

# Preparation and Properties of Waterborne Polyurethane Adhesives Modified by Polystyrene

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**ABSTRACT:** Waterborne polyurethane (WPU) adhesives modified by polystyrene (PS) were prepared through a prepolymer mixing process from diisocyanates, an anionic polyester, internal emulsifiers, a neutralizer, a chain extender, and PS dispersions. The latter was performed via the *in situ* polymerization of styrene in poly(1,4-butanediol adipate) diol. Transmission electron microscopy, Fourier transform infrared spectroscopy, and <sup>1</sup>H-NMR techniques were used to characterize the PS dispersions and polyur-

ethane (PU)–PS prepolymer. Experimental results with respect to the performance of the PU–PS adhesives indicate that suitable PS/polyester diol weight ratios improved the mechanical properties, thermal stability, water resistance, and initial adhesive strength of the pristine WPU adhesives. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3156–3161, 2008

**Key words:** adhesion; adhesives; polystyrene; polyurethanes; strength

## INTRODUCTION

Concerns for low production costs and environmental protection have strongly stimulated the fast development of waterborne polyurethane (WPU) dispersions. Currently, these dispersions are widely used as adhesives and coatings for a great variety of substrates. However, the materials are usually inferior to their solvent-borne counterparts in water resistance, mechanical properties, adhesive strength, and heat stability mainly because of the presence of the ionic groups in polyurethane (PU) chains. The ionic groups damage the integrality of the PU chain and beget a dramatic degradation of these properties.<sup>1–4</sup>

Many attempts have been made to resolve these problems. The utilization of different starting materials with special chemical structures proved to be an effective method. For instance, Murata et al.,<sup>5</sup> Furu-kawa et al.,<sup>6</sup> and Kim and Kim<sup>7</sup> reported that polyester polyols with two ethyl side chain groups were useful for improving the hydrolytic stability and adhesive strength of WPU dispersions. Yoon and Kim<sup>8</sup> indicated that WPU adhesives derived from polyols modified with hydroxyl-terminated polybutadiene

and hydroxyl-terminated acrylonitrile–butadiene copolymer possessed higher tensile strength, modulus, and adhesive strength values. Recently, the hybridization techniques of PU–vinyl polymers have enjoyed great attention. One applied example of these methods is PU–polystyrene (PS) hybrid dispersions because PS has excellent mechanical properties and water-resistant abilities (nonpolar nature of PS). Generally, a one-pot miniemulsion polymerization<sup>9,10</sup> and a two-step emulsion polymerization<sup>11</sup> are feasible approaches for the synthesis of PU–PS hybrid dispersions. In addition to aforementioned routes, the PU–PS hybrid dispersions can also be prepared via other procedures.

It is well known that the stable dispersions of particulate material in a high-molecular-weight polyol are referred to as *graft polymer polyols*.<sup>12</sup> The latter can be produced by the *in situ* polymerization of a vinyl monomer in a base polyol. Actually, the product is a mixture, where the vinyl monomer homopolymer is dispersed in pristine polyol and stabilized by the macromonomer.

In this study, dispersions of PS in poly(1,4-butanediol adipate) diol (PBA) were first prepared. The synthesis of WPU–PS adhesives with these dispersions with various PS contents (different PS/PBA ratios) as one of the polyol components was then conducted through a prepolymer mixing process. The influences of the PS/PBA weight ratio on the chemical and physical properties of the adhesives were studied.

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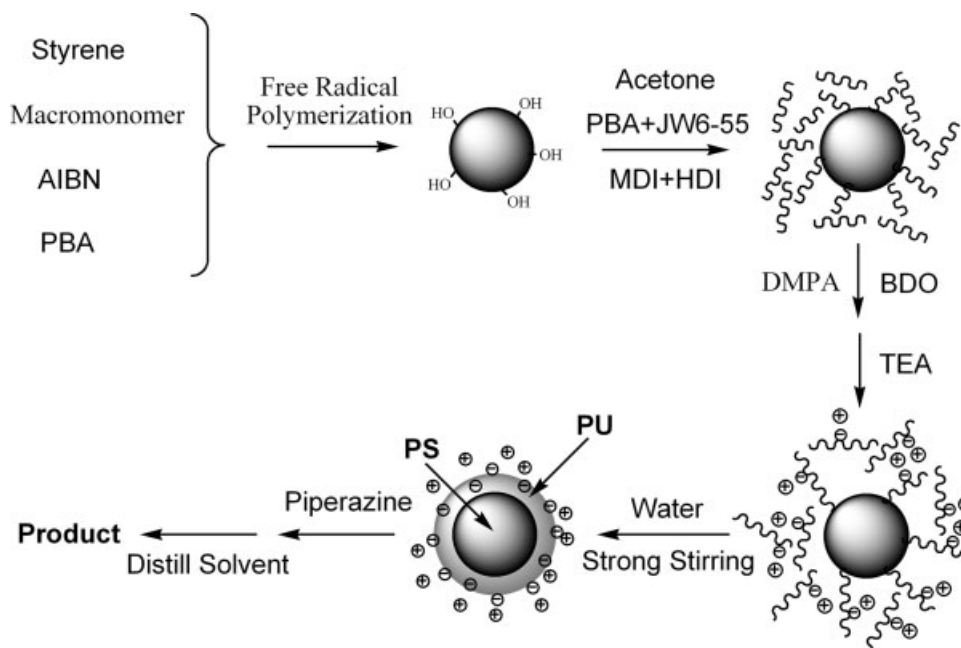


Figure 1 Synthesis scheme of the WPU-PS adhesives.

## EXPERIMENTAL

### Materials

Diphenylmethane-4,4-diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HDI) were supplied by Bayer Co. (Germany). PBA (number-average molecular weight = 2000) and anionic polyester diol (JW6-55, number-average molecular weight = 1970) were commercially available from Shanfeng Polyurethane Co. (Shanxi, China). 1,4-butanediol (BDO), dimethylol propionic acid (DMPA), piperazine, triethylamine (TEA), acetone, styrene (St), and 2,2'-azobisisobutyronitrile (AIBN) were chemically pure and were purchased from Shanghai Chemicals Co. (China). The macromonomer, made in our laboratory, was used as a stabilizer for the PS dispersion in PBA.

### Synthesis of stable dispersions of St polymers in PBA

The experiment was conducted in a 500-mL, four-necked, round-bottom flask with a mechanical stirrer, a thermometer, a condenser, and a N<sub>2</sub> inlet. Under vigorous stirring, the macromonomer, St, PBA, and AIBN with appropriate proportions were introduced and mixed to form a homogeneous mixture. The *in situ* polymerization of St in the PBA medium was carried out for 5 h at 130°C. After the completion of the reaction, the unreacted St monomer was distilled out at reduced pressure.

### Synthesis of the WPU-PS adhesives

Waterborne adhesives based on PU-PS hybrid dispersions were prepared in a 500-mL, round-bottom,

three-necked flask with a mechanical stirrer, a thermometer, and a condenser. The grafted PBA made previously and JW6-55 were first dehydrated in the vessel. When the mixture was cooled to room temperature, MDI and HDI dissolved in acetone were then added and reacted for 1 h under the refluxing temperature. After this, DMPA and BDO in suitable amounts were introduced, and the reaction was kept for 3 h to obtain the NCO-terminated prepolymer. When the desired NCO value was achieved, the neutralization of carboxylic acids with TEA was carried out at room temperature. The previous solution was then dispersed into water in virtue of vigorous stirring and extended by piperazine. At the end of the reaction, the solvent acetone was removed, and aqueous PU-PS adhesives were finally made. In this study, the adhesives prepared were coded as PP0, PP1, PP2, PP3, PP4, and PP5, which represented their PS/PBA weight ratios of 0, 1 : 20, 2 : 20, 3 : 20, 4 : 20, and 5 : 20, respectively. The reaction scheme of the aqueous adhesives is illustrated in Figure 1.

The PU-PS dispersions were molded at room temperature and dried under an IR lamp for 4 days. The resulting films were subjected to further annealing at 60°C for 12 h. In this way, films applicable for property measurement were finally obtained.

### Characterization and measurement

Transmission electron microscopy (TEM, Hitachi, Japan) images were taken with a Hitachi H-600 transmission electron microscope. The PS dispersions in PBA were pretreated by ultrasound in acetone and

were deposited on 200-mesh copper nets for TEM observation.  $^1\text{H-NMR}$  spectra of PBA and PS dispersions in PBA were recorded on a Bruker (Switzerland) DRX-300 spectrometer in  $\text{CDCl}_3$ . Fourier transform infrared (FTIR) spectra were collected on a Nicolet (Thermo Electron Co., USA) 380 spectrometer. The KBr pellet technique was applied to determine the IR spectra of the samples.

Tensile strength, elongation at break, and tear strength measurements were conducted at ambient temperature on an Instron 4201 (Jiangdu Jingyi Test Machinery Company, China) instrument. Hardness (Shore A) measurement was carried out on a sclerometer model J LX-A (Jiangdu Jingyi Test Machinery Company, China). Viscosity measurement was performed on a NDJ-1 (Shanghai Precision & Scientific Instrument Co., China) rotational viscometer at  $25^\circ\text{C}$ .

Thermogravimetric analysis experiments were carried out on a Shimadzu (Japan) TGA-60 instrument. Each sample (4–6 mg) was placed in an aluminum pan and heated from 30 to  $600^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere (50 mL/min).

Differential scanning calorimetry (DSC) measurements were performed in a Shimadzu DSC-60 instrument. The experiments were carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere in the temperature range  $95\text{--}200^\circ\text{C}$ .

The viscosities of the WPU-PS dispersions were measured with a NDJ-1 rotational Brookfield viscometer at  $25^\circ\text{C}$ .

To investigate the water resistance, WPU-PS films ( $20 \times 20 \text{ mm}^2$ ) were immersed in water for 24 h at room temperature. The swelling ratio was calculated as follows:

$$\text{Swelling ratio (\%)} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

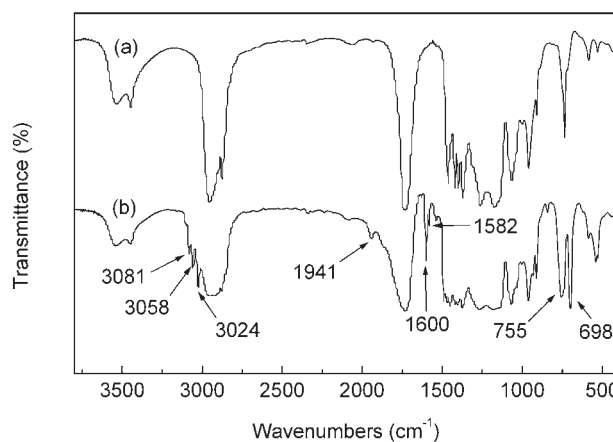
where  $W_0$  and  $W_1$  represent the weights of the dried and swollen films, respectively.

The initial adhesive strengths of the aqueous PU-PS adhesives were measured with an Instron 4201 instrument. The adhesives were applied to each poly(vinyl chloride) (PVC) strip treated with acetone. The two PVC strips were maintained for 10 min at 60, 70, 80, or  $90^\circ\text{C}$ . After heat activation, the strips were fixed in contact and immediately placed on the strips for 20 s at 0.5 MPa. Then, the Instron 4201 instrument was used to obtain the adhesion strength value at a peel rate of 250 mm/min.

## RESULTS AND DISCUSSION

### Characterization of the PS dispersions in the polyester polyol (PBA)

The composition and morphology of the PS dispersions in PBA were characterized by the means of FTIR



**Figure 2** FTIR spectra of (a) PBA and (b) the PS dispersion in PBA.

spectroscopy,  $^1\text{H-NMR}$  spectroscopy, and TEM techniques, and the results are depicted in Figures 2–4.

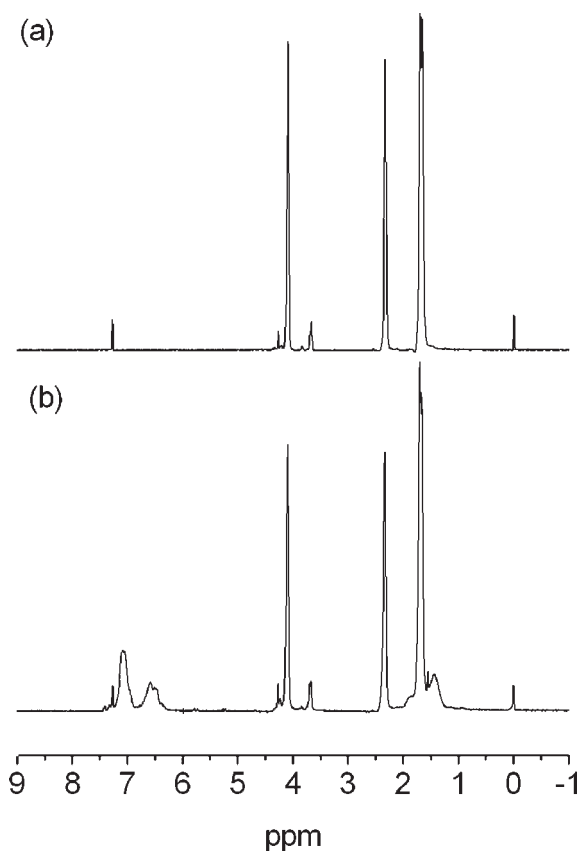
Figure 2(a) shows representative FTIR spectra of PBA. In contrast to these, Figure 2(b) features the emergence of new bands apart from those peaks originated from the base PBA. For example, the characteristic  $\text{C}=\text{C}$  stretching bands of the phenyl at  $1600\text{--}1582 \text{ cm}^{-1}$  were registered. Moreover, IR absorption bands at  $3010\text{--}3100 \text{ cm}^{-1}$  belonging to the  $\text{C-H}$  stretching band of the phenyl and bands at  $755\text{--}698 \text{ cm}^{-1}$  attributed to the  $\text{C-H}$  out-of-plane bending vibrations in phenyl were also observed in Figure 2(b). These revealed that the dispersions of the PS particles in PBA were realized after the *in situ* polymerization of St in PBA.<sup>13</sup>

Figure 3(a) shows the  $^1\text{H-NMR}$  spectra of pure PBA. The peaks displayed at 1.56–1.80, 2.22–2.42, and 4.03–4.15 ppm were related to the protons of the PBA molecule. These were consistent with the results reported in the literature. All of the proton peaks mentioned previously also existed in the spectra shown in Figure 3(b). In addition, two distinct characteristic peaks assigned to the phenyl protons located between 6.30 and 7.50 ppm existed in the spectra shown in Figure 3(b). These results provide additional evidence of the presence of the PS polymer in the base PBA.<sup>14–16</sup>

Figure 4 shows the TEM images of the as-prepared PS dispersions. The PS particles were almost spherical and homogeneously dispersed in the PBA medium. The average dimension of the PS particles was estimated to be about 800 nm. It appeared that the macromonomer used in this study stabilized the PS particles and prevented them from further aggregation.

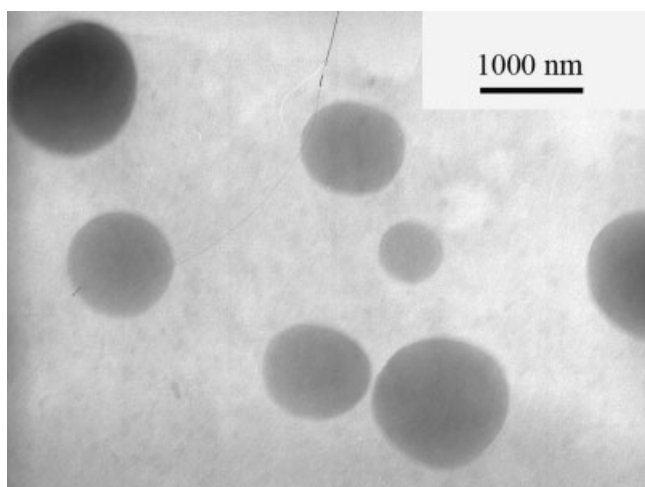
### Characterization of the synthesis process of the WPU-PU prepolymer

Figure 5 shows the IR absorbance bands of the reaction mixtures during the prepolymer synthesis. After

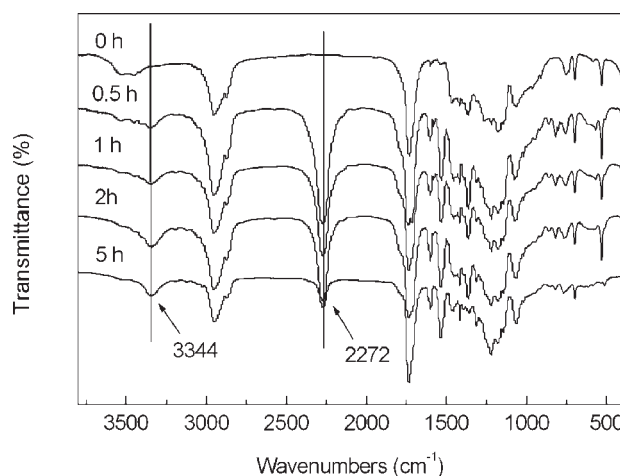


**Figure 3**  $^1\text{H-NMR}$  spectra of (a) pure PBA and (b) the PS dispersion in PBA.

the addition of diisocyanates, characteristic peaks of aromatic urethane links appeared. Isocyanate, phenyl, and urethane group signals, such as  $\text{N}=\text{C}=\text{O}$  ( $2272\text{ cm}^{-1}$ ),  $\text{C}=\text{C}$  bond ( $1599\text{ cm}^{-1}$ ), and  $\text{N-H}$  bond ( $3344$  and  $1530\text{ cm}^{-1}$ ), were observed. With further reaction, the peaks due to the  $\text{N}=\text{C}=\text{O}$  and  $\text{O-H}$  groups ( $3400\text{--}3550\text{ cm}^{-1}$ ) were attenuated gradually to a different extent. At the same time, the



**Figure 4** TEM micrographs of the PS particles in PBA.



**Figure 5** FTIR spectra of the WPU-PU prepolymer synthesis.

characteristic peaks of the urethane groups were enhanced. After 5 h, all of the  $\text{O-H}$  groups were fully consumed by the diisocyanates. This proved that the  $\text{NCO}$ -terminated prepolymers were obtained.

#### Characterization of the WPU-PS adhesives

In this study, WPU-PS dispersions were used as adhesives, and their mechanical properties are listed in Table I. The incorporation of PS into the PU matrix brought about an alternation of the properties. For example, with an increase in the PS/PBA ratio, the surface hardness of the PU-PS films was higher than that of the pure PU film because of the existence of the plastic phase (PS) in the PU-PS films. This meant that the PS particles played an important role in the structural integrity. The percentage elongation at break, tensile strength, and tearing strength were found to first increase and then decrease with increasing PS/PBA weight ratio. Exorbitant PS contents increased the frequency of localized clusters or aggregations, which decreased the elongation, tensile strength, and tearing strength.<sup>17,18</sup> It appeared that PS/PBA weight ratios ranging from 2 : 20 to 3 : 20 were appropriate for the production of WPU-PS adhesives with good mechanical properties.

Figure 6 shows the thermogravimetric analysis data of the different WPU-PS adhesives. With increasing PS/PBA weight ratio, the thermal stability was improved slightly. Generally, the thermal degradation of segmented PUs is a two-step process. The first step is ascribed to the thermal degradation of the hard segment, whereas the second step corresponds to the thermal degradation of the soft segment.<sup>19</sup> In this study, the soft segment of the pure PU substrate was modified by PS particles. The rigid phenyl groups in the soft segments originated from



**TABLE I**  
**Mechanical Properties of the WPU–PS Adhesives**

Sample	Hardness (Shore A)	Elongation at break (%)	Tensile strength (MPa)	Tearing strength (kN/m)
PP0	79	416	9.78	74.33
PP1	94	564.33	10.54	80.35
PP2	94	589.33	11.42	81.97
PP3	94	565.33	12.23	83.50
PP4	95	528	9.93	75.85
PP5	96	480	9.71	73.68

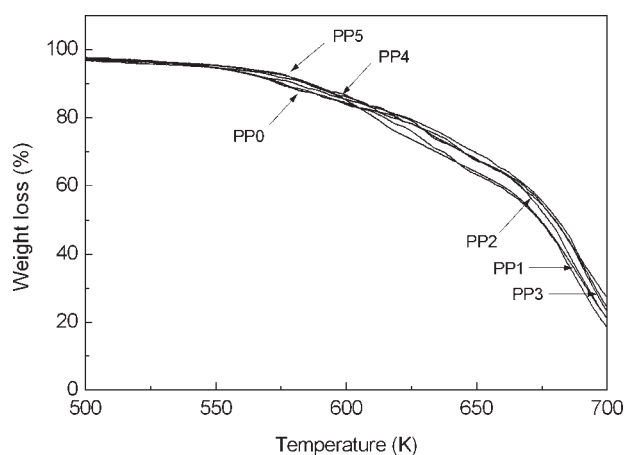
the PS addition improved the thermal stability of the products.<sup>17</sup>

The DSC curves of the WPS–PS adhesives are shown in Figure 7. All of the films showed an obvious melting peak (enthalpy) around 314 K corresponding to the crystalline melting temperature of soft segments. Figure 7 also indicated that the values of enthalpy and crystalline melting temperature of the soft segment of the PP0 film were higher than those of WPU films modified by PS. The reason for this was probably that the increase in the PS/PBA weight ratio induced a decrease in the crystallinity of the soft segments (as determined by soft-segment content). A higher PS/PBA weight ratio increased the crosslinking of PU chains and decreased the soft-segment content.

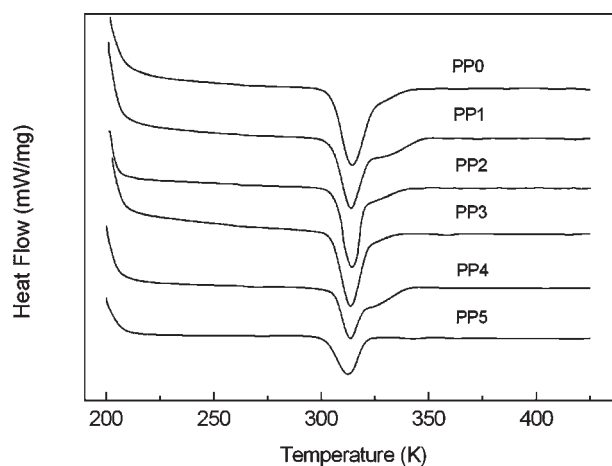
Figure 8 presents the water resistance of the WPU–PS films. As the PS/PBA weight ratio increased, the swelling ratio of the films decreased markedly. The WPU–PS films exhibited much smaller swelling ratios (8.10–11.03%) than the pure WPU film (11.54%). In other words, the water resistance of the pure WPU adhesive was inferior to that of the WPU adhesives modified by PS. These results substantiate the fact that the incorporation of hydrophobic PS blocks decreased the hydrophilicity of the WPU film and ameliorated its water resistance.<sup>11</sup>

The effects of the PS/PBA weight ratio on the viscosity of the WPU–PS dispersions are presented in Figure 9. A core–shell (PS–PU) structure was formed during the synthesis of the dispersions because of the hydrophobicity of PS. The addition of the hydrophobic PS particles made hydrophilic segments transfer to the surface layer of the PU particles, which increased the ionic group density in the surface layer. The higher ionic density in the surface layer enhanced interactions of the particles and, therefore, increased the viscosity of the WPU–PU dispersions. However, overfull hydrophobic PS particles reduced the proportion of ionic groups in the dispersions at a constant solid content, which thus decreased viscosity.

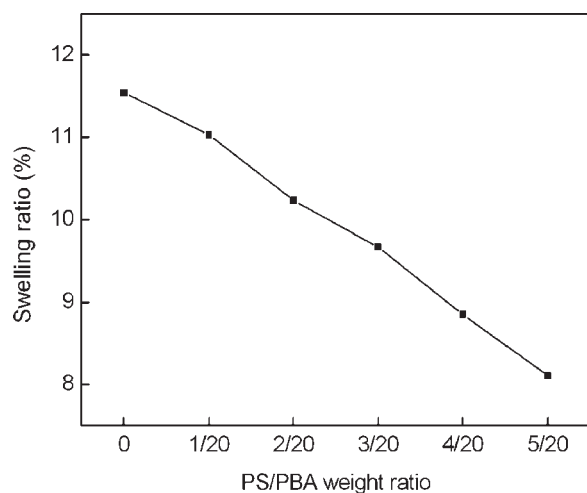
Figure 10 shows initial adhesive strengths of PVC/WPU–PS adhesives/PVC joints, which depended on the activation temperature and the PS/PBA weight ratio. As shown in Figure 10, the initial adhesive strength increased as the activation temperature was increased from 333.15 to 363.15 K. A higher activation temperature should have increase the wettability of the adhesives to the PVC joints and accelerated the evaporation of water in the adhesives. The varieties could be linked to the change in the surface and bulk properties of the adhesives. Also, the initial adhesive strengths



**Figure 6** TG curves of PS–PU films with different PS/PBA weight ratios.



**Figure 7** DSC curves of WPS–PU adhesives with different PS/PBA weight ratios.

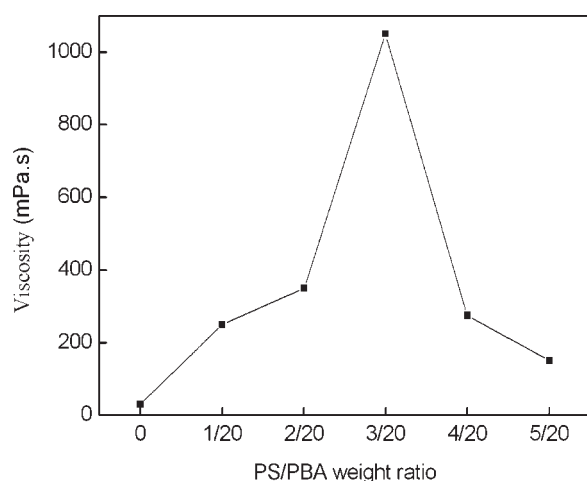


**Figure 8** Swelling ratios of WPU-PS films with different PS/PBA weight ratios.

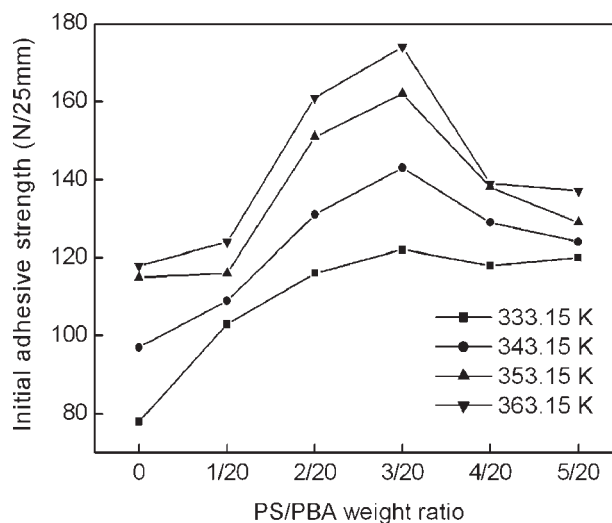
increased first and then decreased with increasing PS/PBA weight ratio. The maximum initial adhesive strength was observed for the WPU-PS adhesive with a PS/PBA weight ratio of 3 : 20. The reason was probably that the incorporation of hydrophobic PS particles sped up the drying process of the adhesive and altered its bulk properties. However, too high a weight ratio of PS/PBA weakened the polarity of the adhesive and decreased the wettability to PVC and the interfacial interaction between PVC and the adhesive.<sup>8</sup>

## CONCLUSIONS

A novel synthetic route to WPU-PS adhesives was presented in this article. The hybridization technique of the PU-vinyl polymer was based on a combination of the preformation of PS in the base PBA and the prepolymer method, which is commonly adopted for



**Figure 9** Effect of the PS/PBA weight ratio on the viscosity of the WPU dispersions.



**Figure 10** Initial adhesive strengths of the WPU-PU adhesives.

WPU preparation. The experimental results indicate that the mechanical properties, water resistance, and initial adhesive strength of the products were strongly influenced by the PS/PBA weight ratio and that a suitable ratio effectively improved the performances. This technique provided a feasible way for synthesizing WPU-PS adhesives with good performance.

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