

Role of the Soft and Hard Segments Structure in Modifying the Performance of Acrylic Adhesives Modified by Polyurethane Macromonomers

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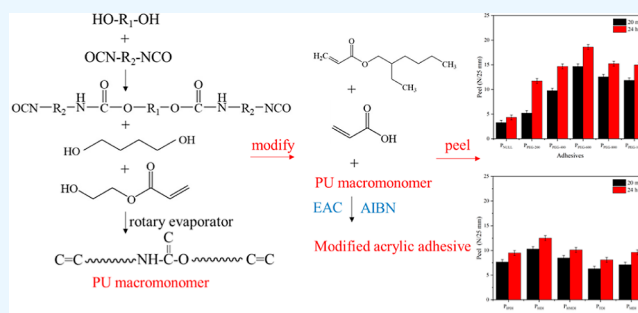
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ABSTRACT: Acrylic pressure sensitive adhesives, modified by polyurethane (PU), achieve selective optimization through the designability of polyurethanes. In this paper, PU macromonomers were prepared by a two-step synthesis method, using polypropylene glycol or polyethylene glycol with different molecular weights as soft segments and different types of diisocyanates: isophorone diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane diisocyanate (HMDI), 2,4-toluene diisocyanate (TDI), and 4,4'-diphenylmethane diisocyanate (MDI) and chain extenders as hard segments. After being terminated by capping agents, a series of PU macromonomers of different molecular weights and structures were obtained and used to modify the acrylic base adhesives. Compared to unmodified adhesives, acrylic adhesives modified by PU macromonomers have improved adhesion performances and heat resistance and show an increasing trend with the increase of molecular weight of diols. Diols with a molecular weight of 600 have the best effect. Diisocyanates containing benzene rings can better improve the thermal performance of adhesives, where P_{MDI} containing a biphenyl ring is the best, while aliphatic isocyanate groups have a greater improvement in adhesion performance, and the adhesion performance of P_{HDI} with a long carbon chain is the best.



INTRODUCTION

Pressure-sensitive adhesives (PSAs) can effectively adhere to the substrate at room temperature. This type of adhesive does not require solvent evaporation or chemical reactions to bond, and the bonding process can be completed at room temperature, making the use of PSAs simple and safe.^{1,2} Among all synthesized PSAs, acrylic adhesives are widely used due to their excellent performances and diverse types.³ Acrylic adhesives can be mainly divided into solvent-borne, solvent-free, water-borne, UV-curing, etc.^{4–6} Solvent-borne acrylic adhesives are well-known for their excellent performances, and they are widely used in applications of medical tapes, pressure-sensitive labels, packaging tapes, etc.^{7,8} However, solvent-borne acrylic adhesives have many drawbacks such as adhesive-cohesive strength balance. Therefore, the performances of solvent-borne acrylic adhesives are usually modified by different types of cross-linking agents,⁹ resins,³ or functional monomers.¹⁰

Polyurethane (PU) is a cohesive polymer with unique structures and properties. Its molecular chains are composed of alternating hard segments of isocyanates, chain extenders, and soft segments of polyester or polyether polyols. The hard segments give polyurethanes rigidity, while the soft segments affect the flexibility of the molecular chains.¹¹ Therefore, by

precisely changing the content and type of hard and soft segments, PU materials of different structures and performances can be obtained, with properties such as good wear resistance, oil resistance, flexibility, hardness, and environmental friendliness.^{12–15} These materials can be used for a wide range of applications, including coatings,¹⁶ adhesives,¹⁷ elastomers,¹⁸ fibers,¹⁹ and rigid materials.²⁰ Due to the designability of PU, it has also been used in the modification of various materials.

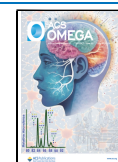
Usually, PU-acrylic PSAs were prepared by modifying acrylates with polyurethanes, which can simultaneously exhibit high hardness and flexibility characteristics of PU while retaining the advantages of acrylic PSAs themselves. For example, performance of adhesives has been strengthened;^{21,22} the scope of application has been expanded;²³ and the pollution to the environment has been reduced.^{24,25} Therefore, studies on the modification of acrylic adhesives by polyur-

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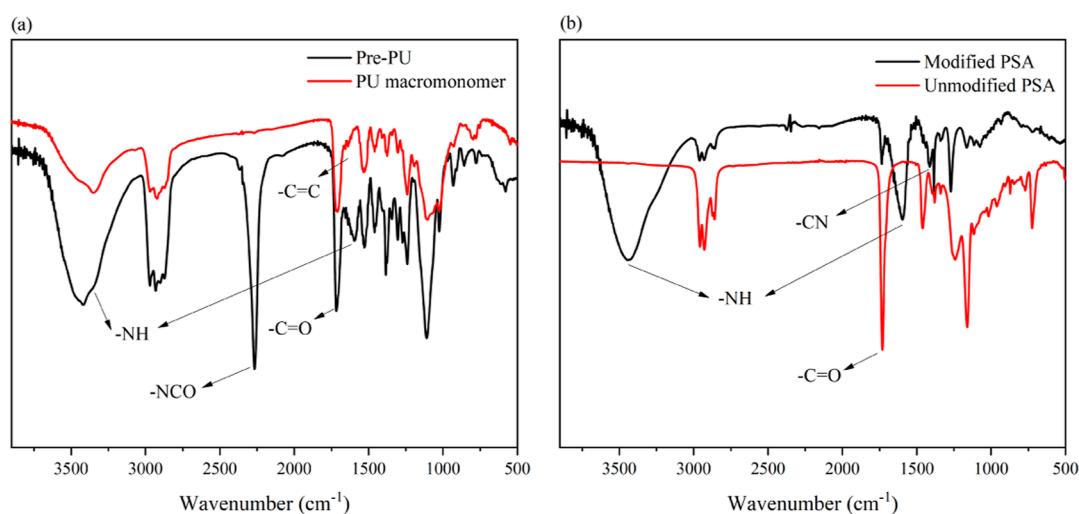


Figure 1. FTIR spectra of (a) PU prepolymer and PU macromonomer and (b) PU-modified PSA and unmodified PSA.

Table 1. Formulas, Molecular Weights, and Cross-Linking Degrees of PSAs with Different Weight Diols

sample	diol	diisocyanate	molecular weight of PUs	molecular weight of PSAs ($\times 10^4$)	cross-linking degree (%)
P_{NULL}	null	null		3.92	
$P_{\text{PEG-200}}$	PEG-200		1635	4.12	0.13
$P_{\text{PEG-400}}$	PEG-400		2487	4.65	0.18
$P_{\text{PEG-600}}$	PEG-600	IPDI	2946	5.44	0.25
$P_{\text{PEG-800}}$	PEG-800		4048	6.88	0.33
$P_{\text{PEG-1000}}$	PEG-1000		4875	8.23	0.32

ethanes provide an important approach to improve the performance of the adhesives. However, most of the studies on PU-modified acrylic adhesives regarded polyurethanes and acrylic adhesives as a whole during the synthesis²⁶ or pursued new structures.²⁷ Seldom has work been aimed on the effects of different diols and diisocyanates on PU-modified acrylic adhesives from the perspective of PU macromonomers separately.

In this work, the influence of PU macromonomers on modified acrylic adhesives is characterized. By changing the molecular weight and structure of soft and hard segments, we investigated the relationships between molecular weight, structure, and performance. PU macromonomers of different molecular weights and structures were synthesized with different diols and diisocyanates and then used to modify acrylic adhesives, resulting in the preparation of PU macromonomers-modified acrylic base adhesives. The physical and thermal properties of modified acrylic adhesives were analyzed by gel chromatography (GPC), a Ubbelohde viscometer, dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA). After the modified acrylic adhesives were coated into adhesive films, strip film samples were prepared. Their adhesion performances were tested, and the relationships among performances, molecular weight, and structures were analyzed. According to the results of this article, it is possible to design PU macromonomer-modified acrylate base adhesives that meet different requirements from a performance perspective; these base adhesives with specific properties can be further modified to simplify subsequent processes and expand the application of acrylic adhesives.

RESULTS AND DISCUSSION

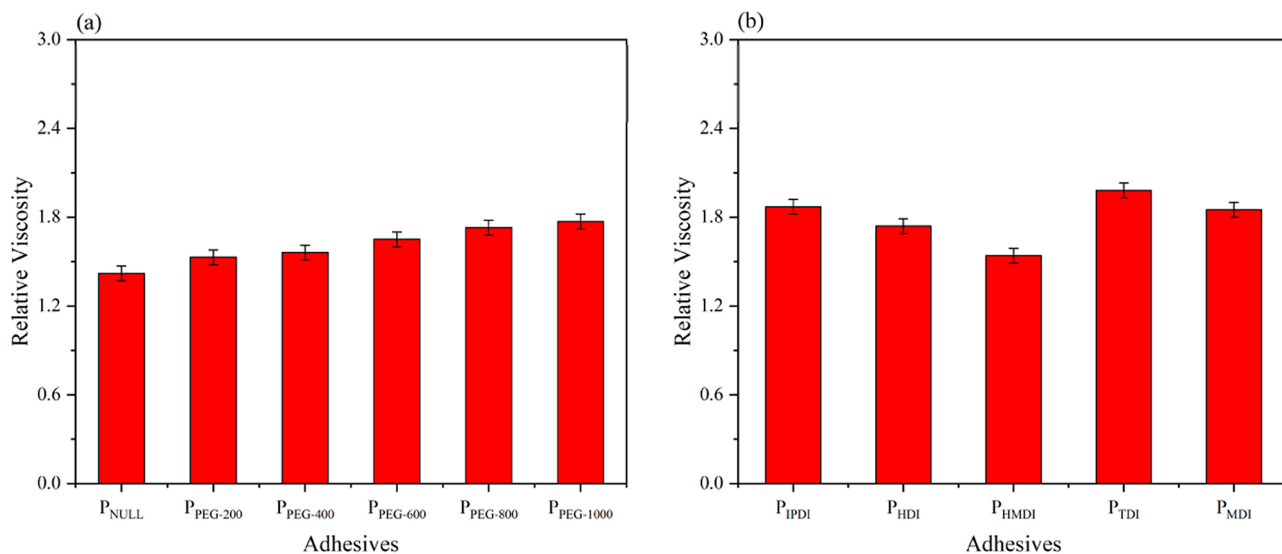
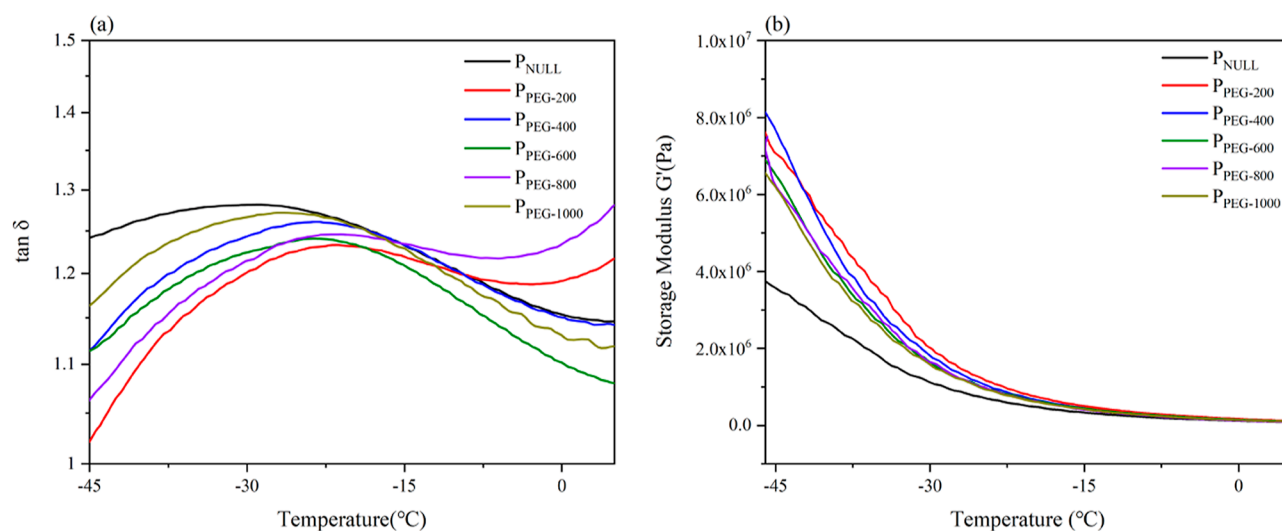
Structural Characterization. PU macromonomers were prepared through a two-step reaction: first, NCO-terminated prepolymers were generated using diols and diisocyanates as raw materials; then, after chain extension, 2-hydroxyethyl acrylate (HEA) was used to consume the remaining NCO, at the same time attaching carbon-carbon double bonds to molecular chains.

Figure 1a shows the Fourier transform infrared (FTIR) spectra of the PU prepolymer (Pre-PU) and the PU macromonomer. The main bands commonly used to characterize PU are the OH absorption at 3500 cm^{-1} , the NH stretching vibration at $3500\text{--}3000\text{ cm}^{-1}$, and the C=O group of urethane at $1800\text{--}1640\text{ cm}^{-1}$. The bands at 3379 and 1532 cm^{-1} evidence the formation of NH in urethane. Simultaneously, the NCO stretching band at 2273 cm^{-1} disappeared as a consequence of the reaction between OH and NCO groups.^{28,29} The small peak of the carbon-carbon double bond at 1633 cm^{-1} is due to the low content of the double bonds. These facts reveal that the designed PU macromonomers were successfully synthesized.

Figure 1b compares the FTIR spectra of unmodified acrylic adhesives with those of PU macromonomer-modified acrylic adhesives. The C=O group peak at 1725 cm^{-1} is caused by 2-EHA, acrylic acid (AA), and esters in the carbamate group. There is no peak at $1620\text{--}1700\text{ cm}^{-1}$, indicating that there is no stretching vibration of the carbon-carbon double bond in the system, meaning that all monomers in the system have reacted.³⁰ Comparing the two curves, the spectrum of the modified acrylic adhesive shows a stretching vibration absorption peak of NH at 3408 cm^{-1} , a bending vibration absorption peak of NH at 1593 cm^{-1} , and a stretching vibration absorption peak of CN at 1420 cm^{-1} , all of which

Table 2. Formulas, Molecular Weights, and Cross-Linking Degrees of PSAs with Different Diisocyanates

sample	diol	diisocyanate	molecular weight of PUs	molecular weight of PSA ($\times 10^4$)	cross-linking degree (%)
P_{IPDI}	PPG-600	IPDI	3517	6.05	0.33
P_{HDI}		HDI	3206	5.75	0.16
P_{HMDI}		HMDI	4076	6.89	0.21
P_{TDI}		TDI	3435	6.33	0.37
P_{MDI}		MDI	3814	6.68	0.29

**Figure 2.** RV of modified PSAs with (a) different molecular weight PU macromonomers or (b) different structure PU macromonomers.**Figure 3.** (a) $\tan \delta$ and (b) storage modulus curves of modified PSAs with different molecular weight PU macromonomers.

prove the presence of carbamate groups in the modified acrylic adhesive.

Viscosity Analysis. Tables 1 and 2 list the formulas, molecular weight, and cross-linking degree of modified acrylic adhesives with different molecular weight PU macromonomers or different structure PU macromonomers. According to these tables, cross-linking degrees of synthesized adhesives are all less than 0.5%, indicating that these adhesives can be used as base adhesives.

The relative viscosity (RV) of PSAs relative to ethyl acetate (EAC) was measured by using a Ubbelohde viscometer. Figure 2 shows the RV of acrylic adhesives modified by different

molecular weights and structures of PU macromonomers. As observed from Figure 2a, RV of the modified acrylic adhesives increases along with increase of the diol molecular weight. As the molecular weight of the adhesives increases, the degree of chain entanglement becomes easier because of the long chain and cross-linked network in the system, which leads to an increase in the viscosity of the system.

In Figure 2b, the change trend of RV is basically the same as that of the molecular weight in Table 2, which also confirms the influence of the molecular weight on the performance of modified acrylate adhesives. However, the viscosity changes of P_{IPDI} and P_{TDI} do not follow the trend of molecular weight

change, and overall, the viscosity of adhesives modified by symmetrical PU macromonomers is lower than that of adhesives with asymmetric structures. Due to the asymmetric structure of PU macromonomers, the entanglement between molecular chains is increased, leading to the detachment of the relationship between viscosity and molecular weight.

Comparing $P_{\text{PEG-600}}$ and P_{IPDI} , it can be seen that the PU macromonomer prepared from polypropylene glycol (PPG) has a higher RV than that prepared from polyethylene glycol (PEG). In addition to the influence of molecular weight, the length of the molecular chain and the methyl branch in PPG are also important reasons.

Dynamic Mechanical Analysis. Polymers are a type of viscoelastic material that undergo reactions in both the elastic and viscous parts under alternating forces, and these reactions vary with temperature. DMA has been employed to obtain information about the viscoelastic properties to investigate the glass transition of adhesives and the movement of chains at various levels. The $\tan \delta$ curves of modified adhesives are shown in Figure 3a, and the peak values of each curve are listed in Table 3.

Table 3. T_g Values of Modified PSAs with Different Molecular Weight PU Macromonomers

sample	P_{NULL}	$P_{\text{PEG-200}}$	$P_{\text{PEG-400}}$	$P_{\text{PEG-600}}$	$P_{\text{PEG-800}}$	$P_{\text{PEG-1000}}$
T_g ($^{\circ}\text{C}$)	-31.58	-21.85	-23.69	-24.44	-24.41	-24.77

Combining Figure 3 and Table 3, the glass transition temperature (T_g) of PU macromonomer-modified acrylic adhesives deviates toward low temperature as the diols molecular weight increases. T_g of $P_{\text{PEG-200}}$ is -21.85 $^{\circ}\text{C}$, while T_g of $P_{\text{PEG-1000}}$ is only -24.77 $^{\circ}\text{C}$, which is still higher than that of the unmodified acrylic adhesive P_{NULL} . The main component in this series of adhesives is 2-EHA, so the T_g of P_{NULL} is relatively low. With the addition of PU macromonomers, T_g increases. As the diols molecular weight gradually increases, the proportion of soft segments in the PU macromonomer also increases, and the flexibility of the molecular chain is improved, leading to a decrease in the glass transition temperature.³¹ When the temperature exceeds 20 $^{\circ}\text{C}$, the adhesive samples could not maintain their original solid

state and began to exhibit viscous flow; the resulting curves under high temperatures show an irregular divergent shape and lose analytical value. This phenomenon confirmed that the modification of acrylic adhesives by PU macromonomers was mainly manifested under the low temperature range.

The storage modulus (G') refers to the ability of a material to absorb energy when subjected to stress or deformation and be restored to its original state after the stress or deformation disappears. Figure 3b shows the curves obtained for the storage modulus as a function of temperature for the synthesized modified adhesives. G' drops sharply before the glass transition temperature; when the temperature is near the glass transition temperature, the downward trend slows down. Under all temperatures, compared to unmodified acrylic adhesives, acrylic adhesives modified by PU macromonomers have a higher storage modulus. The same as the $\tan \delta$ curves, the modulus of the high-temperature section is extremely low, losing the trend under low temperature. Therefore, we only analyzed DMA curves under low temperatures.

As shown in Figure 4a and Table 4, T_g of P_{HDI} is only -29.09 $^{\circ}\text{C}$, while the T_g of P_{MDI} is as high as -20.63 $^{\circ}\text{C}$. When

Table 4. T_g Values of Modified PSAs with Different Structure PU Macromonomers

sample	P_{IPDI}	P_{HDI}	P_{HMDI}	P_{TDI}	P_{MDI}
T_g ($^{\circ}\text{C}$)	-24.31	-29.09	-24.54	-22.71	-20.63

hexamethylene diisocyanate (HDI) is used as hard segments in the PU macromonomer, its long carbon chain structure improves the flexibility of the molecular chains; the biphenyl ring structures in 4,4'-diphenylmethane diisocyanate (MDI) make the molecular chains more stable, resulting in a higher T_g .³²

The modulus of adhesives is related to wettability. The higher the modulus, the poorer the wettability, and hence, the more hindered the contact of the adhesive on the surface.¹¹ In Figure 4b, P_{MDI} and P_{TDI} have higher storage modulus under all temperatures, proving that the presence of benzene rings can increase the rigidity of the adhesives, leading to higher storage modulus. The storage moduli of P_{IPDI} , P_{HDI} , and P_{HMDI} are similar, indicating that the structure of aliphatic isocyanates

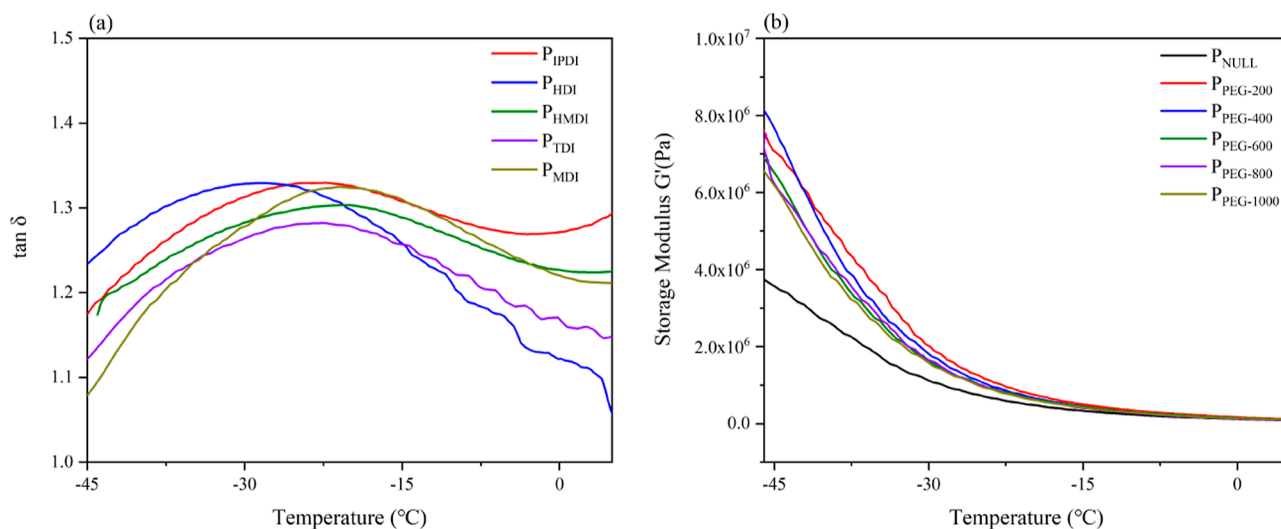


Figure 4. (a) $\tan \delta$ and (b) storage modulus curves of modified PSAs with different structure PU macromonomers.

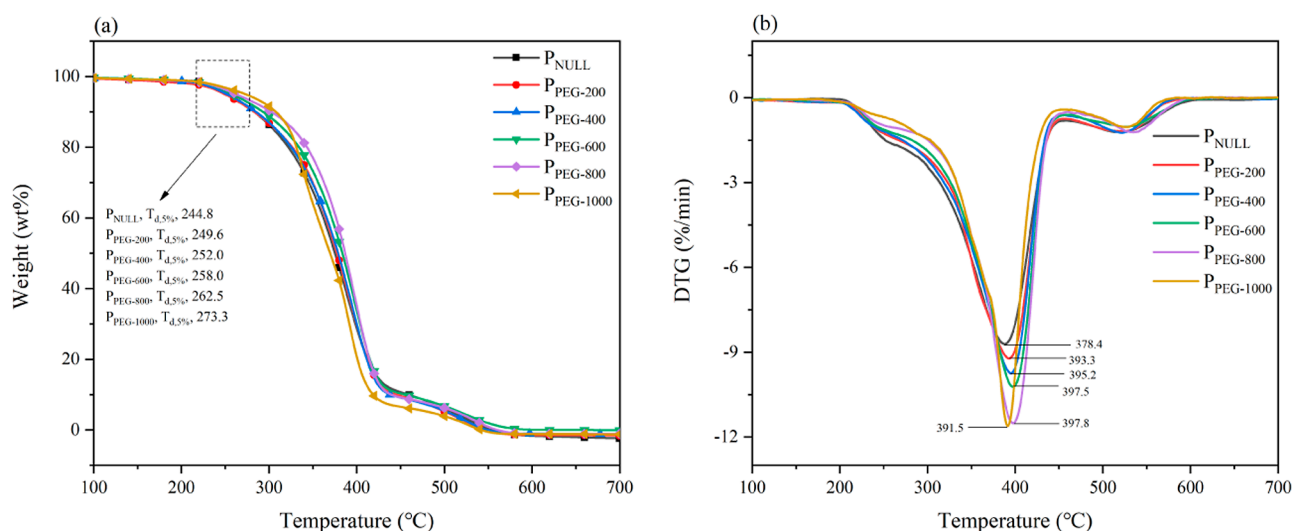


Figure 5. (a) TGA and (b) DTG curves of modified PSAs with different molecular weight PU macromonomers.

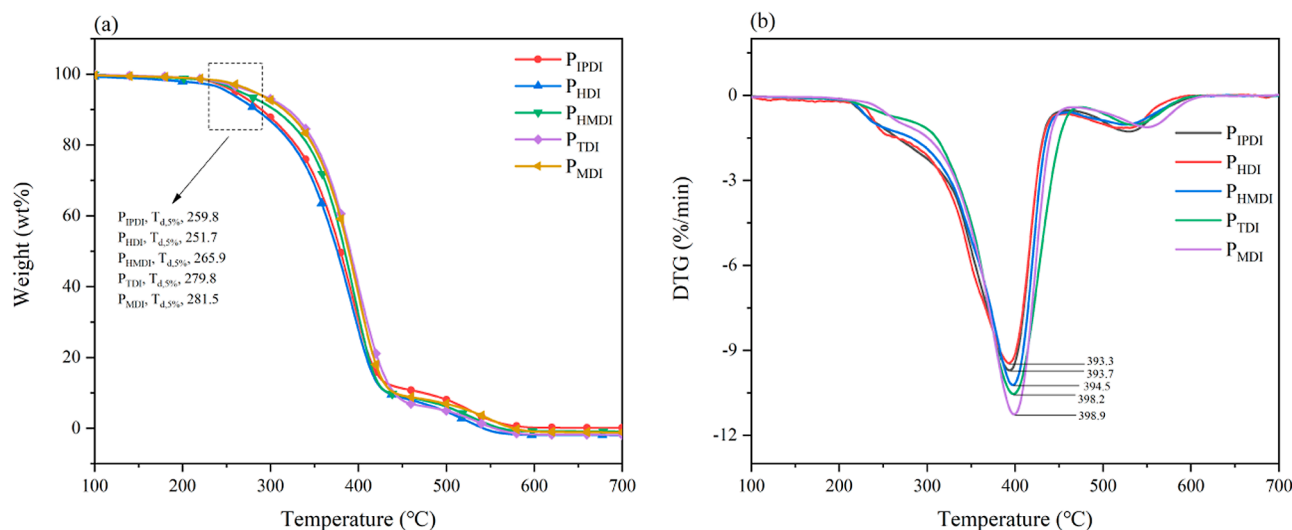


Figure 6. (a) TGA and (b) DTG curves of modified PSAs with different structure PU macromonomers.

has no significant effect on the storage modulus of PU macromonomer-modified acrylic adhesives. Compared to $P_{PEG-600}$, P_{IPDI} has higher T_g and lower storage modulus, indicating that the side chain methyl groups of diols can hinder the movement of molecular chains.

Thermogravimetric Analysis. Thermal degradation of modified acrylic adhesives was analyzed using TGA as the thermal stability of adhesives has a significant impact on application.

The composition of the soft segments of PU materials strongly affects their thermal properties. Figure 5a shows the thermogravimetric curves of acrylic adhesives modified by different molecular weight PU macromonomers. In this figure, the thermal weight loss trend of modified acrylic adhesives remains consistent with that of the unmodified adhesive. Below 200 °C, the weight of the adhesives does not change; 200–420 °C is the main range for weight loss; and between 420 and 550 °C, the trend of weight loss slows down due to the presence of a small amount of cross-linking in the system, which improves its heat resistance. The residue of all samples is very low, approaching 0. This is because the main component of the acrylic adhesive modified by the PU macromonomer is acrylic

ester, which contains a small amount of PU and has a high carbon content. After high-temperature decomposition, there is almost no residue.

Figure 5b shows the differential thermogravimetry (DTG) curves of PU macromonomer-modified acrylic adhesives with different diol molecular weights. Combining Figure 5a,b, it can be seen that the modification of PU macromonomers improves the heat resistance of acrylic adhesives, and as the molecular weight of diols increases, the heat resistance and thermal stability also gradually improve.¹⁴ $T_{d,5\%}$ represents the temperature at which the system loses 5% weight, the $T_{d,5\%}$ of the acrylic adhesive before modification is 244.8 °C, and after the modification, the highest $T_{d,5\%}$ ($P_{PEG-1000}$) that can be reached is 273.3 °C. $T_{d,max}$ represents the temperature at which the weight loss rate of the system is the highest; in the DTG curves, it is displayed as the temperature corresponding to the peak value. From Figure 5b, it can be seen that as the molecular weight of diols increases, the value of the peak gradually increases toward higher temperatures; the maximum weight loss rate before modification occurs at 378.4 °C, and after modification, $P_{PEG-800}$ has the highest $T_{d,max}$, which occurs at 397.8 °C. Although $T_{d,5\%}$ of $P_{PEG-1000}$ is the largest, its $T_{d,max}$

is lower. This is because the molecular weight of diols in the PU macromonomer used in $P_{\text{PEG-1000}}$ is too large, the relative content of the soft segment is high, and when the temperature reaches its decomposition temperature, it decomposes quickly.

In Figure 6a,b, thermal properties of modified PSAs with different structure PU macromonomers have been analyzed by TGA and DTG. As is clearly shown, the initial decomposition temperature of adhesives containing different structures of diisocyanates varies greatly, while the maximum weight loss rate occurs at almost the same temperature, indicating that the heat resistance of modified acrylic adhesives containing a benzene ring structure is higher than that of adhesives without a benzene ring structure, but the influence of the diisocyanate structure on thermal stability is not significant.³³ $T_{\text{d},5\%}$ and $T_{\text{d},\text{max}}$ of P_{TDI} and P_{MDI} are all higher than those of P_{IPDI} , P_{HDI} , and P_{HMDI} , and the adhesive containing MDI has the best thermal stability, whose $T_{\text{d},5\%}$ is 281.5 °C and $T_{\text{d},\text{max}}$ is 398.9 °C, indicating that the appropriate introduction of rigid benzene rings can improve the heat resistance of the adhesives.³² P_{HDI} has the worst heat resistance, whose $T_{\text{d},5\%}$ is 251.7 °C and $T_{\text{d},\text{max}}$ is 393.3 °C; this is mainly attributed to the long carbon chain structure of HDI.

Comparing $P_{\text{PEG-600}}$ and P_{IPDI} , $T_{\text{d},5\%}$ of $P_{\text{PEG-600}}$ is 258 °C and $T_{\text{d},\text{max}}$ is 397.5 °C, $T_{\text{d},5\%}$ of P_{IPDI} is 259.8 °C and $T_{\text{d},\text{max}}$ is 393.7 °C, and the thermal stabilities of PU macromonomer-modified acrylic adhesives prepared by PEG and PPG are similar. The improvement of thermal stability of acrylic adhesives containing PEG were slightly greater than that of adhesives containing PPG.

Contact Angle Analysis. The value of the contact angle (CA) reflects the wettability of droplets on solid surfaces, which can be related to the adhesion of adhesives.

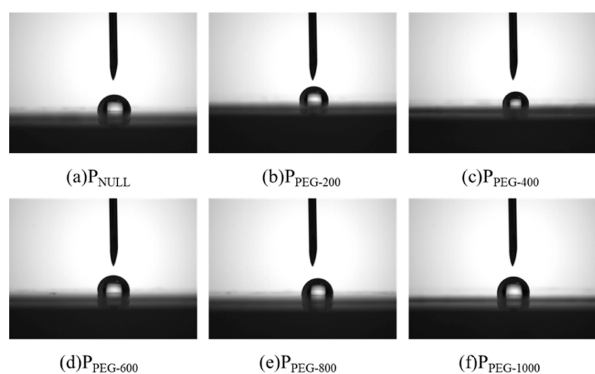


Figure 7. CA of modified PSAs with different molecular weight PU macromonomers: (a) P_{NULL} , (b) $P_{\text{PEG-200}}$, (c) $P_{\text{PEG-400}}$, (d) $P_{\text{PEG-600}}$, (e) $P_{\text{PEG-800}}$, and (f) $P_{\text{PEG-1000}}$.

CA and CA values are shown in Figure 7 and Table 5. From Table 5, after modification with PU macromonomers, the CA of acrylic adhesives increases and is consistent with the trend of molecular weight changes. CA of P_{NULL} is 91.75°, and that of $P_{\text{PEG-1000}}$ can reach up to 100.5°. As the molecular weight of diols increases, the polarity of PEG gradually decreases, and

the molecular chain of PU macromonomers becomes longer. These are all the main reasons for the increase in the CA. The CA can reflect the wettability of the adhesive on the PET film. The larger the CA, the poorer the wettability.

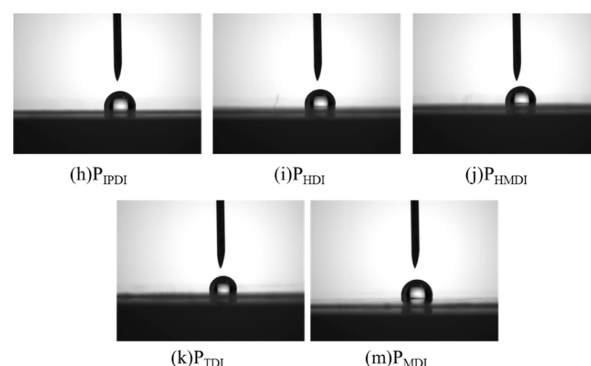


Figure 8. CA of modified PSAs with various structure PU macromonomers: (h) P_{IPDI} , (i) P_{HDI} , (j) P_{HMDI} , (k) P_{TDI} , and (m) P_{MDI} .

Figure 8 and Table 6 present the effect of PU macromonomer structures on the CA of modified acrylic adhesives, and it can be concluded that the CA of modified acrylic adhesives containing aromatic diisocyanates is larger than that of aliphatic ones; the asymmetric structure also increases the CA of the adhesives; the CA of acrylic adhesives modified by PU macromonomers prepared by PPG is higher than that of adhesives modified by PU macromonomers prepared by PEG. The larger the CA, the lower the surface free energies.³⁴ So, wettability of adhesives containing PPG is not as good as that of adhesives containing PEG, and the wettability of P_{HDI} is the best. The wettability also affects the adhesion performance of adhesives.

Adhesion Performance. Adhesion performance, as one of the most important properties of adhesives, has a significant impact on the application of adhesives.

Figure 9a,b shows the peel strength, loop tack, and shear strength of PU macromonomer-modified acrylic adhesives with different molecular weights and structures; all the destruction modes are cohesive failure.

Peel. From Figure 9a, the 180° peel strength after 24 h is generally higher than the 180° peel strength after 20 min, and the trends of both are roughly the same. The addition of PU macromonomers improved the 180° peel strength of acrylic adhesives and showed a trend of first increasing and then decreasing with the increase of molecular weight; $P_{\text{PEG-600}}$ reached the maximum. With the increase of the diols molecular weight, the content of soft segments in PU macromonomers increases, which improves the flexibility of the molecular chains and increases the fluidity of the adhesive. The adhesive films can better contact the substrate, leading to obstruction during peeling. Based on the results of the CA, when the molecular weight of PU macromonomers further increases, the molecular chains become too long, the possibility of

Table 5. CA Values of Modified PSAs with Different Molecular Weight PU Macromonomers

sample	P_{NULL}	$P_{\text{PEG-200}}$	$P_{\text{PEG-400}}$	$P_{\text{PEG-600}}$	$P_{\text{PEG-800}}$	$P_{\text{PEG-1000}}$
CA (°)	91.7 ± 0.5	93.7 ± 1.1	96.2 ± 0.2	96.7 ± 0.8	96.7 ± 0.5	100.5 ± 0.6

Table 6. CA Values of Modified PSAs with Various Structure PU Macromonomers

sample	P_{IPDI}	P_{HDI}	P_{HMDI}	P_{TDI}	P_{MDI}
CA (°)	100.0 ± 0.9	97.3 ± 0.7	99.0 ± 0.5	102.2 ± 1.1	101.2 ± 0.7

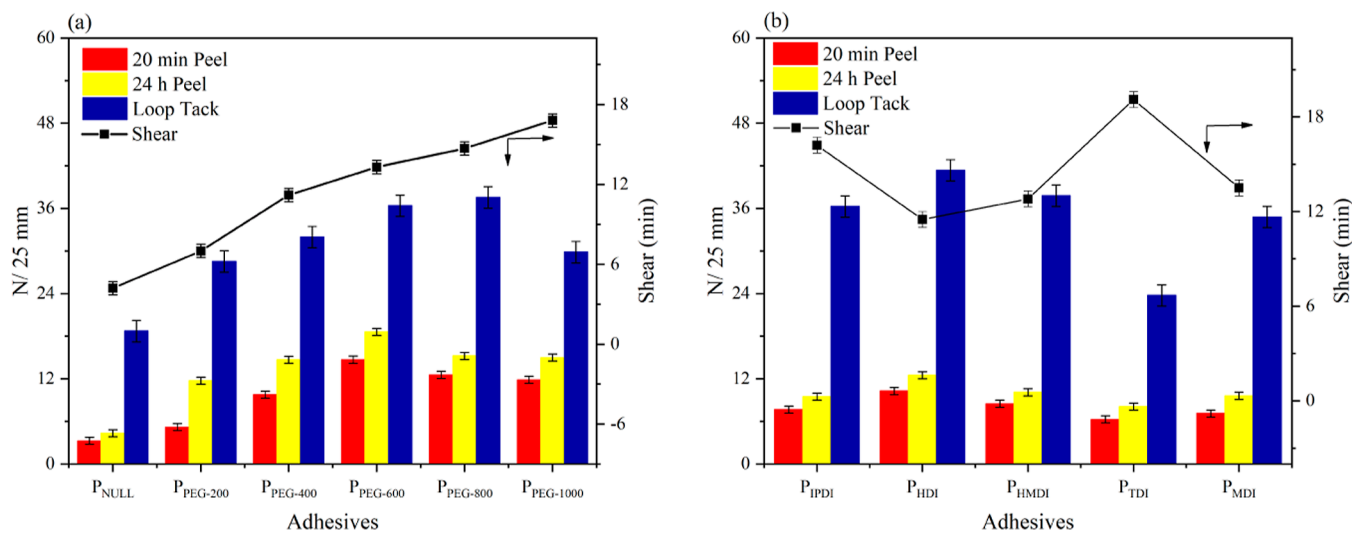


Figure 9. Adhesion performances of modified PSAs with (a) different molecular weight PU macromonomers or (b) different structure PU macromonomers.

entanglements grows, and the flowability decreases. The contact area between the adhesive film and the substrate decreases, resulting in a decrease in peel strength.³⁵

Figure 9b shows that modified acrylic adhesives with symmetric structures have higher peel strength than those with asymmetric structures; adhesives containing benzene rings have lower peel strength than those without benzene rings,³⁶ while P_{HDI} has the best peel strength and P_{TDI} has the worst. In addition, the peel strength of PU macromonomer-modified acrylic adhesives prepared by PPG is lower than that of those modified by PEG. The methyl in the side chain of PPG, benzene ring, and asymmetrical structure all result in poor fluidity of the molecular chains, a large CA, and a rough surface, preventing the formation of a dense adhesive layer between the adhesive films and the substrate surface, so adhesives containing these structures have lower peel strength.

Loop Tack. The loop tack of adhesives is an important basis for evaluating adhesive bonding performance. As shown in Figure 9a, the loop tack of the modified acrylic adhesives gradually increases when the diols weights increase. As the molecular weight increases, the content of soft segments also increases and the modulus of loss during film formation decreases. When the adhesive film briefly contacts the substrate, it can form a better adhesive layer, so greater energy is required for peeling.³⁷ However, when the molecular weight is too large, the separation of segments is obvious, breaking the phase continuity and reducing the loop tack, as shown by $P_{\text{PEG-1000}}$.

The loop tacks of modified acrylic adhesives prepared from PPG and PEG are almost the same, while the loop tack of $P_{\text{PEG-600}}$ is 36.38 N/25 mm and that of P_{IPDI} is 36.27 N/25 mm; the loop tack of adhesives modified with aliphatic PU macromonomers is generally higher than that of adhesives modified with aromatic PU macromonomers. Loop tack of adhesive with the linear symmetric structure (HDI) is the highest (41.37 N/25 mm), while loop tack of adhesive with the asymmetric aromatic structure [2,4-toluene diisocyanate

(TDI)] is the lowest (23.75 N/25 mm), which is only 57% of the former. PU macromonomers are mainly composed of soft and hard segments; the long carbon chain structure of HDI makes the distribution of soft and hard segments relatively tight and orderly, forming a dense adhesive layer when the adhesive film contacts the substrate; and the loss of modulus during separation is also large.²⁸

Shear. Shear strength is also one of the important indicators for evaluating the adhesion performance of adhesives, relating to the entanglement density between molecular chains and the cross-linking degree of the system. The larger the cross-linking degree, the greater the shear viscosity, which also leads to a higher shear strength.^{38,39} To avoid the cross-linker's interference in the investigation of the adhesive structure and performance relationship, PU macromonomer-modified acrylic adhesives prepared in this article were compared to those without the cross-linker (shown in Tables 1 and 2); certainly, a low shear level appears. As shown in Figure 9a, the shear strength of PU macromonomer-modified acrylic adhesives increases with the continuous increase in molecular weight. From the previous text, as the molecular weight of the adhesives increases, entanglement of molecular chains is easier, leading to an increase in the viscosity of the system, which further results in an increase in the shear value.

Shear of P_{IPDI} is larger than that of $P_{\text{PEG-600}}$, indicating that the acrylic adhesive modified by PPG-prepared PU macromonomers has a higher shear strength. From Figure 9b, adhesives containing asymmetric structures, such as isophorone diisocyanate (IPDI) and TDI, have higher shear strength, P_{TDI} has the longest holding time, while P_{HDI} 's holding time is the shortest. The PU macromonomers prepared from aromatic diisocyanates contained benzene rings; when used to modify acrylic adhesives, the benzene rings were implanted into the molecular chains, reducing the flexibility of the molecular chains and increasing the possibility of entanglement between molecular chains, resulting in an increase in shear strength.

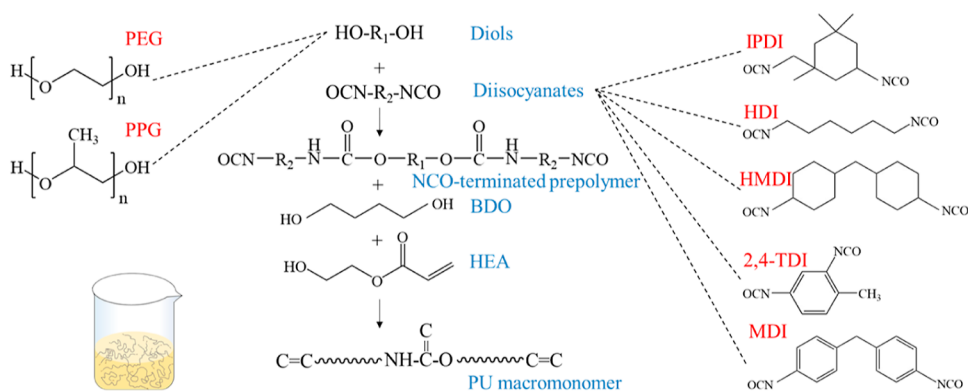


Figure 10. Synthesis of PU macromonomers.

However, shear strength of P_{IPDI} is larger than that of P_{MDI} , the molecular chains are generally longer in adhesives, and the asymmetry of the structure increased the entanglement density of the molecular chains more than that of the benzene ring. Therefore, modified acrylic adhesives containing asymmetric isocyanates have a higher shear strength.

CONCLUSIONS

In this paper, PU macromonomers with different molecular weights and structures were synthesized by using different diols and diisocyanates as raw materials and used to modify acrylic adhesives. The influences of the molecular weight and structure on the thermal and adhesion properties of acrylic adhesives were studied. As the molecular weight of diols in PU macromonomers increases, the glass transition temperature gradually decreases; thermal stability, loop tack, and peel strength all show a trend of first increasing and then decreasing; and surface roughness and shear strength increase continuously with the increase of molecular weight. Taking all performances into account, when the molecular weight of diols is 600, the PU macromonomer prepared has the best modification effect on the acrylic adhesive. The influence of the type of diols on the modified acrylic adhesives is mainly reflected in that the peel strength, shear strength, and storage modulus of PU macromonomer-modified acrylic adhesives prepared by PPG are higher than that of those prepared by PEG.

The structure of diisocyanate also has a significant effect on acrylic adhesives modified by PU macromonomers. Compared to modified acrylic adhesives containing aliphatic diisocyanates, acrylic adhesives modified with PU macromonomers synthesized from aromatic diisocyanates (MDI and TDI) have lower viscosity and surface roughness and better heat resistance and shear strength, suitable for adhesives that require higher temperatures, but the loop tack, peel strength, and glass transition temperature are relatively lower. Modified acrylic adhesives with asymmetrical structure diisocyanates have a higher peel strength and shear strength. On the contrary, their loop tacks are not good. Therefore, HDI can be used to enhance adhesion best, while TDI can be used to reduce adhesion.

EXPERIMENTAL SECTION

Materials. Several PU macromonomers have been synthesized using diisocyanates and diols of different molar weights and structures. Soft segments were composed of poly(propylene glycol) (PPG) or poly(ethylene glycol) (PEG)

with different molecular weights, all supplied by Shanghai Titan Scientific Co. Ltd. (Shanghai, China). Hard segments consisted of five different diisocyanates: IPDI, HDI, dicyclohexylmethane diisocyanate (HMDI), TDI, and MDI, purchased from Wan Hua Group Co., Ltd. (Shandong, China), and the chain extender 1,4-butanediol (BDO), purchased from Shanghai Titan Scientific Co. Ltd. (Shanghai, China). All other reagents, dibutyltin dilaurate (DBTDL), HEA, 2-ethylhexyl acrylate (2-EHA), AA, 2-butanone, EAC, and 2,2'-azobis(2-methylpropionitrile) (AIBN), were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2-Butanone is distilled by CaH_2 before use, and diols were dried under vacuum at 120 °C for 2 h. All other chemicals were kept in dry boxes to avoid water absorption.

Synthesis of PU Macromonomers. Synthesis of PU macromonomers consisted of two steps. First, solvent, diisocyanate, and diol were added at a molar ratio $\text{NCO}/\text{OH} = 2$ into a four-necked flask containing a thermometer and a condenser tube under a nitrogen environment. Reacted at 75 °C for 1 h, catalyst DBTDL was added, generating NCO-terminated PU prepolymers. When the NCO level reached a theoretical value, chain extender BDO was added to extend the chain. Afterward, HEA was added to attach carbon-carbon double bonds to the PU macromonomers. Samples were evaporated for 1 h at 40 °C, and PU macromonomers were obtained after all solvents were removed. The PU macromonomers synthesized from IPDI and PEG of different molecular weights (average molecular weights: 200, 400, 600, 800, and 1000) were named as $\text{PU}_{\text{PEG-200}}$, $\text{PU}_{\text{PEG-400}}$, $\text{PU}_{\text{PEG-600}}$, $\text{PU}_{\text{PEG-800}}$, and $\text{PU}_{\text{PEG-1000}}$, respectively. The preparation process of PU macromonomers is shown in Figure 10.

The PU macromonomers, synthesized by PPG (average molecular: 600) and different structure diisocyanates, were named as PU_X , where X is the diisocyanate employed (PU_{IPDI} , PU_{HDI} , PU_{HMDI} , PU_{TDI} , and PU_{MDI}).

Synthesis of Modified Acrylic Adhesives. 2-EHA as a soft monomer, AA as a hard monomer, PU macromonomers as modifiers, AIBN as an initiator, and EAC as a solvent are used in adhesive preparations. The molar ratio of 2-EHA/AA/PU/AIBN was 90:10:0.5:0.004, and the total solid content was designed as 33%. The solvent and initiator were added into a three-necked flask equipped with a stirrer and a condenser tube and heated to 85 °C. After 15 min, monomers, macromonomers, and initiators were added dropwise using a peristaltic pump. After dripping and maintaining the temperature for 3 h, the modified acrylic adhesives were prepared.

The adhesive without PU macromonomer modification was marked as P_{NULL} . The adhesives modified by PU macromonomers were named P_Y , where Y is consistent with the corresponding PU macromonomer index X.

The synthesized adhesives were uniformly coated on release paper using a coating machine. The samples were heated in a 130 °C oven for 5 min to remove solvents; thus, a dry adhesive film was made and then calendered with the PET film. The adhesive films were cut into standard sample strips (2.5 × 15 cm) for further tests.

Characterization. FTIR spectra were obtained using a Magna-IR 550 infrared spectrometer (Thermo Nicolet Corporation, USA) to characterize the chemical structure of the PU prepolymer, PU macromonomers, and PSAs. Samples were diluted with acetone and then dropped onto KBr flakes. The wavenumber range was set from 400 to 4000 cm^{-1} .

The molecular weight of PU macromonomers and PSAs was measured by a Waters e2695 Gel chromatograph (Waters Technology Co., Ltd., USA). The samples were dissolved in tetrahydrofuran and diluted to 1.5 mg/mL.

RV of PSAs is measured using an FKV1000 Ubbelohde viscometer (Shanghai Qigao Instrument CO., LTD, China). The samples were diluted with EAC to a 0.04% concentration. Pure EAC was used as the control sample. Each sample was tested three times, and the average value was taken as the final result.

DMA of the dried samples was performed with a HAAKE MARs 40 rheometer (Thermo Fisher Scientific, USA). The samples were tested at a constant strain force and heated from -50 to 120 °C at a heating rate of 6 °C/min.

TGA was performed using a TA Instrument TG209F3 (NETZSCH Scientific Instruments Trading, Ltd., Germany) at a heating rate of 10 °C/min within a temperature range from 50 to 800 °C under an air atmosphere. The quantity of each tested sample was approximately 5–10 mg.

Water CA of the PSA films was measured three times by a JC2000D2 CA measuring instrument (JEOL Japan Electronics Co., Ltd., Japan) with the amount of liquid set as 2 μL .

Peel strength was tested under 23 ± 2 °C by using a KJ-1065A testing machine (Guangdong Kejian Instrument Co., Ltd., China) with a speed of 300 mm/min according to ASTM D903. Standard size strips were adhered to the steel plates and pressed five times with a 2 kg roller; tests were conducted after 20 min and 24 h, respectively. Each sample was measured three times; results were averaged.

A KJ-6031 annular tack test machine (Guangdong Kejian Instrument Co., Ltd.) was used to test the loop tack of the adhesives. The instrument rose at a speed of 300 mm/min according to ASTM D6195-03. The average value was calculated after three tests.

Shear strength of the samples was measured by a KJ-6013 SAFT adhesive testing machine (Guangdong Kejian Instrument Co., Ltd., China). Standard size strips were adhered to the steel plates according to ASTM D3645/D3645 M. Each sample measurement was repeated three times; the calculated average value was used as the shear strength.

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Notes

The authors declare no competing financial interest.

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