

# Use of precipitated silica with silanol groups as an inorganic chain extender in polyurethane



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## ABSTRACT

In this study, novel polyurethane/silica (PU/SiO<sub>2</sub>) hybrid materials, prepared without an external crosslinking agent, were developed via the chemical reaction between urethane groups of PU prepolymer and hydroxyl groups at the surfaces of silica. The added inorganic filler-silica thus played the dual roles not only inorganic chain extender but also reinforcing agent in the preparation of the hybrid. Two different blending methods, were compared with respect to the mechanical properties of the PU/SiO<sub>2</sub> hybrid materials: stirring mixing and three-roller shear mixing. The hybridization mechanism was confirmed using Fourier-transform infrared spectroscopy (FT-IR), solid-state <sup>29</sup>Si NMR spectroscopy and X-ray diffraction (XRD). The dispersion of silica particles in the PU matrix was investigated by scanning electron microscopy (SEM). Because of the shear effect of three-roller shear process, the size of the silica aggregates tended to be more uniform. The tensile strength and elongation at break of the PU/SiO<sub>2</sub> hybrid were 51 MPa and 590%, respectively, which represent increases of fourfold and 39% compared to those of neat PU. The thermogravimetric analysis (TGA) results for the PU/SiO<sub>2</sub> hybrids indicated greater thermal stabilities and lower decomposition rates after hybridization. This work contributes new insights into the preparation of high-performance PU/SiO<sub>2</sub> hybrids.

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## 1. Introduction

Since the early 1970s [1] polymer/inorganic hybrid materials have been attracting increasing attention due to the possibilities to increase the performances of polymers with acceptable sacrifices in other properties and cost. In recent 10 years, extensive research has been focused on polyurethane-based hybrid materials [2–6], including polyurethane/modified montmorillonite nanocomposites [7–9], polyurethane hybrid materials using POSS [10], and PU/SiO<sub>2</sub> organic/inorganic hybrid materials [11–17]. To prepare polyurethane/SiO<sub>2</sub> organic/inorganic hybrid materials, the sol–gel method [18–21], in situ polymerization [22–24] and mechanical blending method [25] have been extensively introduced. The sol–gel method has many advantages, such as mild reaction conditions and a tendency to produce small particle with a uniform distribution. Therefore, the sol–gel method has become the primary method to prepare PU/SiO<sub>2</sub> organic/inorganic hybrid materials. However, the precursor in the sol–gel method is normally orthosilicate alkyl ester, which is both expensive and toxic. Furthermore, the evaporation of the solvent and small molecules during the drying process may create shrinkage stress in the material, which can result in embrittlement; in addition,

the preparation of a large-scale or thick hybrid material is difficult [26]. The in situ polymerization and mechanical blending preparation of polyurethane/SiO<sub>2</sub> organic/inorganic hybrid materials usually require modification of the SiO<sub>2</sub> surface via, for example, organic processing to increase the adhesive force between the silica particles and the PU matrix [27–29]. Thus, the process is more complicated and the material cost is increased. A simple method of preparing polyurethane/SiO<sub>2</sub> organic/inorganic hybrid materials with excellent comprehensive performance would reduce the costs associated with producing these materials and expand their range of application.

In this study, a new approach to prepare polyurethane/SiO<sub>2</sub> organic/inorganic hybrid materials without an external chain extender, organic tin catalysts or the surface treatment of silica is presented. The hydroxyl groups on the silica surface react with the NCO groups in the polyurethane prepolymer to yield high-performance polyurethane organic/inorganic hybrid materials. The hybridization mechanism and structure of the hybrid material were investigated using Fourier-transform infrared spectroscopy (FT-IR), NMR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Two mixing methods—stirring mixing and three-roller shear mixing—were used to blend the silica particles in the pre-PU matrix. The morphological structures and mechanical properties of PU/SiO<sub>2</sub> hybrids prepared using these two different methods were compared, and their thermal properties were investigated using thermogravimetric analysis (TGA).

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## 2. Experimental

### 2.1. Materials

Toluene diisocyanate (TDI; the isomer mixture ratio between 2,4- and 2,6-TDI was 80:20) was purchased from BASF Corporation and used without additional purification. Polytetramethylene ether glycol (PTMEG) (1000 g/mol) was acquired from Mitsubishi and dried at 80 °C in a vacuum oven for 12 h before use. Precipitated silica ( $\text{SiO}_2$ ) (average particle diameter: 999.5 nm) was purchased from Wanzai Chemical Company and dried at 60 °C in a vacuum oven for 24 h before use.

### 2.2. Preparation of polyurethane prepolymer and PU/SiO<sub>2</sub> hybrid material

According to the rapid reaction principle of the NCO group and OH group, the silanol groups on the silica were allowed to react with the terminal isocyanate groups of polyurethane prepolymer (pre-PU) to form the hybrid materials. Thus, the PU chains were chemically bonded to the silica particles to increase the crosslink density and reinforce the thermal and mechanical properties of the hybrid materials. The reaction is shown in Fig. 1.

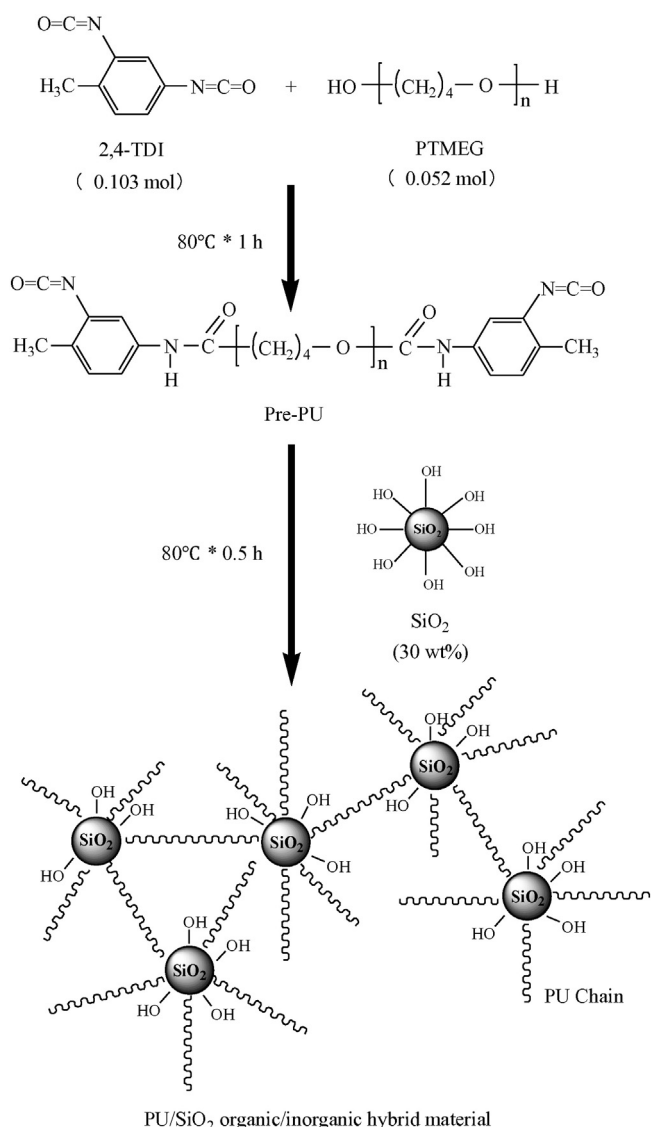


Fig. 1. Synthesis of polyurethane prepolymer and PU/SiO<sub>2</sub> hybrid material.

A typical procedure to prepare polyurethane prepolymer is described as follows. PTMEG was dehydrated under vacuum drying at 80 °C for 12 h before using. Then, 52 g (0.052 mol) of PTMEG was added to a 250 ml three-necked flask, which was equipped with a dropping funnel and a condenser, and stirred at 80 °C for 30 min. Subsequently, 18 g (0.103 mol) of TDI was added to the flask to react with PTMEG. The reaction mixture was subsequently stirred at 80 °C for 1 h to obtain the pre-PU. An appropriate organic extender (1,4-butanediol) was used to crosslink the pre-PU to prepare neat PU as referential samples.

The procedure to prepare PU/SiO<sub>2</sub> hybrid materials with a 30 wt.% SiO<sub>2</sub> loading is described as follows. First, 70 g of pre-PU, which was prepared according to the aforementioned processes, was loaded into a 500 ml three-necked flask. Then, 30 g of SiO<sub>2</sub> was added to the flask and stirred with a speed of 120 r/min at 80 °C for 0.5 h to obtain a mixture of pre-PU and SiO<sub>2</sub>.

### 2.3. Preparation of PU/SiO<sub>2</sub> hybrid material using different methods

Fig. 2 illustrates the different methods to prepare PU/SiO<sub>2</sub> hybrid materials. Method A is a mechanical-stirring mixing method in a three-necked flask, as shown in Fig. 2(a). The mixture of pre-PU and SiO<sub>2</sub> was added to a pre-heated mold and solidified for 30 min at 120 °C. The pre-cured samples were placed in oven at 100 °C for 10 h to finalize the post-curing process.

In method B, three-roller shear mixing was used to improve the dispersion of SiO<sub>2</sub> in the PU mixture, as shown in Fig. 2(b). The PU/SiO<sub>2</sub> mixture that was prepared using method A was mixed with a three-roller mill and exhibited better SiO<sub>2</sub> dispersion. The mixture was then pre-heated and post-cured using procedures identical to those described for method A.

### 2.4. Characterization

FT-IR spectra were collected using a Nicolet Fourier-transform infrared spectrophotometer (Thermo Nicolet Corporation, Nicoletis10, USA). The solid-state <sup>29</sup>Si NMR spectral analyses of silica and the hybrid material were performed using a Bruker Avance AV 400 spectrometer (Bruker Germany). The X-ray diffraction (XRD) measurements were conducted at ambient temperature using a Rigaku Dmax-91 diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a Cu-K $\alpha$  radiation source ( $\lambda = 1.542 \text{ \AA}$ ) operated at 30 kV and 30 mA. The samples were measured from 5° to 80° with a resolution of 0.02°. SEM observations were conducted using an FEI Nano SEM 430 system (FEI, USA) to investigate the structure and morphology of the silica particles and the ruptured surfaces of the PU, PU/SiO<sub>2</sub> hybrid materials. The curing characteristics of the hybrid materials were determined using a U-CAN UR-2030 vulcameter (Taipei, Taiwan). The tensile testing properties, which include the tensile strength and elongation at break, were investigated at 25 °C with compliance to ASTM D421[A] on a U-CAN UT-2060 (Taipei, Taiwan) instrument with a strain rate of 500 mm/s. The tear strength was measured according to ASTM D624[B] specifications using a U-CAN UT-2060 instrument. TGA was conducted on a Q5000 TGA instrument (TA Instrument, USA) over a temperature range from 30 to 600 °C with a heating rate of 10 °C/min and N<sub>2</sub> as the purge gas.

## 3. Results and discussion

### 3.1. Structural characterization of PU/SiO<sub>2</sub> hybrid materials

#### 3.1.1. FT-IR analysis

The FT-IR spectra of silica (a), pre-PU (b) and PU/SiO<sub>2</sub>-Method B (c) are shown in Fig. 3. The spectrum of SiO<sub>2</sub> exhibits bands at 3446 cm<sup>-1</sup> and 960 cm<sup>-1</sup>, which should be attributed to the stretching vibrations of the OH groups on the surface of the silica particles [30]. In the spectrum of pre-PU, the absorption peak at 2260 cm<sup>-1</sup> corresponds

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