Synthesis and Characterization of Water-Borne Crosslinked Silylated Polyurethane Dispersions

S. Subramani,[1] J. M. Lee,[1] I. W. Cheong,[2] J. H. Kim[1]

[1]*Nanosphere Process and Technology Laboratory, Department of Chemical Engineering, Yonsei University, 134, Shinchon-Dong, Sudaemoon-Ku, Seoul 120-749, South Korea*
[2]*Department of Applied Chemistry, Kyung pook National University, 1370 Sankyuk-dong, Buk-gu, Daegu 702-701, South Korea*

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ABSTRACT: A series of water-based polyurethane dispersions were synthesized by the polyaddition of isophorone diisocyanate, poly(oxytetramethylene) glycol, and dimethylol propionic acid as prepolymers, which were end-capped and crosslinked with 3-aminopropyl trimethoxysilane (APTMS) to produce silylated polyurethane dispersions (SPUDs). The dispersion was performed before the end-capping reaction to avoid gelation. Pure and tetraethylene pentamine chain-extended polyurethanes were also synthesized. The length of the soft segment and the ratio of NCO to OH were varied. The properties of these prepolymer dispersions were investigated with Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction, tensile and surface contact-angle measurements, nanoindentation testing, gel content, water and xylene swellability, and storage stability. An increase in the modulus and hardness and a decrease in the tensile properties of SPUDs were noticed in comparison with a pure polyurethane dispersion. This may have been due to the smaller number of hydrogen bonds and the brittleness of the film by the formation of crosslinked siloxane networks through the hydrolysis–condensation reaction of methoxysilane groups of silylated polyurethane, and it was also confirmed by the reactions of APTMS end capping and crosslinking. The gel content of SPUDs increased with the NCO/OH ratio, and all the prepared samples were amorphous in nature. The thermal stability of SPUDs was higher than that of pure and amine-chain-extended polyurethane dispersions. A decrease in the water and solvent swelling and an increase in the water contact angle confirmed the effective crosslinking of the silanol groups of the silylated polyurethane. Storage-stability results showed that all the prepared dispersions were stable for more than 3 months.
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Key words: crosslinking; dispersions; hardness; indentation; polyurethanes; thermogravimetric analysis (TGA)

INTRODUCTION

Because of the ever-increasing needs of modern society, scientists are focusing their attention on the synthesis of specialty materials. Polymers traditionally used for their mechanical abilities are now being developed as specialty materials for specific applications. Polyurethanes (PUs) are proven high-performance engineering materials with excellent mechanical strength, high chemical and solvent resistance, and so forth. Because of these versatile properties, they have an almost unlimited spectrum of applications as specialty polymers for advanced technologies. One of the major applications of polymeric materials is in coatings. Coatings are highly required, providing an aesthetic look to materials and protecting materials from environmental deterioration.

Among the various polymers, PUs are predominantly used in coatings for their excellent chemical, water, solvent, and abrasion resistance as well as outstanding hardness and toughness. Conventionally, these PU coating formulations are diluted with an organic solvent. Because of the rapidly developing environmental regulations controlling air, water, and land pollution, coating industries have changed many of their manufacturing processes and coating formulations as a step toward minimizing the impact on the environment.

Several products are available for the reduction of environmental effects and have added-value applications such as high-solid alkyds, latices, alkyd emulsions, natural paints, and water-borne, photocure, and powder coatings. Water-borne products are attracting a lot of commercial interest because of their technical advantages, which include the following:

- The viscosity of water-borne coatings is low, and this makes their application easier.

Correspondence to: J. H. Kim (jayhkim@yonsei.ac.kr).

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TABLE I
Raw Materials Used to Prepare the Anionic PUDs

Designation	Chemical description	Supplier
PTMG-1000	Poly(oxytetramethylene) glycol (OH functionality = 2.0, MW = 1000)	Duksung Co., Ltd. (Korea)
PTMG-2000	Poly(oxytetramethylene) glycol (OH functionality = 2.0, MW = 2000)	Duksung Co., Ltd. (Korea)
DMPA	Dimethylolpropionic acid	Aldrich Chem., Co. (Milwaukee, WI)
IPDI	Isophorone diisocyanate	Aldrich Chem., Co. (Milwaukee, WI)
APTMS	3-Aminopropyl trimethoxysilane	Aldrich Chem., Co. (Milwaukee, WI)
TEPA	Tetraethylene pentamine	Aldrich Chem., Co. (Milwaukee, WI)
TEA	Triethylamine	Duksan Pharmaceutical Co. (Korea)
NMP	*N*-Methyl-2-pyrrolidone	Lancaster (UK)
DBTDL	Dibutyl tin dilaurate	Aldrich Chem., Co. (Milwaukee, WI)

MW, molecular weight.

- They are cheaper than other products.
- They have better finishing characteristics and are compatible with conventional coating systems.

In water-borne coatings, the molecular weight of the polymer is independent of the dispersion viscosity, and hence high-molecular-weight polymers with relatively low viscosity can be prepared. Because of the high molecular weight and solid content of the dispersions with low viscosity, the properties of the resulting films are superior to those of other coating analogues. PUs are made water-dispersible with external emulsifiers. However, they suffer a few disadvantages, as they require strong shear forces to disperse the polymer, and this results in coarse particles and poor dispersion stability. A unique method of dispersing PU in aqueous media is structural modification,[1] that is, modifying a hydrophobic PU backbone with built-in hydrophilic segments. The introduction of hydrophilic segments into the PU backbone is achieved by the incorporation of nonionic polyether segments such as poly(ethylene glycol) as hydrophilic segments. Dispersions obtained with poly(ethylene glycol) have poor storage-stability and film properties. Hydrophilic segments can also be introduced by the incorporation of ionic groups, which can be anionic,[2,3] cationic,[4,5] or zwitterionic.[6] Dispersions based on ionomers are more stable than nonionic dispersions.

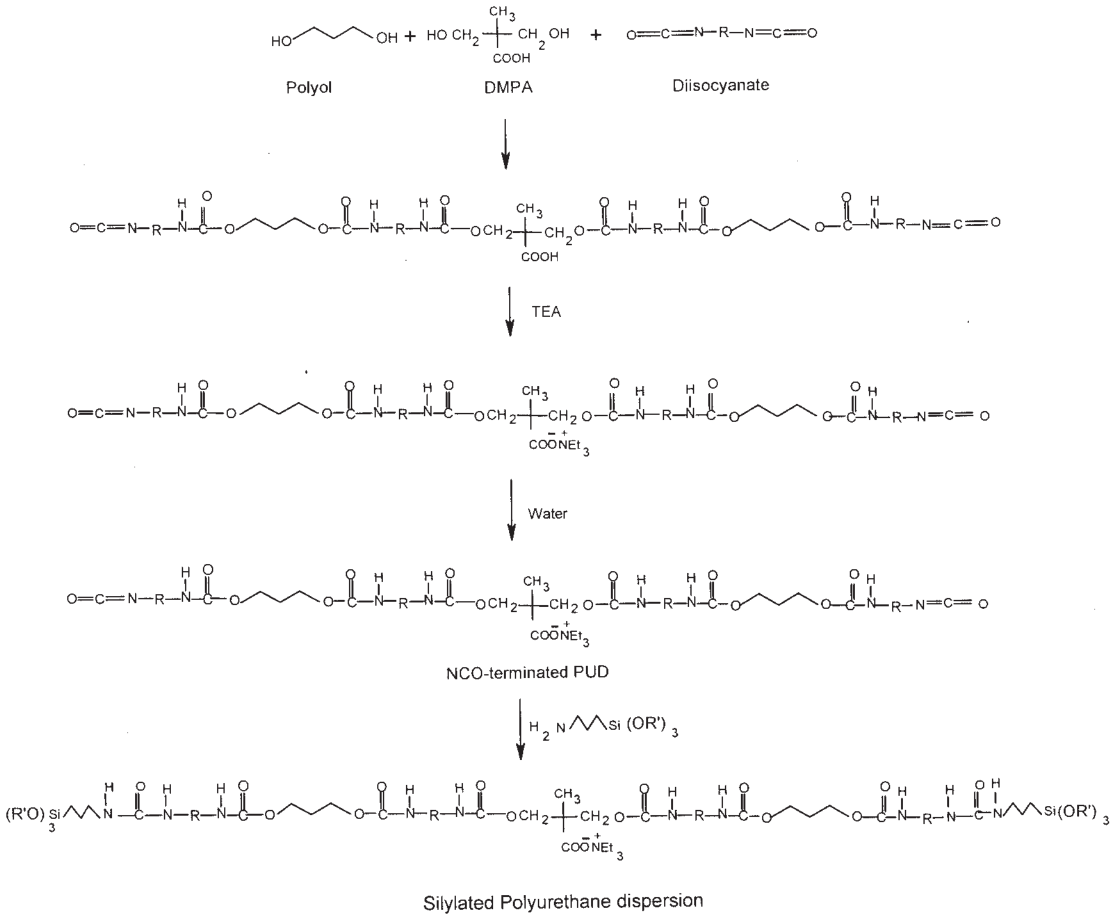
To compete with solvent-borne dispersions, the properties of water-borne dispersions must be improved. Most of the recent research work on PU aqueous dispersions is focused on improving properties such as the tensile strength, toughness, and solvent and water resistance.[7,8] This is achieved via grafting, crosslinking, and blending with other polymers. Crosslinking is widely used because of its simplicity. Many ways of crosslinking have been studied, including UV-crosslinking,[9] heat-activated,[10] and two-component systems. These crosslinking mechanisms have their own disadvantages. Heat-activated systems and UV-crosslinkable systems need either an oven or UV source, and this limits their use in industrial applications, whereas a two-component system has a limited pot life after mixing and involves the handling of carcinogenic crosslinkers such as aziridine. These factors have limited the scope of these systems.

A new method for the hydrophobic modification and crosslinking of polyurethane dispersions (PUDs) at ambient temperatures is described in this article. In the prepolymer–ionomer process, a hydrophilically modified prepolymer with terminated NCO groups is dispersed with water, and chain extension is accomplished by the addition of a diamine to the dispersion. In this work, 3-aminopropyl trimethoxysilane (APTMS) was used as crosslinker (chain extender) in place of diamine chain extenders to produce crosslinked PUDs. Silylated polyurethane dispersions (SPUDs) are generally composed of urethane backbones, containing hydrolysable groups on the silicon and one organic group including an isocyanate-reactive radical most suitable for forming the terminal groups. In the presence of moisture and a catalyst, these terminal groups undergo crosslinking reactions to form a stable siloxane-linked network,[11] which results in the desired solvent and water resistance. SPUDs are fast cure products that are free of residual NCO and exhibit superior physical properties. Products made with these resins exhibit fast curing times, greater durability, and improved adhesion, elongation, tensile strength, elasticity, toughness, abrasion resistance, and chemical resistance. In this work, stable SPUDs were synthesized and characterized, and the results were compared with pure and diamine-chain-extended PUDs.

EXPERIMENTAL

Materials

The raw materials used in this study are presented in Table I. The raw materials were laboratory-grade chemicals and were used as received, except for the polyols. The polyols [poly(oxytetramethylene) glycols (PTMGs)] were dried *in vacuo* at 100°C for 2 days



Scheme 1 Synthesis of anionic silylated PUD.

before use. *N*-Methyl-2-pyrrolidone (NMP) and acetone were stored over well-dried molecular sieves.

Synthesis of aqueous anionic SPUDs

Scheme 1 outlines the synthetic process used to prepare anionically modified water-dispersible silylated PU prepolymers. PTMG (number-average molecular weight = 1000 or 2000 g/mol) and dimethylol propionic acid (DMPA) in NMP were first charged into a reaction kettle equipped with a reflux condenser. The reaction mixture was stirred at 80°C under a nitrogen atmosphere. After complete mixing, isophorone diisocyanate (IPDI) was added slowly to the reaction mixture, and the reaction was allowed to proceed for 4 h. The prepared NCO-terminated PU prepolymers were cooled to 50°C, and the neutralizing agent [triethylamine (TEA)] was added and allowed to react for 30 min. Because of the high viscosity of the prepolymer mixture, acetone (25 mL) was added to dilute the system. At the end, water was added to accomplish the dispersion under vigorous stirring. After 15 min of water addition, APTMS was added and allowed to react with the NCO-terminated anionic PU prepolymer dispersion to produce an anionic SPUD. Finally, acetone was removed by the application of a low vacuum at 60°C to make an aqueous uniform dispersion.

Pure PUD without any chain extender and tetraethylene pentamine (TEPA) chain-extended PUD were also prepared by the same procedure. The compositions of the prepolymer (P1–P6) samples are given in Table II.

Characterization

The particle size was measured with a BI ZPA particle sizer (Brookhaven Instruments Corp., Holtsville, NY). The viscosity of the dispersions was measured with a Brookfield LVDV-II viscometer (Middleboro, MA) at 25°C. The dispersions in a sealed bottle were kept at room temperature to examine the storage stability. Fourier transform infrared (FTIR) spectra for the polymers were recorded with a Bruker Tensor 27 FTIR analyzer (Bruker Optics, Germany) in the range of 400–4000 cm^{-1} at room temperature. The tensile properties of the dispersion-cast films were measured with a universal tensile machine (Model LR101, Lloyds Instruments, Ltd., UK) at a crosshead speed of 100 mm/min. The films were prepared by the casting

TABLE II
Compositions of the Anionic PUDs (Weight in Grams)

Dispersion sample	NCO/OH	PTMG-2000	PTMG-1000	DMPA	IPDI	NMP	TEA	APTMS	TEPA
S1	1.4	57.12	—	3.83	17.78	7.66	2.89	—	—
S2	1.2	66.60	—	4.47	17.78	8.93	3.37	2.89	—
S3	1.4	57.12	—	3.83	17.78	7.66	2.89	4.93	—
S4	1.6	50.00	—	3.35	17.78	6.70	2.53	6.46	—
S5	1.4	—	36.62	2.75	17.78	5.50	2.08	4.93	—
S6	1.4	57.12	—	3.83	17.78	7.66	2.89	—	2.60

of the dispersions on release paper, followed by drying at 60°C for 5 h, and the samples were aged for 1 week before testing. Sample specimens were prepared from the films with a die 10 mm wide and 40 mm long, and the grip distance was set at 20 mm. The thickness of the films was 0.5–1.00 mm. For each film, three specimens were tested, and the average value is reported.

A TA Instruments DSC Q10 differential scanning calorimeter (TA Instruments, New Castle, DE) was used to examine the thermal properties of the PU prepolymers obtained from aqueous dispersions at a heating rate of 20°C/min under a nitrogen purge of 30 mL/min. The sample size was 3–10 mg in a sealed aluminum pan. Thermogravimetric analyses (TGAs) were carried out with a TA Instruments TGA Q50 thermogravimetric analyzer. The sample weight was 3–10 mg. The experimental run was performed from 30 to 600°C at a heating rate of 20°C/min in a nitrogen atmosphere with a gas flow rate of 30 mL/min.

An MTS XP system nanohardness tester (MTS Systems Corp., Eden Prairie, MN) was used to measure the mechanical properties of the SPUD films. In this experiment, a diamond Berkovich-type indenter tip was forced into the material being studied under continuous conditions. The indentation depth was related to the area of contact between the indenter and the tested material. Multiple indentations were made at different locations of the film surface at a fixed and applied load. The load–displacement curve was recorded, from which the effective hardness and modulus could be calculated. X-ray diffraction (XRD) experiments were performed directly on the film samples with a Rigaku D/max Rint 2000 X-ray diffractometer (Rigaku Corp., Japan) at 30 kV and 20 mA with a Cu Kα radiation source (λ = 1.5404 Å) at a scan speed of 4°/min in the range of 5–60°. The PUD samples were measured as films. The film thickness varied from 0.3 to 1.0 mm.

The water and xylene resistance of the films was measured as follows. Preweighed dry slabs (5 × 5 mm) were immersed in deionized water for 50 h to study the water resistance and in xylene for 25 h to study the xylene resistance at 25°C. After being immersed, the samples were blotted with laboratory tissue and weighed. The swelling ratio (water uptake) was expressed as the weight percentage of water in the swollen sample:

$$\text{Swelling ratio} = (W_S - W_D)/W_D \times 100\%$$

where W_D is the weight of the dry sample and W_S is the weight of the swollen sample.

Water contact angles were measured with a Phoenix Image PRO 300 contact-angle and surface-tension analyzer (Surface Electro Optics Co., Ltd., Korea). The data were collected after 1 drop of double-distilled water was placed on the surface of the film. At least three measurements were taken, and the average contact angle was calculated. The freeze–thaw stability of the dispersions was evaluated as follows: 5 mL of the dispersion was placed in a sealed weighing bottle. The bottle was first placed in a convection oven at 70°C for 5 h and was then transferred immediately to a refrigerator at 0°C for 5 h, which concluded a typical testing cycle. At least 10 such cycles were performed for each sample to observe whether any precipitation could be detected in response to the temperature. The gel content (degree of crosslinking) was attributed to that part of the SPUD films that was crosslinked and showed no dissolution upon extraction. The gel content is defined as follows:

$$\text{Gel content}(\%) = \text{Weight of undissolved SPUD(g)}/\text{Initial SPUD weight(g)} \times 100 \quad (1)$$

A sample of approximately 0.1 g (w_1) was wrapped in a 300-mesh stainless steel mesh of known mass (w_2) and exposed to 100 mL of xylene at 100°C for 24 h. The stainless steel mesh was then removed, and the mass was measured after vacuum drying at 80°C for 24 h (w_3). The degree of crosslinking was measured in terms of the gel content (%):

$$\text{Gel content}(\%) = [(w_3 - w_2)/w_1] \times 100 \quad (2)$$

The transparency was measured with a Shimadzu UV-2401 PC ultraviolet–visible spectrophotometer (Shimadzu, Japan) with a film 0.3 mm thick.

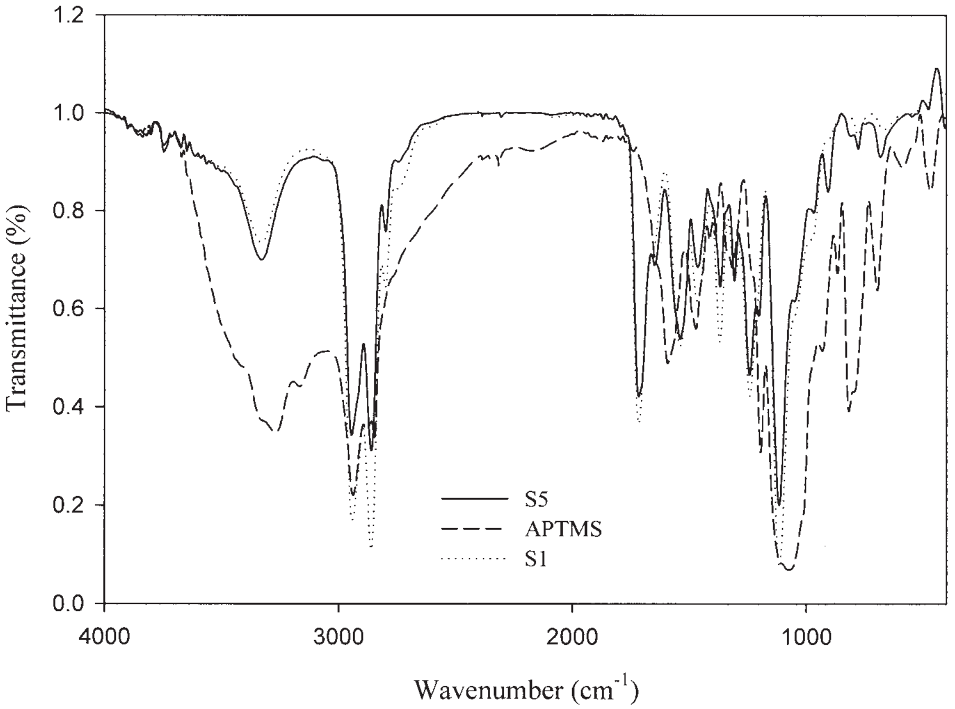


Figure 1 FTIR spectra of anionic pure, amine-chain-extended, and silylated PUDs.

RESULTS AND DISCUSSION

Synthesis of anionic SPUDs

SPUDs were prepared at 1.2, 1.4, and 1.6 NCO/OH ratios with the PTMG-2000 polyol. For a comparative study, pure PUD without chain extension and TEPA-chain-extended PUD were prepared at a 1.4 NCO/OH ratio with the PTMG-2000 polyol. The SPUD at a 1.4 NCO/OH ratio was prepared with the PTMG-1000 polyol to study the effect of the polyol molecular weight. It has been reported that about 60% of free NCO groups of IPDI can be available in the reaction with amine extenders after the dispersion process, and 40% of free NCO groups seem to be consumed by the side reaction with H_2O.[12,13] Hence, in all the experiments, the chain extenders (APTMS and TEPA) were added on the basis of 60% of the remaining NCO content after prepolymer formation. No catalyst was used to avoid any probable side reactions. The DMPA concentration was kept between 4.3 and 4.9 wt % in these experiments. The carboxylic groups of DMPA were neutralized by an equimolar amount of TEA. The solid contents of all the dispersions were measured and adjusted to 30%.

The FTIR spectra of the pure PUD, silylated anionic PU prepolymer, and APTMS are given in Figure 1. All the spectra are identical and show no absorption peak around the 2270-cm^{-1} range; this indicates that the NCO groups of the isocyanate molecule completely reacted with aminosilane. Strong absorptions at 1700 (C═O stretching of urethane and carboxylic groups), 2900 (CH_2 stretching vibration of PTMG), 1100 (C—O—C stretching vibration of PTMG, Si—O—C stretching, and Si—O—Si asymmetric stretching vibration of aminosilane), 3250–3300 (N—H stretching), 1530–1560 (N—H bending), 1210–1240 (stretching vibration of the C═O group of urea combined with the N—H group),[14] and about 800 cm^{-1} (Si—C stretching and Si—O—C deformation) confirmed the formation of the pure and silylated PU prepolymer.

Physical properties of the dispersions

The physical properties of the dispersions, that is, the particle size, viscosity, and pH of the SPUDs, are given in Table III. The pH of the dispersions obtained by the neutralization of weakly acidic pendant COOH groups of DMPA by a strong base, TEA, was weakly basic because of the remnant basicity of the internal salt groups. The pH of all the dispersions was basic in nature. The pH of the TEPA-chain-extended dispersion was more basic than that of the other dispersions. This was due to the greater basicity of TEPA.

The viscosity of all the dispersions was invariant, and this showed that the viscosity was not affected by the APTMS addition. The results also confirmed that the viscosity of the dispersions was not affected by the NCO/OH ratio, that is, the content of APTMS, the polyol molecular weight, and the chain extension with TEPA. The similar viscosities of all the dispersions were mainly due to the same content of carboxylic ions (DMPA content) and the same particle size for all the dispersions. They were also due to the low solid

TABLE III
Physical Properties of the Anionic PUDs

Dispersion sample	Particle size (nm)	Viscosity (Cps)[a]	*p*H	Stability	Transmittance (%) at 633 nm	514 nm	488 nm
S1	48	2.0	7.77	Stable	91.7	90.4	89.5
S2	48	2.0	7.60	Stable	87.4	86.2	85.1
S3	48	2.0	7.74	Stable	87.2	86.6	85.3
S4	49	2.0	7.67	Stable	87.8	86.0	85.5
S5	40	3.0	8.25	Stable	85.4	84.2	83.1
S6	47	2.0	9.03	Stable	71.8	62.3	58.9

[a] Measured at 30% solids.

content of the obtained dispersions and the low concentration of APTMS. The hydrolysis of the silane groups led to extensive crosslinking; the nanoparticle was globular in shape, and the polymer chains possessed covalent crosslinks that prevented free motion of the chains. This restricted motion might have resulted in the reduction of the viscosity. Generally, the particle size of PUDs depends on many factors, such as the type of isocyanate, the polyols, DMPA (hydrophilicity), and the viscosity of the prepolymer, and varies with their content and neutralization degree. The neutralization degree is the percentage of carboxylic groups that are neutralized to become carboxylic ions by a reaction with TEA, and it is proportional to the molar ratio of TEA to carboxylic groups. The carboxylic groups were neutralized by a reaction with equimolar amounts of TEA, and so the content of carboxylic ions was proportional to the content of carboxylic groups. The particle sizes of all the dispersions (S1–S6) were almost the same, except for S5. This result shows that the particle size of the dispersions was not affected by silylation, and this may have been due to the small amounts of APTMS used in the prepolymer preparation. Moreover, the complete hydrolysis and condensation of the silane groups occurred after the film formation, and hence there was not much variation in the particle size in the dispersion stage. The dispersion prepared with PTMG-2000 (S1–S4 and S6) showed a larger particle size than those prepared with PTMG-1000 (S5) because of the lower ionic content. Factors such as a high prepolymer molecular weight also favored a larger particle size in PTMG-2000-based dispersions.[15]

The storage stability of PUDs, which is an important parameter, depends on many functions, such as the pH, solid content, particle size, and viscosity of the medium. Because DMPA was used in this study and acted as an internal emulsifier, the resulting dispersion end-capped with aminosilane exhibited satisfactory stability in the whole range of testing temperatures of the freeze–thaw-stability test. No precipitation was observed. This feature might be desirable for their future applications. The SPUDs stored at room temperature for 6 months were also stable. All these results confirmed that the silylation of PUDs was not affected by APTMS and its concentration at various NCO/OH ratios.

Nanoindentation test

The mechanical properties (modulus and hardness) of a film mostly depend on the crosslinking density of the film. The changes in the depth, modulus, and hardness with an applied load of pure, amine-chain-extended, and SPUD films are summarized in Table IV, and load–displacement curves of the films obtained from nanoindentation testing are illustrated in Figure 2.

As shown in Table IV, with an applied load (target load = 50,000 μN), the penetration decreased in the order of S1 $>$ S2 $>$ S3 $>$ S5 $>$ S6 $>$ S4, and both the modulus and hardness increased in the order of S1 $<$ S2 $<$ S3 $<$ S5 $<$ S6 $<$ S4. From these data, it was known that the SPUD prepared at a 1.6 NCO/OH ratio and the amine-chain-extended PUD showed better properties than the other samples. For samples S3 and S5, which were prepared with different polyols at a 1.4 NCO/OH ratio, the properties were comparable. For samples S3 and S6, which were prepared at a 1.4 NCO/OH ratio, the modulus and hardness of sample S6 were higher than those of S3. On the basis of these results, we concluded that the physical and mechanical properties of the films could be easily adjusted through the formulation of the monomers and silanes to obtain better properties like those of amine-chain-extended PUs in PUDs.

TABLE IV
Nanoindentation Data of the Pure, Diamine-Chain-Extended, and Silylated Anionic PUD Films

Sample	Load (mN)	Depth $\times 10^{-4}$ (nm)	Modulus $\times 10^{2}$ (GPa)	Hardness $\times 10^{3}$ (GPa)
S1	27.8	5.4	1.1	1.3
S2	34.7	3.3	2.3	2.1
S3	36.2	3.1	2.5	2.5
S4	40.6	2.0	8.6	5.8
S5	35.8	3.1	2.8	2.6
S6	40.3	2.1	7.7	5.9

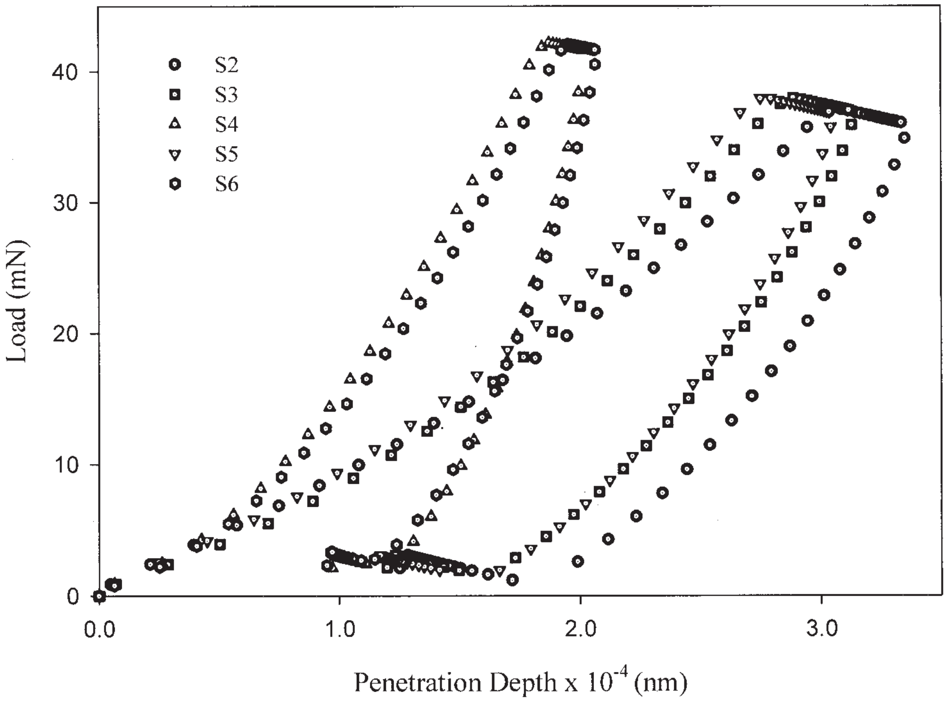


Figure 2 Indentation response of anionic silylated and amine-chain-extended PUD films with an applied load of 50,000 μN.

The hardness and gel content of the films were measured and are given in Tables IV and V, respectively.

The films of the SPUDs and TEPA-chain-extended PUDs (S2–S6) were less flexible than that of pure PUD (S1), and this was probably due to the reaction of —NCO end groups of the PU prepolymer with —NH_2 groups of aminosilane and TEPA, respectively. The aminosilylated PUD hydrolyzed rapidly (according to the pH of the medium) in the presence of water by generating less stable silanol groups, which could crosslink through a condensation reaction, forming siloxane networks. In the case of TEPA, it formed more urea groups in the chain-extension step. The urea groups had two nitrogen atoms suitable for forming hydrogen bonds. Therefore, the presence of the urea groups increased the rigidity (brittleness) of the material (by the formation of strong hydrogen bonding) and, consequently, resulted in an increase in the hardness of the film.[16] The film hardness of SPUDs increased with an increase in the NCO/OH ratio. This was probably due to an increase in the silane content of the dispersions from S2 to S4, which increased the crosslinking density (gel content). The greater hardness of S5, compared with that of S3, was due to the low soft-segment content and high crosslinking density of S5, which was prepared from PTMG-1000 with greater silane content. The film derived from dispersion S6 was harder than the other samples. This might have been due to the formation of the higher hard-segment content and higher gel content (crosslinking density) of the resulting film. Moreover, the short-chain diamine chain extender increased the hard-segment content (urea content) and, therefore, increased the hardness of the system. Compared with the TEPA-chain-extended PUs, the silylated PUs were more flexible. Generally, silicones are flexible (siloxane bond) in

TABLE V
Tensile and Swelling Properties of the Pure, Diamine-Chain-Extended, and Silylated Anionic PUDs

Film sample	TS (N/mm^2)	EL (%)	Water uptake (%)	Water contact angle (°)	Swelling in xylene (%)	Gel content (%)
S1	20.6	1255	12.2	62.28	1425	Dissolved
S2	7.0	530	6.4	74.80	319	38
S3	8.6	218	4.4	81.90	169	69
S4	9.8	95	3.4	84.50	108	89
S5	11.3	190	6.8	88.60	121	87
S6	4.9	138	8.7	70.00	87	90

TS, tensile strength; EL, elongation at break.

nature, whereas urea bonds are tough. Among the SPUD samples, S4 was harder than the other samples because of its higher crosslinking density (gel content).

Tensile properties

The mechanical properties of the SPUDs were determined from measurements of the tensile strength and elongation at break. The dispersions were poured into silicone troughs and dried in an air-circulating oven at 60°C for 5 h, and the dried films were kept under atmospheric conditions to effect the moisture-induced crosslinking of silane groups. These films were again dried at 100°C for 1 h before the tensile measurements, and the results are given in Table V. The tensile strength and elongation at break of the pure PUs were good. It has been generally observed that PTMG gives PUs with superior mechanical properties, mainly because of its regular chain structure and ability to crystallize upon extension.[17] Overall, the tensile properties of the crosslinked SPUD were lower than those of the pure PUD, mainly because of the greater hardness of the crosslinked polymers. Moreover, in the crosslinked SPUD, the siloxane units reduced the close packing and order of the hard segments. This might have been the cause of the reduction of the tensile properties of the crosslinked PUs.[18] However, the hardness and gel content (crosslinking density) of the SPUDs increased with an increase in the NCO/OH ratio, as shown in Tables IV and V, respectively.

In the aminosilane-end-capped PUD (S2–S4) series, the tensile strength increased and the elongation at break decreased with an increasing NCO/OH ratio; that is, an increase in the content of APTMS resulted in an increase in the crosslinking density (gel content) of the films. The increase in the tensile strength and the decrease in the elongation at break were mainly due to the self-crosslinking of functional alkoxysilane present at the chain end by the hydrolysis–condensation mechanism in the presence of atmospheric moisture. In the case of polyols, PTMG-1000-based PU (S5) showed a higher tensile strength and a lower elongation percentage than PTMG-2000-based PUs (S3), which were prepared at a 1.4 NCO/OH ratio. The high tensile strength and low elongation of the PTMG-1000-based samples were due to a higher hard-segment content and a greater aminosilane content, which resulted in a higher crosslinking density. Both the tensile strength and elongation of the films of the TEPA-chain-extended dispersion (S6) were lower than those of the other dispersions (S1–S5) of this series. This could be due to the greater toughness of the TEPA (containing two primary and three secondary amine functionalities)-chain-extended films resulting in a high crosslinking density (gel content). This was confirmed by the higher crosslinking density and hardness of S6 in comparison with those of the other samples (S1–S5). The higher crosslinking density made the film tougher, and it also might have been due to hydrogen-bonding interactions between the chains of S6.[19]

Swelling in water and xylene

As shown in Table V, the dispersion-cast films exhibited different swelling ratios in water and xylene. The aminosilane-end-capped PU samples exhibited much lower swelling ratios than that of pure unmodified PU because siloxane networks that formed in aminosilane-end-capped PUs migrated to the surface and prevented the solvent (water or xylene) molecule from getting into the bulk.[18] In particular, the siloxane group was hydrophobic in nature and hence reduced the water swelling to a major extent. The table also shows that the water and xylene swelling decreased from S2 to S4 with an increase in the aminosilane content (NCO/OH increased). There was not much difference in the water swelling of films S3 and S5. The swelling in xylene of S5 was lower than that of S3 because of an increase in the aminosilane content (crosslinking density) of S5. In comparison with TEPA-chain-extended PU (S6), aminosilane-end-capped PU exhibited lower water uptake and higher xylene swelling. The nature of the bond, the bond length, and the crosslinking density were the main factors responsible for this property. The siloxane bonds were flexible and highly hydrophobic in nature, so the water uptake of S3 was much less than that of tough TEPA-chain-extended PU (S6). The polar nature of S6 and water was also one of the reasons for more water uptake. More xylene swelling of S3 and less xylene swelling of S6 were due to the flexibility of the siloxane bonds and the toughness of the urea bonds, respectively.

Water contact angle

The water-contact-angle data of the prepared films are presented in Table V. The contact angle increased with increasing aminosilane content. The contact angle of the film of sample S5 prepared from PTMG-1000 was higher than those of the other samples. Generally, polymer molecules at the surface have greater freedom because of the mobility and flexibility of their constitutional units to rearrange themselves to accommodate the change in the chemical potential in the surrounding environment.[20] Owen et al.[21] proposed the following ways for the hydrophobic recovery of a polymer surface:

1. Reorientation of surface hydrophilic groups away from the surface.
2. External contamination of the polymer.
3. Changes in the surface roughness.

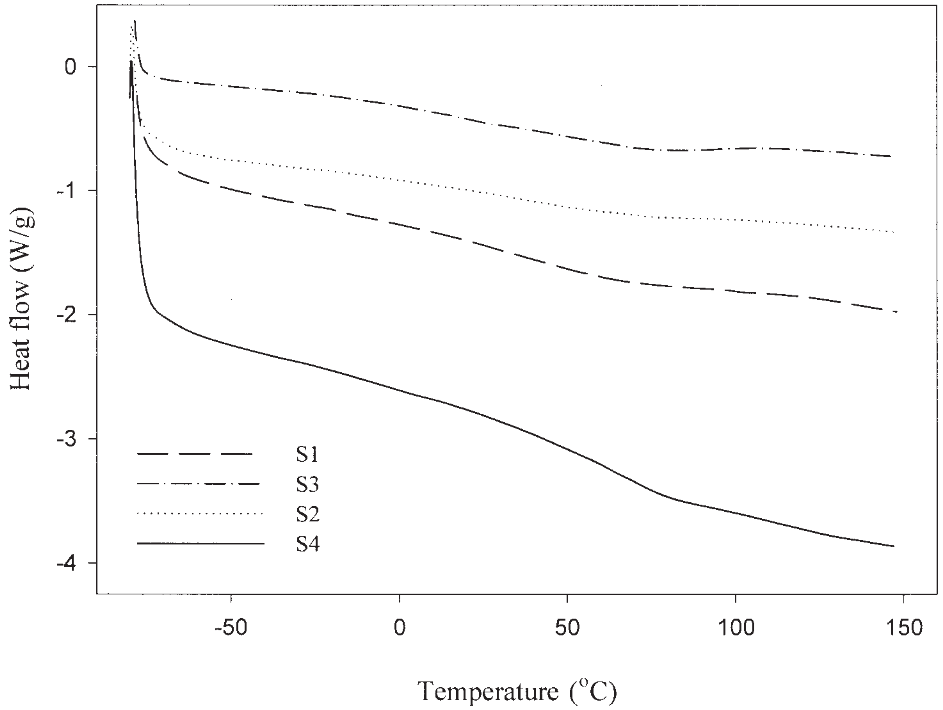


Figure 3 DSC curves of anionic pure and silylated PUDs.

Thus, a polymer can restructure or reorient its nonpolar components if it is exposed to an environment of air, creating a hydrophobic surface to minimize the free energy. If the polymer is exposed to a highly polar environment, the polar components orient toward the interface.[22,23] In this work, a hydrophilic PU in the form of a dispersion was cast as a film, which underwent moisture-induced curing that resulted in hydrophobic siloxane networks. The experimental results show that the contact angle increased with an increase in the aminosilane content. The increase in the contact angle indicates that the surface polarity decreased. This must have been due to the migration of low-energy chemical groups to the polymer–air interface to minimize the interfacial energy of the polymer–air interface. Hence, the aminosilane-end-capped PU films exhibited higher contact angles than the pure PU and TEPA-chain-extended PUs. In a comparison of the pure PU and TEPA-chain-extended PUs, the latter exhibited higher contact angles. This could be due to the chain extension and increase in the hydrophobicity of the TEPA-chain-extended PUs in comparison with the pure PU.

Thermal properties

A differential scanning calorimetry (DSC) technique was used to study the effect of silylation (APTMS) on the polyether soft-segment glass-transition temperature (T_g) of anionic PU prepolymer dispersions. Figures 3 and 4 show the DSC thermograms of anionic PU prepolymers. The T_g transition in the crosslinked PUs did not exhibit a typical sharp baseline shift; however, it showed T_g over a broad temperature range. These T_g's were detected for S1, S2, S3, and S6. T_g's of S4 and S5 could not be detected from DSC scans, probably because the transition extended over a wide interval and because of the high crosslinking density of these samples. The glass transition is due to molecular movement. However, in the crosslinked networks, these movements were arrested, and hence T_g's of the polymers could not be detected. T_g's of the silylated PU were higher than those of pure PU and TEPA-extended PU and also increased with an increase in the silane content (an increase in the NCO/OH ratio). The T_g values of pure, TEPA-chain-extended, and silylated PU prepolymers are given in Table VI.

TGA is a suitable technique for evaluating the thermal stability of PU materials. TGA curves are depicted in Figures 5 and 6. Figure 5 represents the degradation of pure PU prepolymer dispersion-cast films and silylated PU dispersion-cast films prepared at various NCO/OH ratios. The initial degradation temperature of pure, TEPA-chain-extended, and silylated PU prepolymers were 248, 239, and 260–265°C, respectively. There was a significant difference in the onset point of degradation between pure PU and silylated PUs. Among silylated PU films (S2–S5), there was no appreciable difference in the onset point of degradation. The thermal stability of silylated PUs was higher than that of TEPA-chain-extended PU. These results show

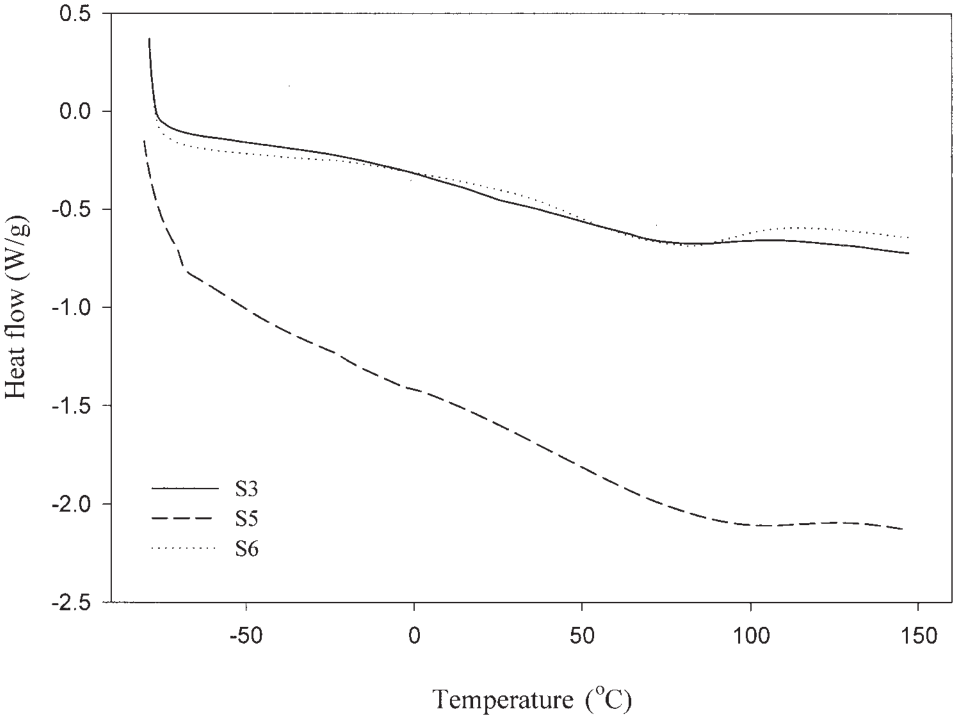


Figure 4 DSC curves of anionic amine-chain-extended and silylated PUDs.

that the silylation of PU increased the thermal stability of PU films, probably because of the higher thermal stability of the siloxane bond and crosslinking density of the silylated PU polymer obtained by a hydrolysis–condensation curing process with atmospheric moisture. The molecular weight of the polyol, the NCO/OH ratios, and the APTMS content showed no significant effects on the initial degradation temperature of the silylated PU. The silylated PU, prepared with a higher silane content, had higher retention of the weight percentage. The initial thermal degradation temperature of pure, TEPA-chain-extended, and silylated PU prepolymers are summarized in Table VI.

Crystallinity study and optical clarity

Figure 7 presents XRD curves of the PUD samples (S1, S2, and S4). All the samples (S1–S6) showed a broad band centered around a diffraction angle of 20°. This indicated that no significant crystallinity existed in any of the samples and that all the samples were amorphous materials. These results suggested that the soft segment was of insufficient length to crystallize and that the unsymmetrical nature of the diisocyanate was unlikely to form hard-segment crystallites. The results also implied that soft-segment/hard-segment phase mixings could disturb the soft-segment crystallization. The transparency of the nanocomposite films was measured and is presented in Table III. As shown in Table III, the transparency was not affected very much by the addition of a very small amount of aminosilane.

TABLE VI
T_g and Initial Decomposition Temperature Values of Pure, Diamine-Chain-Extended, and Silylated Anionic PUDs

Sample	T_g (°C)	Initial decomposition temperature (°C)
S1	−20	248
S2	−7	260
S3	−18	263
S4	—	265
S5	—	264
S6	−12	239

CONCLUSIONS

Stable, water-dispersible anionic SPUDs were synthesized and characterized. The particle size and viscosity of the prepared dispersions were the same and comparable. The mechanical properties of the SPUD films were good in comparison with those of the TEPA-extended PU films. The tensile properties of the SPUD films were lower and the film hardness of the SPUD films were higher than those of pure PUD. This may have been due to the lower number of hydrogen bonds and the brittleness of the film by the formation of crosslinked siloxane networks through the hydrolysis–condensation reaction of methoxysilane groups of silylated PU; it was also confirmed by the reactions of APTMS end capping and crosslinking. The gel content

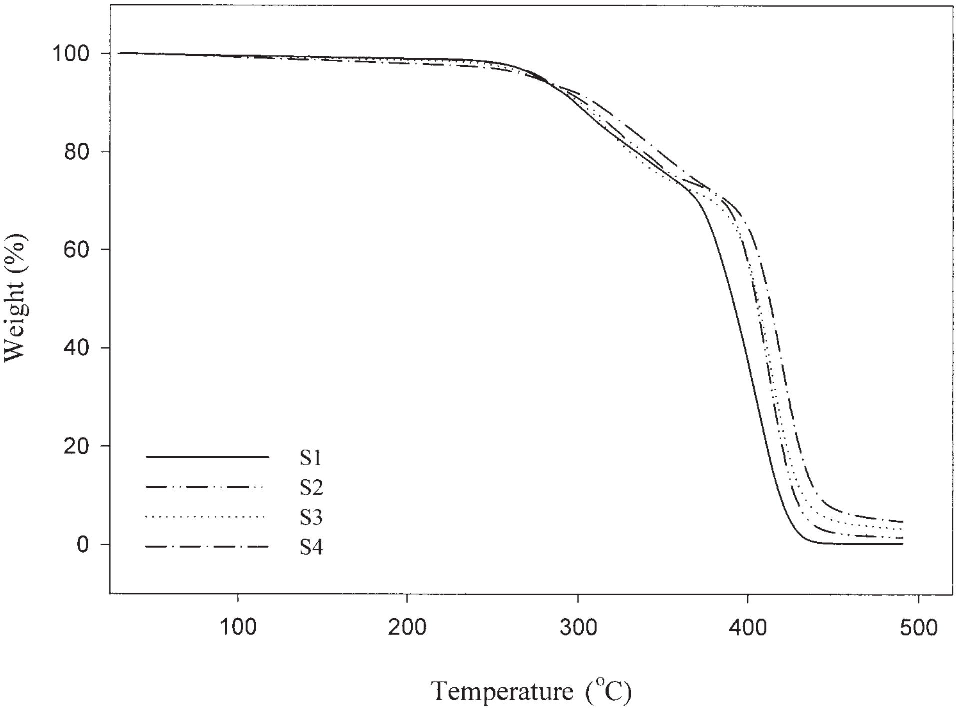


Figure 5 TGA curves of anionic pure and silylated PUDs.

of the SPUDs increased with the NCO/OH ratios, and the prepared samples were all amorphous in nature. The thermal stability of the SPUDs was higher than that of the pure and TEPA-chain-extended PU dispersions. A decrease in the water and solvent swelling and an increase in the water contact angle confirmed the effective crosslinking of silanol groups of silylated PU. The results of freeze–thaw-stability and storage-stability testing at room temperature showed that all prepared dispersions were stable for more than 6

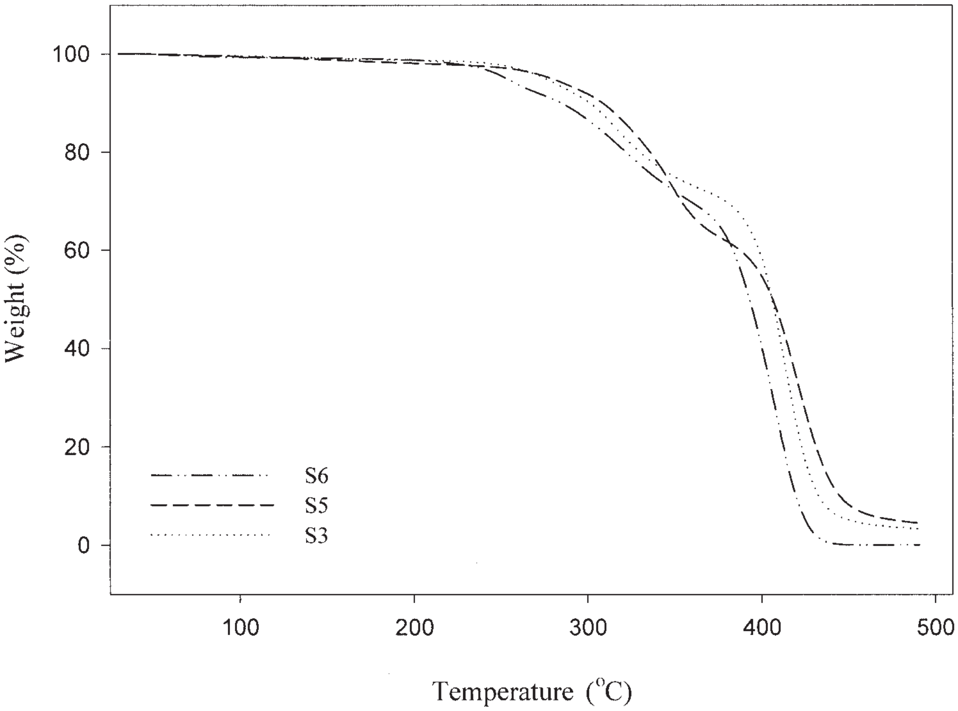


Figure 6 TGA curves of anionic amine-chain-extended and silylated PUDs.

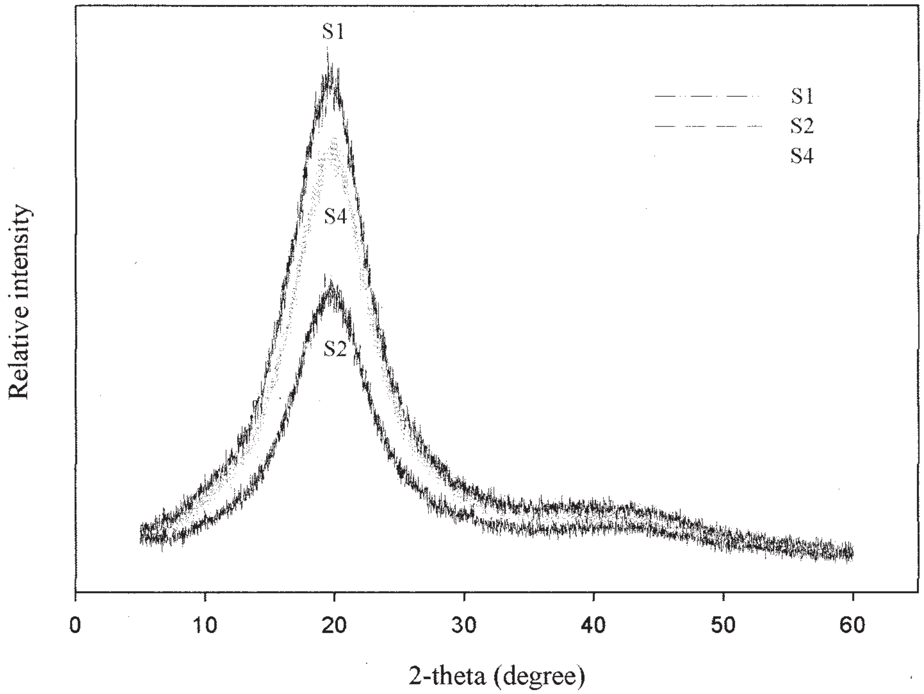


Figure 7 XRD profile of some dispersion-cast films.

months. This study effectively describes a way of preparing anionic aqueous SPUDs with remarkable storage stability. One-package silylated PU can be used as a coating material. The physical and mechanical properties of the films can be easily adjusted through the formulation of the monomers and silanes used in the urethane polymerization. The crosslinking density of the polymer can be tailored by the control of the silane derivatives reacted with the prepolymer.

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