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Synthesis and characterizations of waterborne polyurethane–silica hybrids using sol–gel process

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Abstract

Using a sol–gel process nanometer-scale silicas were incorporated into waterborne polyurethanes (PUs) which were synthesized from isophoronediisocyanate (IPDI), poly(tetramethyleneglycol) (PTMG), dimethylolpropionic acid (DMPA), triethylamine (TEA), diethylenetriamine (DETA) and 3-aminopropyltriethoxysilane as coupling agent. Thermal, mechanical, and dynamic mechanical properties of the hybrid composite have been studied. ^{29}Si-NMR spectra gave evidence of condensation reaction between silica and silanes encaping the PU prepolymers, whereas transmission electron microscopy (TEM) showed the high connectivity of hybrid composites. It was found that greater thermal and mechanical properties of waterborne PU/silica hybrid composite were obtained when chemical networks were formed between PU and silica.

Keywords: Polyurethanes; Silicas; Hybrids; Crosslinking

1. Introduction

In recent years, there have been intensive studies on the production of composite materials having hybrid or nanostructure in the fields of metals, ceramics, and polymers. The synergistic combination of organic polymers-inorganic silica via a sol–gel process has recently attracted great attention in the field of material science because it has the potential for the development of new materials with designed properties, by structural manipulation at the molecular level [1–7].

Inorganic silica is brittle but shows a number of beneficial properties such as surface hardness, transparency, high physical properties, and heat resistance. In contrast, organic polymers show good flexibility, low density, ease processing but are thermally unstable. The hybrid can be formed by simply blending or by synthesis of a dedicated co-polymer. In materials formed by simple blending there is little crosslinking between the organic and inorganic polymers with the result of phase separation which is usually detrimental to one or more of the properties of the coating. In copolymers the inorganic segments are chemically attached to the organic segments, but the degree of crosslinking is still low. It is now generally accepted that the preferred hybrid structure is one in which there is intimate crosslinkings between the organic and inorganic materials [8]. Therefore, considering the synergistic effect of two different materials, hybrid techniques via sol–gel process have been proposed [9–11].

The use of the sol–gel process to prepare highly intermingled inorganic-organic hybrid polymer networks using coupling agents 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 [12]. To obtain stronger interaction between the organic and inorganic components, functionalized silanes are used as coupling agents. These can react with functional groups already present on the polymer molecules and also can react with silanol groups on the silica surface (Aerosil 200).

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties [13,14]. Because a wide range of monomeric materials are now commercially available and tailor-made properties can be obtained from well-designed combination of monomeric materials, PUs can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fiber, foams, and

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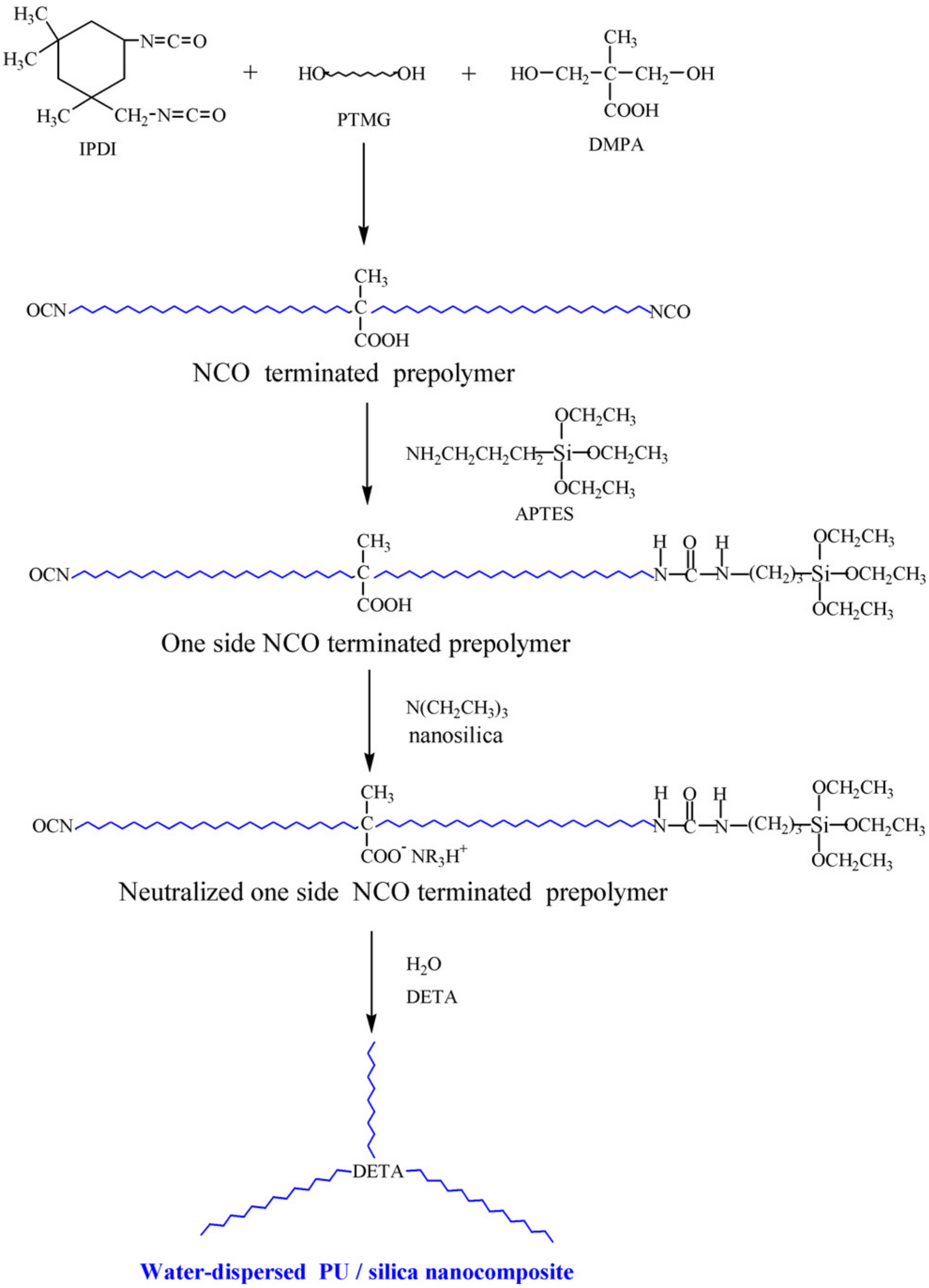
thermoplastic elastomers. Also, waterborne PUs have received increased attention recently because they are non-toxic, non-flammble and do not pollute the air [15–17]. Some inferior properties of waterborne PUs such as low mechanical strength and water resistance can be improved by hybridizing them with other materials [17].

In this study, we report preparation of water dispersible PUs-based hybrid composites through the sol–gel process. This approach assumes both homogeneous dispersion of silica nanoparticles within a continuous polymer matrix and advantage of the autocatalytic effect of basic groups of a polyurethane (TEA, DETA) in the polycondensation reaction.

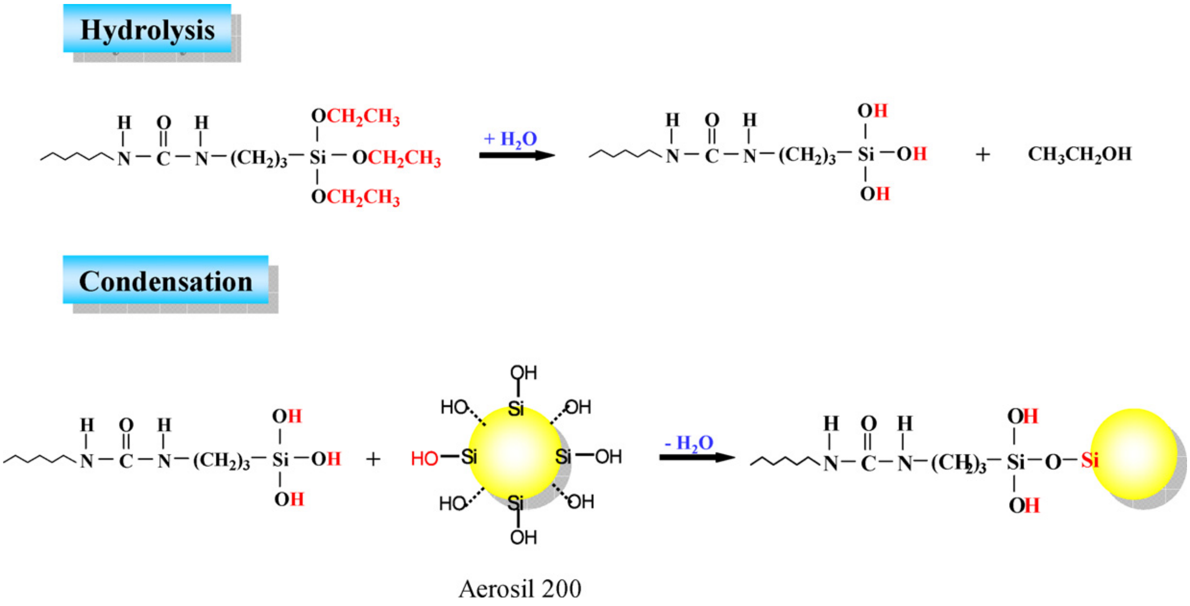
2. Experimental

2.1. Materials

Poly(tetramethylene glycol) (PTMG; 1000 g/mol; Korea PTG) was dried and degassed at 80 °C under vacuum for 3 h. Dimethylol propionic acid (DMPA; Aldrich) was dried at 50 °C for 48 h in vacuum oven. Isophorone diisocyanate (IPDI; Aldrich) and dibutyltin dilaurate (DBT; Aldrich) were used as received. Diethylene triamine (DETA; Junsei Chemical) and triethylamine (TEA; Fluka) were dried over 4 Å molecular sieve before use. Nano-size hydrophilic silica (Aerosil 200) with



Scheme 1. Overall reaction scheme to prepare waterborne PU/silica hybrid composites.



Scheme 2. The scheme for the sol–gel process of waterborne PU/silica (Aerosil 200) hybrid composites.

average particle size of 12 nm and nano-size hydrophobic silica (Aerosil R812) with average particle size of 8 nm were obtained from Degussa-Hüls. 3-Aminopropyltriethoxysilane (APTES; Aldrich) was used as a coupling agent. Silcones, silicates and silanes are commonly blended with organic resins to prepare coatings with improved weathering and thermal resistance [18].

2.2. Preparation of polyurethane/hybrid composite

A 500 ml round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube was used as reactor. The reaction was carried out in a constant temperature oil bath.

The overall reaction scheme is shown in Scheme 1. PTMG, IPDI, and DMPA (4 wt.% based on PUs) were mixed and reacted in the presence of DBTDL (0.03 phr based on the total solid) for 2 h at 80 °C to obtain NCO-terminated prepolymer of number average molecular weight (M_n) 3000 calculated by feed composition. Subsequently to cap one terminal of NCO group of prepolymer, 3-aminopropyltriethoxysilane as a coupling agent was added and reacted for another 2 h at 50 °C. After cooling the reaction mixture to room temperature, TEA and nanosilicas were fed into the reactor and mixed thoroughly for 3 h to neutralize DMPA unit and to disperse nano-sized silicas in PUs.

An aqueous dispersion of NCO-terminated prepolymer was obtained by adding water (30 °C) to the mixture. Since the water addition rate is a critical parameter to obtain a stable emulsion, water was fed for 20 min with a tubing pump at a constant flow rate. The sol–gel process is occurred at this step. APTES 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 (Aerosil 200) to form siloxane. The Si atom in APTES is tri-functional in terms of reactive ethoxy groups and is therefore able to form a three-dimensional chemical bondings between PU and nanosilica (Aerosil 200). The scheme for the sol–gel process of PU and nanosilica (Aerosil 200) is summarized in Scheme 2.

DETA dissolved in water (3 wt.%) was then fed to the emulsion at 50 °C and chain extension with DETA was carried out for 1 h. The resulting product was a PU emulsion with a solid content of about 30%.

The recipes to prepare of PU/nanosilica composites are shown in Table 1.

2.3. Measurement

A Fourier transform infrared transmission spectrophotometer (The Satellite FTIR Spectrometer, Mattson Instruments) was used to verify the incorporation between NCO and APTES or DETA. Samples for infrared analysis were prepared by drying emulsion directly on KBr pellet. IR spectra were recorded to detect the absorption peaks that are characteristic of the resins during synthetic procedures. Part of the reacting mixture was taken every 0.5 h for IR analysis.

^{29}Si cross-polarization magic-angle-spining (CP/MAS) NMR spectra were recorded using a 7 mm rotor probe on a Bruker Avance 300.

Number average diameter of polyurethane emulsion was measured by light scattering (Autosizer, Malvern II C), where a He–Ne type laser with wavelength 633 nm was used. The sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion.

TEM (Transmission Electron Microscopy) was performed on a Hitachi-7600 operating at 120 kV. For viewing morphology, film was floated off from the mica substrates onto deionized water and collected on TEM grids.

Films were cast from emulsion on a Teflon plate at 60 °C for 24 h. The remaining moisture was removed at 30 °C under vacuum for the next 2 days.

Table 1
Recipe for the preparation of waterborne PU/silica hybrid composites

Designation	Feed												
	Soft segment		Hard segment								Neutralizer		Nanosilica; Aerosil 200 (Aerosil R812) (Phr)
	PTMG		IPDI		Aminosilane		DMPA		DETA		TEA		
	mol	wt.%	mol	wt.%	mol	wt.%	mol	wt.%	mol	wt.%	mol	wt.%	
A200-0 (A812-0)	0.0294	59.5	0.0588	26.1	0.0147	6.5	0.0147	3.9	0.0049	1.0	0.0147	3.0	0
A200-2 (A812-2)													2
A200-5 (A812-5)													5
A200-10 (A812-10)													10

Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometry Scientific DMTA MK III), using a bending mode at a heating rate of 4 °C/min and 10 Hz.

Tensile test was done using a Tinius Olsen Series 1000. Micro-tensile specimens of 25 mm (length) × 5 mm (width) × 1 mm (thickness) were used. The specimens were elongated at 500 mm/min.

Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyzer (TA Instrument). 5 mg of each sample in an alumina crucible was used with a heating rate of 20 °C/min under N2.

Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75.

Transparency was measured with an UV–vis spectrophotometer (Hitachi U-2010) using a film with 0.2 mm thickness.

Water swell was measured by emerging a film in water. The water swell (%) as a function of immersion time was calculated by the following equation, where W_o is the original film weight and W is the film weight after water absorption.

$$\%\ \text{Swell} = \frac{W - W_o}{W_o} \times 100$$

3. Results and discussion

3.1. FTIR spectroscopy

The absorption peak of the NCO group (2270 cm^{-1}) of PU prepolymers decreases during the capping reactions of NCO groups with APTES on one terminal, and eventually disappears upon coupling by DETA. The results indicate that NCO groups of the PU prepolymer have completely been reacted with the amine groups in APTES and DETA as shown in Fig. 1.

3.2. ^{29}Si CP/MAS NMR spectroscopy

Three peaks are evident in the ^{29}Si NMR spectra (Fig. 2), at approximately −58, −66 and −93 to −112 ppm, respectively. The peak at −58 ppm is assigned to P^2 and the one at −66 to P^3 species [19] i.e., they represent silicon atoms with two and three siloxane linkages, respectively. Also, the peak at around −93 to −112 ppm is for nanosilica (Aerosil 200 or Aerosil R812). There is no evidence of any further peaks associated with P^1 (−49 ppm) or P^0 (−40 ppm) species indicating that condensation reactions have proceeded rapidly and almost completely. Because the APTES monomer has three ethoxy groups it can, in principle, form 100% P^3 species when it is fully condensed. TEA and DETA in PU structure are basic in nature and the increase in pH on their addition would be expected to accelerate the condensation reactions of the silanol groups.

3.3. Emulsion particle size and morphology

Fig. 3 shows that particle size of the emulsion increases with increase of nanosilica content. This is primarily due to the inclusion of inorganic filler in PU particle implying that the silicas are effectively encapsulated by the PUs. Due to the hydrophobic

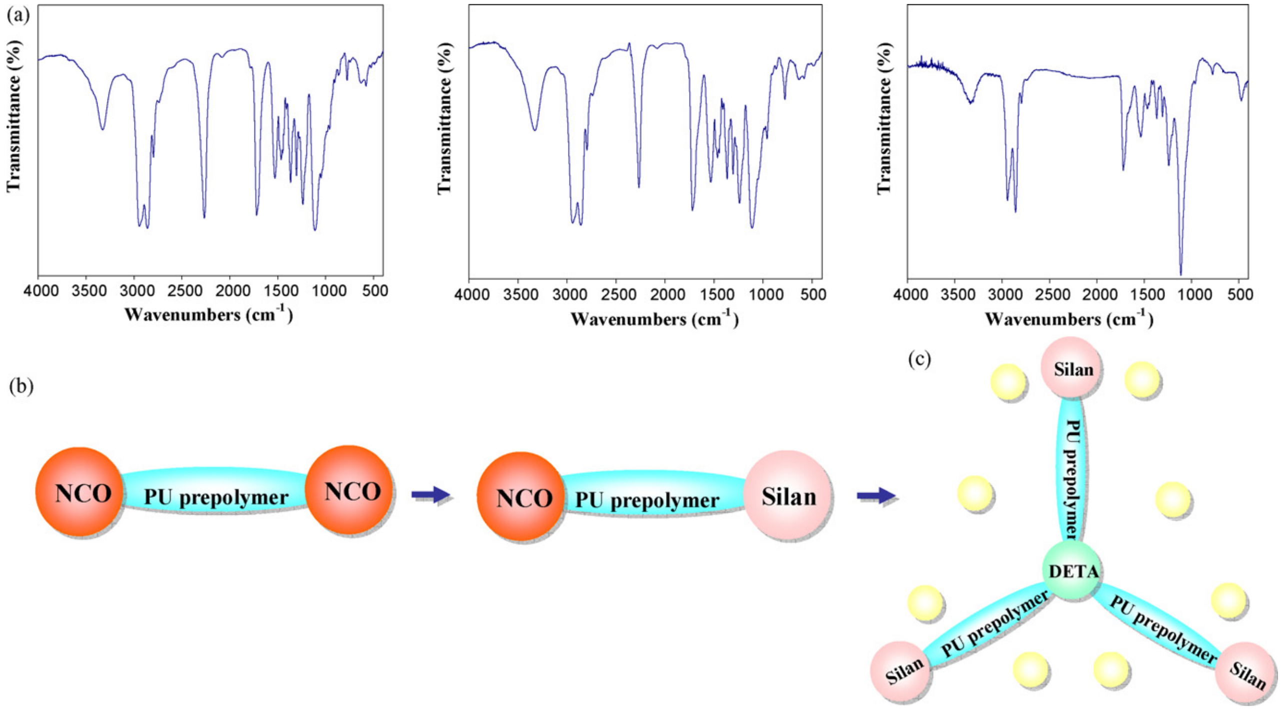


Fig. 1. FTIR spectra of PU (a) before and (b) capping with APTES, and (c) capping with DETA.

nature of nanosilica (Aerosil R812), silicas should form the core of particles and the particles are stabilized by the ionic groups of PUs forming the shell of the composite particles. As expected particle size of the emulsion increases more with addition and increase of hydrophilic nanosilica (Aerosil 200) as compared with hydrophobic one due probably to the increased swell of water.

Fig. 4 shows the transmission electron micrograph of PU/silica hybrid composites. It is seen that silicas (dark spheres), regardless of their types are well dispersed in PU matrix.

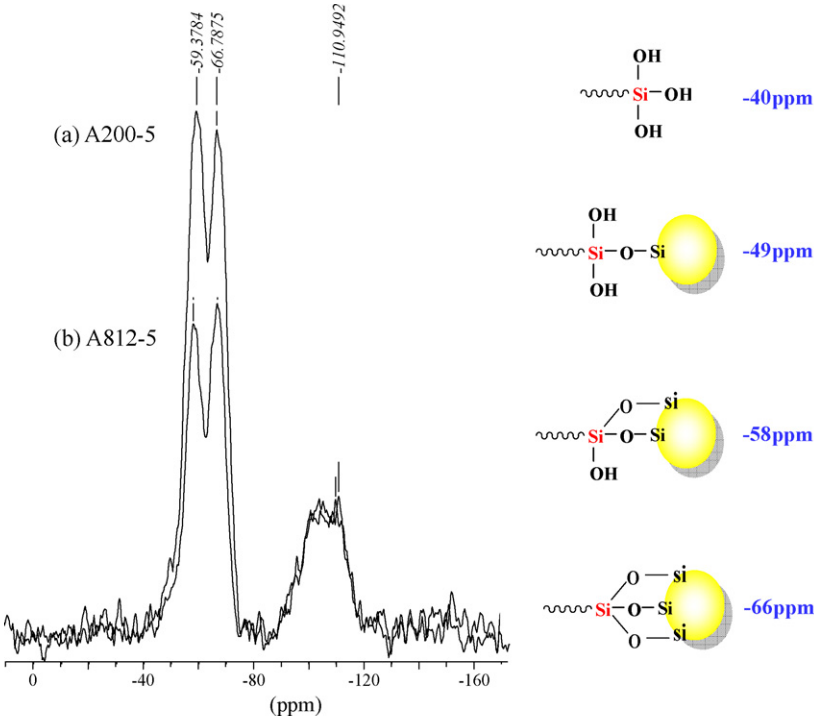


Fig. 2. ^{29}Si solid-state NMR spectra of waterborne PU/silica hybrid composites with 5 phr silica contents: (a) Aerosil 200 and (b) Aerosil R812.

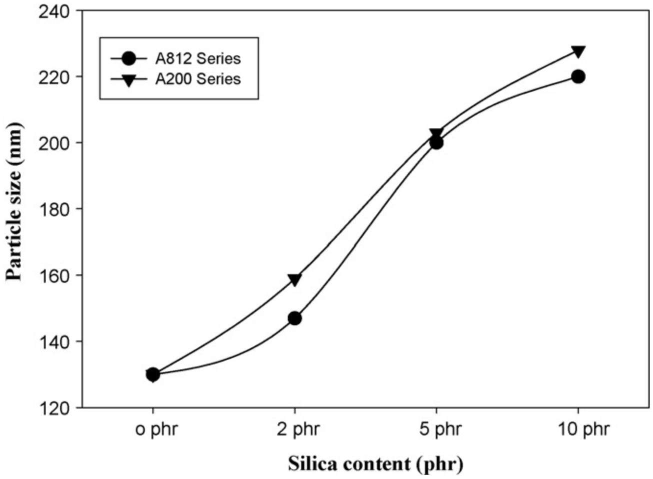


Fig. 3. Variation of emulsion particle size by the amount of added silica.

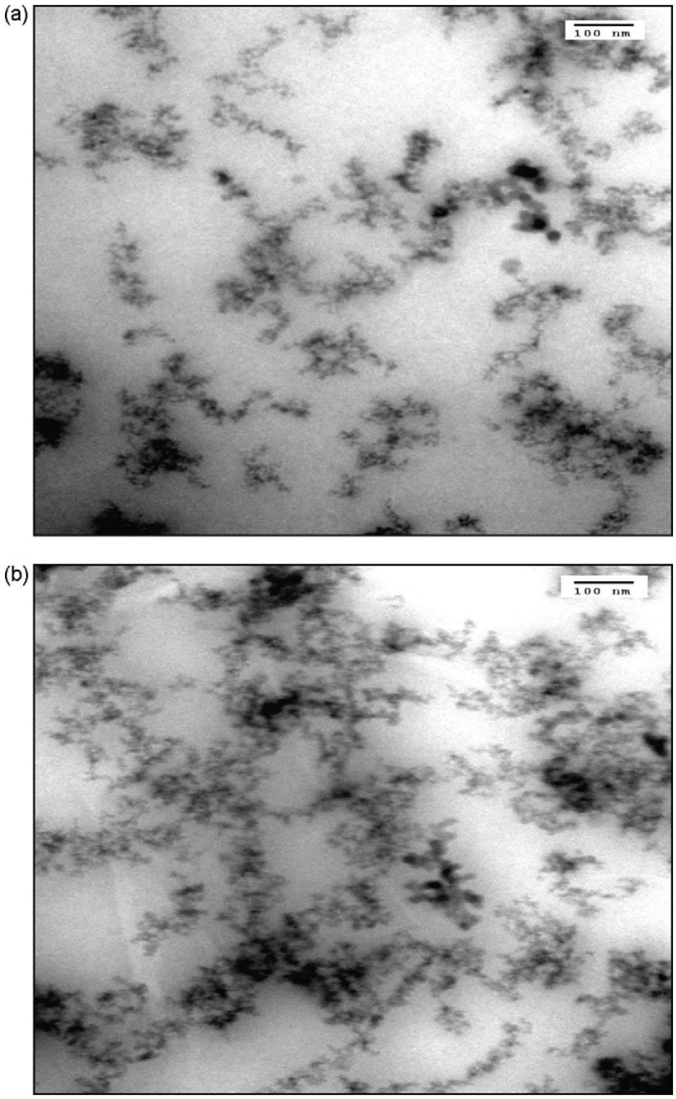


Fig. 4. Transmission electron microscope images of (a) A200-10 and (b) A812-10.

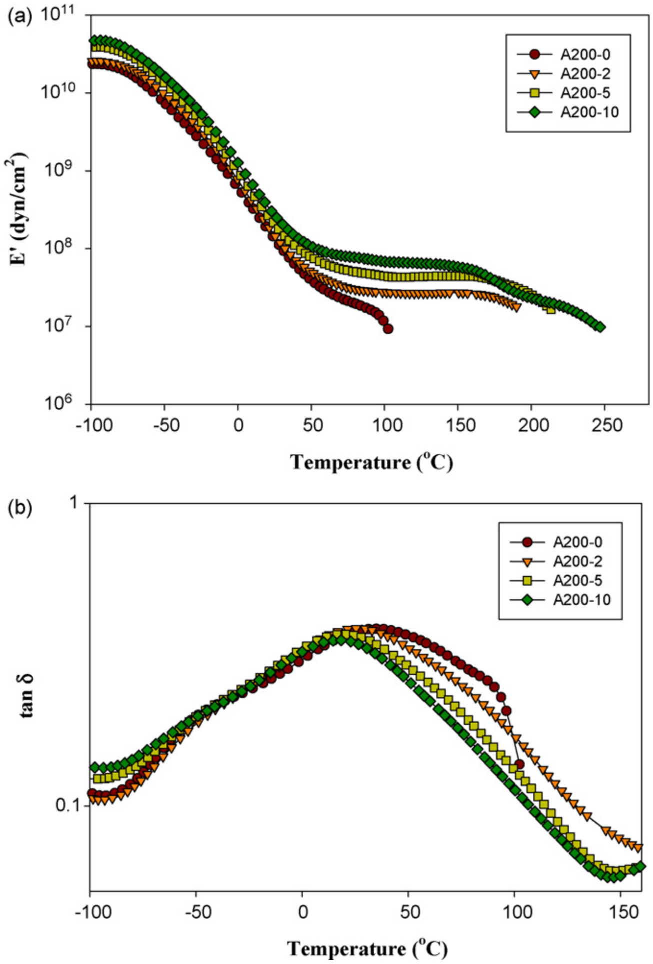


Fig. 5. (a) Storage modulus (E') and (b) tan δ of A200 series.

3.4. Mechanical and dynamic mechanical properties

Dynamic mechanical properties of PU/silica hybrid composites based on Aerosil 200 are shown in Fig. 5. A200-0 shows two broad damping peaks around −45 and 41 °C, which indicates that A200-0 has phase separated morphology, each temperature corresponding to the glass transition temperatures (T_g) of soft and hard segment domains, respectively. Since the T_g of PTMG is about −88 °C [20], a bit high T_g of soft segment and broad shape of damping peaks suggest that there are partial phase mixings between soft and hard segments. Relatively low T_g of hard segment is most likely due to the low molecular weight of A200-0 (9000) as compared with these (ca. 70 °C) of crosslinked PUs consisting similar soft and hard segment [21,22]. The peak temperature varies much in PU/silica hybrid composite. Although T_g of soft segment is virtually unchanged, T_g of hard segment significantly decreases with increasing contents of silica. This implies that the degree of partial phase mixing between soft and hard segment increases in the presence of hydrophilic silica (Aerosil 200).

With the addition and increasing amount of nanosilica, rubbery plateaus are well defined and increase in magnitude and extend to higher temperature. The increase of rubbery modulus is an indication of effective reinforcement of PU by nanosili-

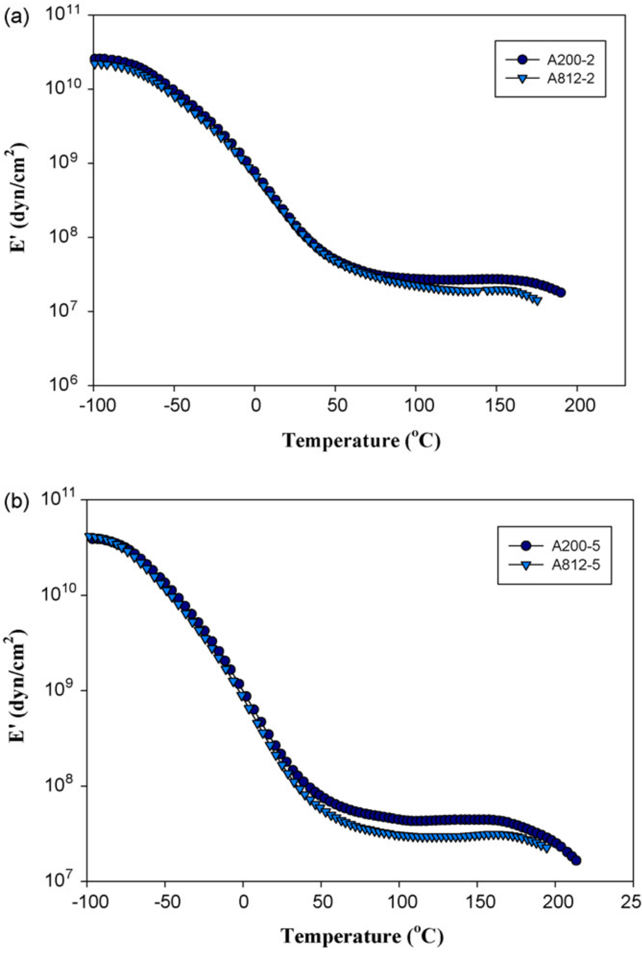


Fig. 6. Storage modulus (E') of (a) A200-2 vs. A812-2 and (b) A200-5 vs. A812-5.

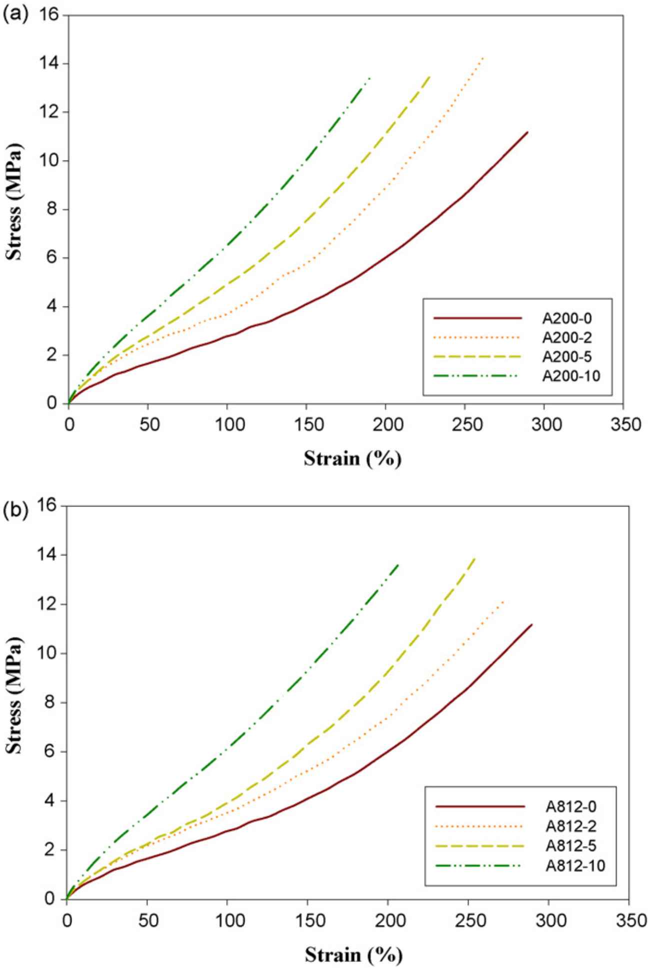


Fig. 7. Stress–strain curves of (a) A200 series and (b) A812 series.

cas. On the other hand, extension of prateau modulus to higher temperature is an indication of increased thermal resistance to flow. In our PU/nanosilica composites, the chemical connection between PU and hydrophilic silica (Aerosil 200) seems to suppress the flow of PU and sustain the rubbery state even at temperature higher than the T_g of hard segment domain.

Fig. 6 shows that A200 series gives much greater reinforcing effects than A812 series. This implies that chemical bonding between PU and silica (Aerosil 200) is essential for better reinforcement of PU with silica. With chemical bonding, thermal resistance as well as mechanical reinforcement is also increased.

Stress–strain curves of PU/nanosilica composites are shown in Fig. 7 and the tensile properties and hardness are summarized in Table 2. The 100% modulus and tensile strength increase generally with increase of nanosilica, whereas the elongation at break shows the opposite tendency. It is seen that the reinforcing effect of nanosilica is more evident in tensile properties at large deformation due to the fact that alignment and exten-

Table 2
Mechanical properties of PU/silica Hybrid composites

Sample	100% secant modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness
A200 series				
A200-0	2.76	11.2	289.6	69
A200-2	3.66	14.4	263.0	75
A200-5	4.89	13.5	228.6	80
A200-10	6.50	13.6	192.0	86
A812 series				
A812-0	2.76	11.2	289.6	69
A812-2	3.47	12.3	274.2	71
A812-5	3.95	14.0	255.4	75
A812-10	6.13	13.6	206.4	79

Table 3
Physical properties of PU/silica hybrid composites

Sample	30% weight loss temperature (°C)	Water swell (%) after					Transmittance (%) at		
		1 day	2 day	3 day	4 day	5 day	633 nm	514 nm	488 nm
A200 series									
A200-0	351.4	6.49	7.91	9.14	10.05	10.74	91.93	89.72	86.50
A200-2	373.4	6.10	7.80	9.00	9.80	10.50	87.80	83.69	81.16
A200-5	380.5	5.91	7.33	8.27	9.09	9.37	87.53	83.22	80.80
A200-10	387.7	5.73	7.21	8.08	8.78	9.27	86.10	82.58	79.88
A812 series									
A812-0	351.4	6.49	7.91	9.14	10.05	10.74	91.93	89.72	86.50
A812-2	360.2	6.39	7.85	9.04	9.90	10.62	88.93	85.54	84.63
A812-5	363.8	6.09	7.74	8.92	9.80	10.42	86.35	84.17	81.00
A812-10	369.4	5.88	7.43	8.60	9.44	10.05	83.50	81.55	80.08

sion of PU chains in rubbery state contribute to the improved performance of nanosilica [23]. Also, A200 series show much higher modulus and tensile strength than A812 series, whereas the elongation at break is the opposite. This is primarily due to crosslink formations between PU and silica (Aerosil 200).

Hardness (Table 2) is increased as the content of nanosilica is increased by the reinforcing effect of dispersed nanosilica. These mechanical properties are similar to those of PU/organoclay hybrid composites [24]. Also, A200 series give better properties than A812 series.

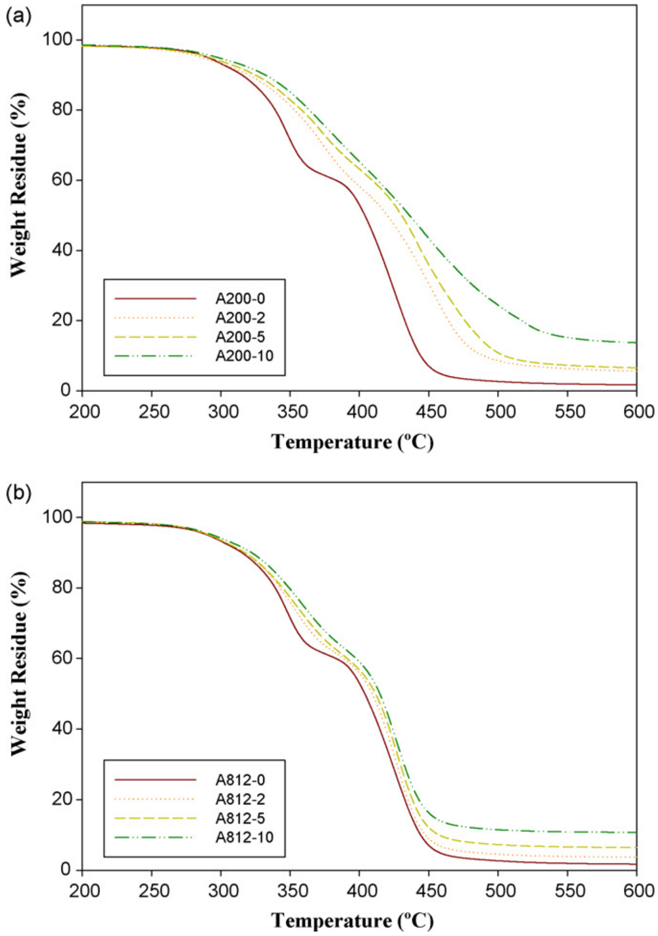


Fig. 8. TGA thermograms of (a) A200 series and (b) A812 series.

3.5. Physical properties

In order to examine the effect of nanosilica on the thermal stability, thermogravimetric analysis (TGA) was carried out and results are shown in Fig. 8 together with temperatures of 30% weight loss in Table 3. The results show that thermal resistance is enhanced with nanosilica, due probably to the thermal insulation effect of nanosilica, as we observed in the nanocomposite of organoclay [24]. Also, A200 series show better thermal properties than A812 series due to chemical bonding by sol–gel process.

Table 3 shows that the presence of impermeable nanosilica in PU matrix reduces the water swell and enhances the resistance to water, results similar to PU/oraganoclay nanocomposites. Such results are expected due to the increased mean free path of water molecules to pass through the hybrid composite when silicas are dispersed in PU matrix. Also, despite hydrophilicity of Aerosil 200, water swell of A200 series is less than A812 series. This result indicated that A200 series have network structure by sol–gel process.

In Table 3, we can see that the transparency of the film is not damaged seriously by the presence of nanosilica. This is simply due to the small size of dispersion as compared with the wavelength of visible light regardless of silica species. This transparency, together with water and solvent resistance, is especially attractive for waterborne PU because such dispersions have many applications in coatings and films.

4. Conclusions

Waterborne PU/silica (Aerosil 200) hybrid composites are synthesized by sol–gel process. ^{29}Si solid-state NMR spectroscopy was used to prove the degree of molecular connectivity between PU and silica (Aerosil 200).

Thermal, mechanical properties and water resistance of PU/Aerosil 200 hybrid composite are better than those of

PU/Aerosil R812 due to chemical network formations between PU and silica (Aerosil 200).

With increasing silica content, thermal and mechanical properties are improved without impairing clarity seriously.

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