Structure and Property of Polyurethane/SiO$_2$ Composite Elastomer Prepared via *In Situ* Polymerization

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ABSTRACT: A series of polyurethane (PU)/SiO$_2$ composites were prepared via *in situ* polymerization through a prepolymer process. The effect of SiO$_2$ content on mechanical and solvent-resistant properties of PU/SiO$_2$ composites was investigated. It was found that with increasing SiO$_2$ content, the tensile strength and toughness, hardness, and modulus of PU composites increased. PU/SiO$_2$ composites exhibited only one loss peak corresponding to the glass transition temperature of the soft-segment of PU, which shifted insignificantly with increasing SiO$_2$ content. The equilibrium swelling ratio and swelling rate constant in cyclohexanone and xylene were reduced by increasing SiO$_2$ content, indicating the enhancement of the solvent resistance of the PU elastomer. Morphology observation of PU/SiO$_2$ composites showed that the acicular SiO$_2$ dispersed uniformly in PU matrix, and there was no obvious aggregation even at 9 wt % loading of SiO$_2$. The reinforcing and toughening effects depended largely on the dispersion of SiO$_2$ in PU matrix and the interfacial layer formed between the two phases. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Casting polyurethane elastomers (CPUEs) are crosslinked, segmented copolymers consisting of alternating hard and soft segments. From a morphological standpoint, they consist of crystalline or glassy hard domains of the segregated polyurethane (PU) so-called hard segments in an elastic matrix of the so-called soft segments.[1] The hard segment is composed of alternating diisocyanate and short chain extender molecules (i.e., diol or diamine), whereas the soft segment is formed from a linear, long-chain diol. The incorporation of low molecular weight crosslinker into PU structure would result in the formation of chemical crosslinks. Thus, the physical properties of PUs are predominantly the result not only of a two-phase morphology but also of the chemical crosslinker concentration.[2–4] PU nanocomposites filled with inorganic fillers have been widely studied. Zilg et al. reported that PU nanocomposites, containing synthetic fluoro-mica, exhibited enhanced tensile strength and elongation at break. Liang et al. prepared PU/MWCNT (multi-walled carbon nanotube) nanocomposites, whose modulus and tensile strength presented an ascend trend first and descend afterward with the content of MWCNT. Lee et al. prepared PU/silica nanocomposites. The nano-silica particles were well dispersed in PU matrix up to 3 wt %. Elongation at break of the nanocomposite film containing 1 wt % nano-silica was 3.5 times greater than that of the pure PU film.[5–7]

CPUEs have been widely used as rollers in printing, papermaking and food processing, and high mechanical property, low hardness, and especially solvent-resistant property are required for these applications. Bai et al. prepared PU/zeolite composite via pre-polymerization method. The results showed that the mechanical property of PU elastomer was enhanced obviously by filling zeolite. But the improvement of the solvent-resistant property was not obvious. Yang et al. studied the effect of different fillers on mechanical properties, heat-resistant, and solvent-resistant property of PU elastomer. The results also showed that the molecular sieve was an ideal filler to improve solvent-resistant property.[8,9] But few studies have been devoted to the system of PU/silica nanocomposite elastomers on solvent-resistant property.

Acicular silica is a new type of functional inorganic filler, which can increase hardness, tensile strength, impact strength, and improve thermal stability and dimensional stability of materials. With the same size, silica with large aspect ratio has better carry ability than granular fillers to enhance properties of composites. The properties of composites are also related to particle size and density of silanol groups on silica surface.[10,11]

In this work, casting PU elastomer filled with acicular SiO$_2$ were synthesized via *in situ* polymerization process, which was beneficial for dispersion of nanofillers in PU matrix. The interfacial bonding of the two phases can thus be improved. The structure and properties of the composite were investigated in terms of morphology, mechanical and solvent-resistant properties.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) mixture was purchased from Wanhua Polyurethane (Yantai, China) and used as received. Polyethylene adipate as polyols ($\overline{Mn}$ = 2000) was purchased from Huada Chemical Engineering (Yantai, China). Trimethylolpropane (TMP) was supplied by Bodi Chemical (Tianjin, China). Acicular silica with size of 10 μm and aspect ratio of 10:1 was provided by Harbin Mining (Liaoning, China).

Preparation of Materials

Synthesis of Casting PU/SiO$_2$ Composite Elastomer. The casting PU/SiO$_2$ composite elastomer was prepared via *in situ* polymerization and prepolymer process. The stoichiometric amount of the polyols (80 g) was dried under vacuum at 120°C for 2 h. Then 20.96 g of TDI (isocyanate index: 1.05) was added into this bulk by vigorously stirring at 80°C. Afterwards SiO$_2$ with varying dosage was added and mixed homogeneously. After the prepolymer was prepared, 3.08 g of TMP was added and the mixture was poured into a preheated mould and casting molded at 120°C. The product was conditioned for 1 week at room temperature before test.

Synthesis of SiO$_2$ Grafted with TDI (SiO$_2$-g-TDI). The mixture of SiO$_2$ and TDI were vigorously stirred at 80°C for 3 h, and then the mixture was poured into a preheated mould and reacted at 120°C, which process was the same with synthesis of the PU composites. The product was washed with tetrahydrofuran (THF) for several times, and dried under vacuum.

Measurements

FTIR Analysis. The interaction of SiO$_2$ and PU matrix was analyzed with a Nicolet-560 Fourier-transform infrared spectrometer (FTIR) (Madison, USA). The scanning rate was 20 min^{-1}.
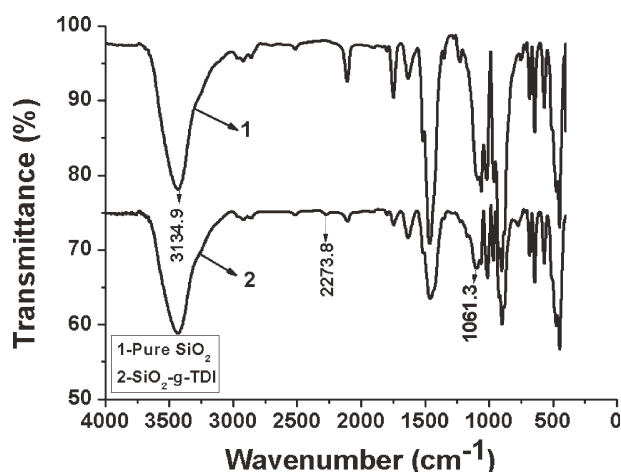

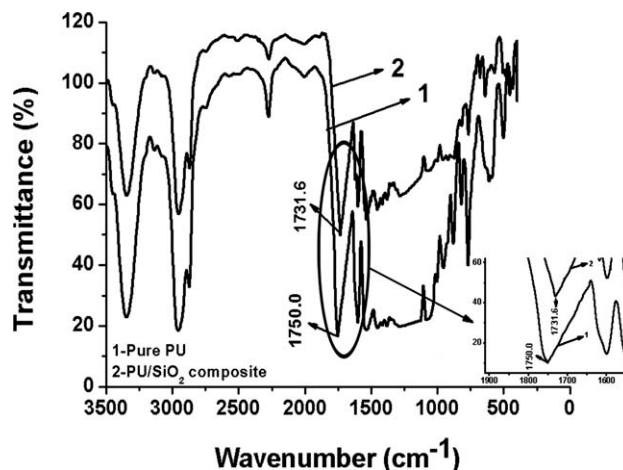**Figure 1.** FTIR of pure SiO$_2$ and SiO$_2$-*g*-TDI.

Figure 2. FTIR of pure PU and PU/SiO$_2$ composite.

Tensile Properties. The tensile properties of PU samples were measured with a 4302 material testing machine from Instron Co. (Gardena, USA) according to ISO 37:94. The tensile speed and temperature were 100 mm/min and 23°C, respectively.

Hardness. The hardness of the sample was measured with shore A method at 23°C on a XY-1 hardness tester from No.4 Chemical Machinery Company (Shanghai, China) according to standard ISO 7619:1986.

Solvent Resistance. According to the standard ISO 1817:2005, PU samples were cut into small pieces with the area of 25 × 25 × 2 mm^3 and immersed into various solvents (cyclohexanone, xylene) for 48 h. The temperature and relative humidity were 25°C and 50%, respectively.

Dynamical Mechanical Analysis. The normal dynamical mechanical test was performed on a TA Instrument Q800 Dynamical mechanical analysis (DMA) (New Castle, USA). The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of PU samples were measured with a tension mode at a heating rate
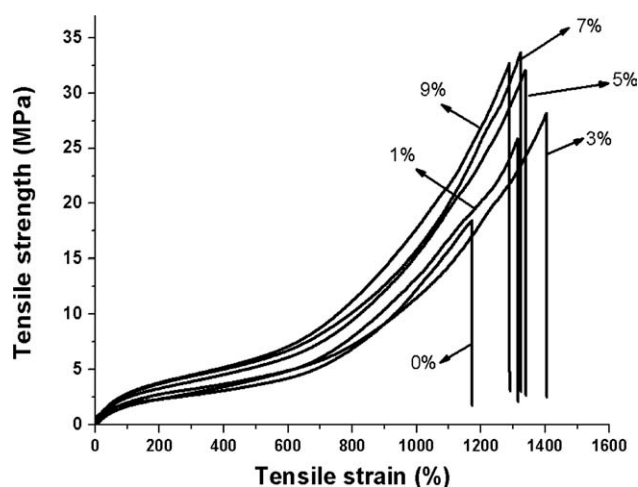

Figure 3. Stress–strain curves of PU/SiO$_2$ composite with varying SiO$_2$ content.
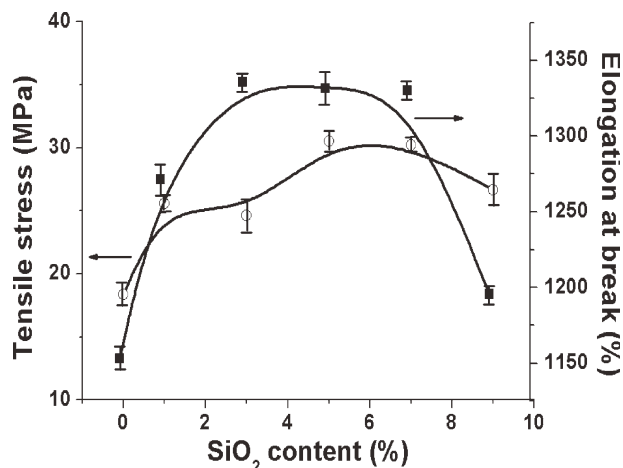
Figure 4. Mechanical properties of PU/SiO$_2$ composite with varying SiO$_2$ content.

Figure 5. Hardness of PU/SiO$_2$ composite with varying SiO$_2$ content.

of 3°C/min and a frequency of 1 Hz. The sample size was 20 × 4 × 2 mm^3.

Scanning Electron Microscopy Analysis. Cryogenically fractured in liquid nitrogen, the fracture surfaces of PU composites were sputter-coated with a thin gold layer to make samples electric conductive, avoiding charge accumulated, and then observed by a JEOL SM-5900LV (Osaka, Japan) scanning electron micros-
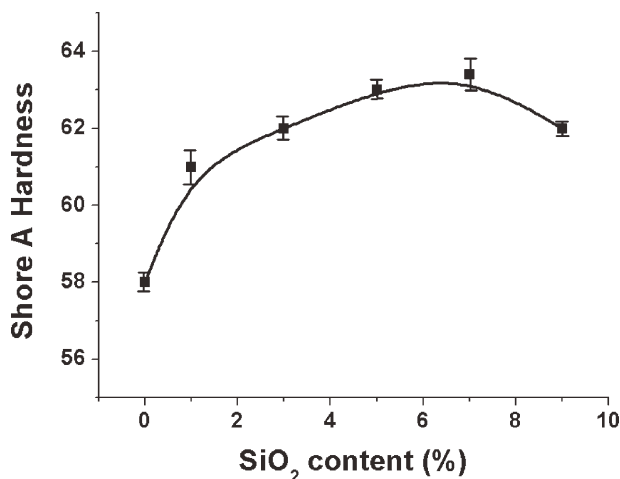
copy (SEM) instrument with an acceleration voltage of 20 kV. To study the reinforcing mechanism, the tensile-fractured surface of the composites was directly observed under the same condition.

RESULTS AND DISCUSSION

The FTIR absorption peak at 3134.9 cm^{-1} ascribed to silanol group on the surface of SiO$_2$ can be observed, as shown in Figure 1. To investigate the chemical interaction of SiO$_2$ and PU
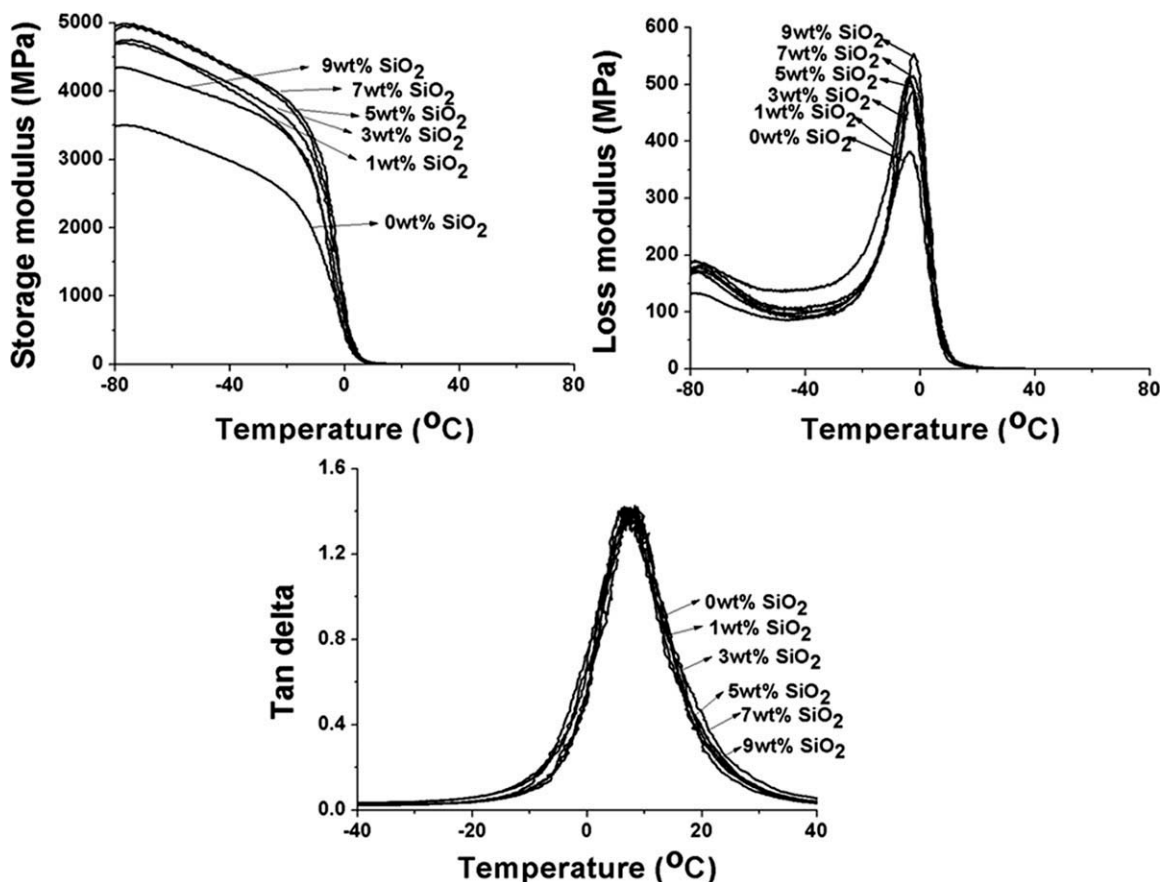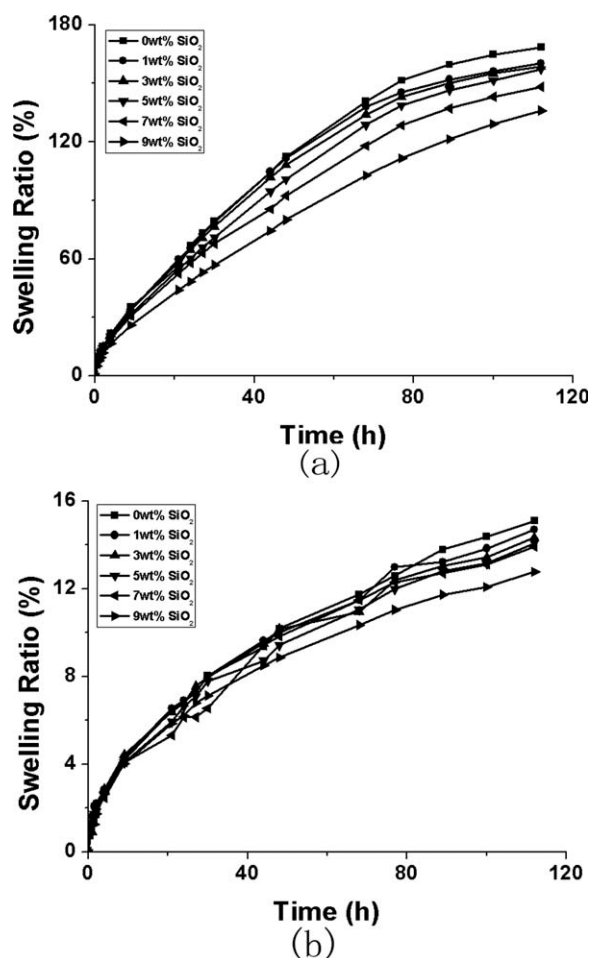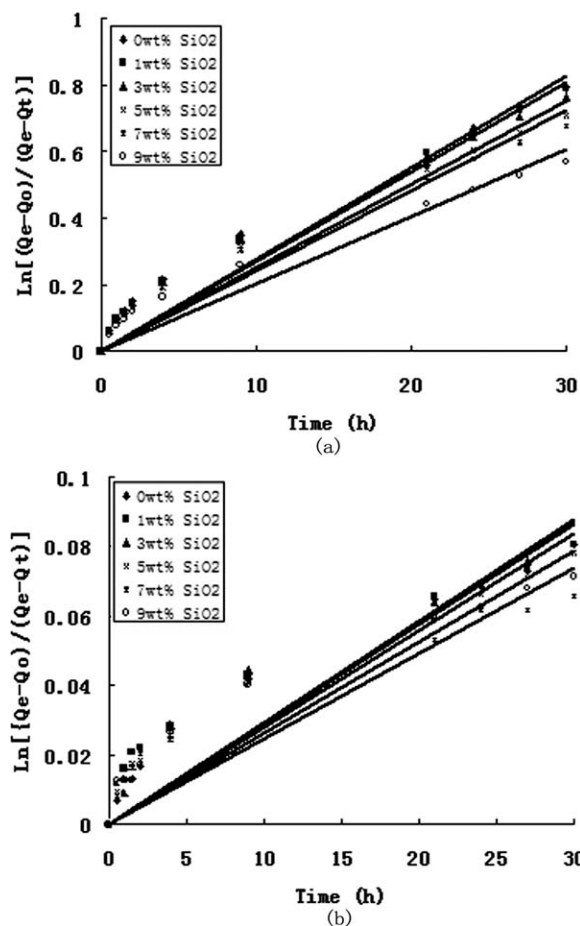

Figure 6. Dynamical property of PU/SiO$_2$ composite with varying SiO$_2$ content.

Table I. DMA Parameters of PU/SiO$_2$ Composite with Varying SiO$_2$ Content

SiO$_2$ content (wt %)	Initial storage modulus (MPa)	T_g (°C)	Tan δ
0	3479	7.34	1.31
1	4689	8.43	1.42
3	4700	7.89	1.39
5	4873	7.89	1.38
7	3419	6.25	1.39
9	3802	6.25	1.34

matrix, the reaction of SiO$_2$ with TDI was conducted. It can be seen from Figure 1, the peak at 2273.8 cm^{-1} was ascribed to C≡N groups on the molecule of TDI, and the peak at 1061.3 cm^{-1} was ascribed to C—O groups produced by the reaction of silanol group of SiO$_2$ with isocynate group of TDI. Therefore, TDI was evidenced to be grafted onto the surface of SiO$_2$.

As shown in Figure 2, the hydrogen bonding also emerged between silanol group of SiO$_2$ and urethane carbonyl groups of PU matrix, which was evidenced by the red shift of the peak of C=O groups of PU from 1750.0 to 1731.6 cm^{-1}.

Figure 7. Swelling ratios of PU/SiO$_2$ composite with varying SiO$_2$ content [(a) in cyclohexanone, (b) in xylene].

Figure 8. Swelling kinetics of PU/SiO$_2$ composite with varying SiO$_2$ content [(a) in cyclohexanone, (b) in xylene].

Mechanical Property of PU/SiO$_2$ Composite Elastomer

Figure 3 showed the tensile stress–strain curves of PU/SiO$_2$ composite with varying SiO$_2$ content. It can be seen that for all PU samples, the stress increased with strain, and exhibited strain-harden characteristic. With increasing SiO$_2$ content, such behavior became more remarkable, indicating of the reinforcing and toughening effect of SiO$_2$ on PU matrix at low SiO$_2$ content.

Figure 4 showed the mechanical properties of PU/SiO$_2$ composite as a function of SiO$_2$ content. It can be seen that the tensile strength and elongation at break first increased and then decreased with SiO$_2$ content, and the mechanical properties reached maximum in the range of 5–7 wt % SiO$_2$. The strong chemical interaction of SiO$_2$ and PU matrix resulted in the enhancement of the mechanical properties. On the other hand, silica with large aspect ratio showed better reinforcing effect than granular fillers.[11] However, high content of SiO$_2$ led to poor dispersion and agglomerization of SiO$_2$ in PU matrix, resulting in stress concentration and decline of mechanical properties.

The shore A hardness of PU/SiO$_2$ composite elastomer as a function of SiO$_2$ content was shown in Figure 5. The hardness of PU samples had an ascending trend with increasing SiO$_2$ content, and slight decrease occurred at 9 wt % SiO$_2$. All

Table II. Swelling Kinetics of PU/SiO$_2$ Composite with Varying SiO$_2$ Content

SiO$_2$ content (wt %)	K		Swelling ratio (%)	
	Cyclohexanone	Xylene	Cyclohexanone	Xylene
0	0.0277	0.0029	168	15.11
1	0.0276	0.0029	160	14.71
3	0.0270	0.0029	158	14.34
5	0.0252	0.0028	157	14.08
7	0.0241	0.0025	148	13.93
9	0.0203	0.0026	136	12.77

samples of PU/SiO$_2$ composite elastomer had a reasonable low hardness, which was in the range of shore A 58–65, and required when used as printing roller.

Dynamic Mechanical Property of PU/SiO$_2$ Composite Elastomer

Dynamical mechanical analysis provides information on the glass transition and damping properties of a polymer. Storage modulus (E') reflected flexibility of flexible and stick material, a sign of stiffness; loss modulus (E'') reflected stickiness of flexible and stick material; tan δ is the ratio of E' to E'', a sign of dampening performance of materials.

The dynamical mechanical properties of PU/SiO$_2$ composite elastomer with varying SiO$_2$ content were shown in Figure 6. It can be seen that the storage modulus increased with SiO$_2$ content in the range of 0–5 wt %, and above 5 wt % SiO$_2$, the storage modulus decreased. All the samples exhibited only one loss peak corresponding to the glass transition temperature (T_g) of soft-segment of PU elastomer. The loss peaks changed insignificantly with SiO$_2$ content, and addition of SiO$_2$ had little influ-

Solvent-Resistant Property of PU/SiO$_2$ Composite Elastomer

The time-dependent solvent-resistant property of PU composite elastomer with varying SiO$_2$ content in cyclohexanone and xylene at room temperature and 50% RH was plotted in Figure 7. It can be seen that in the initial swelling stage, all samples of PU elastomer absorbed solvent rapidly, and the swelling ratio increased dramatically with time. The solvent absorption rate and equilibrium swelling ratio were significantly reduced by increasing SiO$_2$ content, and the equilibrium swelling ratio of PU elastomer in cyclohexanone and xylene decreased from 168% to 15.1% for pure PU to 136% to 12.7% for PU in presence of 9 wt % SiO$_2$, respectively, indicating that addition of SiO$_2$ facilitated the enhancement of solvent-resistant property of PU elastomer.

Swelling kinetics of PU/SiO$_2$ composite elastomer was analyzed by assuming that the swelling process met the first order kinetic equation[12]:

$$dQ_t/dt = k(Q_e - Q_t) \tag{1}$$

where t is swelling time; Q_t, swelling ratio at time t; Q_e, the equilibrium swelling ratio, and dQ_t/dt, swelling rate; and k, the swelling rate constant. The swelling kinetics equation can be obtained by integral of eq. (1):

$$Q_t = Q_e - (Q_e - Q_0)/e^{kt} \tag{2}$$

Another form of the equation can be written as:

$$\ln(Q_e - Q_t) = -kt + \ln(Q_e - Q_0) \tag{3}$$

The plot of $\ln[(Q_e - Q_t)/(Q_e - Q_0)]$ of PU/SiO$_2$ composite elastomer versus time t in cyclohexanone and xylene was shown in Figure 8, respectively, which exhibited good linear relationship. The slope represented the swelling rate constant k. As listed in Table II, it can be seen that with increase of SiO$_2$
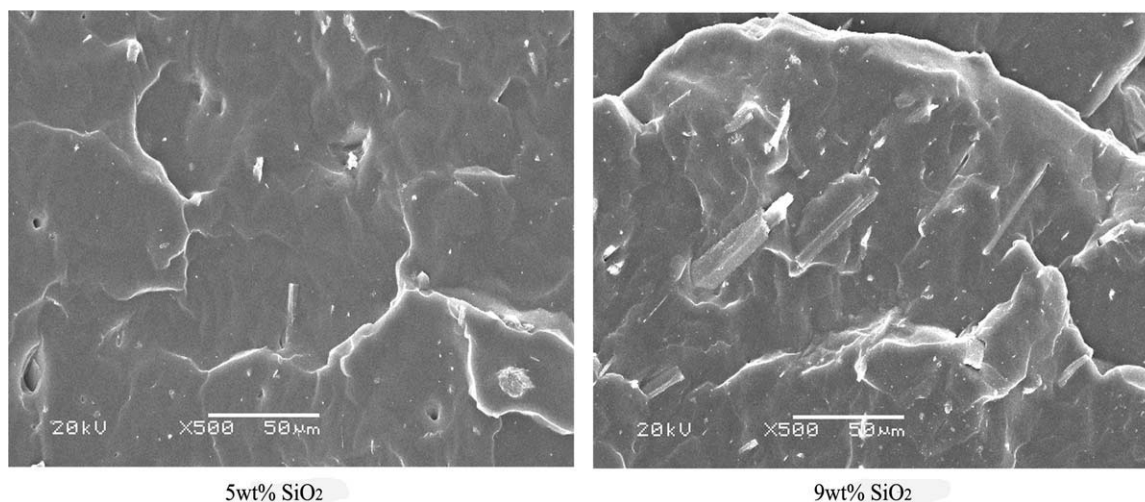
Figure 9. SEM of PU/SiO$_2$ composite with varying SiO$_2$ content.
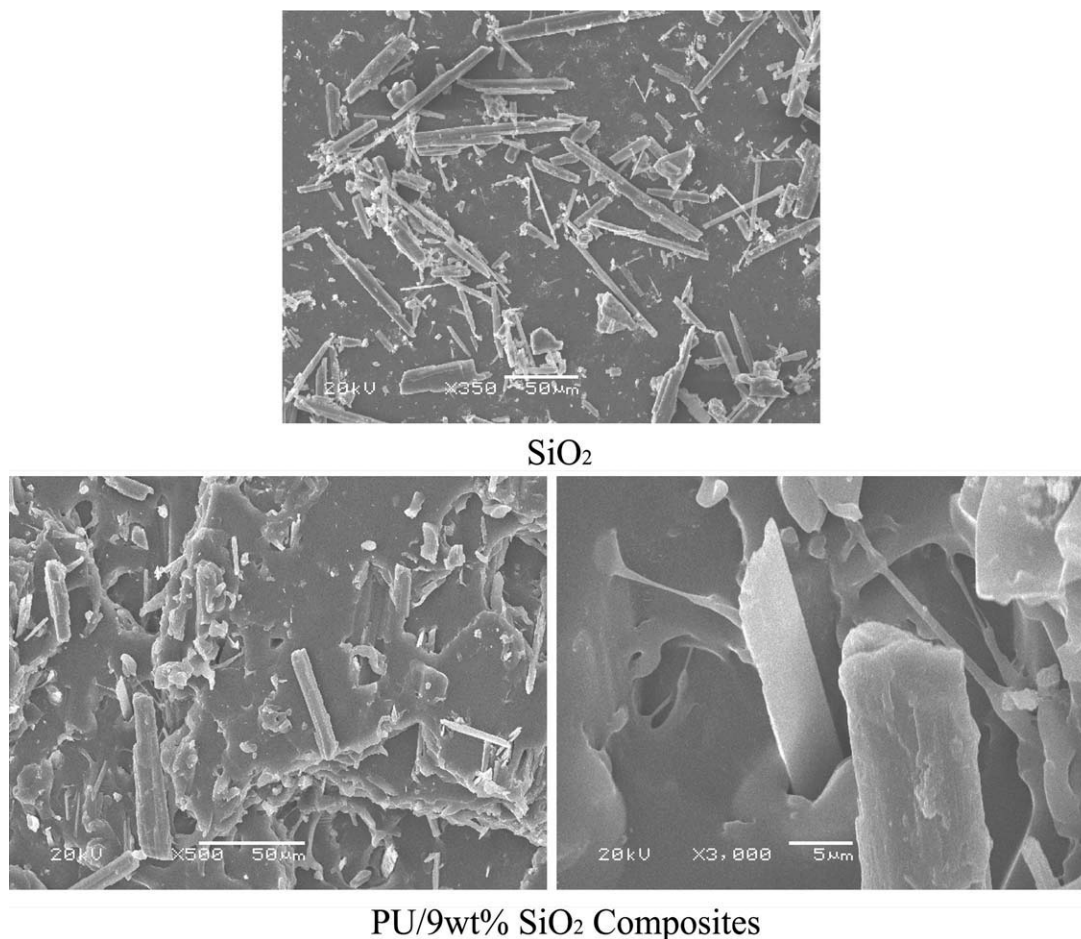
5wt% SiO$_2$ 　 9wt% SiO$_2$

Figure 10. SEM of the tensile-fractured surface of PU/SiO$_2$ composite.

content, the swelling rate constant k of PU elastomer decreased, indicating that addition of SiO$_2$ enhanced the solvent-resistant property of PU elastomer in cyclohexanone and xylene.

Morphology of PU/SiO$_2$ Composite Elastomer

SEM images of cryogenically fractured surface of PU/SiO$_2$ composite elastomer with varying SiO$_2$ content were shown in Figure 9. It was found that acicular SiO$_2$ dispersed uniformly in PU matrix and there was no obvious aggregation even at 9 wt % loading of SiO$_2$. The boundary of PU/SiO$_2$ was diffused, indicating of the formation of the strong interfacial bonding between the two phases.

To further characterize the internal structure of composites, SEM observation of tensile fracture surfaces of PU/9 wt % SiO$_2$ composite elastomer was shown in Figure 10. The black area was PU matrix, and the well-dispersed bright dots and sticks were the ends of SiO$_2$ and SiO$_2$ pulled out from the matrix, respectively.

It can be seen that under shear stress, some of SiO$_2$ were pulled-out. The surface of some of them was still covered with PU resin. As shown in Figure 10, the average diameter of the pulled-out SiO$_2$ was substantially larger than that of pure SiO$_2$, which was 10–15 μm, 7 μm, respectively, indicating of the for-

mation of skin-core structure. Moreover, the resin in the interfacial layer was torn into a continuous tape, which can absorb energy under load. Therefore, the failure mode of the composite was the deformation and destruction of PU matrix around the
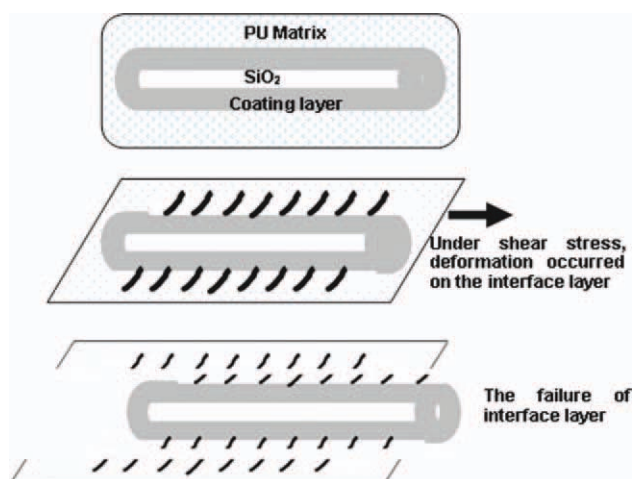

Figure 11. Failure mode of PU/SiO$_2$ composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interfacial layer, and the inorganic particle can hinder crack propagation and passivation, and terminate crack eventually, as shown in Figure 11.

On the other hand, the reinforcement mechanism could be summed up as load transferring. When adding SiO_2, stress can be transmitted to SiO_2 through the PU matrix, because the modulus of SiO_2 was far higher than PU elastomer, and thus it showed good reinforcing effect. The reinforcing and toughening effect depended largely on the dispersion of the SiO_2 in PU matrix and the interfacial layer formed between the two phases.

CONCLUSIONS

A series of casting PU/SiO_2 composite elastomers were prepared via *in situ* polymerization and prepolymer process. The composites were studied in terms of mechanical and solvent-resistant property for its application as printing rollers. The result showed that with increasing SiO_2 content, the tensile strength and hardness of PU/SiO_2 composites increased, whereas the elongation at break had the same trend. For the sample with 5 wt % of SiO_2 content, the tensile strength can reach 30.5 MPa and the elongation at break kept as high as 1331.7%. The storage modulus increased with SiO_2 content in the range of 0–5 wt %, and above 5 wt % SiO_2, the storage modulus decreased and all samples exhibited only one loss peak corresponding to the glass transition temperature of the soft-segment, which shifted insignificantly with increasing SiO_2 content. The equilibrium swelling ratio and swelling rate constant k in cyclohexanone and xylene were significantly reduced by increasing SiO_2 content, indicating that more content of stiff inorganic particles facilitated the enhancement of solvent-resistant property of PU/SiO_2 composites. The acicular SiO_2 dispersed uniformly in PU matrix and there was no obvious aggregation even at 9 wt % loading of SiO_2. The interfacial bonding of the two phases was strong; and SiO_2 presented obvious reinforcing and toughening effect on PU matrix.

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