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Preparations and Properties of Waterborne Polyurethane / Nanosilica Composites

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Summary

Aqueous dispersion of polyurethane(PU) ionomers, based on poly(tetramethylene glycol) as soft segment, isophorone diisocyanate as diisocyanate, 1,4-butanediol as chain extender, dimethylol propionic acid as potential ionic center, triethylene tetramine as crosslinker, and triethyl amine as neutralizer, were reinforced with hydrophobic nanosilica to give waterborne PU/nanosilica composites. The reinforcing effects of nanosilica were examined in terms of mechanical, dynamic mechanical, and thermal properties together with water swell and transparency of the dispersion cast films. With the addition of nanosilica to PU, tensile modulus and strength increased, and the rubbery modulus increased in magnitude and extended to higher temperature, and these enhanced mechanical and thermal properties, together with increased swell resistance were obtained without scarifying the transparency of the films.

Introduction

Nanostructured hybrid organic-inorganic composites based on organic polymer and inorganic mineral have attracted 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].

On the other hand waterborne polyurethanes have received increased attention in coatings because they are non-toxic, non-flammable and do not pollute the air [8-10]. Some inferior properties of waterborne polyurethanes such as low mechanical strength and water resistance can be improved by hybridizing them with other materials [10]. In our previous study [11], we prepared the waterborne polyurethane / organoclay nanocomposites and found that mechanical properties, thermal and water resistance of waterborne polyurethanes can be improved with marginal reduction in transparency, when reinforced with exfoliated nanometer scale organoclay layer [11].

The nanosilica 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 nanosilica compared with micronsilica [4]. However, 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; 1000g/mol; Korea PTG) and 1,4-butanediol (BD; Junsei Chemical) were dried and degassed at 80°C under vacuum for 3hr. Dimethylol propionic acid (DMPA; Aldrich) was dried at 50°C for 48hrs 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 4Å molecular sieve before use. Hydrophobic nanosilica, Aerosil R812, with average particle size of 8nm was obtained from Degussa-Hüls.

Preparation of polyurethane / nanosilica composite

A 500ml 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.

Nanosilicas were fed into the reactor and agitated with PTMG at 70°C. To obtain NCO- terminated prepolymer of number average molecular weight 5000g/mol calculated by feed, the above polyol / nanosilica mixture was reacted with IPDI and DMPA in the presence of DBT (0.03phr based on the total solid) for 1hr at 80°C. Subsequently BD was added and reactions proceeded for another 1hr at 80°C. After cooling the reaction mixture to room temperature, TEA was fed into the reactor and agitated for 1hr to neutralize DMPA unit in polyurethane.

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

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

Table 1. Recipe for the preparation of polyurethane / nanosilica composite

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

Measurements

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

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

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 10Hz.

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

Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyzer (TA Instrument). 5mg of each sample in an alumina crucible was used at a heating rate of 20°C/min under N_2.

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

Transparency was measured with an UV-visible spectrophotometer (Hitachi U-2010) using a film with 0.3mm 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 (1), where W_o is the original film weight and W is the film weight after water absorption

$$\%swell = \frac{W - W_0}{W_0} \times 100 \qquad \textbf{(1)}$$

Results and discussion

Dispersion particle size and morphology

Table 2 shows that particle size of the dispersion increases with the addition and increase of nanosilica content. This is primarily due to the inclusion of inorganic filler in PU particle implying that the nanosilicas are effectively encapsulated by the PUs. Due to the hydrophobic nature of nanosilicas, nanosilicas should form the core of particles and the particles are stabilized by the ionic groups of PUs forming the shell of the composite particles.

Table 2. Emulsion particle size and mechanical properties of PU / nanosilica composite

Series	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

Mechanical and dynamic mechanical properties

Fig. 1 shows the dynamic mechanical properties of the PU/nanosilica composites. Film containing no silica shows a broad damping peak at about 5°C, corresponding to the glass transition temperature (T_g) of soft segment rich phase. A small mere shoulder may be seen at about 90°C, corresponding to the T_g of hard segment. However, due to the insignificant extent of microphase separation, T_g of soft segment rich phase dominates the damping.

With the addition and increasing amount of nanosilica, rubbery modulus increases and extends to higher temperature. The increase of rubbery modulus is an indication of effective reinforcement by nanosilicas. On the other hand extension of plateau modulus to higher temperature is an indication of increased thermal resistance to flow. Above T_g, polymer chains are in there rubbery state and only the entanglements sustain the elasticity. As temperature goes up, relaxation of the entanglement occurs quickly and the polymers are subject to irreversible viscous flow. In our PU/nanosilica composites, the interaction between PU and nanosilica seems to suppress the flow of PU and sustain the rubbery state even at temperature higher than the T_g of hard segment domain.

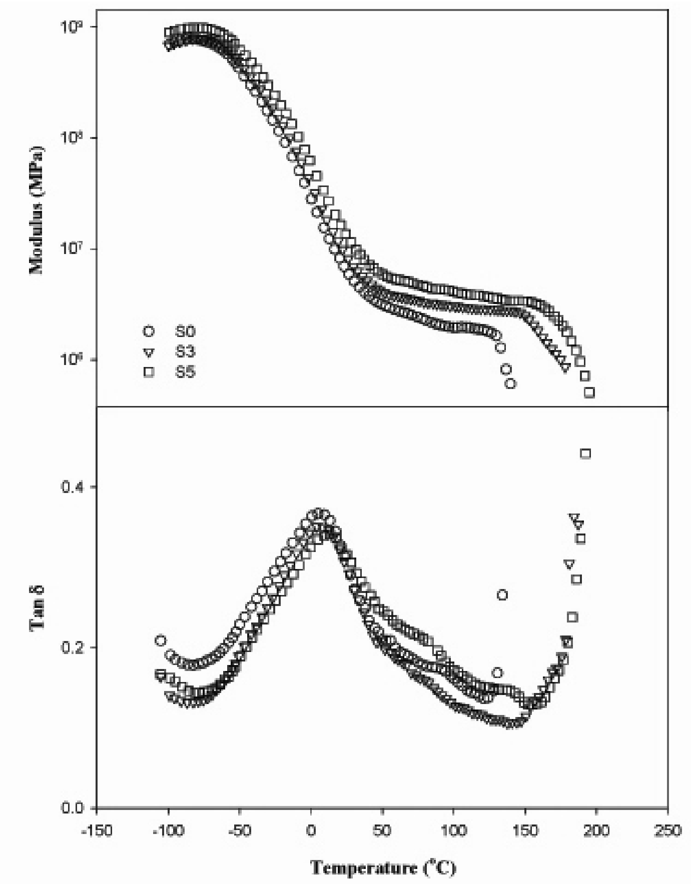

Fig. 1. E’ and tan δ of S0 (○), S3 (▽) and S5 (□)

Stress-strain curves of PU/nanosilica composites are shown in Fig. 2 and the tensile properties and hardness are summarized in Table 2. The 100% secant modulus and tensile strength increase generally with the addition and 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 alignment and extension of PU chains [2].

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 nanocomposites reported earlier [11, 12].

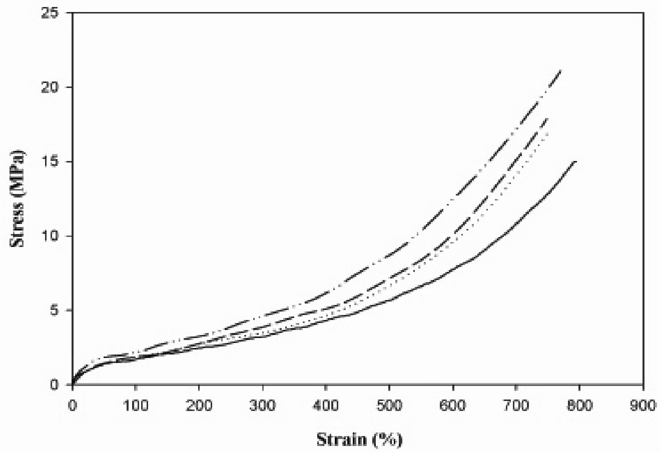

Fig. 2. Stress-strain curves of S0 (—), S1 (· ·), S3 (‒‒) and S5 (–· ·)

Physical properties

In order to examine the effect of nanosilica on the thermal stability thermogravimetric analysis (TGA) was carried out (Fig. 3) and the temperatures of 10% weight loss are given in Table 3. The results show that thermal resistance is enhanced with

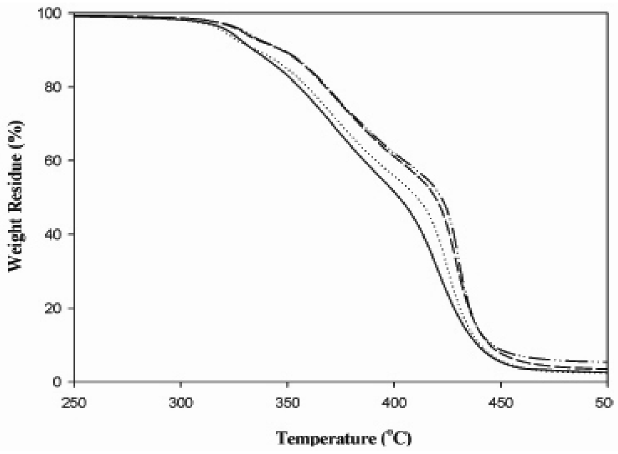

Fig.3. TGA thermograms of S0 (—), S1 (· ·), S3 (‒‒) and S5 (–· ·)

nanosilica, due probably to the thermal insulation effect of nanosilica, as observed in the nanocomposite of organoclay [7, 13].

Hydrophobic nanosilica in PU matrix reduces the water swell and enhances the resistance to water (Table 3), results similar to PU / oraganoclay nanocomposites [11]. Such results are expected due to the increased mean free path of water molecules to pass through the nanocomposite when organoclay layers are dispersed in nanometer scale in PU matrix [7].

Due to the small particle size of dispersion as compared with the wavelength of visible light, transparency of the film is not damaged seriously. Transparency, water and solvent resistance are especially attractive for waterborne PU because such dispersions have many applications in coatings and films.

Table 3. 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	633nm	514nm	488nm
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

Conclusions

When waterborne PU was reinforced with nanosilica, rubbery modulus increased in magnitude and extended to higher temperature due respectively to the reinforcing effect and thermal resistance to flow of the inorganic fillers in rubbery state. Increased thermal resistance was again verified with TGA analysis. These enhanced mechanical and thermal properties with increased swell resistance were obtained without scarifying the transparency of the films.

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