

Effect of Nanosilica Content on Properties of Polyurethane/Silica Hybrid Emulsion and Its Films

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ABSTRACT: Polyurethane/silica hybrid emulsion (PUSi) was synthesized by the reaction of isophorone isocyanate, polyether polyol, hydrophilic nanosilica (A200), dimethylol propionic acid, trimethylol propane, and 3-aminopropyltriethoxysilane (KH550). The films of the waterborne polyurethane (WPU) were prepared. The structure of the polyurethane was characterized by Fourier transform infrared spectrometer (FTIR), thermogravimetry (TG), and differential scanning calorimetry (DSC). The particle size distribution and morphology of emulsion were examined. Influence of nanosilica content on the mechanical properties and solvent absorption of the cast films were also measured quantitatively. FTIR indicates that $-\text{NH}_2$ of KH550 reacted with $-\text{NCO}$ of polyurethane. TG analysis

indicates that nanosilica can improve thermal stability of polyurethane. There is no clear effect of nanosilica on the glass transition of soft segments. It was found that greater mechanical properties of WPU were obtained when chemical networks were formed by sol-gel process. As the nanosilica content increases, water absorption and ethanol absorption decreased. The particle size increases with increase of A200 content. PUSi hybrid emulsions are endowed with pseudo-plasticity. The apparent viscosity of emulsions increased and then decreased with addition of A200. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3521–3530, 2011

Key words: polyurethanes; silicas; thermal properties; crosslinking

INTRODUCTION

Due mainly to the environmentally friendly nature and versatile structure-property relationships of polyurethane (PU), polyurethane dispersions (PUDs) are steadily expanding their usages in coatings, adhesives, textile sizing, etc.^{1–4} However, some inferior properties of waterborne PUs such as low mechanical strength, solvent, and chemical resistance restrict utility for high performance applications of waterborne polyurethane (WPU) to some extent. It is important to modify the WPU by various methods to improve the solvent and chemical resistance, thermal, and mechanical properties of the waterborne PU. To improve the properties, some researchers have made many reports about their synthesis and modification.^{5,6}

In the past decade, nanosilica particles have been widely introduced into polymers to improve the heat resistance, radiation resistance, and mechanical and electrical properties of the polymer materials.^{7–10} For

example, Zhou et al.¹¹ found that nanosilica particles could more effectively improve the hardness, abrasion resistance, and scratch resistance of acrylic-based polyurethane coats than microsilica particles. Wu et al.¹² indicated that nanosilica particles could simultaneously provide PP with stiffening, strengthening, and toughening effects at rather lower filler content (typically 0.5% by volume). Manna et al.¹³ found that the storage modulus and T_g of epoxidized natural rubber increased through addition of silica. Properties of polyurethane such as rigidity, toughness, heat resistance are improved by SiO_2 because silanol groups on the nanosilica can react with the urethane group and other groups of polyurethane.¹⁴

In addition, the use of the sol-gel process to prepare highly intermingled organic-inorganic hybrid polymer networks is of current scientific interest since it offers the possibility of tailoring the properties of the materials by variation of the relative composition of the inorganic and organic phases.^{15–17} Depending on the desired application, polymers with different mechanical properties can be obtained because of their versatility in the formulation variables. Additionally, because of the hybrid character, they present superior thermal and weathering resistance, and more excellent abrasion than traditional polymers.^{18–21}

Lately, polyurethane has attracted great attention for the preparation of hybrid sol-gel materials and functional materials. For instance, PU- SiO_2 hybrid

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materials have been prepared by suspension²² and an acid-catalyzed sol-gel process.²³ Ho Tak Jeon²⁴ synthesized WPU-silica composites using both hydrophilic and hydrophobic silica. Jui-Ming Yeh²⁵ prepared amino-terminated anionic waterborne-polyurethane-silica hybrid materials through a sol-gel process in the absence of an external catalyst. Tzong-Liu Wang²⁶ synthesized a series of polyurethane/polyaniline/silica organic/inorganic hybrids via the conventional polyurethane prepolymer technique. Mohammad Mehdi Jalili, Siamak Moradian²⁷ used nano-silica particles to improve and optimize properties of 2-pack polyurethane clearcoats based on acrylic polyol. However, polyurethane/silica hybrid emulsion (PUSi) prepared by a sol-gel process where tri-functional trimethylol propane (TMP) is used as an internal crosslinker have not been mentioned. The aim of this work is to prepare water-based polyurethane with highly crosslinked hybrid polymer networks. The tri-functional TMP is able to form a three-dimensional chemical bondings between PU prepolymer, leading to the increasing crosslinking density of the prepolymer. With this understanding, the nanosilica particles (Aerosil 200) were introduced into polyurethane and silane coupling agent 3-aminopropyltriethoxysilane (KH550) was used as an inorganic precursor for the preparation of polyurethane hybrid emulsions (PUSi). It is an organofunctional alkoxy silane monomer that can undergo both the sol-gel polymerization of the alkoxy groups and the reaction with NCO functionality in the prepolymer to form a hybrid network with covalent bonds between organic and inorganic phases. Hydrolysis of ethoxy groups in PUSi hybrid emulsion gives silanol groups which can subsequently condense with silanol groups on the nanosilica (A200) to form siloxane. Accordingly crosslinking density of PUSi can be further improved. The solidified films of PUSi hybrid emulsions were prepared. The modified PUSi were characterized by Fourier transform infrared spectrophotometer (FTIR) and thermogravimetric analysis (TGA) instruments.

The emulsion, as the basic material of coatings, plays an important role in the coatings' properties. On the one hand, their particle size and morphology exert a great influence on the film-forming properties and mechanical properties. On the other hand, their rheological properties not only affect workability but also have something with their stability and some other properties.

Therefore, it is important to study the particle size, morphology and rheological properties of the dispersions. The effects of the nanosilica particles on the particle size and rheological behavior of the dispersions were studied. Finally, the effects of Aerosil 200 content on mechanical properties and water absorption were studied in this work.

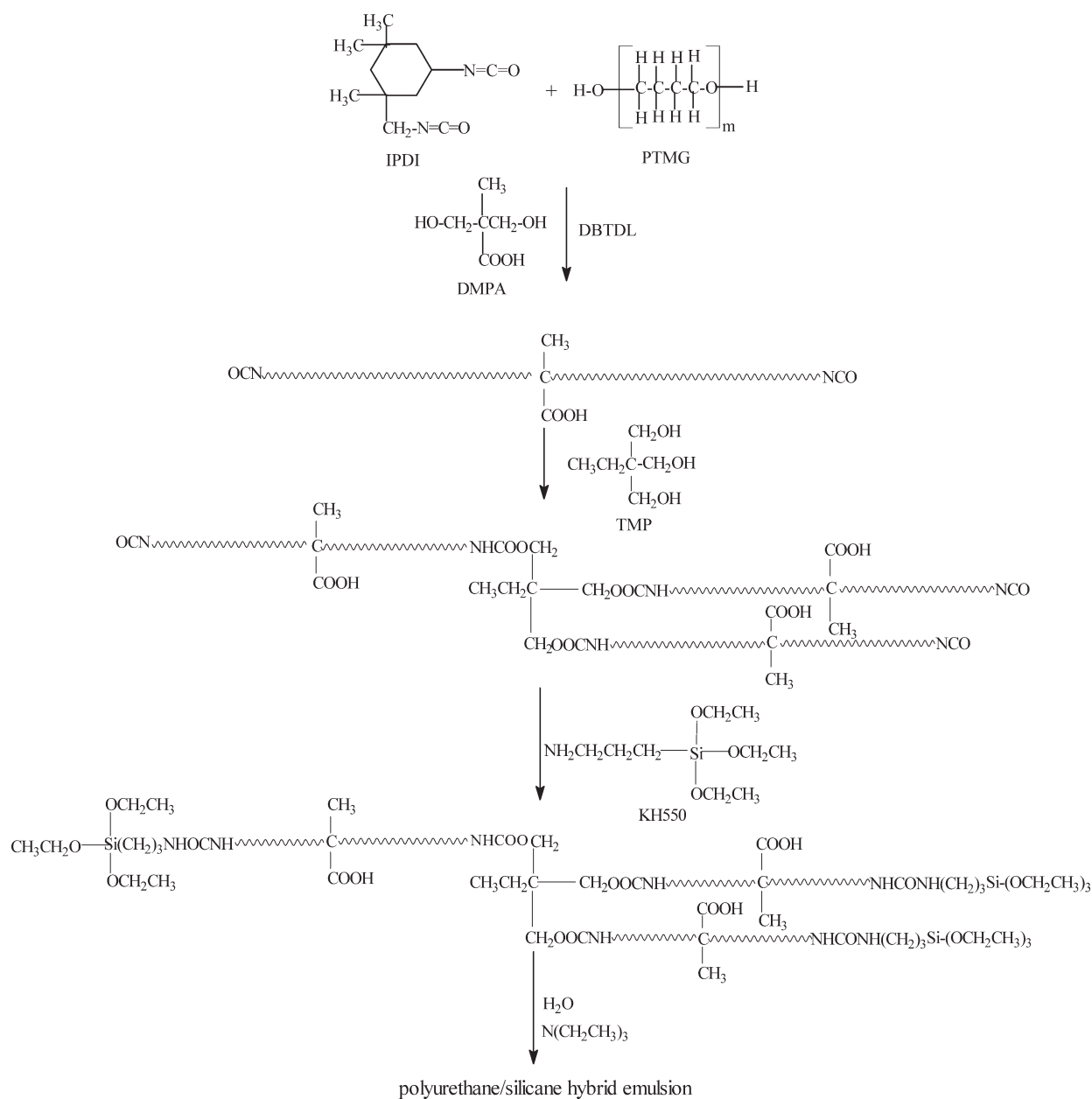
EXPERIMENTAL

Reagents and materials

Isophorone isocyanate (IPDI) were vacuum distilled before use. Poly(tetramethylene glycol) (PTMG; 1000 g/mol) was dried and degassed at 80°C under vacuum for 3 h. 2,2-bis(hydroxymethyl) propionic acid (DMPA) and TMP were dried at 50°C for 48 h in vacuum oven. Dibutyltin dilaurate (DBTDL) were used as received. 3-aminopropyltriethoxysilane (KH550) was used as a coupling agent. 1-methyl-2-pyrrolidone (NMP) and triethylamine (TEA) were dried over 4°A molecular sieve before use. Nano-size hydrophilic silica (Aerosil 200) with average particle size of 12 nm was obtained from Degussa (Hanau, Germany).

Preparation of PUSi emulsion

A 500 mL round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser with nitrogen in/outlet, and a pipette outlet was used as a reactor. The polymerization was carried out in a constant temperature oil bath. PTMG, A200 and IPDI were charged into the dried flask at 70°C. While stirring, NMP was added and stirring was continued until a homogenized mixture was obtained. DMPA and DBTDL were added and stirring was continued for 2 h at this temperature. Then TMP was added to the flask. The mixture was heated to 80°C for about 2 h to afford an NCO terminated prepolymer. The NCO content during the reaction was determined using a standard dibutylamine back titration method. Upon obtaining a theoretical NCO value, the prepolymers were cooled to 30°C, 3-aminopropyltriethoxysilane as a coupling agent and NMP were added and reacted for 30 min, then the neutralizing solution, i.e., TEA (DMPA equiv) dissolved in NMP (2 wt %) was added and stirred for 30 min. Since the water addition rate is a critical parameter to obtain a stable emulsion, distilled water was added dropwise at a constant flow rate to the flask under vigorous magnetic stirring. After all of the distilled water had been dropped into the flask, polyurethane/silica hybrid emulsion was obtained. The sol-gel process is occurred at this step. KH550 can undergo a variety of reactions during the preparation of a hybrid by a sol-gel route. Hydrolysis of ethoxy groups in PU gives silanol groups which can subsequently condense with silanol groups on the nanosilica (A200) to form siloxane. The resulting product was a PU/silica hybrid emulsion (PUSi) with a solid content of about 30%. The reaction scheme of PUSi hybrid emulsion is shown in Scheme 1 and the sol-gel process of PUSi is summarized in Scheme 2. Composition of PUSi emulsion is summarized in Table I.



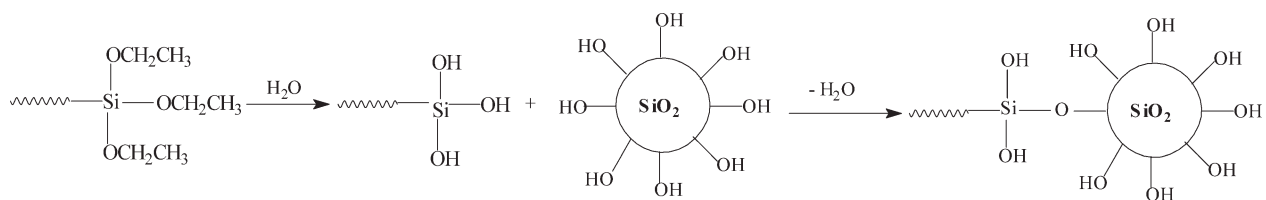
Scheme 1 The reaction scheme of PUSi hybrid emulsion.

Preparation of PUSi films

Films were obtained by casting the aqueous dispersions onto Teflon surfaces and allowing them to dry at room temperature for 5 days and then at 60°C for 12 h. After demoulding, the films were stored in a desiccator to avoid moisture.

FTIR spectroscopy

A Fourier transform infrared transmission spectrophotometer was used to verify the reaction between NCO and KH550 and the formation of Si—O—Si structure by sol-gel process. Samples for infrared analysis were prepared by drying emulsion directly on KBr discs.



Scheme 2 The sol-gel process of PUSi.

TABLE I
Composition of PUSi Emulsion

Designation	A200/g	IPDI/g	PTMG/g	DMPA/g	TMP/g	KH550/g	TEA/g
PUSi0	0	17	12	1.8	0.6	4	1.4
PUSi0.3	0.3						
PUSi0.4	0.4						
PUSi0.5	0.5						
PUSi0.6	0.6						
PUSi0.8	0.8						

Thermogravimetric analysis

Thermogravimetric experiments were performed on a Germany Netzsch 209 TG analyzer. Film samples about 5 mg were placed in a platinum sample pan and heated from 30 to 530°C, under N₂ atmosphere, at a heating rate of 10°C/min.

DSC analysis

The thermal properties were measured with use of a Germany Netzsch differential scanning calorimeter DSC-204 in a nitrogen atmosphere. All samples of 10 mg were initially scanned over the temperature range from -110 to 150°C at a heating rate of 10°C min⁻¹.

Mechanical property tests

Tensile test was done using a Tinius Olsen Series 1000. Microtensile specimens of 25 mm (length) × 5 mm (width) × 1 mm (thickness) were used. Pencil hardness was measured using a QHQ hardness tester according to GB/T 6739-1996.

Determination of water absorption

The PUSi films, with a thickness of 0.4–0.8 mm, were cut into circular disks by using a sharp-edged stainless steel die with inner diameter of 20 mm. The samples were dried in vacuum oven for 24 h to determine their dry weight (W_d). Water absorption of the PU membranes was determined by immersing the membranes in a baker of water at 37°C. The wet weight with different immersion times (W_t) was determined by wiping off the surface water with a piece of filter paper. The water absorption (WS) of the films was calculated by²⁸

$$WS = [(W_t - W_d)/W_d] \times 100$$

The ethanol absorption was calculated similarly.

Particle size measurement

The particle size of modified emulsions was analyzed by a dynamic light scattering (DLS) (Zeta-plus, Brookhaven Instruments). All samples were first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion.

Transmission electron microscopy

The morphology of the polyurethane/silica hybrid emulsion was examined by Transmission electron microscopy (TEM). The testing was performed on a Hitachi-7600 operating at 120 kV.

Rheology of PUSi emulsions

The rheology of PUSi emulsions were analyzed in an American Brookfield DV-III Ultra Programmable Rheometer. 100 cm³ of emulsions were used in the measurements. Controlled shear rate (CSR) experiments were carried out as follows: shear rate was increased from 50 to 300 s⁻¹ and maintained for 300 s to provide a uniform and standardized state in all the emulsions. Some experiments were repeated and an excellent reproducibility was always obtained.

RESULTS AND DISCUSSION

FTIR spectroscopy

The FTIR spectrum is shown in Figure 1(A–E), and show the FTIR spectra of PU prepolymer, PU prepolymer with KH550, PUSi0, PUSi0.4, and PUSi0.5,

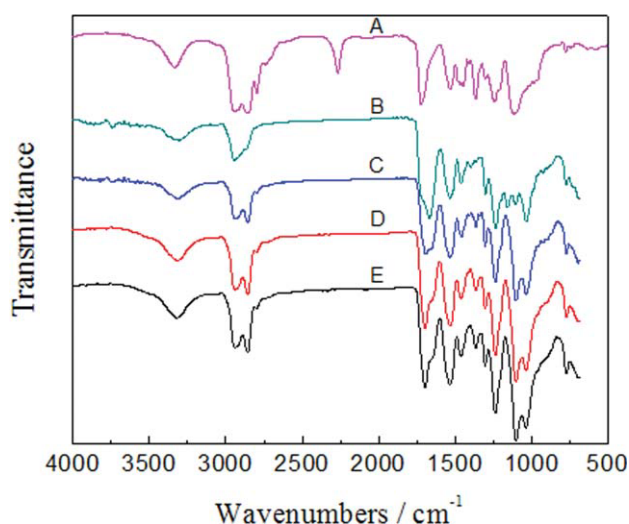


Figure 1 The FTIR spectrum. (A) PU prepolymer, (B) PU prepolymer with KH550, (C) PUSi0, (D) PUSi0.4, and (E) PUSi0.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The absorption peak of at 3310 cm^{-1} indicates the N—H stretch in polyurethane. The peaks at $2980\text{--}2850\text{ cm}^{-1}$ are associated to C—H stretch of CH_3 , CH_2 , and CH. The characteristic absorption peaks at 1690 cm^{-1} is the C=O carbonyl stretchings of urethane. The absorption peak of the NCO group (2270 cm^{-1}) of PU prepolymer (A) disappeared in spectrum B, C, D, and E during the reactions of NCO groups with KH550. The results indicate that NCO groups of the PU prepolymer have completely been reacted with the amine groups in KH550. The characteristic absorption peaks at 1100 cm^{-1} of C, D, E was due to the asymmetric vibration modes of Si—O—Si formed by the sol-gel reaction.²³ The absorption peak at 1200 cm^{-1} was due to the symmetric deformation of Si—O—Si. Which implies the Si—O—Si structure has formed during the sol-gel process. As the nanosilica content increases, the characteristic absorption peaks of the asymmetric vibration modes of Si—O—Si at 1100 cm^{-1} is stronger and wider ($\text{PUSi}0 < \text{PUSi}0.4 < \text{PUSi}0.5$), it can be inferred that the asymmetric vibration of Si—O—Si and C—O—C are interactional. It also shows that KH550 has reacted with PU prepolymer and hydrolysis of ethoxy groups in KH550 gives silanol groups which can subsequently condense with silanol groups.

Thermogravimetric analysis

To examine the effect of nanosilica on the thermal stability, thermogravimetric analysis (TGA) was carried out. Figure 2 shows typical TGA curves for as-prepared PUSi and Figure 3 shows the behavior of differential weight loss (DTG) curves for the samples, as measured under a nitrogen atmosphere. The thermal stability of polyurethane is generally not high, especially above their softening temperatures,²⁹

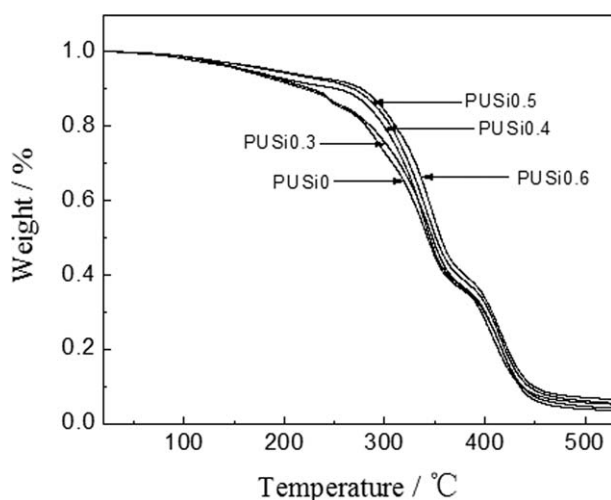


Figure 2 TGA curves of polymer.

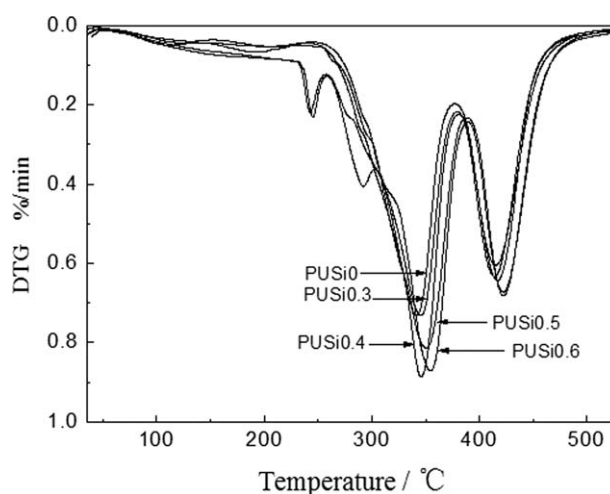


Figure 3 DTG curves of polymer.

and the degradation mechanism is very complex due to the variety of products formed in the process. Usually, at a low heating rate, the degradation process results in differential weight loss (DTG) curves with several peaks, which indicates the complexity of the degradation. Those peaks correspond to the temperatures at maximum rate of weight loss in the corresponding step. The temperatures at weight loss of 10, 30, 50% and maximum decomposition of the samples are shown in Table II.

It was verified from Table II that the thermal stability was influenced by nanosilica content. According to Table II, $T_{0.1}$, $T_{0.3}$, $T_{0.5}$, and T_{\max} of PUSi0.3, PUSi0.4, PUSi0.5, and PUSi0.6 are higher than PUSi0, and $T_{0.1}$, $T_{0.3}$, $T_{0.5}$, and T_{\max} for the PUSi films increased gradually with increasing $w(\text{A200})$, indicating that the addition of nanosilica enhances the product's thermal stability. The DTG curves show that there are different stages of degradation which are not perceptible in TGA curves, showing the close relation and mutual influence between degradation process of hard and soft segments. It is shown that the films present three stages and even more degradation-step profile. In general, the TGA curve exhibits three distinct weight loss stages,

TABLE II
Effects of Nanosilica on the Heat Resistance
of PUSi Films

Designation	$T_{0.1}/^{\circ}\text{C}$	$T_{0.3}/^{\circ}\text{C}$	$T_{0.5}/^{\circ}\text{C}$	$T_{\max}/^{\circ}\text{C}$
PUSi0	220.73	308.10	343.07	341.40
PUSi0.3	226.99	314.99	347.80	345.29
PUSi0.4	252.96	319.51	345.05	345.55
PUSi0.5	269.34	324.40	351.25	350.19
PUSi0.6	277.36	331.08	356.21	354.63

$T_{0.1}$, $T_{0.3}$, $T_{0.5}$, and T_{\max} refer to the temperature at weight loss of 10%, 30%, 50%, and maximum decomposition of the polymer, respectively.

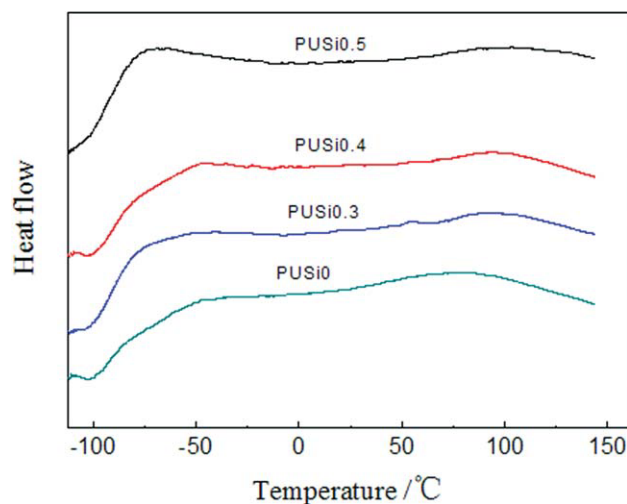


Figure 4 DSC thermogram curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

starting at 30°C and ending at ~ 550°C. The first weight loss stage in the temperature range of 25–300°C, results from vaporization of residual water and loss of oligomer and by-products existing in the PUSi films. The second weight loss step, around 300–350°C, might be starting the decomposition of the urethane group as the hard segments degradation. The third weight loss step, about 350–450°C might be attributed to the decomposition of the soft segment of polyurethane.^{30–33}

The weight loss in temperature range of 30–550°C is shown that the thermal decomposition of these PUSi films shift toward the higher temperature range than that of PUSi0, which confirms the enhancement of thermal stability of modified polyurethanes. The modified PUSi may have an interpenetrated network nature generated in the sol-gel process. The reason limits the segmental movement of PUSi, leading to the increase in the thermal stability. In addition, there is Si–O bond in the PUSi molecule after reacting with tri-functional KH550 and A200, and bond energy of Si–O bond is greater than that of C–O bond, which can also improve thermal resistance of PU. In a word, PUSi show better thermal properties than PUSi0 due to the higher crosslinking density and formation of –Si–O–Si– linkage by sol-gel process.

DSC analysis

The glass transition temperatures (T_g 's) of polyurethane/silica hybrid films can be carefully measured using DSC instrument. Figure 4 shows the T_g 's. The transitions around –60°C may be due to the glass transition of PTMG as soft segment in polyurethane chains in Figure 4. Since the silica has the –OH groups on its surface, it should have the interaction with PUSi macromolecular chains via hydrogen bonding between –OH groups of silanol and –NH–CO– or –COO groups from resin molecules. But, these weak electrostatic interactions can not significantly influence the segmental motion of soft poly(tetramethylene glycol) molecular chains at the addition of silica particles. Thus, the PU-silica hybrid films have similar values of T_g 's. Since the T_g of PTMG is about –88°C,³⁴ a bit high T_g of soft segment suggest that there are partial phase mixings between soft and hard segments. Although T_g of soft segment is virtually unchanged by increasing $w(A200)$, this implies that the degree of partial phase mixing between soft and hard segment increases in the presence of hydrophilic silica (A200).

Influence of the A200 content on the mechanical properties

Table III shows the static mechanical properties and hardness of polyurethane films containing different nanosilica content. The tensile strength of polyurethane films increased with increase of $w(A200)$, whereas the elongation at break shows the opposite tendency. On the whole, the tensile strength increase while $w(A200)$ increases from 0 to 0.6 g. However, the tensile strength will decrease when $w(A200)$ is more than 0.6 g. The excessive nanosilica particles is disadvantageous to tensile strength improvement. The nanosilica can improve the mechanical properties of PU films by increasing crosslinking density of the polymer. Increasing $w(A200)$ leads to higher cross-linking density between crosslinking points. Excessive crosslink structure of macromolecule leads to the increasing particle size of PU emulsion and PU emulsion will be unstable due to the severe aggregation of the sample. Unstable PU emulsion is a great disadvantage to the film-forming properties, which result in the decrease of tensile strength of

TABLE III
Effects of $w(A200)$ on the Mechanical Properties of PUSi Films

$w(A200)/g$	0	0.3	0.4	0.5	0.6	0.8
Tensile strength (MPa)	18.5	21.8	22.8	25.9	28.1	25.6
Elongation at break (%)	289.8	263.5	236.5	228.6	215.0	196.8
Pencil hardness	HB	H	2H	2H	2H	2H
Emulsion appearance	Bluish	Opalescent	Opalescent	Opalescent	Milky	Deposit

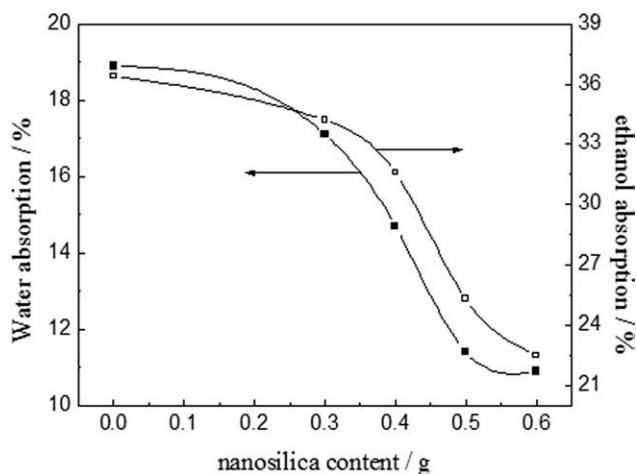


Figure 5 Influence of the nanosilica content on the water absorption and ethanol absorption of films.

films. Hardness is increased as the content of nanosilica is increased by the reinforcing effect of dispersed nanosilica and crosslink structure of macromolecule.

Influence of the nanosilica content on water absorption

Influence of the nanosilica content on the water absorption and ethanol absorption of films is shown in Figure 5. The water absorption and ethanol absorption of films decreases monotonically with increasing A200 content. As the nanosilica content increases, water absorption and ethanol absorption decreased, indicating the forming of siloxane structure enhances the resistance to water and ethanol. Despite hydrophilicity of Aerosil 200, water swell of PUSi films decreased with $w(\text{A200})$, this result indicated that PU films have hydrophobic network structure by sol-gel process. The films prepared with higher A200 content exhibited better water resistance, and this may be ascribed to the higher cross-linking density between cross-linking points. Because there are silanol groups on the nanosilica, and hydrolysis of ethoxy groups in PU gives silanol groups which can subsequently condense with silanol groups on nanosilica to form $-\text{Si}-\text{O}-\text{Si}-$ linkage. On the other hand, the Si atom in KH550 is trifunctional in terms of reactive ethoxy groups and is therefore able to form a three-dimensional chemical bondings between PU polymer molecules, leading to the increasing crosslinking density of the polymer and decreasing free volume of the molecular chain, thus the water and ethanol molecules were hard to penetrate into the films, therefore the water and solvent resistance increased.

Effects of nanosilica on particle size distribution and morphology of emulsion

The particle size and distribution of PUSi0 and PUSi0.4 emulsions are shown in Figure 6. The average particle size of PUSi0 is only 80.3 nm with very narrow distribution width, and the average particle size of PUSi0.4 is 104.9 nm. The morphology of the as-prepared hybrid emulsion was examined by TEM as shown in Figure 7. It is shown that the emulsion particles of PUSi0 are well dispersed. When nano-SiO₂ are introduced onto the particles, the sizes of particles become larger. Increasing $w(\text{A200})$ leads to more hydrophobic structure and higher cross-linking density in the macromolecular chains, consequently it is difficult to emulsify the polyurethanes with a constant COOH content in the polymer chain and the particle size increases. It is found that the particle size of PUSi0 is small. However, When $w(\text{A200})$ increases from 0 to 0.6, the dispersions' average size increase from 80.3 to 152.1 nm. According to

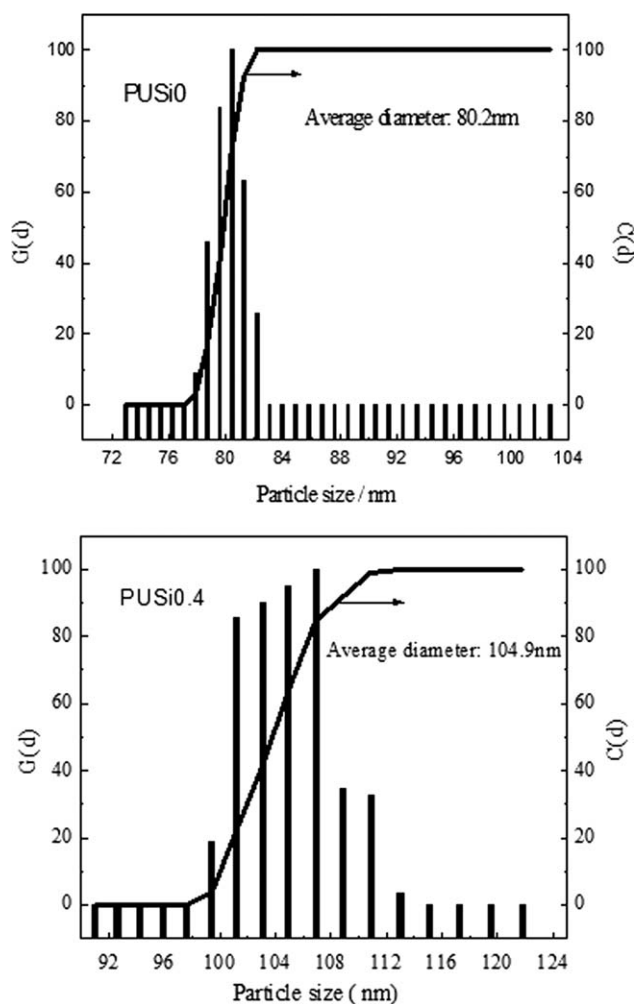


Figure 6 Particle size and particles size distribution of PUSi0 and PUSi0.4 emulsion.

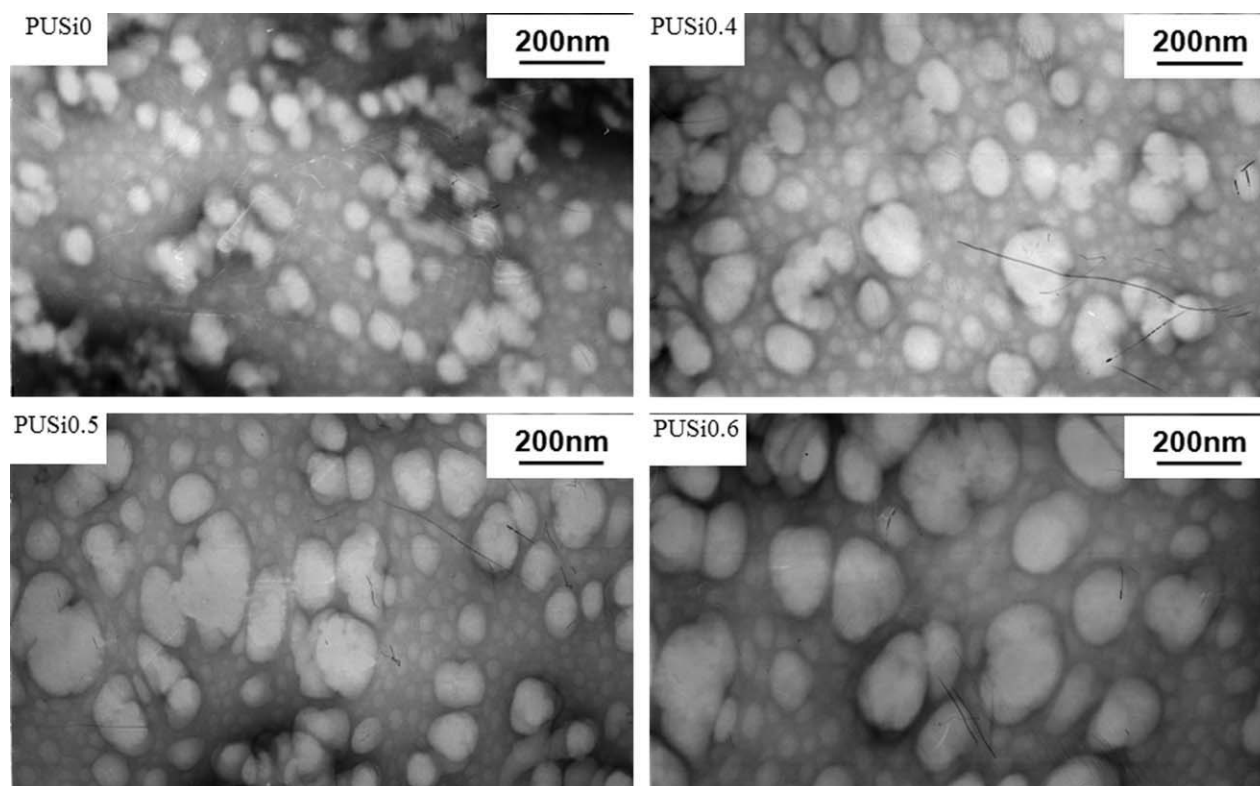


Figure 7 Transmission electron micrograph of polyurethane/silica hybrid emulsion.

thermodynamic law, eq. (1) can be used, when polymer was dispersed into water with temperature and pressure kept constant.

$$\Delta G = \sigma \times \Delta A \quad (1)$$

where ΔG represents variation in free enthalpy; σ represents interfacial tension between polymer and water; ΔA represents variation in interfacial area.

In general, if the polymer can be well dispersed into water, ΔA would be positive, as well as σ . And therefore ΔG would be positive, as a result, the dispersion can't process spontaneously until in virtue of external force. To increase ΔA , that is, to obtain smaller particles, the interfacial tension should be low enough when the external force is the same. As to a polymer with good hydrophilicity, such as pure WPU, σ is relative small, so accordingly ΔA can be bigger, and particle size is just the opposite. While with the increase of hydrophobic Si—O—Si, the interfacial tension would increase, leading to the increase of particle size.

Effects of nanosilica on rheological properties

Figure 8 displays viscosity variation as a function of the shear rate of PU emulsion with different silica content. It is found that η_a decreased greatly at the beginning and then become invariable with increasing shear rate, which manifest that PUSi emulsions

are endowed with pseudoplasticity. Mooney equation can explain this phenomenon, which was described as follow:

$$\ln \eta_a = \ln \eta_e + k_e V_i / (1 - V_i / \phi) \quad (2)$$

where η_a is systematic apparent viscosity, V_i is particles' interior phase volume, ϕ is stacking

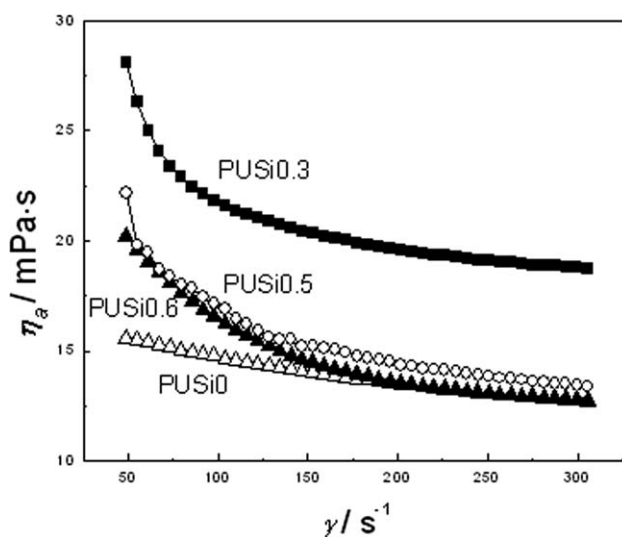


Figure 8 Viscosity variation as a function of the shear rate of PUSi emulsions with different silica content.

coefficient, k_e is shape factor, η_e is particle's outside viscosity. Deformation took part in particles with the action of shear stress, k_e decreased and ϕ increased which eventually lead to the decrease of η_a . And accordingly η_a keeps invariable when the particles keep steady shape. Furthermore, due to the existence of polar groups in polymer molecular chain, hydrogen bond and solvation are produced, and eventually forming hydrated layer. The hydrated layers would be destroyed with the increase of shear rate, which make the particles' relative movement more easily and therefore η_a decreases, but when shear rate increases to a certain degree, the hydrated layers would be totally destroyed, η_a wouldn't decrease any longer.

According to Ostwald-de Wael Power-law equation, the rheological behavior can be described as follows:

$$\eta_a = k \times \gamma^{n-1} \quad \text{or} \quad \sigma = k \times \gamma^n \quad (3)$$

where σ is shear stress, γ is shear rate, n is flow-behavior index, k is consistency coefficient whose apparent viscosity increases with increasing k , η_a is apparent viscosity.

Equation (4) can be obtained by eq. (3):

$$\lg \sigma = \lg k + n \lg \gamma \quad (4)$$

Since there exists linear relationship between $\lg \sigma$ and $\lg \gamma$, n , and k value can be calculated by linear regression approach.

Figure 9 shows the flow curves of emulsions with different silica content and n and k were calculated from Figure 9, n and k value are shown in Table IV. The n value of the emulsion is less than 1 and decreased with addition of nanosilica. This indicates that PU emulsion exhibits a non-Newtonian liquid behavior with SiO_2 addition. At the same time, addi-

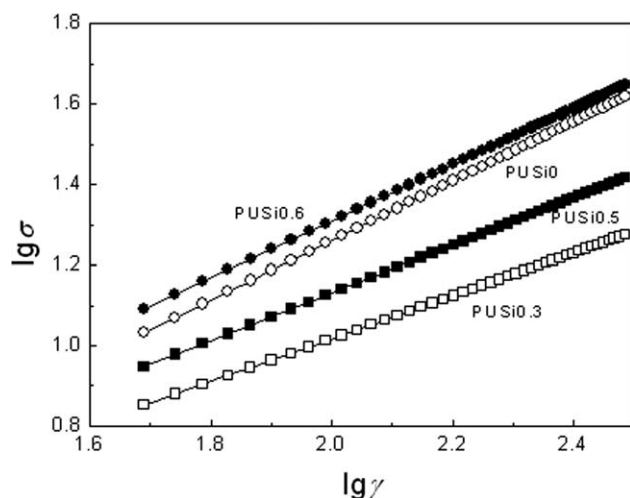


Figure 9 Flow curves of PUSi emulsions.

TABLE IV
The n , k Values for PUSi Emulsions

Designation	n	K
PUSi0	0.74	0.61
PUSi0.3	0.53	0.90
PUSi0.5	0.59	0.89
PUSi0.6	0.70	0.81

tion of more hydrophilic silica results in a decrease in the apparent viscosity of PUSi emulsions. The consistency coefficient (k) decreased from 0.90 to 0.81 when nanosilica content increased from 0.3 to 0.6 g. The reason is that the difference in structure and polarity of Si—OH and PU lead to the change of interaction force between the polymer's latex particles. On the one hand, due to solvation and hydrogen bond action of polar polyurethane in water phase, the viscosity increases. On the other hand, the solvation of Si—O—Si is feeble, and Si—O—Si group content increases with increasing silica content, which make particle's crustaceous hydrated layer thin. Therefore the interaction force between latex particle and water declines, manifesting the decrease of the apparent viscosity.

CONCLUSIONS

A series of polyurethane/silica hybrid emulsion (PUSi) was synthesized by sol-gel process. The films of the WPU were prepared by casting emulsions on Teflon surfaces. The structure of the polyurethane was characterized by Fourier transform infrared spectrometer (FTIR), which implies the Si—O—Si structure has formed during the sol-gel process. Thermogravimetric analysis (TGA) indicates that nanosilica can improve thermal stability of polyurethane. Differential scanning calorimetry (DSC) shows there is no clear effect of nanosilica on the glass transition of soft segments. The morphology of the polyurethane/silica hybrid emulsion was examined by transmission electron microscopy (TEM). It was found that greater mechanical properties of waterborne PU were obtained when chemical networks were formed by sol-gel process. As the nanosilica content increases, water absorption and ethanol absorption of the PUSi films decreased. The particle size increases with increase of A200 content. PUSi hybrid emulsions are endowed with pseudoplasticity. The apparent viscosity of PUSi emulsions increased and then decreased with addition of nanosilica.

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