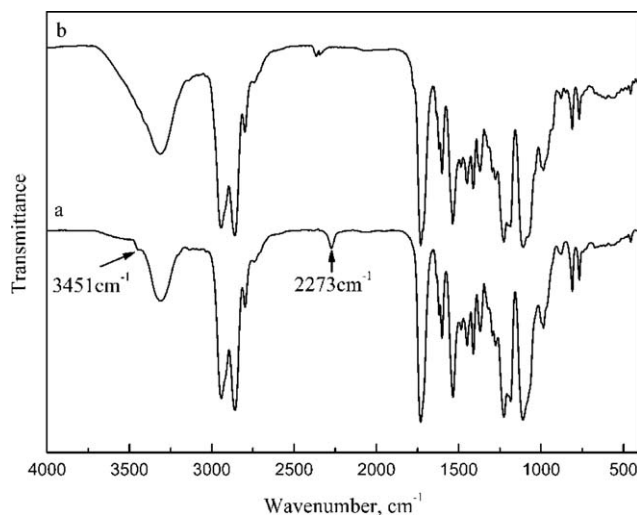
Figure 1 FTIR spectra of prepolyurethane with reaction time of the second step: (a) 5 hrs; (b) 7 hrs.

Effect of prepolyurethane on dynamic mechanical property of poly(acrylates-*co*-urethane)

Figure 3 shows the DMA results of the copolymers with different prepolyurethane content. Only one T_g occurring at 30–40°C indicates a good compatibility of PU and polyacrylates phase, which benefits the bonding of copolymers as adhesives to substrates. With prepolyurethane content increasing, T_g decreases a little, which results from higher soft segment content. It indicates that the flexibility of copolymers is improved because of introduction of PU. Figure 3 also shows that introduction of PU brings about higher tan δ, which indicates that these copolymers have a better damping property and flexibility than that of the polyacrylates without PU.
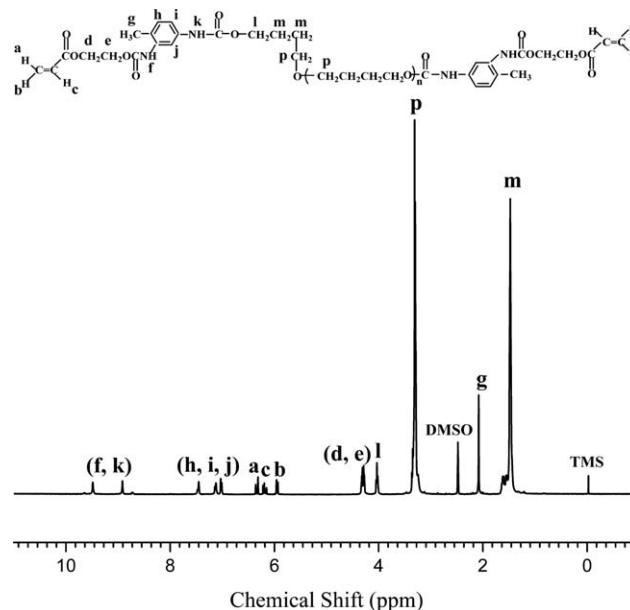
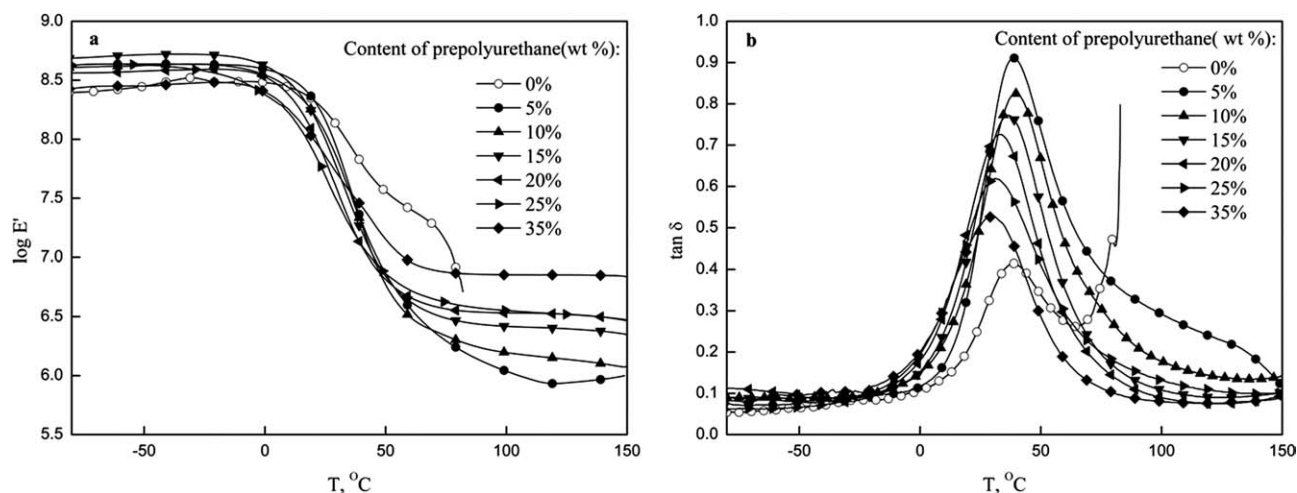

Figure 2 ^{1}H-NMR spectrum of the prepolyurethane.

Figure 3 DMA curves of the copolymers with different prepolyurethane content: (a) storage modulus E' curves; (b) loss tangent tan δ curves.

Although tan δ at glass transition zone decreases with prepolyurethane content increasing, the decrease of half-width of loss peak suggests that compatibility of PU and polyacrylates is improved because of the increasing degree of crosslinking. Tan δ of copolymer at high temperature decreasing with the prepolyurethane content increasing also proves that it results from the higher degree of crosslinking. But, the influence of crosslinking degree on tan δ at high temperature becomes weak when prepolyurethane content exceeds 15 wt %.

From Figure 3, storage modulus E' decreases sharply from about 0°C because of low T_g of the copolymers, which indicates that the copolymers as adhesives aren't suitable for utilization at high temperature. On the other hand, E' of all copolymers is close to that of polyacrylates at or below room temperature, which suggests that the introduction of PU does not result in decrease of cohesive strength of copolymer. When the copolymers are in low temperature, E' shows the trend of first increase followed by decrease with the prepolyurethane content increase because of the higher degree of crosslinking and the better flexibility of PU. E' of copolymer increases with the prepolyurethane content increasing at high temperature, which also proves the crosslinking degree of copolymer increase. The DMA results suggest that the brittleness of polyacrylates is improved by the introduction of PU on the condition of keeping its cohesive strength.

Effect of prepolyurethane on phase structure of poly(acrylates-*co*-urethane)

The morphology of poly(acrylates-*co*-urethane) copolymer is vital to excellent bonding as adhesives. Possessing a good dispersity of two phases in the adhesives is necessary to achieve a good bonding of

adhesives. The electron micrographs of copolymer containing 5 and 20 wt% prepolyurethane are shown in Figure 4. The dark and white zones represent the PU and polyacrylates phase respectively. Figure 4 shows a relative good dispersity of PU in polyacrylates for two copolymers. From Figure 4(a,b), the dispersity of PU in polyacrylates is improved with prepolyurethane content increasing, which results from the higher crosslinking degree of the copolymer with higher prepolyurethane content. The higher degree of crosslinking would promote the compatibility of PU and polyacrylates phase. The PU phase size in the copolymer containing 20 wt % prepolyurethane is also smaller than that in the copolymer containing 5 wt % prepolyurethane. The reason is that the lower content prepolyurethane leads to the lower degree of crosslinking, which results in PU phase agglomeration insisting of prepolyurethane and polyurea (product of reaction between decomplexer and complex). Better dispersity and lower phase size are in favor of increasing cohesive strength and impact performance of adhesives.

Effect of prepolyurethane on bonding property of poly(acrylates-*co*-urethane)

The effect of prepolyurethane content on LSS of copolymer adhesives bonding PP or PE is discussed in Figure 5. Whether for PP or PE bonding, the figure suggests that the adhesives containing prepolyurethane have a better bonding to the substrates than that without PU, especially when the prepolyurethane content is among 10 to 40 wt %. LSS for PP and PE bonding both have the trend of first increase followed by decrease. The maximum of LSS for PP and PE bonding are 8.0 MPa and 3.0 MPa, respectively. With the prepolyurethane content increasing, the degree of crosslinking increases because of the
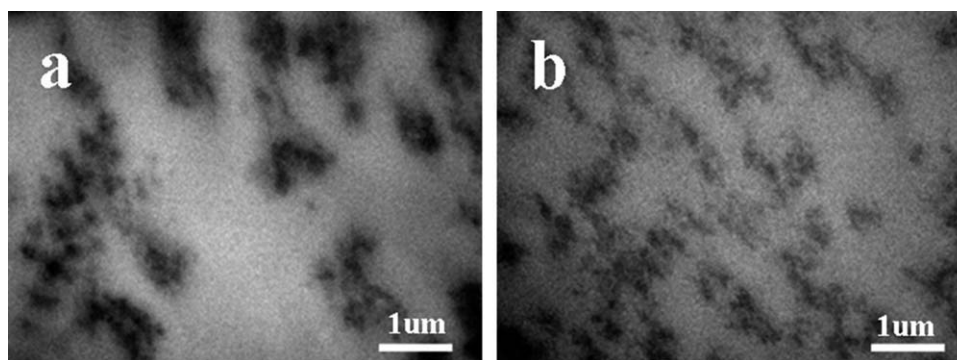
Figure 4 TEM micrographs of the copolymers containing (a) 5 wt % prepolyurethane; (b) 20 wt % prepolyurethane.

terminated acrylate content increasing, and the cohesive strength of adhesives increase, which results in the increasing of LSS. When the prepolyurethane content reaches some extent, the viscosity of the adhesive system increases quickly because of fast crosslinkage, and the contents of acrylates decrease a lot. It results in larger difficulty of TBB and acrylate monomers migration to the interface of adhesive and substrate. So, the interaction between TBB and substrate becomes weaker, which results in the decrease of LSS. Moreover, the fast crosslinkage brings about the trouble of coating, which results in a bad infiltration to substrate and a short work time. As a result, LSS decreases and the bonding failure for PP substrate turns into adhesive failure from cohesive or substrate failure seen from Figure 6. From Figure 6, the failure mode for PP bonding turned into cohesive or substrate failure from adhesive failure of pure polyacrylates, which indicates that it is favorable for PU introduction to coordinate the interaction between TBB and substrate. On the other hand, the higher content of hard segment isn't benef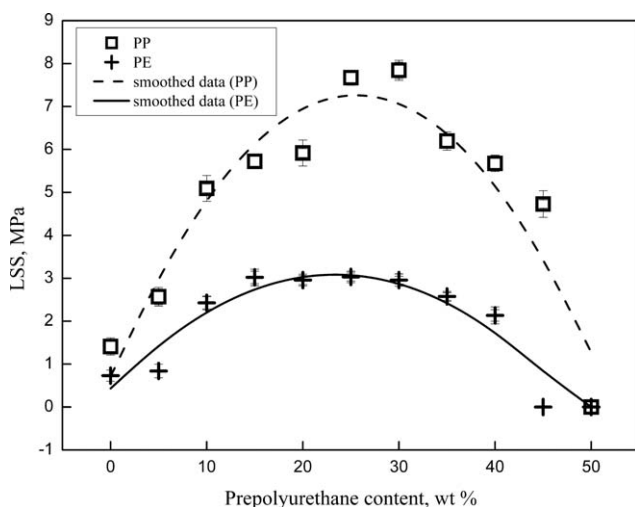it for the infiltration of adhesives to substrate with the PU content increasing, which also is a factor to result in LSS decrease. On the contrary, the higher content of PTMG segment resulted from the increasing PU content promotes the infiltration of adhesives to substrate because of the lower polarity of PTMG than polyacrylates.[41] The effect of PU on the infiltration performance is the overall results of the influences of soft and hard segment in PU.

According to the comparison of LSS of the copolymers with that without PU, the introduction of prepolyurethane not only increases the cohesive strength of copolymer, but also more importantly, coordinates the phase structure of copolymer to be in favor of promoting the interaction among substrates, TBB, and acrylates.

Serviceability temperature of poly(acrylates-*co*-urethane) as adhesives

The serviceability temperature is an important performance of adhesives for applications. LSS of the copolymer adhesives containing 5 and 20 wt% prepolyurethane with temperature are shown in Figure 7. The figure shows that the LSS decreases sharply with temperature increasing whether for PP or PE bonding, which indicates that the copolymer adhesives are not suitable for utilization at high temperature. It is in agreement with the DMA result very well. The figure also shows that the copolymer adhesive containing 20 wt % prepolyurethane is more sensitive to temperature than that containing 5 wt % prepolyurethane, which suggests that the copolymer containing 20 wt % prepolyurethane is more flexible. The result also indicates that the flexibility of copolymer is improved with prepolyurethane content increasing.

Working life of poly(acrylates-*co*-urethane) as adhesives

The application fields of adhesives also depend on the working life of the adhesives. Because of good preparing process and relatively high LSS of the
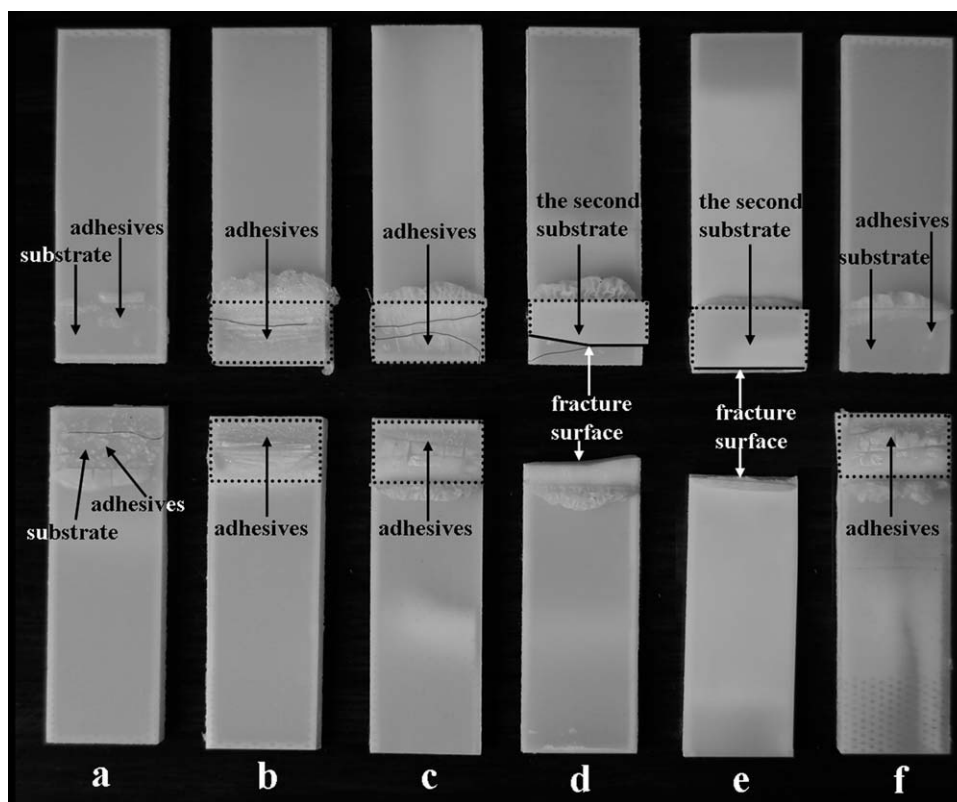

Figure 5 LSS of the adhesives with prepolyurethane content to bond different substrates.

Figure 6 Photos of the lapped samples (PP as substrate) after LSS test. Prepolyurethane content in the adhesives (wt %): (a) 0%; (b) 5%; (c) 10%; (d) 20%; (e) 30%; (f) 40%.

copolymer adhesive containing 20 wt % prepolyur-ethane, LSS of samples bonded by the copolymer adhesive containing 20 wt % prepolyurethane at different lapping times are shown in Figure 8. Whether for PP or PE bonding, LSS both have the trend that decreases sharply before 5 min, then keeps at a platform of about 4.7 MPa and 1.7 MPa respectively before 30 min, and finally decreases again. The result indicates that the copolymer adhesive has a relatively long working life that exceeds 30 min for PP or PE adhesion when the content of prepolyur-ethane is lower than 20 wt %. With the prepolyur-ethane content increasing, the working life of adhesives must be decreased because of faster crosslinkage. Especially when the prepolyurethane content exceeds 35 wt %, the working life of copolymer adhesives is lower than 1 min according to our experiment results.
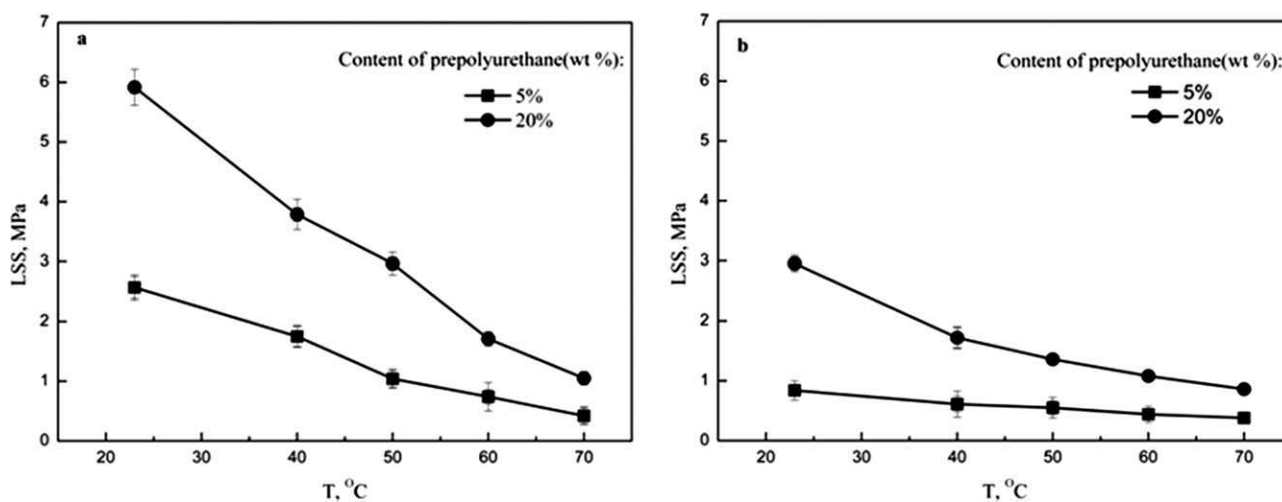

Figure 7 LSS of the copolymer adhesives at different temperature to bond: (a) PP; (b) PE.
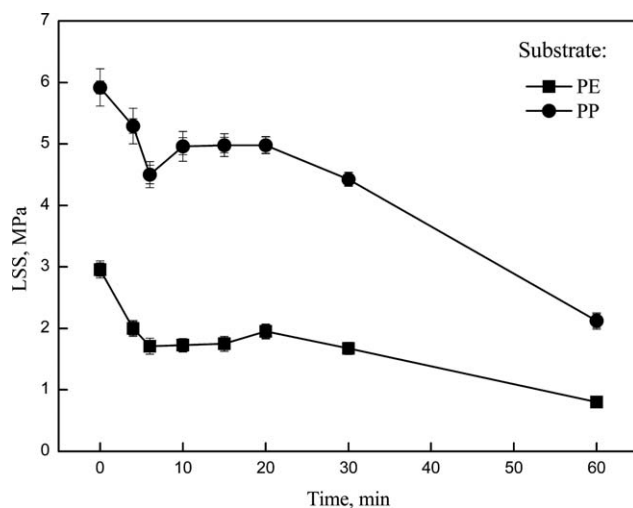
Figure 8 LSS of the adhesive containing 20 wt % prepolyurethane at different lapping time.

CONCLUSIONS

Poly(acrylates-co-urethane) copolymers were synthesized by the polymerization of acrylates and polyurethane macro-monomer (prepolyurethane) at room temperature. The copolymers were found to bond low surface energy materials well because of introduction of PU in polyacrylates. The effect of PU on LSS was summarized to be in three aspects: increasing cohesive strength of copolymers, coordinating the interactions among TBB, acrylates and substrates when PU content was lower than 30 wt %, and then weakening the interactions when PU content was further increased. Because of PU existed in the copolymers, the copolymers possessed higher damping and flexibility properties than that of pure polyacrylates. The copolymers had a relatively homogeneous morphology structure though PU introduction. The copolymers were also shown to have a long working time and be suitable for utilization at low temperature especially at room temperature when they were used as adhesives. The copolymer adhesive properties achieved have not been previously found in any single-phase polyurethane or acrylate adhesives for low surface energy materials bonding.

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