

Properties of Waterborne Polyurethane/Nanosilica Composite

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Abstract: Aqueous emulsion of polyurethane (PU) ionomers were reinforced with hydrophobic nanosilica to give composites. The aqueous emulsion was stable and the particle size increased as the content of hydrophobic nanosilica was increased. The reinforcing effect of nanosilica in mechanical properties of these composites were examined by dynamic mechanical and tensile tests, and the Shore A hardness was measured. Enhanced thermal and water resistance and marginal reduction in transparency of these composites were observed compared with pristine polymer. These results were similar with those of our previous studies on waterborne PU/organoclay nanocomposites.

Keywords: waterborne polyurethane, nanosilica, composite, emulsion particle size, mechanical properties, physical properties.

Introduction

Nanostructured hybrid organic-inorganic composites, based on organic polymer and inorganic mineral, have attracted the great interest of researchers, because they exhibit the enhanced performance properties compared with conventional composites, owing to the maximized interfacial contact between the organic and inorganic phases.¹⁻⁷

Waterborne polyurethane coatings have received increased attention in recent coating technology development, because it is non-toxic, non-flammable and does not pollute the air.⁸⁻¹⁰ Some defects of waterborne polyurethanes, for example low mechanical strength and water resistance, can be improved by hybridizing with other materials.¹⁰ In our previous studies, we prepared the first examples of waterborne polyurethane/organoclay nanocomposites and observed that mechanical properties, thermal and water resistance of waterborne polyurethanes can be improved with marginal reduction in transparency, when reinforced with exfoliated nanometer scale silicate layer.^{11,12}

The nano-size silica is another candidate of inorganic filler which can enhance the performance properties of waterborne polyurethanes, and it was reported that the tensile properties of polyurethane can be improved more effectively by nano-size silica compared with micron-size silica.⁴ How-

ever, to the best knowledge of present authors, there is no information about the preparation and properties of waterborne polyurethanes reinforced with nanosilica. So, we report here the preparation and the physical properties of waterborne polyurethane/nanosilica composites.

Experimental

Materials. Poly(tetramethylene glycol) (PTMG; 1,000 g/mol; Korea PTG) and 1,4-butanediol (BD; Junsei Chemical) were dried and degassed at 80°C under vacuum for 3 hrs. Dimethylol propionic acid (DMPA; Aldrich) was dried at 50°C for 48 hrs in vacuum oven. Isophorone diisocyanate (IPDI; Aldrich) and dibutyltin dilaurate (DBT; Aldrich) were used as received. Triethylene tetramine (TETA; Junsei Chemical) and triethylamine (TEA; Fluka) were dried over 4 Å molecular sieve before use. Nano-size hydrophobic silica, Aerosil R812, whose average particle size is 8 nm, was obtained from Degussa-Hüls.

Preparation of Polyurethane/Nanosilica Composite. A 500 mL round-bottomed, 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.

Nanosilica were fed into reactor and agitated with PTMG at 70°C. To obtain NCO-terminated prepolymer, whose number average molecular weight calculated by feed is 5,000 g/mol, the above polyol/nanosilica mixture was reacted

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with IPDI and DMPA in the presence of DBT (0.03 phr based on the total solid) for 1 hr at 80°C, and then with BD for another 1 hr at 80°C. After cooling to room temperature, TEA was fed into the reactor and agitated for 1 hr to neutralize DMPA unit in polyurethane.

An aqueous emulsion 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 10 min with pump at a constant flow rate. TETA dissolved in water (3 wt%) was then fed to the emulsion at 50°C and chain extension with TETA was carried out for 1 hr. The resulting product was a polyurethane emulsion with a solid content of about 30%.

The recipes for the preparation of polyurethane/nanosilica composites are shown in Table I.

Measurements. Number average diameter of polyurethane emulsion was measured by light scattering (Autosizer, Malvern IIC), 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.

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

Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometric 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 tensile tester (Tinius Olsen Series 1000). Micro-tensile specimen for the test had the dimensions of 25 mm length, 5 mm width, and 1 mm thickness. The specimens were elongated at the rate of 500 mm/min.

Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyzer (TA Instrument). The samples of 5 mg each in an alumina crucible were 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 UV-visible spectropho-

tometer (Hitachi U-2010) using a film with 0.3 mm thickness.

Water swell, i.e., the degree of water absorption, was measured by preserving a film in water. The water swell (%) was calculated by the following equation, where W_o is the original film weight and W is the film weight after water absorption:

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

Results and Discussion

Emulsion Particle Size. Table II shows that polyurethane (PU) emulsion particle size is increased as the content of nanosilica is increased. In PU emulsion, because the particle size is governed by the hydrophilicity of PU ionomer,¹³ the increase of hydrophobicity by the presence of hydrophobic nanosilica seems to be a cause of particle size increase. Stable emulsion suggests that hydrophobic nanosilica is effectively encapsulated by PU ionomer to be dispersed in water.

Mechanical Properties. Dynamic mechanical properties of PU/nanosilica composites are shown in Figure 1. S0 shows a broad damping peak around 5°C. This shows that S0 has phase mixed morphology, and this temperature is the glass transition temperature (T_g) of soft and hard segments mixed phase. The peak temperature positions do not vary much in PU/nanosilica composite compared with pristine polymer. This suggests that the degree of phase mixing between soft and hard segment does not vary much in the presence of nanosilica compared with pristine polymer. In Figure 1, we can see a large drop of tensile storage modulus, E' , occur on heating at the T_g of soft and hard segments mixed phase. The improvement of E' by added nanosilica is marginal at the temperature range below the T_g . However, at the temperature range above the T_g , the presence of nanosilica evidently enhances the E' values to develop rubbery plateau. The interaction between PU polymer and nanosilica seems to prohibit the flow of PU polymer and sustain the rubbery state even at the temperature range above the T_g . In

Table I. Recipe for the Preparation of Polyurethane / Nanosilica Composite

Designation	Feed													
	Soft Segment				Hard Segment						Neutralizer		Nanosilica	
	PTMG		IPDI		BD		DMPA		TETA		TEA		Aerosil R812	
	mol	wt%	mol	wt%	mol	wt%	mol	wt%	mol	wt%	mol	phr	phr	
S0	1	65	1.75	27	0.02	1	0.45	4	0.14	3	0.45	3	0	
S1	1	65	1.75	27	0.02	1	0.45	4	0.14	3	0.45	3	1	
S3	1	65	1.75	27	0.02	1	0.45	4	0.14	3	0.45	3	3	
S5	1	65	1.75	27	0.02	1	0.45	4	0.14	3	0.45	3	5	

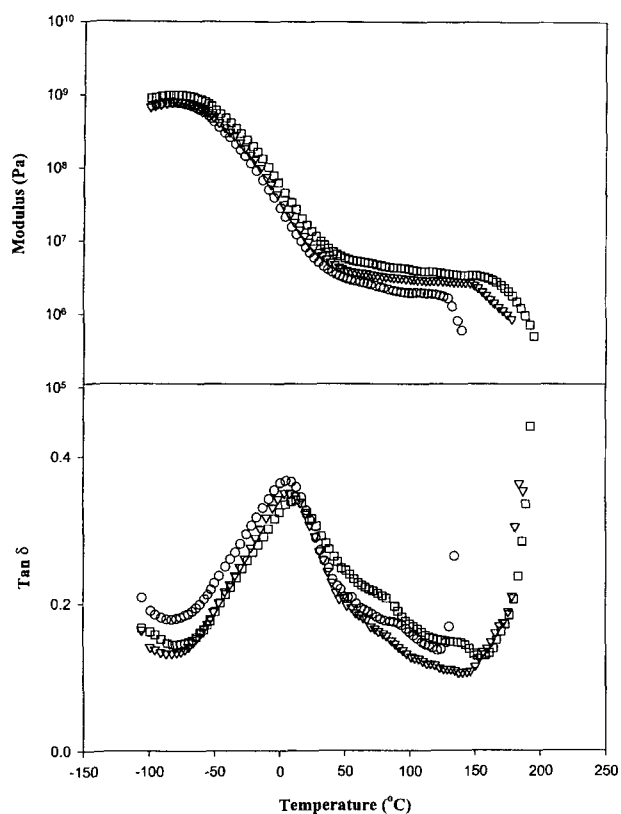


Figure 1. E' and $\tan \delta$ of (○) S0, (▽) S3, and (□) S5.

epoxy/clay nanocomposite, the improvement of tensile modulus and tensile strength was more evidently observed at the temperature range above T_g compared with that below T_g , because the shear deformation and stress transfer to the platelet particles are enhanced by the increased elasticity of

the matrix above T_g .² This explains the above our result on E' , and similar results were observed in our previous studies on PU/organoclay nanocomposites.^{11,12}

The tensile properties measured are summarized in Table II. The 100% secant modulus and tensile strength increase generally as the content of nanosilica is increased, and the elongation at break is reduced in the presence of nanosilica compared with pristine polymer. These results of tensile properties measured at room temperature (20 °C) show that the reinforcing effect of nanosilica is more evidently observed in tensile test with large deformation compared with E' measured with small deformation by DMTA. This seems to be due to the fact that alignment and extension of PU polymer in rubbery state under large strain may cause the improved performance of nanosilica.²

In Table II, we can see that the Shore A hardness is increased as the content of nanosilica is increased by the reinforcing effect of dispersed nanosilica. These results of tensile properties and Shore A hardness is similar with our previous studies on PU/organoclay nanocomposites.^{11,12}

Physical Properties. In order to examine the effect of nanosilica on the thermal stability, thermogravimetric analysis (TGA) was carried out, and the temperatures where 10% weight loss occurs are given in Table III. The results show that thermal resistance is enhanced in the presence of nanosilica, and this seems to be due to the thermal insulation effect of nanosilica as we observed in the nanocomposite of organoclay.^{7,14}

Table III shows that the presence of hydrophobic nanosilica in PU matrix reduces the water swell, and enhances the resistance to water. Similar results were observed with PU/organoclay nanocomposites,^{9,10} and the results were explained to be due to the increase of the mean free path of water

Table II. Emulsion Particle Size and Mechanical Properties of PU / Nanosilica Composite

Sample	Particle Size (nm)	Tensile Properties			Shore A Hardness
		100% Secant Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	
S0	180	1.68	15.0	794	75
S1	200	1.81	16.8	748	77
S3	225	1.91	17.9	745	81
S5	250	2.17	21.1	769	83

Table III. Physical Properties of PU / Nanosilica Composite

Sample	10% 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
S0	330	9.8	17.1	23.9	29.8	36.9	87.1	86.4	86.3
S1	332	6.9	14.2	18.4	20.8	23.8	88.0	87.0	86.5
S3	347	6.8	12.3	15.6	17.5	20.1	85.2	84.6	83.6
S5	350	6.5	11.7	14.5	16.4	18.3	86.1	85.3	84.5

molecules to pass through the matrix of PU/organoclay nanocomposite when organoclay layers are dispersed in nanometer scale in PU matrix.⁷

In Table III, we can see that the transparency does not reduce so much in the presence of nanosilica, because its particle size is less than the wavelength of visible light. This transparency is, together with water or solvent resistance, especially attractive for waterborne PU, because waterborne PUs have many application in coatings and films.

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