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The varying mass ratios of soft and hard segments in waterborne polyurethane films: Performances of thermal conductivity and adhesive properties

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ABSTRACT

Waterborne polyurethanes (WPU) with different mass ratios of soft and hard segments were synthesized by toluene diisocyanate, polypropylene glycol (PPG) and ethylene glycol (EG). It was shown that the PPG-based WPU with a mass ratio of soft and hard segments of 3:2 expressed a highest thermal conductivity (~ 0.374 W/m·K), but showed a lowest T-peel strength (21.55 N/25 mm). As the mass ratio of soft and hard segments increased to 4:1, the T-peel strength was increased to 136.14 N/25 mm and thermal conductivity was decreased to a lowest value (~ 0.306 W/m·K). To gain more understandings a number of analytic were carried out, such as FTIR, TG, DSC, DMA, AFM and XRD. Furthermore, mechanical properties of the PPG-based WPU coatings were tested as well. A possible explanation for the change in properties is due to the degree of phase separation and crystallinity, which was increased with the increasing of hard segment content. As a result, the hard and soft segments formed orderly oriented stacked structures by owing to the increasing of phase separation.

1. Introduction

Solvent-based polyurethane (PU) is recognized as a fast growing area in modern coating. However, due to environmental factors the removal of volatile organic compounds (VOCs) becomes mandatory [1], many studies of waterborne polyurethane coating which possesses the same performances as traditional solvent polyurethane are increasingly attracted most attentions. Linear thermoplastic polyurethane chains are dispersed in water to form emulsion due to the ionic groups either in chain structure, as internal emulsifier, or by an amphiphilic additive (emulsifier). Excellent performances of coating such as abrasion resistance, flexibility at low temperature and chemical resistance, giving the corresponding films a wide applicability in flexible coatings, hard coatings, as well in adhesives, such as leather, textiles, wood, electronic devices and metallic surfaces [2]. Currently, the multifunctional applications of WPU on a basis of general performances are further been studying which exhibits the inflaming retarding [3], conductive responding performances (e.g. electronic conduction, magnetic conduction) [4,5], and biomedical materials for 3D printing scaffold and tissue engineering, etc. [6,7]. However, studies that focus the internal structure on heat transfer performances of WPU coating are rare, which is probably due to the low intrinsic thermal conductivities and its relation

to the complex structure. There has been done much work on the preparation of hybrid compositions in which based on carbon-based nanofillers with higher thermal conductivities [8], such as graphite [9], graphene [10], carbon black [11], carbon nanotube [12–15], and metallic fillers [16] (Ag, Cu, Al [17]), ceramic fillers (BN [18], Si [19]), and so forth [20]. But, the enhanced thermal conductivity is still insufficient which is probably due to the defects and phonon scattering in two phases [21], because of the incompatibility of the fillers and the resin. Along with the miniaturization and intelligent developments of electronic devices, a fast heat transfer in high power density electronics such as integrated circuits, supercapacitors, LEDs and lasers is crucial, importantly requiring the coatings and bonding materials express a high thermal conductivity to facilitate heat dissipation [22]. It has found that the appropriate degree of microphase separation in WPU can facilitate to form orderly orientation of polymer chains in a way of long-range order, short-range order and microcrystal zones, which creates more free pathways for phonon conductivity and enhances the thermal conductivity accordingly [23–25].

To the best of our knowledge, the essential feature of WPU coating is expressing an excellent adhesive properties on most materials, and it is mainly affected by the diisocyanate moieties compared to other components. Previous studies mainly concentrated on the expensive

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Table 1

Specific heat of three chain extenders and thermal conductivity of corresponding WPU films synthesized with these extenders.

Chain extender	Specific heat capacity/(J/Kg·°C)	Thermal conductivity/(W/m·K) ^a
EG	2.35	0.272
BDO	2.41	0.245
DG	2.31	0.216

diisocyanates, such as isophorone diisocyanate (IPDI), tetramethylxylene diisocyanate (*m*-TMXDI), and 1,6-hexamethylene diisocyanate (HDI) [26,27], accordingly, the high prices of these diisocyanates may hinder its applications. So, in this work, we mainly studied the performances of heat conduction and adhesive properties in polypropylene glycol (PPG)-based toluene diisocyanate (TDI) typed WPU (PPG-based WPU) coating with respect to different mass ratios of soft segment (SS) and hard segments (HS). In addition to this, the micro-structures of WPU films were analyzed with various techniques as well.

2. Experimental

2.1. Materials

Polypropylene glycol (PPG, $M_n = 2000$, Nanjing, China) was dried 3 h at 110 °C with a connection of vacuum to remove the residual water. Dimethylolpropionic acid (DMPA, Perstop Chemical Co. Ltd.) was dried 48 h at 50 °C in vacuum oven. 2,4-toluene diisocyanate (TDI, BASF) was used as received without any treatments. Ethylene glycol (EG), 1,4-butanediol (BDO) and diethylene glycol (DG) were reagent grade and purchased from Chengdu Kelong Co. Ltd. Acetone and trimethylamine (TEA), all reagent grade, were dried over 4 Å molecular sieves before use. Deionized water was produced in laboratory by ourselves. Herein, the prepolymer of three WPU emulsions was same, and the only

Table 2

The amounts of monomers in synthesis of WPUs.

Soft-to-hard (mass ratio)	TDI/mmol	PPG/mmol	DMPA/mmol	EG/mmol	TEA/mmol	H ₂ O/mol
3:2	33.33	5.40	4.93	13.55	4.93	2.33
7:3	33.33	8.55	6.87	8.07	6.87	3.17
3:1	33.33	10.65	8.06	5.08	8.06	3.68
4:1	33.92	14.10	10.15	0.00	10.15	4.56

^aSolid content is 30%, R (NCO/OH) = 1.4.

Fig. 1. Particle size distributions of WPU emulsions.

difference of WPU emulsion was adopted three chain extenders to extend polymeric chains. As a result, the thermal conductivity value was obtained from corresponding WPU films and shown in Table 1. Finally, EG was selected as chain extender to synthesize WPUs in next experimental parts.

Scheme 1. Synthetic route of waterborne polyurethane emulsions.

Table 3
Appearance of WPU emulsions and corresponding films.

WPU samples	Emulsion stability	Emulsion color	Film
3:2	Stable	White	Translucence/hard
7:3	Stable	White and blue light	Transparence/flexible
3:1	Stable	White and blue light	Transparence/soft
4:1	Stable	White and blue light	Transparence/soft

Fig. 2. Water absorption curve of WPU films.

Fig. 3. Mechanical properties of WPU films.

Fig. 4. The FTIR spectrum of WPU films.

2.2. Synthesis of WPU emulsions

WPU emulsions were synthesized with four different mass ratios of soft and hard segments ($m_{SS}:m_{HS} = 3:2/7:3/3:1/4:1$). Briefly, according to the previous studies (see Ref. [23], including the various monomers

selections in synthetic process), stoichiometric amounts of PPG, TDI and DMPA were dosed into four-neck flask under 200–300 rpm stirring at 80–85 °C (oil-bathing) for 3–5 h. Next, the inner temperature was decreased to 70–73 °C, followed by the addition of stoichiometric amount EG to continue another 1 h. Then, the temperature was cooled down to room temperature (RT), followed with addition of the mixture of TEA and less amount acetone to neutralize 10 min. Finally, deionized water was added under a high shear speed to form stable emulsion. The emulsion was kept at 50 °C (oil-bathing) for 30 min with a connection of vacuum pump to remove the residual acetone. The synthetic scheme of WPU and list of monomers' consumption were depicted in Scheme 1 and Table 2, respectively.

2.3. Preparation of WPU films

WPU films were prepared by casting the emulsions into Teflon dishes, followed by dried 2–4 days in fume hood. The molding films were then kept overnight in vacuum oven at 70 °C and stored in dryer for following analyses.

2.4. Particle size distribution and appearance of WPU emulsions

Emulsion particle sizes were measured with Zettersizer Nano ZS (Model ZEN 3600). Wherein, WPU emulsions were diluted with deionized water to 0.5%, followed by using ultrasonic wave treatment to homogenize the emulsions, among the method using uniform shaking to get homogeneous emulsion was a control to measure.

2.5. Water absorption

Water absorption percentages of WPU films were calculated by the weight (W) increased at different time, and referring to the immersing time in water to obtain time-water absorption relation. Eq. (S-1) was used to calculate the water absorption percentages.

$$\text{The water absorption percentage} = (W - W_0)/W_0 \times 100\% \quad (\text{S-1})$$

wherein, W_0 was initial membrane weight and W was the weight after some time immersion.

2.6. FTIR spectra

WPU films were recorded using a Nicolet iS10 spectrophotometer equipped with a total reflection device, wherein the wavenumber range was set from 4000 to 400 cm^{-1} with the scan rate of 4 cm^{-1} and scan number of 32 times.

2.7. X-ray diffraction

X-ray diffraction (XRD) was carried out in X'Pert Pro MPD DY129 X-ray diffractometer (Netherlands) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) as the X-ray source. And the film was tested from 5° to 70° with the scan rate of 2°/min.

2.8. Thermal properties analysis

Differential scanning calorimetry (DSC) was carried out with DSC 200PC (NETZSCH, Germany) at a heating rate of 5 °C/min from −100 to 100 °C under N_2 . A fast heating process (20 °C/min) was used to eliminate heat history and then cooled down to prescribed temperature ~ -100 °C to measure the thermal properties. Thermogravimetric analysis (TGA) was performed on TG 209 F1 thermo-gravimetric analyzer (Germany) to measure the thermal stability of films at a heating rate of 10 °C/min from 50 to 600 °C under N_2 .

Fig. 4a. FTIR spectrum and curve fittings of WPU films for $\text{C}=\text{O}$ stretching vibrations.

2.9. Dynamic mechanical analysis

The dynamic mechanical properties of WPU films were measured under a stretching mode using dynamic mechanical analyzer (DMA 242) with a heating rate of $2^\circ\text{C}/\text{min}$ from -100 to 100°C . The operating conditions were at a frequency of 1 Hz , static force of 20 N and a strain amplitude of $20\ \mu\text{m}$.

2.10. Tensile properties and elongation at break

The preparation of specimens was referred to ASTM D-1822 standard, and mechanical properties of WPU films were tested three times with universal testing machine at a rising speed of $50\text{ mm}/\text{min}$ in room temperature. The average was reported.

2.11. Morphological analysis

The surface morphologies of WPU films were observed using atomic force microscope (AFM SPM-9600, SHIMADZU, Japan) to obtain the 3D morphology. The operating parameters were followed as the scope size of $4\ \mu\text{m} \times 4\ \mu\text{m}$, scan frequency of 1 Hz and resolution ratio of 512×512 .

2.12. Thermal conductivity tests

Referring to the steady-state method theory (referring to Ref. [23] description), the thermal conductivities of WPU films were measured at least five times with thermal conductivity coefficient instrument (DRP-II) and the average was reported.

2.13. T-peel strength tests

The T-peel strengths of WPUs were obtained on leather/WPU/leather joints. The dimension of leather stripe was $150 \times 25 \times 2\text{ mm}^3$. Cleaned surface was evenly coated with 2 mL WPU emulsion to form an adhesive areas of $100 \times 25\text{ mm}^2$, which was quickly heated to 80°C and kept 10 min (for initial T-peel strength) and 24 h (for final T-peel strength) under 0.8 MPa pressure respectively. Wherein, T-peeling strength testing was referred to ASTM D1876 – 08 standard (Test Method for Peel Resistance of Adhesives).

3. Results and discussion

3.1. Particle sizes and morphology of emulsions

The ionic groups in ionomers enable polyurethanes to disperse in water, and producing stable dispersion. The stabilizing effect of ionic sites is due to their hydrophilic character in water, resulting in formation of tiny spheres which contain a core of aggregated hydrophobic segments and a shell carrying the ionic groups [26]. In Fig. 1, it is shown that the average particle sizes increase as increasing HS content in WPU. The average particle size of WPU emulsion (SS:HS = 3:2, mass ratio, $\sim 190\text{ nm}$) is bigger than those of other emulsions. Moreover, the particle sizes of emulsions decreased with the increasing SS/HS ratio from 7:3 ($\sim 58.5\text{ nm}$) to 3:1 ($\sim 43.8\text{ nm}$) and to 4:1 ($\sim 32.7\text{ nm}$). That is because the higher HS content in WPU can form longer hydrophobic segments in tiny spheres, on the other hand, due to the chain flexibility decreased and chains rigidity increased accordingly, resulting in more difficult for emulsion particle deformation in shear process [28–30]. Therefore, WPU emulsion contained more HS content shows a bigger

Fig. 4b. FTIR spectrum and curve fittings of WPU films for $-NH$ stretching vibrations.

Table 4
H-bonding degree determination.

WPU films	H-bonding degree (R)	
	R_{NH}	$R_{C=O}$
3:2	10.27	3.81
7:3	6.63	3.18
3:1	5.44	2.75
4:1	3.62	2.29

average particle size than that of WPU emulsion synthesized with less HS content. The chain flexibility reduces the solution viscosity and that contributes to a fine dispersion of emulsion during phase inversion process, naturally appearing a narrow distribution of particle size in WPUs.

In addition to this, the emulsion particle size shows no difference by using ultrasonic dispersion and uniform shaking to get homogeneous emulsion, indicating the stable of emulsions. The appearances of emulsions and corresponding films are listed in Table 3. It shows that the emulsion color contained higher HS content is more white because

Fig. 5. Thermogravimetric curve of WPU films.

Fig. 5c. DSC curve of WPU films.

Table 5

Thermal decomposed temperature (T) of soft segments (SS) and enthalpy (ΔH) in thermal analysis.

Samples	Maximum T of SS/°C	Enthalpy (ΔH)/J·g ⁻¹
3:2	349	6.278
7:3	371	6.148
3:1	379	4.965
4:1	386	4.771

of the bigger particle size. As expected, the corresponding film also is hard as well.

3.2. Water-resistance property

Fig. 2 shows the water absorption curve of WPU films at different immersion time in water. It can be seen (Fig. 2) that WPU film with a high ratio of SS:HS (4:1) displays poorer water-resistance properties than those of other films. While the water-resistance property is enhanced in turns by an order of SS:HS ratio of (3:1), (7:3) and (3:2).

As expected, the water-resistance property has a direct relationship with DMPA content. The more DMPA amount is used in synthesis, the worse water-resistance properties of WPU film exhibits, which is due to the increases of hydrophilicity [31]. However, the same DMPA amount was contained (4 wt% of prepolymer (TDI + PPG)) in four WPU films and the reason of different water-resistance properties can be ascribed to the difference in structure-property relationship, such as the different

cross-link density, chain mobility and hydrogen bonding interactions [32,33]. It is known that water can diffuse into hard segment domains more easily since as the domains have more disordered structures [34]. So, with the increasing of HS content the physical cross-link density in HS domains increases, because the more hydrogen bonding between urethane and urea groups are formed. Moreover, hydrogen bonding can also contribute to form ordered orientation structures in HS and SS domains, resulting in the aggregation of HS chains in HS domains and SS chains in SS domains respectively, appearing a high degree of phase separation naturally. To this end, it lowers the surface free energy and enhances the water-resistance property of WPU film [35,36].

3.3. Mechanical properties

According to the ASTM D-1822 standard, the tensile strength and elongation at break (%) of WPU films were measured. It is shown that the tensile strength and elongation at break (%) displays an opposite relationship as increasing ratio of SS:HS in Fig. 3. Among the WPU film (3:2) has a highest tensile strength (~ 8.62 MPa), while the elongation at break ($\sim 138.60\%$) is lowest. The higher HS content in WPU film can result in a higher tensile strength, which is attributed to the higher interior cohesion, chain rigidity and cross-linked density (hydrogen bonding) in HS domains. Conversely, these effects can also restrict the mobility of polymer chains and decrease the elongation at break (%) of WPU films.

3.4. FTIR spectrum analysis

The chemical structures of WPU films are analyzed by FTIR spectroscopy, and the spectrum is shown in Fig. 4. A broad —NH stretching band can be observed at $3300\text{--}3600\text{ cm}^{-1}$, while the —C=O stretching band can be observed at $1600\text{--}1750\text{ cm}^{-1}$ as well. More importantly, FTIR spectroscopy can demonstrate the H-bonding degree in WPU [37]. The H-bonding strength can be calculated from the peak area of free and hydrogen bonded —NH or —C=O groups which shift from high wave-number to low wave-number accordingly. On the other hand, the peak-fit processing of —C=O stretching region and —NH stretching region is done and the best presumed peak-fits obtained using a Gaussian–Lorentzian sum are seen in Figs. 4a and 4b.

Fig. 4a indicates that the higher wave-number of deconvoluted peak is assigned to free —C=O stretching (about 1729 cm^{-1}) and the bonded (about 1704 cm^{-1}) is assigned to hydrogen bonded —C=O stretching [38,39]. The Eq. (S-2) is used to calculate the H-bonding degree (R) of WPU films, and Eq. (S-3) is used to measure the degree of phase separation (DPS).

Among

Fig. 6. Storage modulus (left) and tan δ (right) curve of WPU films.

Fig. 7. XRD pattern of WPU films: (the right diagram is partly enlarged drawing of $2\theta = 45^\circ$).

Table 6
Crystalline sizes (Å) of WPU films.

Samples	Full width at half maximum (FWHM)	Crystalline sizes (Å)
3:2	10.14	0.146
7:3	19.92	0.074
3:1	22.88	0.065
4:1	23.03	0.064

$$R = \frac{A - \text{NH} / -\text{C} = 0, \text{bonded}}{A - \text{NH} / -\text{C} = 0, \text{free}} \quad (\text{S-2})$$

$$\text{DPS} = \frac{R}{R + 1} \quad (\text{S-3})$$

It can clearly be seen that the DPS of WPU film (3:2) is higher than those of other films, followed with the order of 7:3, 3:1 and 4:1 successively, which is also consistent with the results of Table 4. The H-bonding in HS domains acts as physical cross-link points which brings the difficult for polymer chain motions shifting into SS domains, and reducing the mix degree of two phases, naturally the more significant phase separation between hard and soft segments are formed. As a result, the higher SS content in WPU becomes to continuous phase and creates more mutual interaction forces in HS and SS domains, decreasing the DPS of WPU film directly. Similarly, the free $-\text{NH}$ stretching (about 3500 cm^{-1}) and hydrogen bonded $-\text{NH}$ stretching (about 3297 cm^{-1}) shows the same result of H-bonding degree as $-\text{C}=\text{O}$ stretching demonstrated, which is depicted in Fig. 4-b.

3.5. Thermal analysis

Thermal analysis of four WPU films with different HS contents was tested below. Fig. 5(a) and (b) shows the thermogravimetric curves of WPU films. It shows that there exists two thermal decomposition stages, with respect to the HS decomposition at $200\text{--}280^\circ\text{C}$ and the SS decomposition at $300\text{--}400^\circ\text{C}$ [40] respectively. Clearly, it can be seen that the weight percent of WPU film (3:2) remains more than those of other films after thermal testing, which is due to the hydrogen bonding interactions in urethane and urea segments can resist to polymer chains destroy heavily and improve the thermal stability of WPU film accordingly. While for higher SS content in WPU film we can see that the maximum thermal decomposed temperature of SS in film (4:1, $\sim 386^\circ\text{C}$) is higher than those of other films, followed with the order of 3:1 ($\sim 379^\circ\text{C}$), 7:3 ($\sim 371^\circ\text{C}$) and 3:2 ($\sim 349^\circ\text{C}$). This is because that phase mixing can encapsulate the HS chains into SS domains, and the wrapped HS chains are acted as physical cross-linking points in SS

domains to resist thermal decomposition, showing a high mass-temperature trend in weight loss stage [26], which is consistent with the FTIR analysis, as well.

Fig. 5(c) depicts that there appears endothermic peak in all WPU films, indicating the crystallinity of WPU films. The T_g of SS (PPG) in WPU film obtained from DSC analyzer can indicate the mixing degree of HS and SS, among the T_g of film (3:2) is lowest compared to other films, indicating a higher degree of phase separation in WPU film (3:2). In addition to this, the enthalpy (ΔH) calculated from DSC thermogram can also indicate the same conclusion. The ΔH of WPU film (3:2, $\sim 6.278 \text{ J/g}$) is highest in four WPU films, suggesting the higher degree of crystallinity and phase separation. As a summary, the data of thermal analysis are given in Table 5.

3.6. DMA analysis

Fig. 6 shows the dynamic mechanical thermal analysis curves of four WPU films. Among the left graph shows the plot of the temperature versus storage modulus (E') and in the right graph the $\tan \delta$ is plotted as function of the temperature.

The general feature in Fig. 6(left) can be seen is that the storage modulus (E') of WPU film decreases with the increasing of temperature, which mainly caused by the disruption of intermolecular forces in molecular structures [41]. As expected, the E' increases with increasing HS content, which is similar as the result of tensile strength. That is because the high HS content in WPU provides more intermolecular forces (e.g. hydrogen bonding) to improve the stiffness of polymer chain [42]. The decreases of E' as the HS content decreased may be related to the decrease of structural order which resulting from the difficulty in regular molecular packing, and also depended on the molecular flexibility and regularity in the given temperature range [43]. Besides, Fig. 6 (right) depicts the glass transition temperature (T_{gs}) of WPU films. It shows the order of WPU films as $T_{gs}(4:1) < T_{gs}(3:2) < T_{gs}(3:1) < T_{gs}(7:3)$. To some extent, the more higher SS content will become to continuous phase and wrap the HS chains inside of SS domains as alone points with less effects on T_{gs} , especially in WPU film with 80% SS content. Certainly, the increasing HS content in WPU can restrict the mobility of SS chain and thereby increase the T_{gs} . Similarly, the well phase separated WPU film (3:2), as FTIR and DSC demonstrated, will reduce the interactions from HS chain on SS chain mobility, and showing a lower T_{gs} in comparison to other two WPU films (3:1 and 7:3) naturally.

3.7. XRD analysis

The crystallinity of WPU films was determined using XRD analysis.

Fig. 8. Topography observation of WPU films.

Fig. 9. Thermal conductivity of WPU films.

Fig. 7 shows the X-ray diffraction curves of WPU films. There appears a broad diffraction peak at near $2\theta = 23^\circ$ in four WPU films, indicating the crystallinity of WPU films [44]. Also, there appears another wide diffraction peak at near $2\theta = 45^\circ$ in film (3:2), which is ascribed to the ordered aggregations of SS chains, in spite of the bad crystalline

behavior of SS (PPG). For other WPU films, the wide diffraction peak gradually disappeared with the increasing of SS content. Moreover, referring to Scherrer equation to calculate the crystalline sizes ($\text{\AA}$) and the results are listed in Table 6, clearly it can conclude that the degree of crystallinity of film (3:2) is higher than those of the other films (7:3, 3:1, 4:1), as same as the results of DSC and FTIR demonstrations.

3.8. Morphological analysis

Atomic force microscope (AFM) is a simple and direct device to observe phase separation of multi-phase samples. HS chains aggregate together and form the bright spots in AFM graph, due to the high interior cohesion and polarity. While the gray spots indicate the aggregation of SS domains [45]. Compared to other three WPU films, the film (3:2) shows an apparent distribution of bright and gray zones in Fig. 8, showing a higher degree of phase separation than other WPU films. And also this is consistent with above analytic methods demonstrations. That is, the higher HS content in WPU film, the stronger hydrogen bonding forces are formed in HS domains, which reduces the interferences on SS chains mobility and arrives to the maximum equilibrium of HS and SS chains respectively, forming ordered structures in two phases and showing the well phase separation naturally [46].

Fig. 10. T-peel strength of WPU films.

3.9. Thermal conductivity tests

We used the steady-state method to measure thermal conductivity of WPU films, and the results can represent the heat transfer properties of corresponding films. Among the results of thermal conductivity of WPU films are depicted in Fig. 9. It shows that the thermal conductivity of WPU film (3:2) is higher than those of other films, followed by film (7:3), film (3:1) and film (4:1), which indicates that the increases of HS content can contribute to increasing heat transfer performances. The reason can be ascribed to the differences of DPS and crystallinity in WPU films. As above results reported, the H-bonding degree increase as HS content increases from 20% to 40%, which is owing to the more sites existed in HS domains and SS domains respectively act as hydrogen bond acceptors or donors to mutually increase the hydrogen bonding behaviors. As a result, the DPS and crystallinity of WPU film is increased with increasing HS content. On one hand, the well DPS and crystallization performances in WPU can result in the long-range order, short-range order and oriented ordered structures formed in HS and SS regions respectively, creating more free pathways for phonon conduction to reduce concentrated heat flux and much more heat delays phenomena [12,47]. On the other hand, the ordered structures are acted as many small lattices in soft segment and hard segment domains which reduces the phonon scattering and accelerates the phonon propagation accordingly. As a result, the thermal conductivity of WPU film is increased with increasing HS content.

3.10. T-peel strength test

The adhesive properties of WPU emulsions are obtained from T-peel strength tests of leather/WPU/leather joints. The results of initial adhesive strength and final adhesive strength are given in Fig. 10. Fig. 10 shows that adhesive strength increases with the increasing of SS content in WPU, especially the final adhesive strength of WPU (4:1) is reached to 136.14 N/25 mm, while the adhesive strength of WPU (3:2) is 21.55 N/25 mm. Likewise, a number of articles [26,48–50] showed the same findings as our study. Here, we used PPG to be as SS chain in this study, which possessed a methyl side-group and affect the crystallization behavior of SS regions, to some extent. Interestingly, the T-peel strength of adhesive joints still increases with the increasing of SS content, even though the crystallinity in SS domains is low. This is mainly because the higher SS content in WPU generates smaller particles in emulsions, which is easily penetrated into the natural pores of leather substrate to form strong bonding points, boosting the adhesive properties accordingly.

4. Conclusion

In this study, heat transfer performances and adhesive properties of

PPG-based WPUs with different mass ratios of soft and hard segments were measured. The perspective of structure-property relationships were analyzed using FTIR, TG, DSC, DMA, AFM and XRD. It was found that the phase separation and crystallinity of WPU were increased with the increasing of hard segment (HS) content, which enhanced the heat transfer performance of WPU film accordingly. The experimental results showed that the WPU film ($m_{SS}:m_{HS} = 3:2$) expressed a higher thermal conductivity (~ 0.374 W/m·K) than those of other WPU films, while the T-peel strength (21.55 N/25 mm) of leather/WPU/leather joints was lowest. FTIR, XRD, DSC and AFM demonstrated that the higher HS content in WPU showed more hydrogen bonding degree and higher phase separation and crystallinity than less HS content in WPU, which contribute to form more ordered stacked structures in two phases, as a whole.

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Conflicts of interest

None.

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