Study on High-Solid Content Si/PU Polyurethane Dispersion with PES/PPG Composite Soft Segment

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ABSTRACT: A polyol consists of silicone chains and epoxy acrylate structures, referred to as silicon polyether (PES), was used to prepare crosslinked Si/PU dispersions. Both PES and propylene oxide glycol (PPG) were mixed as soft segments. The effects weight ratios of PES to PPG on properties of the resultant polyurethane dispersions were studied. Morphology and properties of the Si/PU dispersions were characterized by particle size, transmission electron microscopy (TEM), and viscometer. It is shown that the Si/PU dispersions possessed wider particle size distribution and higher average particles diameter because of the use of PES, which contains crosslinked silicone side chains. The Si/PU dispersions have higher solid content as compared to the conventional water-based polyurethane, because of the volume fraction ratio of bigger particle to small particle from the Si/PU dispersions. As increasing weight ratio of PES to PPG, the solid content of the Si/PU dispersions increased firstly, and then decreased. When the ratio ranges from 4 : 10 to 5 : 10, solid content of the Si/PU dispersions is up to 55%. It was also noticed that apparent viscosity of the Si/PU dispersions decreased with increasing PES to PPG ratio. In the Si/PU dispersions, solid content was increased and viscosity was decreased by the use of PES. Therefore, PES is a potential compound for the application of PU dispersions. In addition, stability of the crosslinked Si/PU dispersions decreases slightly at high- and low-temperature; however, which can meet the basical requirements. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polyurethane materials have been generally used in the automobile, paint, furniture, and textile industries, as well as in biomass foam incorporated with renewable raw materials.[1–4] Water-based polyurethanes (WPU), as nontoxic and nonflammable materials, have been abundantly used as environmental friendly coating and adhesives show an excellent range of properties.[5–10] In the past two decades, extensive investigations have been carried out, resulting in numerous articles, patents, and books on synthesis, manufacturing, characterization, and applications of polyurethanes. The wide application of polyurethanes in different fields has brought about higher requirements of their properties. In particular, WPU is now of great interest due to environmental considerations, especially replacing solvent-based polyurethanes. Developing high-performance WPU tautly, therefore, is always of great importance.

However, at a given solid content remaining unchanged, WPU dries at a slower than a solvent-based polyurethanes because of

latent heat of evaporation of water is higher than one of organic solvent, which cannot meet fast-paced modern production line of requirement. To solve this problem, the focus of international research mainly focus on enhancing solid content of WPU to reduce water of evaporation load and shorten drying time. It is the only way possible to promote environmental friendly water-based coatings and adhesives replace the corresponding organic solvent-based products.[11] Moreover, WPU with high-solid content mainly has the following advantages relative to WPU with low solid content,[12] such as drying quickly, better mechanical properties, higher capacity utilization, lower transportation costs, and lower energy consumption per unit of product, and so on. Therefore, production of high-solid content products (solid mass fraction of 50% or more), is one of the development of WPU.

In recent years, it is still at an early stage for the research on WPU with high-solid content. Some of work has been done on WPU with solid content less than 50%; however, few studies on
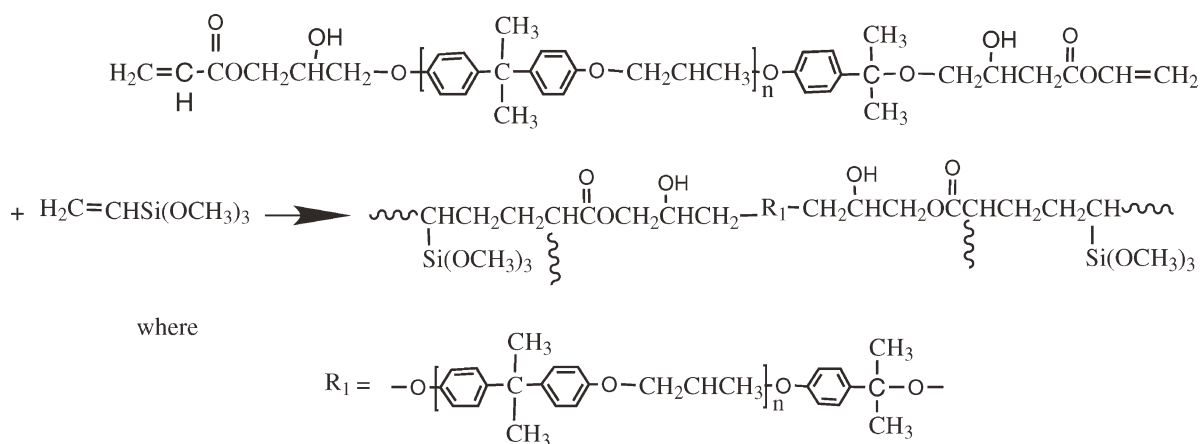
Figure 1. Schematic representation of PES.

WPU with solid content more than 55% can be found in the literatures. Methods have been employed to enhance solid content of WPU, such as mixing polyether diols with sulfonic acid based and polyester diol as soft segments,[13] mixing two kinds of isocyanate as hard segment blending Hybrid olefin polymer.[14] Our groups have reported the preparation of WPU with high-solid content more than 70% and low viscosity less than 300 mPa s^{-1} (HSLV-WPU).[15] However, it was found that the HSLV-WPU was poor in water resistance and heat resistance because of the use of sulfonate groups. Therefore, it is necessary to improve the abovementioned properties of HSLV-WPU.

The initial aim of this study was to prepare a new crosslinked Si/PU dispersions with high-solid content and excellent properties. A polyol consisting of trifunctional siloxane and epoxy acrylate of structure, referred to as silicon polyether (PES), had been synthesized by the use of acrylic resin and vinyl siloxane as monomers via free radical copolymerization in our lab. In this work, PES and propylene oxide glycol (PPG) were used as the composite soft segment of the crosslinked Si/PU polyurethane dispersions. The influence of PES content on the properties of the Si/PU dispersions was considered. Morphology and properties of the dispersions were examined by particle size, transmission electron microscopy (TEM), and viscometer, etc. The work will provide a new method to prepare WPU with high-solid content, which is promising for the application of WPU.

EXPERIMENTAL

Materials

The diisocyanate used was toluene diisocyanate (TDI, 98% purity, supplied by Shanghai Chemical, China). A polyol consisting of silicone chains and epoxy acrylate structure (PES, $M_W = 1100$, prepared in the lab) and PPG ($M_W = 1200$, supplied by Jinlin Chemical, China) and were used as mixing soft segment, which were vacuum-dried at 110°C during 2 h. Dimethylol propionic acid (DMPA, 98% purity, supplied by Chengdu Polyurethane, China) and 1,2-dihydroxy-3-propanesulfonic acid salt (DHPS, 95% purity, prepared in the lab) were used as hydrophilic chain-extending agents. Triethylamine (TEA, analysis reaction purity supplied by Tianjin Bodi Chemical) was used as neutralization agent, N-methyl-2-pyrrolidone (NMP, analysis

reaction purity Shanghai Guanghua Technology, China) was used as solvent, dibutyltindilaurate (DBTDL; Sn content is 19%, supplied by Beijing Chemical, China) was used as catalyst. γ-aminopropyl methyl dimethyoxysilane (KH-550, 97% purity, supplied by Tianjin Chemical, China) was used as termination agent and chain extender. The chemical structure of PES is shown in Figure 1.
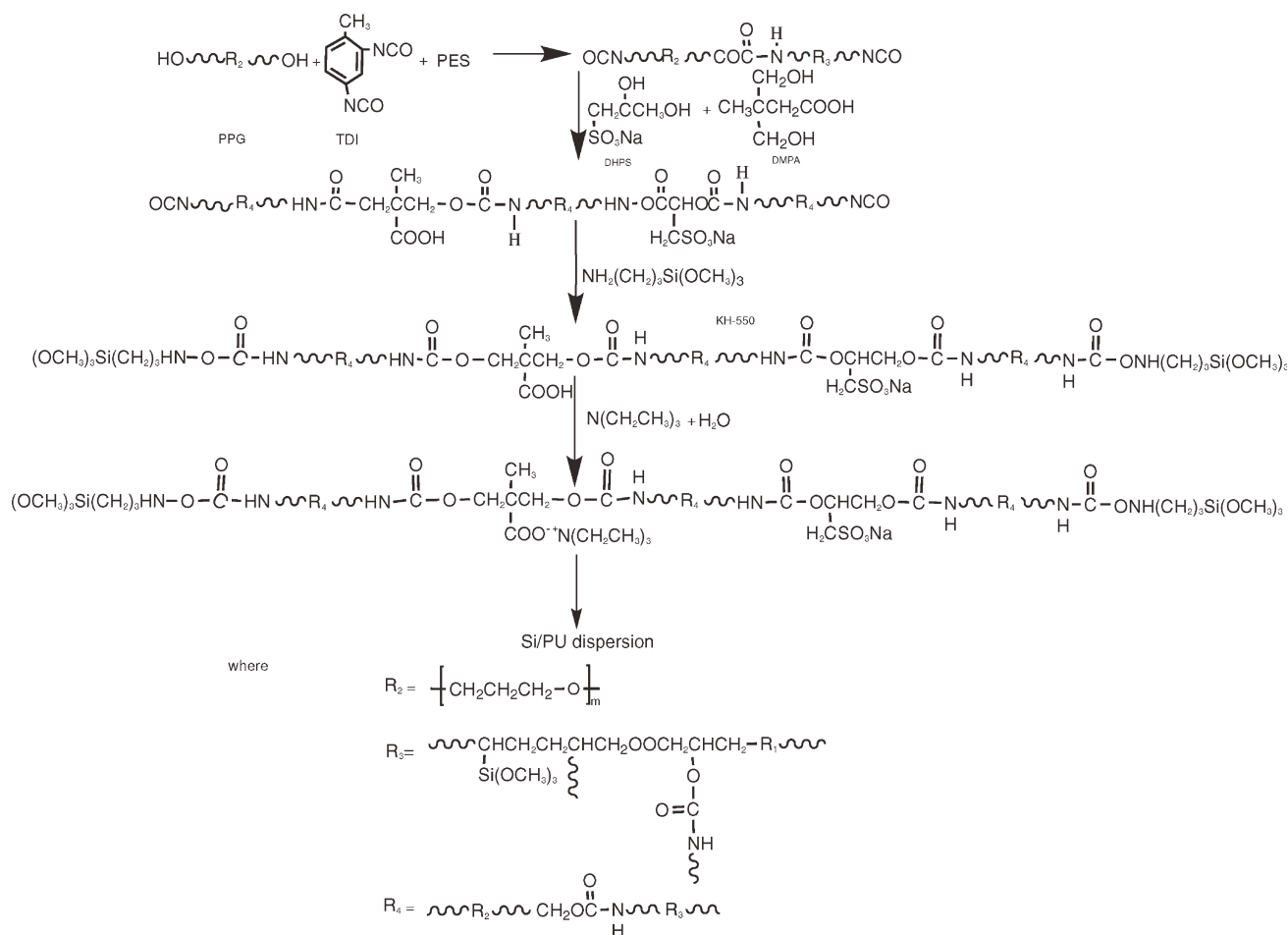
Synthesis of the Crosslinked Si/PU Dispersions

The crosslinked Si/PU dispersions were prepared by material formulations as shown Table I, and the prepolymer mixing process as shown in Figure 2. According to the weight ratio, PES and PPG were added in a four flask equipped with a thermometer, a reflux condenser tube and stirrer, and were degassed under vacuum at 110°C for 1 h. TDI was added to the flask, the goal is to obtain an NCO-capped intermediate. The mixture was allowed to cool to 30°C under moderate stirring (175–200 rpm). One drop of DBTDL was added at this temperature. Then DHPS/DMPA/NMP (5/10/15, w/w/w) were added to the flask, the goal is to introduce hydrophilic groups and chain extending prepolymer. The reaction mixture was heated to 75°C under moderate stirring (175–200 rpm) and was allowed to react at 75°C until the theoretical NCO content was reached. KH-550 was added to the flask to react with the NCO-terminated urethane prepolymer. Then the mixture was cooled to 45°C, TEA was added to the reaction mixture to neutralize the carboxy group of amino siloxane-terminated urethane

Table I. Synthetic Constitutions of Si/PU Prepolymer

Samples	PES/PPG	NCO/OH	HGC (%)	DHPS/DMPA
Si/PU-1	2/10	2 : 1	6.0	5/10
Si/PU-2	3/10	2 : 1	6.0	5/10
Si/PU-3	4/10	2 : 1	6.0	5/10
Si/PU-4	5/10	2 : 1	6.0	5/10
Si/PU-5	6/10	2 : 1	6.0	5/10
Si/PU-6	7/10	2 : 1	6.0	5/10
Si/PU-7	8/10	2 : 1	6.0	5/10

HGC is the hydrophilic chain-extending agents content.

Figure 2. Schematic representation of the cross-linked Si/PU dispersions.

prepolymer. After 30 min of neutralization, distilled water was added to the reaction mixture with vigorous stirring (1200–1500 rpm). Finally, the crosslinked Si/PU dispersions with high-solid content were obtained. The compositions of Si/PU prepolymer are listed in Table I.

Characterization

The mean particle size and particle size distribution of the crosslinked Si/PU dispersions were measured in a Zeta size analyzer. A small amount of aqueous dispersion was added into a deionized water tank and this was followed by the pinhole being set at 200 μm. The average particle diameters were measured at 25°C. Polydispersity index (PDI) was calculated in accordance with the following formula.[15]

$$PDI = -[(\mu - 2)/\Gamma + 2] \qquad (1)$$

where $\mu - 2$ is the second central moment of the distribution, Γ is the line width, Γ has an average meaning, it is generally a function of the concentration C, and angle θ. PDI is able to measure the distribution width of the diffusion coefficient, and PDI is a dimensionless quantity. PDI values of mono-disperse system is about 0.002. With an increase PDI value, distribution becomes wider. When PDI value range between 0.2 and 0.25, which means the polydispersity of the sample has be quite large.

Particle morphology was measured by TEM, dispersion solid content was determined according to international standard GB6743-86. Apparent viscosity of dispersion was measured using the NDJ-8S digital viscometer.

Storage stability of dispersion was described by observing the appearance of dispersion placed at room temperature for six months. Freeze-thaw stability of dispersions was determined as follows: a certain amount of dispersion were placed in the −20°C refrigerator to freeze for 18 h, and then thawed at room temperature lasting 6 h, such operations were repeated about 5 times or more. Finally, the times of dispersion gels were recorded. High temperature stability of dispersion was determined as follows. The dispersion samples were placed in sealed glass bottles at 80°C under the constant temperature, and then time of appearing sedimentation, or flocculation were viewed and recorded.
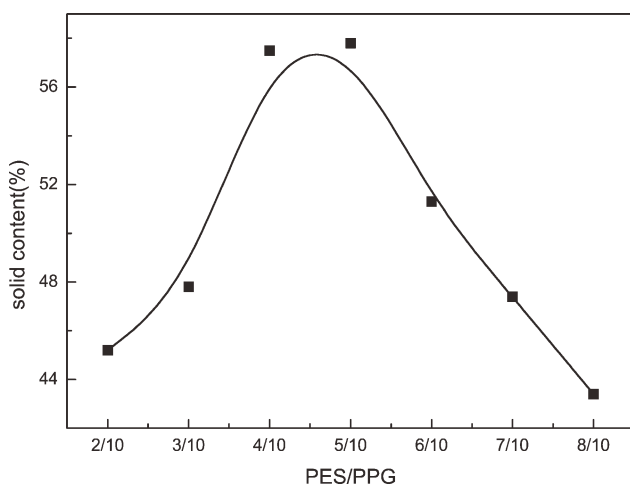
RESULTS AND DISCUSSION

Average Particle Diameters and Distribution of the Dispersions

Figure 3 shows distribution of particle size from Si/PU dispersions with different PES to PPG ratio. It is noticed that the Si/PU dispersions possessed multivariate and wide particle size distribution. According to the Ref. [16] high-solid content and low
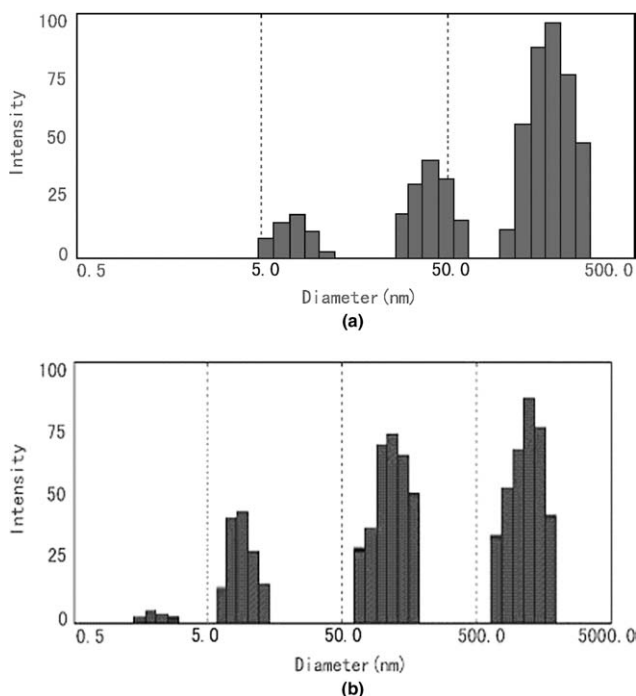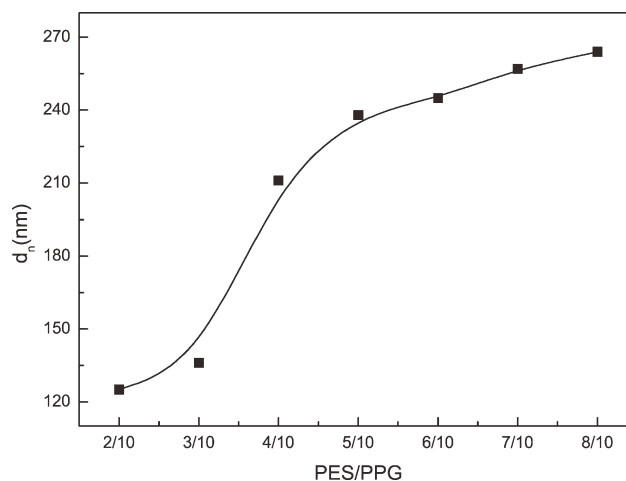
Figure 3. Particle size distribution of Si/PU dispersions with different weight ratio of PES and PPG (a) PES/PPG = 4/10; (b) PES/PPG = 6/10.

Figure 5. Average particle diameters of the Si/PU dispersions with different weight ratio of PES and PPG.

viscosity of the polymer dispersion depends on the distribution of particle size and the volume fraction ratio of large to small particles. In the experiment, mix soft segment of the Si/PU prepolymer is composed of PES and PPG. There is lots of organic siloxane on the PES side chains, the organic siloxane can induce crosslinking reactions, resulting in formation of crosslinked components in the structure of the Si/PU prepolymer. These crosslinked components can make molecular weight of Si/PU prepolymer increase, resulting in bigger particles in emulsification process. On the contrary, there is few of crosslinked groups on the PPG side chains, resulting in smaller particles in emulsification process. So, the content of PES has important influence

on particle size distribution. With increasing weight ratio of the PES to PPG, volume fraction of big particles increases and volume fraction of small particles decreases in emulsification process. As long as the content of PES is controlled in a certain range, the gaps between large particles can be filled with small particles all. Under such condition, the dispersion may possess higher solid content. However, if the weight ratio of PES and PPG is too large or too small, small particles will be not enough to fill the gaps between big particles. So, solid content of system will decrease. Therefore, we can obtain high-solid content Si/PU dispersions by adjusting weight ratio of PES and PPG. As shown in Figure 4, when the ratio of PES and PPG ranges from 4 : 10 to 6 : 10, solid content of the dispersion can reach 55%.

Figure 5 shows average particle diameters of the dispersions with different weight ratio of PES and PPG. At a weight ratio of DHPS and DMPA remaining unchanged, with higher weight ratio of PES and PPG, Si/PU dispersions possess bigger average particle diameters shown as Figure 5. The reason is analyzed as follows. According to the laws of thermodynamics,[17] when

Figure 4. Solid content of Si/PU dispersions with different weight ratio of PES and PPG.
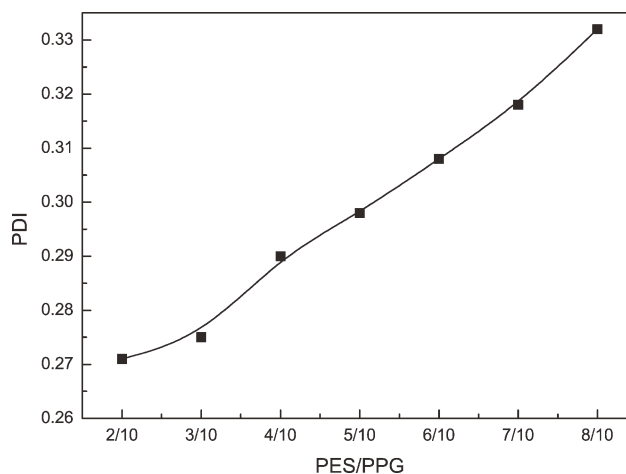
Figure 6. Particle polydispersity index (PDI) of the Si/PU dispersions with different weight ratio of PES and PPG.
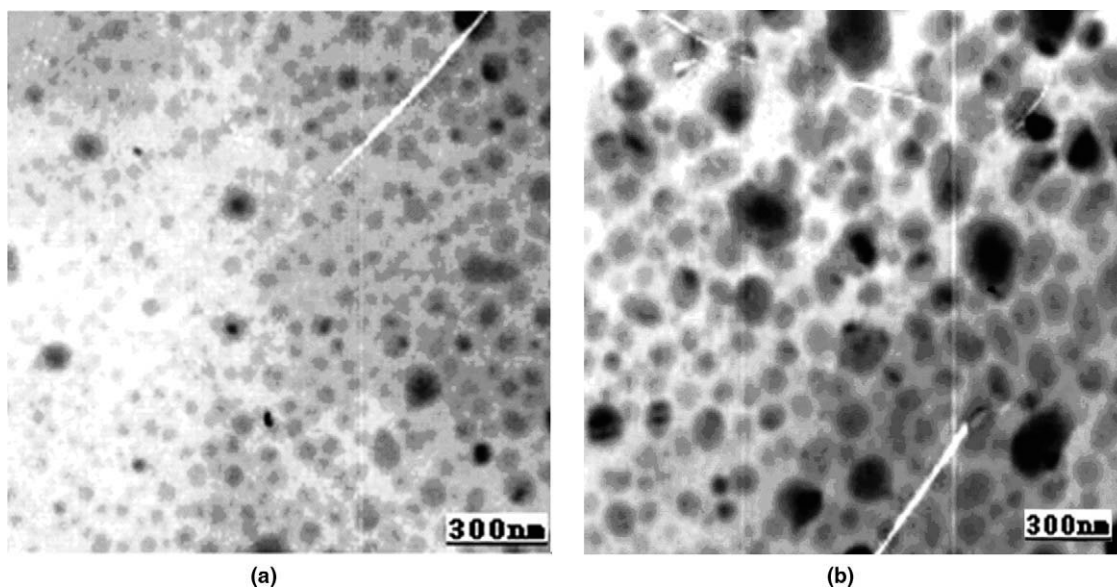
Figure 7. TEM photograph of dispersion particle with different weight ratio of PES and PPG (a) PES/PPG=4/10; (b) PES/PPG=6/10.

polymer is dispersed into the water, the temperature and pressure remaining unchanged, free enthalpy of the dispersion process can be expressed as $\Delta G = \sigma \Delta A$. Here, σ is the interface between the polymer and water, ΔA is the change value of two-phase interfacial area after the polymer dispersed into the water. Because WPU emulsification process is carried out by means of external force, this process is nonspontaneous. That is, ΔG value is positive. At a external force remaining unchanged (stirring speed r/min), if we hope to get smaller particles size, namely increasing ΔA value, σ must a smaller value. As for a polymer, if it is good hydrophilicity, such as pure WPU, its σ is smaller and ΔA value is bigger, so average particle diameter of the polymer is smaller. However, as for Si/PU dispersions in the experiment, with an increase weight ratio of PES and PPG, the relative content of hydrophobic component on the Si/PU molecule chains increase. These make emulsification process more difficult, resulting in an increase particle diameter of the Si/PU dispersions.

Figure 6 shows that particle PDI of the Si/PU dispersions with different weight ratio of PES and PPG. As shown, the Si/PU dispersion with higher PES content possesses higher PDI and wider particle size distribution, but PDI value remains between 0.2 and 0.4, which further illustrates the Si/PU dispersion with characteristics of wide particle size distribution was obtained.

**Table II.** The Values of k and n of Si/PU Dispersions

Samples	N	K
Si/PU-1	0.517	0.892
Si/PU-2	0.521	0.875
Si/PU-3	0.584	0.798
Si/PU-4	0.691	0.633
Si/PU-5	0.753	0.479
Si/PU-6	0.883	0.465
Si/PU-7	0.897	0.441

Particle Morphology of the Dispersions

Figure 7 is the TEM photographs of dispersion particle with different weight ratio of PES to PPG. From the photographs (a) and (b), it is shown that the shape of the particle is spherical and generally possesses a core-shell structure. On two TEM photographs, black spots can be considered hydrophobic components; the lateral can be considered hydrophilic components. Comparing two pictures, it can be found that particle size in (b) photograph is larger, dispersion is more uneven, and core-shell structure is more obvious than those of (a) photograph. But in the two pictures, there is all relatively dense accumulation of particles, and gaps between large particles are filled with small particle, which further validates the previous conclusions.

Rheology of the Dispersions

WPU can be considered as a binary dispersion of PU ionomer and water, and the apparent viscosity of it is able to be a characteristic of shear-thinning. In general, the power-law model
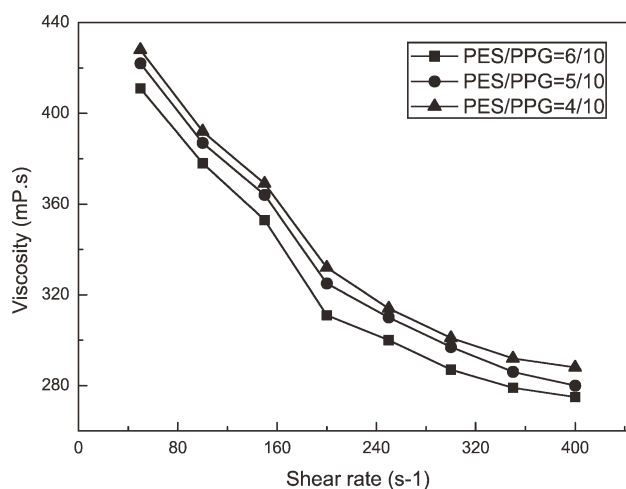
Figure 8. The viscosity and rheological of Si/PU dispersions.

Table III. The Stability of Si/PU Dispersions at Low Temperature, High Temperature, and Room Temperature

Samples	−20°C Gel/times	80°C Appearance	25°C Storage time/month	−20°C Appearance
Si/PU-1	2	Less delamination	>6	Translucence
Si/PU-2	2	Less delamination	>6	Translucence
Si/PU-3	3	Less delamination	<6	Milky
Si/PU-4	3	Less delamination	<6	Milky
Si/PU-5	3	Stratified and milky	<6	Turbidity
Si/PU-6	4	Stratified and milky	<3	Gel
Si/PU-7	4	Stratified and milky	<2	Gel

reflects the rheological properties. According to the Ostwald–Dewael power-law equation, rheological behavior is described as the following equations.[18]

$$\eta_a = k \cdot \gamma^{n-1} \text{ or } \sigma = k \cdot \gamma^n \qquad (2)$$

The above equation after taking logarithm can be described as follows.

$$\lg \sigma = \lg k + n \lg \gamma \qquad (3)$$

where σ is the shear stress, γ is the shear rate, n is the flow index, $n = 1$ means the Newtonian fluid, $n < 1$ represents the non-Newtonian fluids, k is the consistency coefficient (the larger k values, the greater the apparent viscosity), and value k can reflect the impact of structure on the viscosity, η_a is the apparent viscosity values n and k values can be obtained by using linear regression. Experimental dates are shown in Table II.

Table II shows that with increasing weight ratio of PES to PPG, n-value increases, and is closer to 1. This result shows Si/PU dispersions change from the non-Newtonian fluid to Newtonian fluid, shown as Figure 8 but in fact, is still a non-Newtonian fluid. With the weight ratio of PES and PPG increasing, consistency coefficient k decreases from 0.892 to 0.441. The reasons might be explained as follows. There are many crosslinked organic siloxane and linear PU chains in the Si/PU structure, but the polarity of PU chain is different from crosslinked organic siloxane, resulting in the interaction force changed between particles in Si/PU dispersions. As for the polarity PU copolymer units, there are the solvation and hydrogen bond in the aqueous phase, which results in an increase of the apparent viscosity. But solvation of nonpolar PES copolymer units is weaker than that of PU copolymer units. Therefore, the higher PES content makes hydration layer thinning and the interface force between water and particles decreasing, resulting in the lower the apparent viscosity.

The Stability of Dispersion
The stability data of the Si/PU dispersions measured at low temperature, high temperature, and room temperature is shown in Table III. It is observed that the stability of dispersion decrease with the increase in the weight ratio of PES to PPG.

The explanations are that the dispersion with higher PES content is more unstable due to possessing bigger particle diameter and higher hydrophobic component content. On the other hand, organic siloxane from side chain of PES was hydrolyzed and OH group was formed in water. After that, crosslinking among OH groups occurred and polymer was achieved by condensation reaction. Therefore, the crosslinking polymer is more difficult to be dispersed in water. However, as long as weight ratio of PES and PPG is less than 5 : 10, it is sufficient for the basic requirements.

CONCLUSION

A series of the crosslinked Si/PU dispersions with high-solid content were prepared by self-emulsification, which were modified via the self-made PES and PPG as mixing soft segments. The Si/PU dispersions possess wider particle size distribution and higher average particles diameter due to adding PES containing crosslinked silicone side chains. There is higher solid content in Si/PU dispersions as compared with conventional WPU. It was observed that the solid content in the Si/PU dispersions increased firstly and then decreased with increasing weight ratio of PES to PPG. When the ratio ranges from 4 : 10 to 5 : 10, the solid content in the Si/PU dispersions is up to 55%. The apparent viscosity of the Si/PU dispersions decreases with increasing weight ratio of PES and PPG, and the dispersions change from the non-Newtonian fluid to Newtonian fluid. In the Si/PU dispersions, solid content was increased and viscosity was decreased by the use of PES. Additionally, the stability of the crosslinked Si/PU dispersions with higher-solid content decreased at high temperature, low temperature, and room temperature; however, which can meet the basic requirements.

REFERENCES

1. Wei, X. Y.; Yu, X. H. *J. Appl. Polym. Sci.* **1998,** *70*, 1621.

2. Hai, N.; Jeremy, L. D.; Pauline, R. T. *Prog. Org. Coat.* **2002,** *45*, 49.

3. Temtchenko, T.; Turri, S.; Novelli, S. *Prog. Org. Coat.* **2001,** *43*, 75.

4. Yang, C. H.; Yang, H. J.; Wen, T. C. *Polymer* **1999,** *40*, 871.

5. Chinwanitcharoen, C.; Kanoh, S.; Yamada, T. J. *Appl. Polym. Sci.* **2004,** *91*, 3455.

6. Lu, M. G.; Lee, J. Y.; Shim, M. J. *J. Appl. Polym. Sci.* **2002,** *86*, 3461.

7. Chen, Y.; Chen, Y. L. *J. Appl. Polym. Sci.* **1992,** *46*, 435.

8. Hirose, M.; Zhou, J. H.; Nagai, K. *Prog. Org. Coat.* **2000,** *38*, 27.

9. Dong, C. S.; Chung, Y. J. *Chem. Ind. Eng.* **2009,** *60*, 496.

10. Jin, Q.; Huan, Q. C. *J. Chem. Ind. Eng.* **2003,** *54*, 868.

11. Kong, L. F.; Lin, H. Y. *J. Chem. Bon.* **2007,** *29*, 425.

12. Li, Q. A.; Dong, C. S.; Yu, X. W. *J. Polym. Mater. Sci. Eng.* **2007,** *23*, 59.

13. Qu, J. Q.; Chen, H. X. *J. Chem. Ind. Eng.* **2003,** *54*, 60.

14. Lee, H. T.; Wu, S. Y. *Colloid Surf.* **2006,** *27*, 65.

15. Wei, X. L.; Zhang, F. X.; Xiao, Z.H. *L. Acta. Polym. Sin.* **2009,** *1*, 26.

16. Hsu, C. K.; Chuang, W. P.; Chen, M. A. *J. Mater. Sci.* **2005,** *40*, 180.

17. Charoen, C. C.; Shigeyoshi, K.; Toshiro, Y. *Macromol. Symp.* **2004,** *32*, 120.

18. Lee, D.; Lee, S. H.; Sangcheol, K. J. *Polym. Sci.* **2003,** *41*, 20.