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SHORT COMMUNICATION

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Nanosilica-reinforced UV-cured polyurethane dispersion

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Abstract UV-curable polyurethane dispersions (UV–PUDs) have been reinforced with hydrophobic and hydrophilic modified silicas, respectively, and the effects have been studied with dispersion and dispersion cast films. It has been found that particle size increased and water swell decreased, tensile modulus, strength, and thermal stability increased with the addition and increasing amount of silica. These effects were more pronounced with the hydrophilic modified one than the hydrophobic modified one.

Keywords Polyurethane dispersion · UV curing · Nanosilica · Composite · AFM · Swelling

Introduction

Polyurethane dispersions (PUDs) are steadily expending their usages in coatings, adhesives, textile sizing, etc. due to their environmentally friendly nature and versatile structure–property relationships. PUDs are typically prepared via prepolymer mixing process because their properties are easily tailor made [1, 2]. In addition, high molecular weight is built up without impeding dispersion viscosity. In this process, the isocyanate-terminated prepolymers are chain-extended in aqueous media using typically tetramine providing PU with crosslinking sites [3, 4]. However, reactions within the particles which are dispersed in aqueous media do not occur stoichiometrically, leaving a certain amount of unreacted isocyanate groups which slowly react with moistures and cause property change with time in use. In addition, high molecular weight of prepolymer which is linear also poses limits on such coating properties like hardness and abrasion resistance due to the low crosslinking density.

Conventionally, 100% UV cure system, which is composed of polyester or PU oligomer of molecular weight of about 1,000 and acrylate monomers, provides coatings with high hardness, high solvent and stain resistance, and high gloss due to the high crosslinking density [5]. However, high crosslinking density of UV cure system inevitably gives poor flexibility, and its formulation before cure is subject to tack due to its low average molecular weight. UV cure of PUD (UV–PUD) benefits from the advantages of both UV and PUD without suffering from any of their obvious disadvantages [6].

Nanostructured hybrid organic–inorganic composites based on organic polymer and inorganic mineral have attracted great interest because they exhibit enhanced performance properties as compared with the conventional composites owing to the maximized interfacial contact between the organic and inorganic phases [7–9]. Works on nanocomposite with PUD are sparse in open literature [10, 11]. Regarding the nanosilica-reinforced PUD, enhanced moduli especially in rubbery state, strength, thermal stability, and water swell resistance were obtained without scarifying the transparency [10] of dispersion cast film.

In this study, nanosilica-reinforced UV–PUDs were prepared following the prepolymer mixing process where two types of silica, viz., hydrophilic and hydrophobic ones,

Table 1 Formulations to prepare HEA-capped PUD

PTMG 650	H_{12}MDI	DMBA	HEA	TETA	TEA
1.44	2.87	0.54	0.89	0.22	0.54

were respectively added up to 6 phr, and the effects were analyzed in terms of dispersion size, surface, and various physical properties of the dispersion cast films.

Experimental

Polytetramethylene ether glycols (PTMG, M_n=650, Korea Polyols, Korea) were dried and degassed at 80 °C, 1–2 mmHg for 2 h before use. Dimethylol butanoic acid (DMBA, Aldrich) was dried at 50 °C for 48 h. Extra pure grades of 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI, Bayer), dibutyltin dilaurate (DBT, Aldrich), 2-hydroxyethylacrylate (HEA, Aldrich), and triarylsulfo-

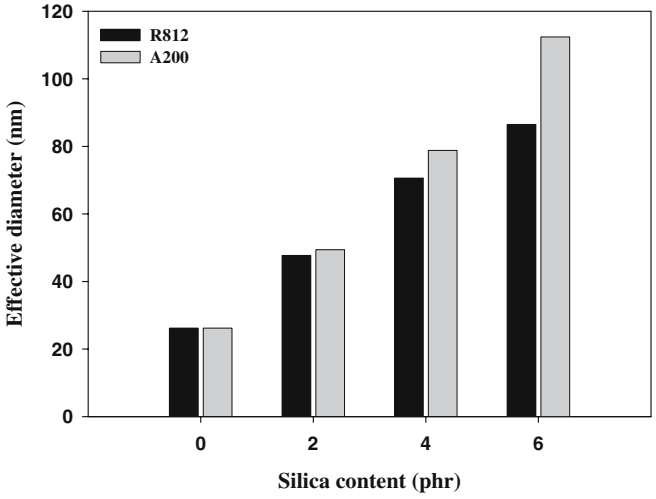
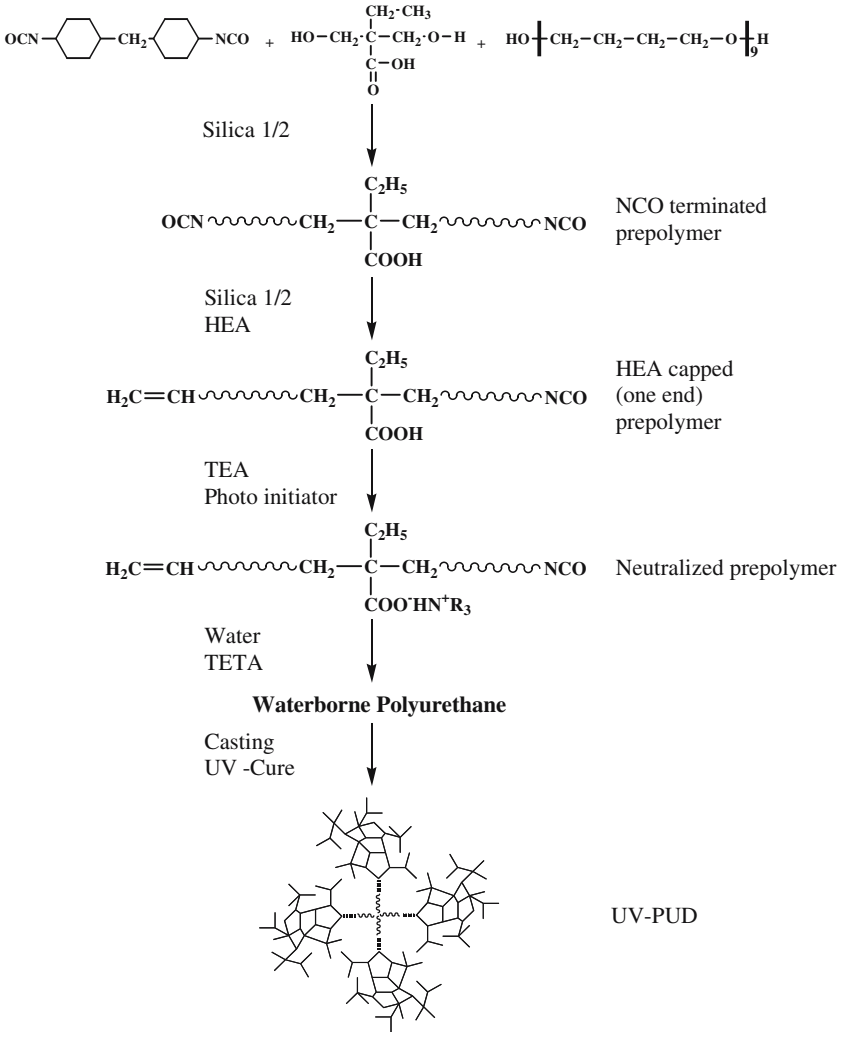


Fig. 1 Dispersion size vs. nanosilica content

Scheme 1 Overall procedure to prepare UV–PUD/nanosilica composites



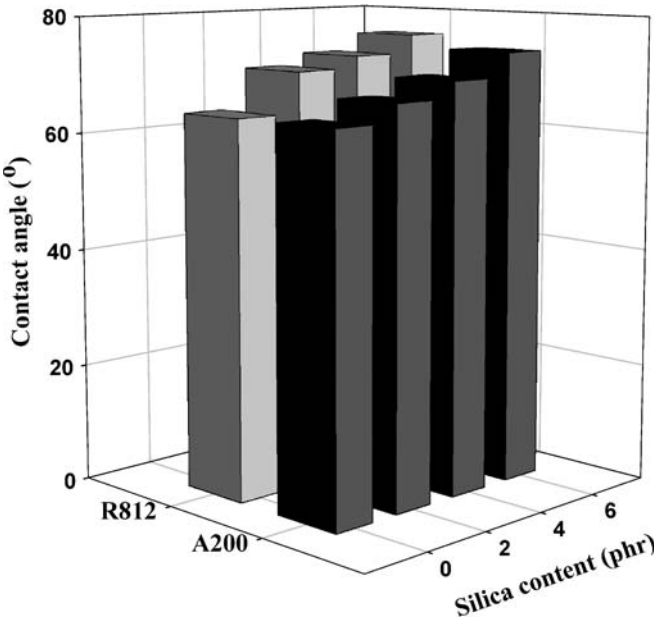


Fig. 2 Contact angle of the cast film vs. silica content

nium hexafluoroantimonate (Cyracure UVI-6974, Union Carbide) were used as received. Triethylamine (TEA, Aldrich) and triethylene tetramine (TETA, Junsei Chemicals) were dried over 4 Å molecular sieves before use. Two types of nanosilica, i.e., hydrophobic one (Aerosil R812, average diameter 8 nm, Degussa) and hydrophilic modified one (Aerosil A200, average diameter 12 nm, Degussa), were used. Basic formulation and procedure to prepare silica-reinforced UV–PUD are respectively given in Table 1 and Scheme 1.

A 500-ml round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube and N_2 inlet was used as reactor. The reaction was carried out in a constant temperature oil bath. DMBA, PTMG, and molar excess of H_{12}MDI were charged into the dried flask and stirred at 80 °C for about 2 h to obtain the NCO-terminated prepolymer of desired molecular weight. These NCO-terminated prepolymers were added with about half of the silica, and one of the two NCO termini of the prepolymer was capped with HEA, with the reaction followed by the absorption peak of NCO group at 2,270 cm^{-1} in FTIR measurement. When the reaction was completed, prepolymers were cooled down to 50 °C and a neutralizing agent (TEA) and remaining half of the silica were added and stirred for the next 1 h while maintaining the temperature at 50 °C. PUDs were obtained by adding water to the mixture using a tubing pump, followed by chain extension by TETA. The resulting product was a stable dispersion with a solid content of about 30 %. To this, 3 wt % of photoinitiator (Cyracure UVI-6974) was added before the dispersion was cast and dried for UV cure.

Average particle size was measured with an electrophonetic light-scattering spectrophotometer (Otsuka Electronics, ELS-8000). Films were prepared by casting the dispersion onto Teflon plate, followed by drying at 30 °C for 24 h. The resulting films were then heated overnight in

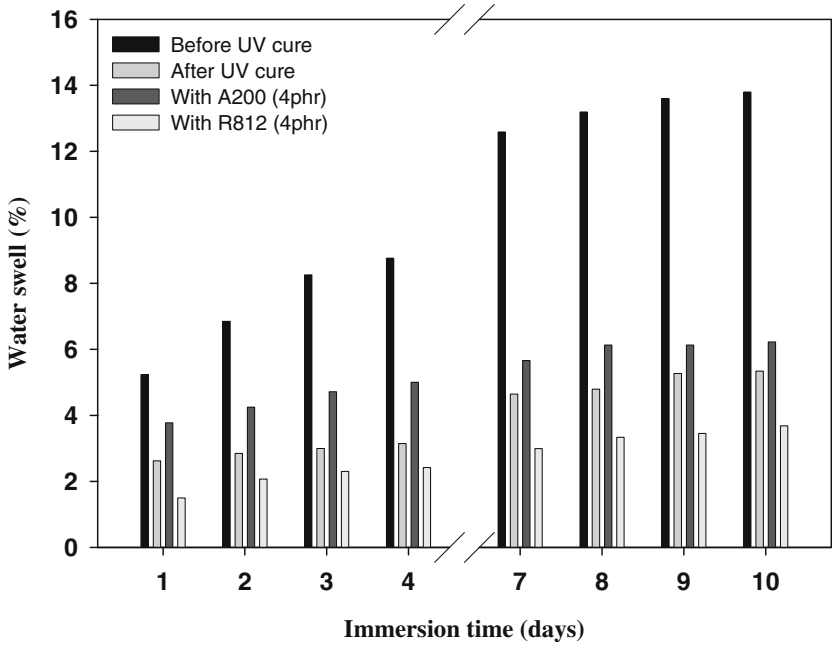


Fig. 3 Water swell of the cast film vs. immersion time

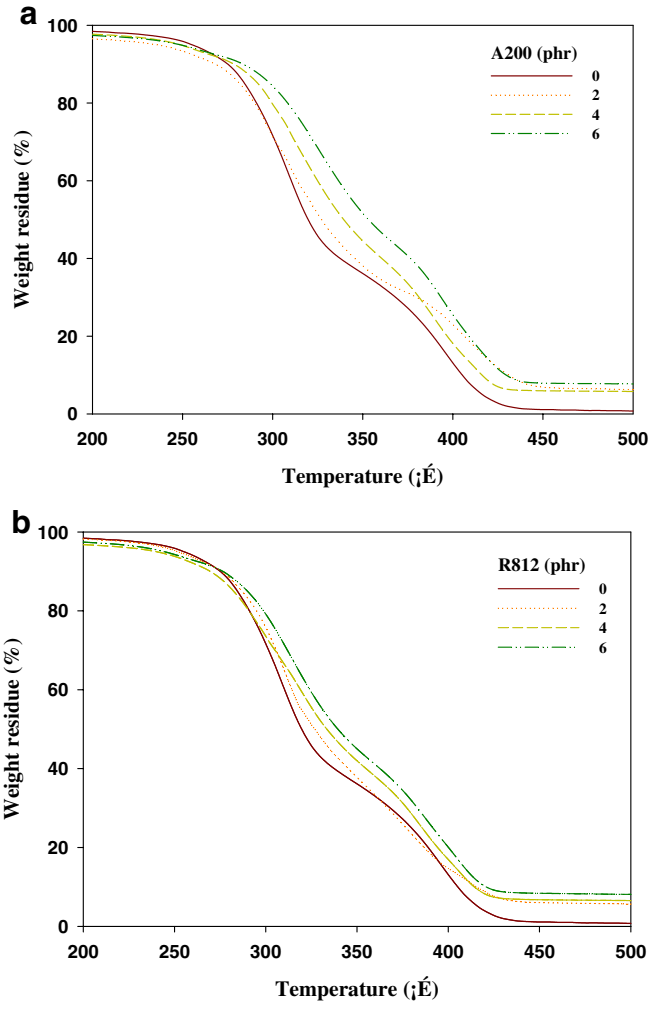


Fig. 4 TGA diagram of the cast film: A200 (**a**) and R812 (**b**)

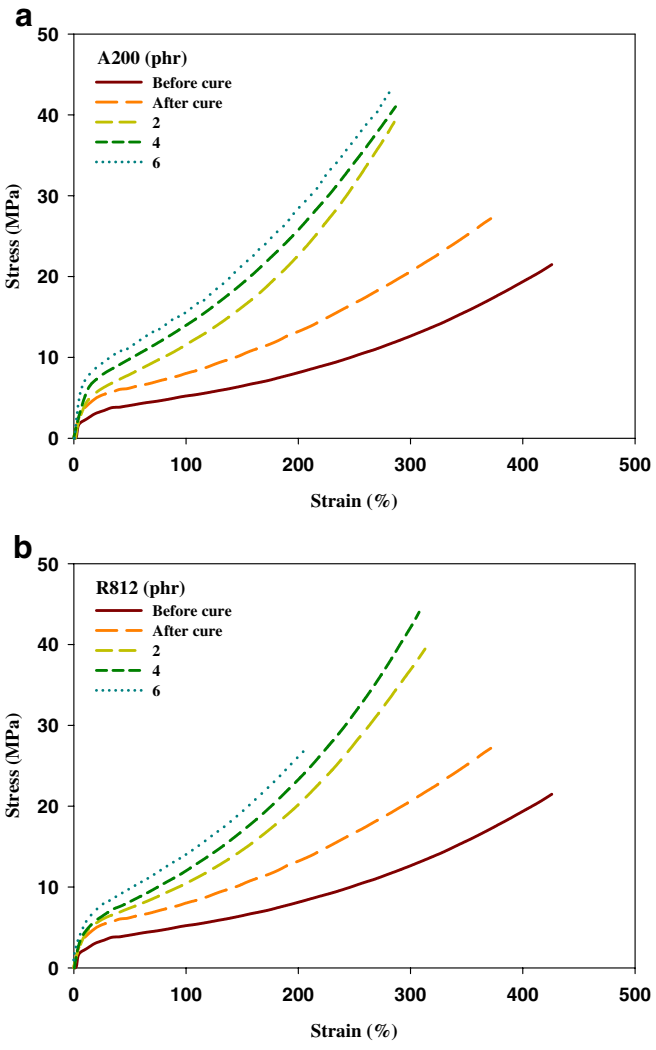


Fig. 5 Stress–strain behavior of cast film: A200 (**a**) and R812 (**b**)

an oven at 50 °C under 2–3 mmHg. Films were irradiated from one side using an 8-W UV (365 nm) lamp for 4 min at room temperature [12]. Contact angle of the dispersion cast film with a drop of water was measured using an Erma (G-1). Film surface has been characterized by an AFM using a Nanocope III equipped with 1553D scanner (Digital Instruments).

Tensile properties were measured with a universal testing machine (Tinius Olsen 1000) at a crosshead of 500 mm/min using specimens prepared according to ASTM D-1822. Tests were made at room temperature, and at least five runs were made to report the average. For thermogravimetric analysis (TA Instruments, TGA Q50), 5 mg of sample was put in an alumina crucible and heated at 20 °C/min under N_2 atmosphere. To measure the abrasion resistance, a film of 1-mm thickness had been rubbed with a glass edge loaded by 3 kg until the film is fractured. The number of cycle to arrive fracture is defined as abrasion resistance of the coating.

Water swell was measured by immersing a film in water at room temperature for over 10 days, and percentage swell

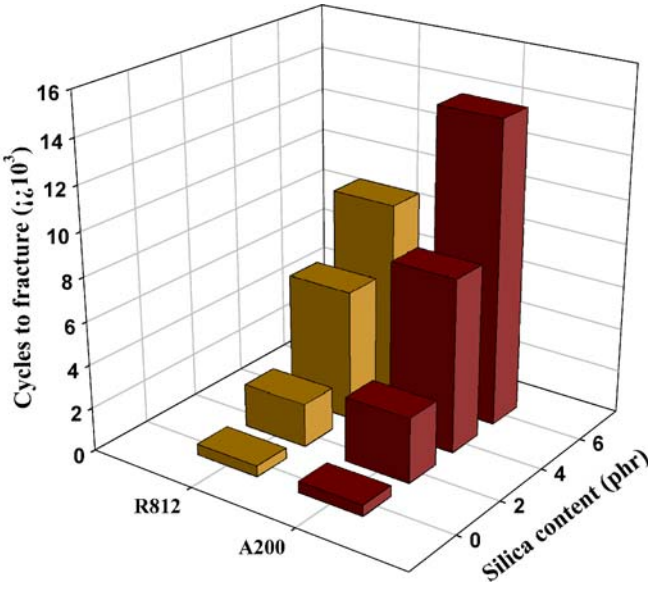


Fig. 6 Abrasion resistance of the cast film

as a function of immersion time was calculated by the following equation:

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

where W_o is the weight of dried film and W is weight after water absorption.

Results and discussions

Figure 1 shows that particle size monotonically increases with the addition and increasing amount of silica. This implies that silicas are well included within the particles of polyurethane dispersions. Among the two types of silica, hydrophilic one (A200) gives larger particle than the hydrophobic one (R812) due possibly to the greater swell of water by hydrophilic modified silicas.

Figure 2 shows that contact angle of the dispersion cast film with a water drop increases with the addition and increasing amount of silica, and the effect is a bit more pronounced with hydrophobic one. This implies that even the hydrophilic modified silica is hydrophobic in nature.

Swells of the films as a function of immersion time up to 10 days are given in Fig. 3 which shows a significant decrease of water swell upon UV cure. UV cure provides the film with additional crosslinks to the one provided by TETA, and the molecular weight between crosslinks corresponds to the prepolymer molecular weight which is about 2,000 based on our formulation. Swell is further

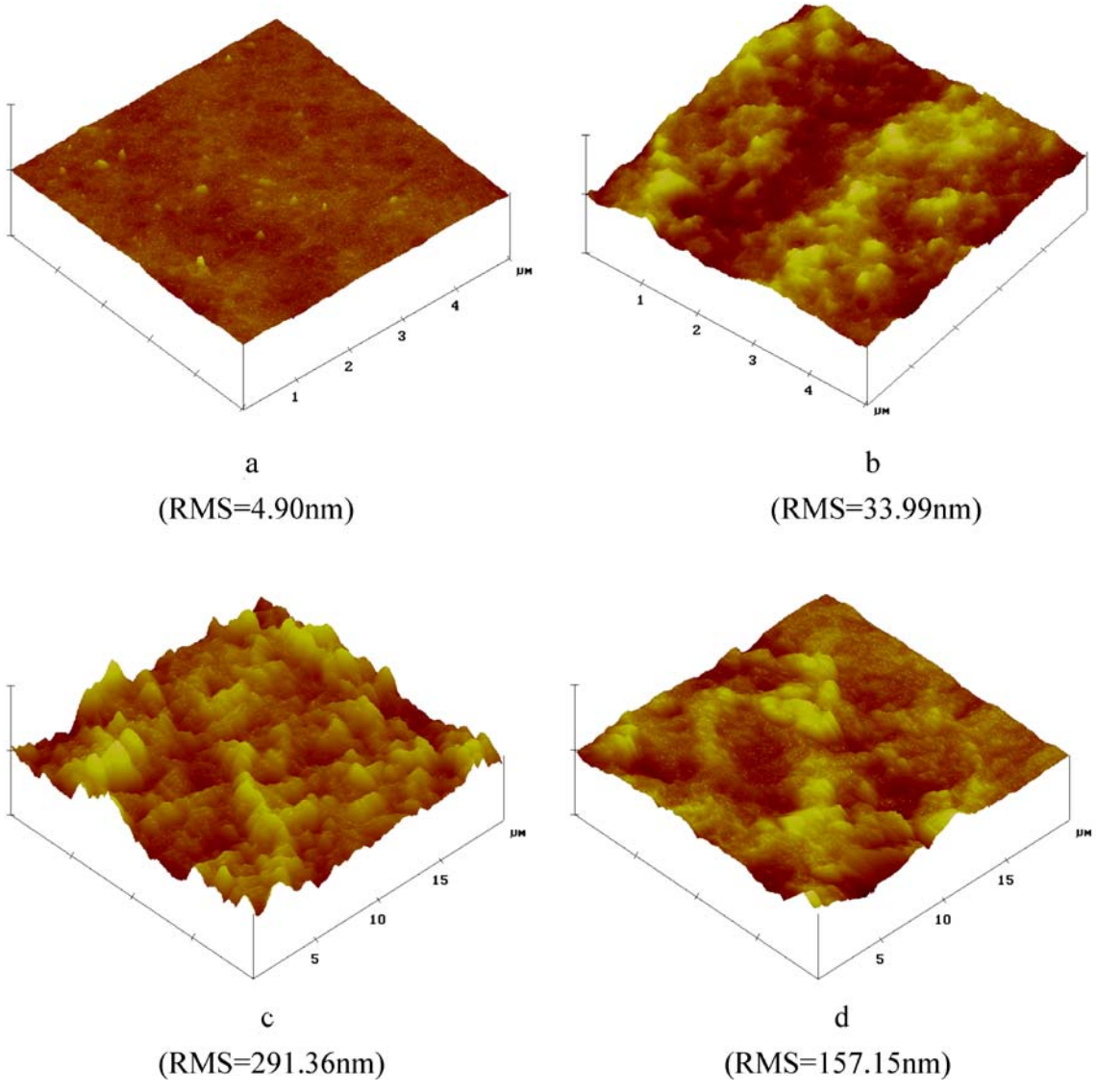


Fig. 7 AFM images of the film: as-cast without silica (**a**) and with A200 (4 %) (**b**), abrasion tested a (**c**) and b (**d**)

decreased with the addition of silica, implying that silica provides barrier to the migration of water, and the effect is more pronounced with hydrophobic one as noted from the contact angle measurements. Similar results have also been reported for waterborne PU/clay nanocomposite [11].

The effect of nanosilica on the thermal stability of UV–PUD cast film has been studied by the TGA measurements (Fig. 4). It has been reported that segmented PUs are thermally degraded in two steps, that is, hard segments at 200–260 °C and soft segments at 300–350 °C depending on the chemical structures of the segments [13, 14]. Our results show that soft, as well as hard segment, has significantly been thermally stabilized with the addition and increasing amount of silica, and again the effect is more pronounced with hydrophilic silicas, possibly implying a better dispersion of hydrophilic modified silica in PU ionomers where the ionic groups are hydrophilic in nature.

Based on the TGA diagrams, increase of decomposition temperature with silica is greater for hard segment than soft segment, which is especially true with hydrophilic modified one. This does not necessarily mean that silicas are preferentially embedded in hard segment domains; however, preferential reinforcement of hard segment necessarily means the reinforcement of segmented PU.

Stress–strain behaviors of the UV–PUD cast films are shown in Fig. 5 where a monotonic increase in initial modulus and strength and decrease in elongation at break with the addition of silica are seen. However, the difference between the two types of silica is marginal perhaps except for the initial modulus which is a bit greater with hydrophilic one. As expected, the abrasion resistance (Fig. 6) is dramatically increased with the addition and increasing amount of silica, and again the effect is much more pronounced with the hydrophilic modified silica.

The AFM images of the cast films (Fig. 7) were taken to examine the effect of silica on surface morphology. The surface of as-cast film is very smooth when silica is not added, but it becomes rough and uneven with silica inclusion due to the existence of silica particles at the surfaces. However, when the film is subjected to abrasion cycles, silica-reinforced one gave much smooth surfaces than the unreinforced one. Surface roughening is mainly caused by plastic deformation [15], and such mechanism has been greatly suppressed by the inorganic fillers probably by the increased thermal stability.

Conclusions

UV–PUD/nanosilica hybrid composites have been synthesized and tested for dispersion size and various properties of dispersion cast films, and the following conclusions have been obtained.

Dispersion size and contact angle of the cast film increased with the addition and increasing amount of silica, indicating that silica particles are included inside the PU dispersion and augmented the hydrophobicity of the cast film. Water swell decreased to about half upon UV cure and further decreased with the addition of silica, especially with hydrophobic one.

The decomposition temperatures of PU, especially that of hard segment, increased with the addition and increasing amount of silica, thus reinforcing the thermal stability of segmented PU. The increased thermal stability seemingly suppressed the plastic yield deformation during abrasion cycle and provided high resistance with smooth surface. Tensile modulus and strength increased, and elongation at break decreased with the addition and increasing amount of silica.

The above effects were more pronounced with hydrophilic modified silica indicating a better dispersion of this type of silica in PU ionomers where the ionic center is hydrophilic in nature.

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