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Synthesis and Characterization of a New UV Cross-linkable Waterborne Siloxane-polyurethane Dispersion

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A new cross-linkable waterborne siloxane-polyurethane dispersion (PEDA-SiPU) was synthesized by incorporating the acrylate groups into the side chain of the polyurethane using the pentaerythritol diacrylate (PEDA) and introducing polysiloxane groups into the soft segment of the polyurethane using dihydroxybutyl-terminated polydimethylsiloxane (PDMS). They can form the cross-linking structure by UV radiation in the presence of a photo-initiator. Fourier transform infrared spectroscopy (FTIR) was used to identify the chain structure of PEDA-SiPU. The effect of the PDMS content and the PEDA content on the C=C conversion behaviors under UV irradiation was investigated. Water resistance and the mechanical properties of the UV cured films were also studied. Through the controlling of suitable content of PDMS and PEDA introduced in the chain, the obtained PEDA-SiPU films were proved to possess both good water resistance and mechanical properties.

Keywords: UV cross-linkable; siloxane-polyurethane; waterborne

1 Introduction

Waterborne polyurethane has been found a variety of applications in recent years for their excellent properties and prominent environmental friendly usefulness (1–6). In order to improve the water resistance and surface hydrophobicity of the films for waterborne polyurethane, the polyurethane was often modified by the polysiloxane. But the incorporation of polysiloxane often had a negative effect on the physical-mechanical properties of the polyurethane. It is known that polysiloxanes demonstrate superior flexibility, resistance to humidity but poor physical-mechanical properties, and on the other hand, the waterborne polyurethanes are more hydrophilic, but have excellent physical-mechanical characteristics. In order to combine the valuable properties of the two types of polymers, the siloxane-polyurethane systems were often designed to form the cross-linking structure. However the cross-linked siloxane-polyurethane systems reported until now were prepared by the cross-linking of Si-O-Si through the hydrolysis condensation process (7, 8) or by the polymerization of multifunctional oligosiloxane polyols with the polymethane polyphenyl polyisocyanate,

respectively (9), or by the incorporation of polyhydric alcohols into the polyurethanes (10). The above mentioned systems formed the cross-linking structure in the process of synthesizing. Therefore, they cannot design a high cross-linking structure, since the viscosity of the system was too high to flow, and the high cross-linking structure would limit the chain movement of the siloxane in the subsequent film forming and curing process.

In this paper, we introduce a new UV cross-linking method for the siloxane-polyurethane system. We introduce the acrylate groups into the side chain of the polyurethane using the pentaerythritol diacrylate (PEDA) and they form the cross-linking structure by UV radiation. Using this method, the siloxane molecules can migrate into the surface without any restraint and be fixed by the cross-linking structure in the subsequent curing process. Moreover, this UV cross-linking method has the advantages of efficient, energy-saving and environmental-friendliness, it can form the cross-linking structure rapidly within one minute or even a shorter time under the UV radiation (11, 12). The effect of the PDMS content and the PEDA content on the properties of PEDA-SiPU films had been investigated in this paper. Through the controlling of a suitable content of PDMS and PEDA introduced in the chain, the obtained PEDA-SiPU films proved to possess both good water resistance and mechanical properties.

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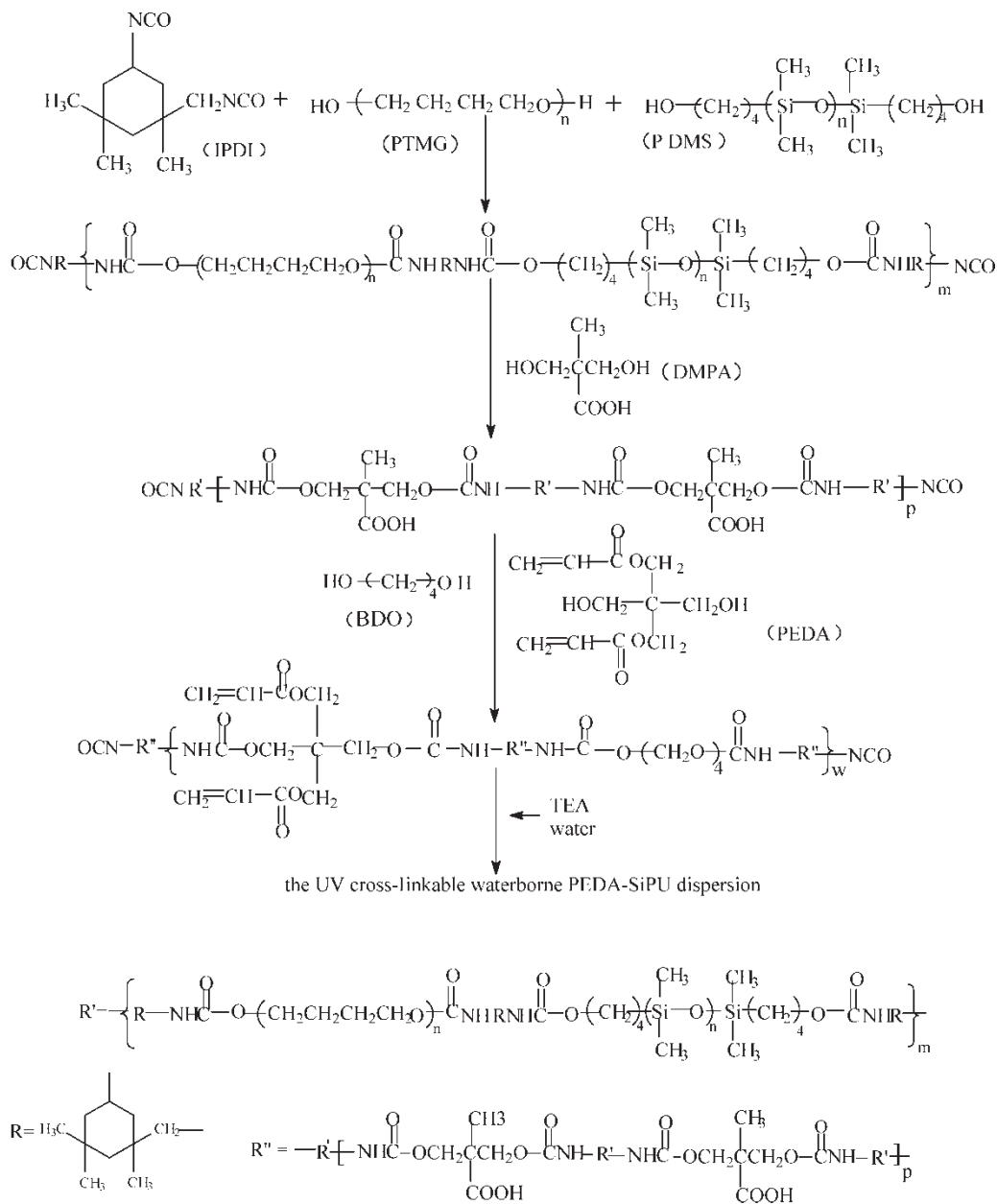


Fig. 1. The preparation process of UV cross-linkable PEDA-SiPU.

2 Experimental

2.1 Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co. Ltd.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_n = 2000$, Daicel Chemical Industries Ltd., Japan) and dihydroxybutyl-terminated polydimethylsiloxane (PDMS, $M_n = 2000$, self-made) were desiccated at 110°C before use. Pentaerythritol diacrylate (PEDA, self-made, the acid value is 1.3 mgKOH/g), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacur2959 from Ciba Specialty Chemicals Inc., used as photo-initiator), butanediol (BDO, Aldrich Chemical Co.), α,α -dimethylol propionic acid

(DMPA, Aldrich Chemical Co.) and triethyl amine (TEA, Shanghai Chemical Reagent Co., Ltd.) were used as received. Di-n-butyltin dilaurate (DBT, Shanghai Chemical Reagent Co., Ltd.) was used as catalyst. Hydroquinone (Luoyang Reagent Co., China) was used as inhibitor.

2.2 Synthesis of the UV Cross-Linkable Waterborne PEDA-SiPU

The synthesis process of the UV cross-linkable waterborne PEDA-SiPU was shown in Figure 1. IPDI, PTMG and PDMS were first added into the reactor according to a suitable mole ratio. The prepolymerization of polyurethane

was carried out at 80°C under N₂ atmosphere until the content of NCO reached the theoretical value. Acetone was added to reduce the viscosity. Then DMPA was added into the system and reacted at 70°C until the NCO reached the theoretical value. Subsequently, PEDA and BDO were added into the system and reacted at 60°C, the inhibitor hydroquinone and the catalyst DBT were needed during the process. As a neutralization agent, TEA was added to react with the carboxylic group in the side chain of the polymer, and the mole ratio of TEA to DMPA was fixed at 1.2:1 to secure the 100% neutralization degree. Finally, a high speed shearing rate (1200 r/min) was used to emulsify the solution for 5 min after suitable deionized water was added into the reaction system. The UV cross-linkable waterborne PEDA-SiPU dispersion was obtained after removal of the acetone from the emulsion by rotary vacuum evaporation. The solid content and pH value of the emulsions were 35% and 7.8–8.2, respectively.

Two series of PEDA-SiPU samples were synthesized. A-series samples were the weight content of PDMS varying from 0% to 16.5% based on the polymer with the PEDA content fixed at 15.2%; B-series samples were the weight content of PEDA varying from 8% to 17.6% based on the polymer with the PDMS content fixed at 7.9%, and their compositions were shown in Table 1.

2.3 UV Cross-linking Process

The UV cross-linking reaction was the polymerization of acrylate double bond under the UV radiation in the presence of photo-initiators. The UV cross-linked siloxane-polyurethane films were formed by casting the dispersions adding 3% photo-initiator Irgacur 2959 based on the solid content onto a glass plate at room temperature, and drying the sample at 60°C to reach a constant weight then irradiating under medium pressure mercury lamp (125 mw/cm²). The obtained film thickness was 60 μm.

Table 1. Compositions of the PEDA-SiPU

Samples	PDMS (wt%)	PEDA (wt%)	First stage IPDI:PTMG:PDMS (mol: mol:mol)	Second stage DMPA (mol)	Third stage PEDA:BDO (mol:mol)
A0	0	15.2	1:0.17:0	0.207	0.451:0.104
A1	4.4	15.2	1:0.155:0.015	0.207	0.451:0.104
A2(B3)	7.9	15.2	1:0.141:0.03	0.207	0.451:0.104
A3	11.9	15.2	1:0.126:0.044	0.207	0.451:0.104
A4	16.5	15.2	1:0.111:0.059	0.207	0.451:0.104
B1	7.9	8	1:0.141:0.03	0.207	0.237:0.318
B2	7.9	12.3	1:0.141:0.03	0.207	0.363:0.192
B3(A2)	7.9	15.2	1:0.141:0.03	0.207	0.451:0.104
B4	7.9	17.6	1:0.141:0.03	0.207	0.533:0.022

Note: The mole ratio of TEA to DMPA was fixed at 1.2:1 to secure the 100% neutralization degree.

2.4 Characterization

FTIR spectra were measured in the range from 4000 to 400 cm⁻¹ by a FTIR spectrometer (MAGNA-IR 750, Nicolet Instrument Co., U.S.A.).

The C=C conversion was measured by a modified CDR-1 DSC (made by Shanghai Balance Instrument Co.) under irradiation using a UV Spotcure System BHG-250 (Mejiro Precision Co., Japan). The digitized data, based on the traces on a strip chart recorder, were analyzed by the software Origin 6.1 on a personal computer.

Polymerization was carried out in an inert atmosphere. The C=C conversion (*P*) was calculated by the following formula: $P = H_t/H_\infty$, where *H_t* is the heat effect within *t* second, *H_∞* is the heat effect of 100% conversion of C=C.

Water resistance (13) was determined as follows: the cross-linked films were cut into 3 cm × 1 cm pieces and dried in a vacuum oven for 24 h to determine their dry weight (*W_d*). Then the film was immersed into distilled water for 72 h, followed by wiping off the surface water with a piece of filter paper to determine their weight (*W_t*). The absorbed water content was then calculated by the formula: $W(\%) = (W_t - W_d)/W_d \times 100\%$.

Tensile property was measured by Instron (Model No 4301) with a cross head speed of 20 mm·min⁻¹ at 25°C. All measurements had an average of 5 runs.

3 Results and Discussion

3.1 PEDA-SiPU Structure by FTIR

The chain structure of PEDA-SiPU was confirmed by FTIR analysis. As examples, the FTIR spectra of A0, A2(B3) and A2 after UV curing were shown in Figure 2. The typical absorption peaks of polyurethane at 3330 cm⁻¹ [ν (NH)], 2855–2955 cm⁻¹ [ν (CH₂) and ν (CH₃)], 1720–1780 cm⁻¹ [ν (C=O)], 1540 cm⁻¹ [δ (NH)] and 1110 cm⁻¹ [ν (C-O-C)] can be seen clearly in the spectra. Compared with the pure polyurethane sample A0 (PDMS% is zero and PEDA%

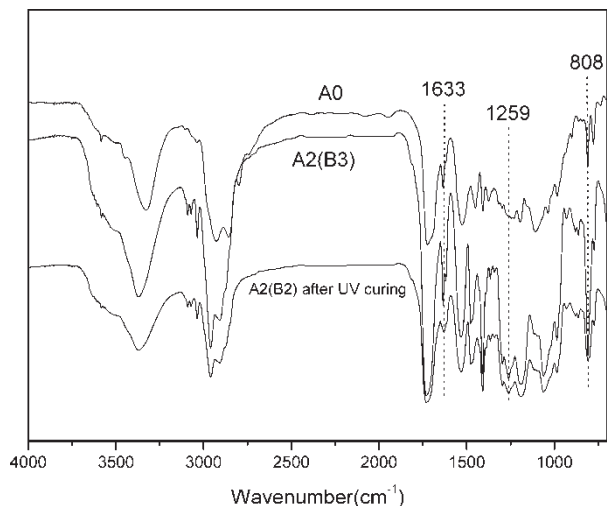


Fig. 2. The spectra of A0, A2(B3) and A2(B3) after UV curing.

is 15.2%), the peaks at 1259 cm^{-1} [$\nu(\text{CH}_3)$ in Si-CH_3] and 808 cm^{-1} ($\text{CH}_3\text{-Si}$ rocking) can be clearly detected in the spectra of A2(B3), indicating that siloxane groups had been successfully introduced into the polyurethane chain. At the same time, it can be seen the typical absorption peaks of $\text{C}=\text{C}$ bond in A0 and A2(B3) spectra at 1633 cm^{-1} ($\text{C}=\text{C}$), 1410 cm^{-1} ($=\text{CH}_2$) and 808 cm^{-1} ($=\text{CH}$), which illustrated that the acrylate $\text{C}=\text{C}$ bond had been incorporated in the polyurethane chains. In addition, it was found that the $\text{C}=\text{C}$ bond absorption peaks in A2(B3) after UV curing spectra decreased significantly after UV radiation.

3.2 The $\text{C}=\text{C}$ Conversion Behavior

The properties of UV cross-linked PEDA-SiPU films strongly depend on the final $\text{C}=\text{C}$ conversion achieved after UV radiation. The higher the $\text{C}=\text{C}$ conversion, the stronger the cross-linking structure. For instance, the mechanical

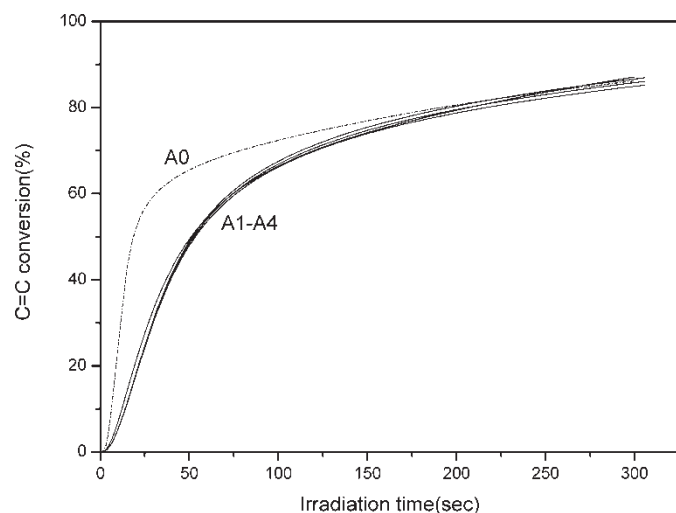


Fig. 3. $\text{C}=\text{C}$ conversion behavior for A-series PEDA-SiPUs.

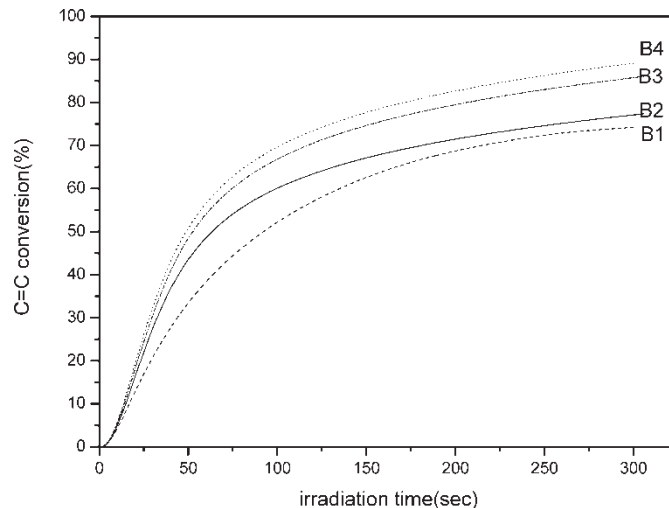


Fig. 4. $\text{C}=\text{C}$ conversion behavior for B-series PEDA-SiPUs.

property and solvent resistance depend on the cross-linking structure of the films which is directly related to the final $\text{C}=\text{C}$ conversion. Figure 3 (for A-series) and Figure 4 (for B-series) show the $\text{C}=\text{C}$ conversion behavior depending on the UV irradiation time. It can be clearly observed from Figure 3 that the final $\text{C}=\text{C}$ conversion of A-series samples was almost at the same value of 86%. But the slope of the curves, which represent the conversion rate of $\text{C}=\text{C}$ bond, had some difference between A0 and A1-A4 samples. The $\text{C}=\text{C}$ conversion rate of A0 sample was higher than that of A1-A4 samples, which was ascribed to the incorporation of PDMS in A1-A4 samples. Therefore, it can be said that the incorporation of PDMS decreased the $\text{C}=\text{C}$ conversion rate, but the PDMS content had no effect on conversion rate and the final conversion values.

It can be seen from the Figure 4 that the conversion behaviors of B-series samples were obviously different.

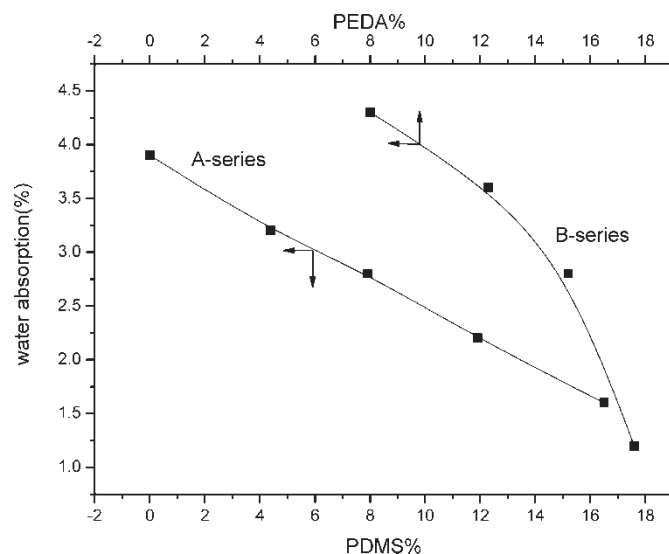


Fig. 5. Water absorption of PEDA-SiPUs.

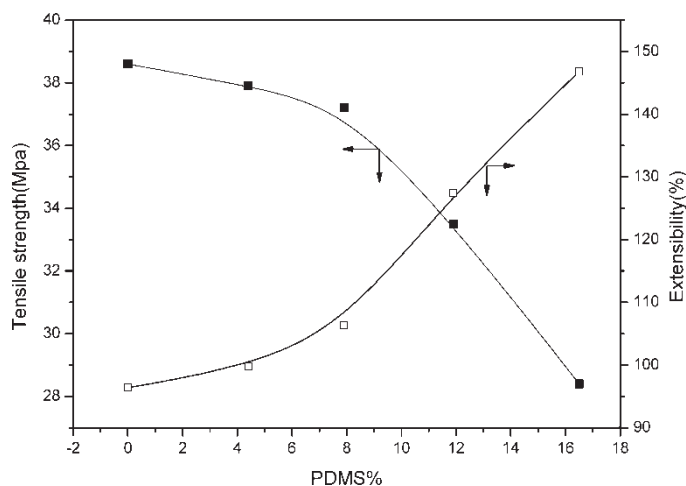


Fig. 6. Tensile properties of A-series samples.

When the PDMS content was constant, with the increasing of PEDA content, the final C=C conversion and the conversion rate increased accordingly, and in the order of B1 < B2 < B3 < B4. The final C=C conversion for B4 sample was 83.2%, while it was 73.9% for the B1 sample. In addition, it was found from both Figures 3 and 4 that the conversion rate (the slope of curves) decreased with the increasing of radiation time, which showed a restriction of molecular chain motion at high cross-linking structure. It is the restriction of chain movement that the conversion ratio can't reach 100%.

3.3 Water Resistance

Water resistance of UV cross-linked film for PEDA-SiPUs was investigated by the solvent absorption in water. As shown in Figure 5, the relationship curves between the content of PDMS and PEDA and water absorption exhibited some differences in a wide range. It could be seen that the water absorption both for A-series and B-series samples decreased with the

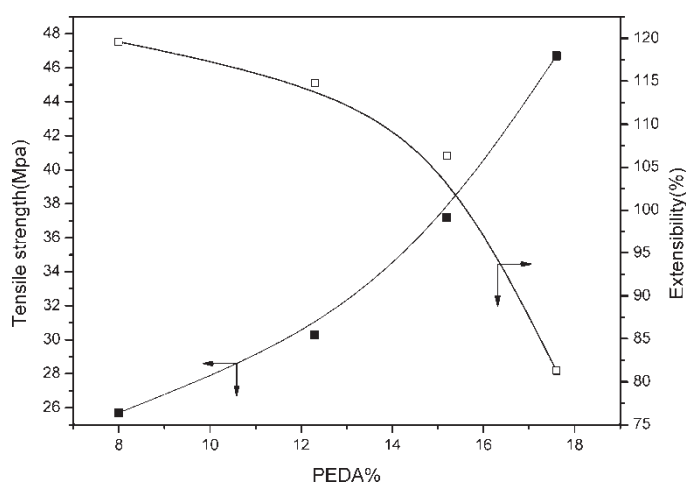


Fig. 7. Tensile properties of B-series.

increasing of PDMS content and PEDA content, and the increasing of PEDA content or PDMS content could both improve the water resistance of the films. Comparing with A-series, the water absorption of B-series samples had an obvious decrease with the increasing of PEDA content, which indicated that the increasing of PEDA content had a more effective effect on the improve of the water resistance than PDMS.

3.4 Mechanical Property

It is known that the polysiloxane is very flexible and has good low temperature properties, but poor physical-mechanism properties, and the formation of cross-linking structure is expected to intensify the physical-mechanism properties. Figure 6(A-series) and Figure 7(B-series) show the tensile property for PEDA-SiPUs. It could be seen from Figure 6 that the tensile strength decreased with the increasing of PEDA content but the extensibility had the reverse trend, and when the PDMS content was below 7.9%, the reduction degree of the tensile strength was lower than that of above 7.9%. In Figure 7, the tensile strength increased with the increasing of PEDA content, while the extensibility in the opposite trend. With the increasing of PEDA content, a stronger cross-linking structure was formed which led to the increase in tensile strength and the reduction in extensibility.

4 Conclusions

The UV cross-linkable waterborne PEDA-SiPUs have been synthesized by introducing the UV curable acrylate C=C bond into the side chain of polyurethane using PEDA, and incorporating polysiloxane into the soft segment of polyurethane using PDMS. The FTIR spectra had confirmed the chain structure. The investigation of the C=C conversion under UV irradiation indicated that the incorporation of PDMS and the PDMS content had no effect on the final C=C conversion, and with the increasing of PEDA content, the final conversion increased accordingly. By measuring the water resistance, it was found that the increasing of PEDA content or PDMS content could both improve the water resistance. The investigation of tensile property indicated that the increasing of PEDA content could improve the tensile strength while the increasing the PDMS content reduced the tensile strength. In addition, the films with 15.2% PEDA and 7.9% PDMS could exhibit both good mechanical property and water resistance.

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