Synthesis and characterizations of silylated polyurethane from methyl ethyl ketoxime-blocked polyurethane dispersion

S. Subramani, I.W. Cheong, J.H. Kim *

Nanosphere Process and Technology Laboratory, Department of Chemical Engineering, Yonsei University, 134, Shinchon-Dong, Sudaemoon-Ku, Seoul 120-749, South Korea

Abstract

Water-dispersible blocked polyurethane dispersions (BPUD) were synthesized by prepolymer mixing process using toluene 2,4-diisocyanate (TDI), 4,4′-diphenylmethane diisocyanate (MDI), poly(tetramethylene glycol) (PTMG), dimethylol propionic acid (DMPA), and methyl ethyl ketoxime (MEKO). The particle size, viscosity, pH and storage stability of the BPUDs were studied and compared. The aqueous dispersions were characterized by FT-IR, GPC, DSC and TGA techniques. De-blocking temperatures of the BPUDs were measured and end-capped with phenylamino propyl trimethoxysilane (PAPTMS) at different de-blocking temperatures. The thermal analysis revealed that both MDI- and TDI-based BPUDs started to de-block at about 60–85 °C. The average molecular weights of the MDI-BPUDs were higher than that of the TDI-BPUDs due to the high reactivity of MDI. It was noticed that the tensile strength increased and elongation at break decreased in the silylated BPUD compared to pure BPUDs, which confirmed that the BPUDs were de-blocked and end-capped with PAPTMS. The T_g values of the silylated BPUD were higher than the BPUD and pure PTMG as well as thermal stability. Storage stability results showed that all BPUDs containing PAPTMS were stable. Water and xylene resistance tests and gel content studies confirmed that silylated PU cross-linked well after silylation of blocked PUDs.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Water-dispersible; Silylated polyurethane dispersions; Thermal properties; Endcapped; De-blocking

1. Introduction

Polyurethanes (PUs) are noted for their high performance due to their excellent chemical, solvent, and abrasion resistance as well as outstanding hardness and toughness combined with low temperature flexibility. These desirable properties make PUs suitable for many coating applications. In the raw material stage diisocyanate or polyisocyanate used in the synthesis is highly moisture sensitive. Conventional PU coatings and adhesives contain significant amounts of volatile organic solvents and some also contain free isocyanate monomers. The effects of volatile organic solvents on the environment are detrimental and hence there is a growing concern about solvent emissions. In addition to the environmental issues, escalating prices of petroleum-based solvents have led to an increased emphasis towards the development of water-borne coatings.

* Corresponding author. Tel.: +82 2 2123 4162; fax: +82 2 312 0305.

*E-mail address:* jayhkim@yonsei.ac.kr (J.H. Kim).

Basically, PUs are hydrophobic. However, it is possible to emulsify, disperse or even dissolve the PUs in water if necessary structural modifications are done. PUs can be dispersed in water with the aid of a protective colloid, external emulsifier or by structural modification [1]. The first two methods suffer a few disadvantages, as they require strong shear force to disperse the polymer, which results in coarse particles and poor dispersion stability. A unique method of dispersing PU in aqueous media is by structural modification, i.e., modifying hydrophobic PU backbone with built-in hydrophilic groups [2,3]. PUs with built-in hydrophilic groups are termed internal emulsifiers or self-emulsifiers. The advantages of the latter method are:

- The hydrophilically modified PU can be dispersed under mild conditions.
- Dispersions with finer particle size are obtained and hence the stability of the dispersion is subsequently increased and
- The films formed from the dispersion have improved solvent and water resistance.

Depending on the type of ionic group incorporated, dispersions can be classified as anionic [4,5], cationic [6,7] and zwitterionic [8]. Anionic dispersions are commercially predominant [9,10].

In industrial practice, there are different methods available for the preparation of water-borne PUs such as the acetone process, prepolymer–ionomer process, and melt dispersion process, among others [11,12]. The critical step in which the various processes differ is the high molecular weight build-up during the chain extension step. This may result in the instability of the final dispersion. 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 diamine to the dispersion. Due to the reaction of NCO groups with water, there is a loss of available NCO groups for chain extension and also the process is highly applicable to aliphatic isocyanates having low reactivity toward water molecules. The above said disadvantages and requirements of one-package systems have led to the development of blocked isocyanate containing urethane prepolymers as precursors for water-borne urethane coatings. Merging the technologies of aqueous PU dispersions and blocked PU could result in high quality, one-package systems and low VOCs, coatings with long pot-life and low film formation temperature. Blocked isocyanates are derivatives of isocyanates, formed by the reaction of an isocyanate with an active hydrogen atom. When heated, the blocked isocyanate dissociates into isocyanate and the blocking agent and the isocyanate then reacts with an active hydroxyl func-

tional resin to form thermally stable bonds. The overall reaction can be seen as:
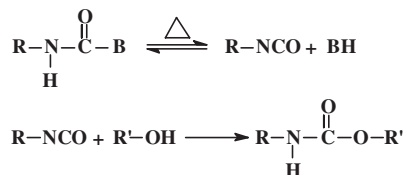
(where the BH is the blocking agent). Commercial blocking agents are phenol, ε-caprolactam, methyl ethyl ketoxime (MEKO), dimethyl pyrazoles, diethyl malonates, sodium bisulfite, etc. Imidazoles and amines were also used as blocking agents [13–16].

Recently, research work is oriented towards improving mechanical properties including solvent, water, scratch, and abrasion resistance properties. Water-based polyurethane dispersions (PUDs) are generally made of linear PU chains having ionic groups. Due to the linear structure, solvent resistance properties are poor and hydrophilic modifications lead to poor water resistance. Both drawbacks can be improved by cross-linking the PU chains.

A novel method for the hydrophobic modification and cross-linking of PUDs at ambient temperatures has been described in this paper. An extension to existing conventional urethane technology, silylated polyurethanes allow us to produce fast cure products that are free from residual NCO and exhibit superior physical properties. Silane endcapping extends the property range of polyurethane backbones. Products made by using these resins exhibit fast curing time, greater durability, improved adhesion, elongation, tensile strength, elasticity, toughness, abrasion, water, heat and chemical resistance. The silane-endcapped compounds are generally comprised 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. These terminal groups undergo cross-linking reactions to form a stable siloxane-linked network in the presence of moisture and/or catalyst. The prepolymers can be formulated into one-pack moisture or room temperature curable products with other polymers and additives.

In general, alkoxysilanes undergo slow hydrolysis leading to cross-linking thus forming siloxane networks in moisture-borne environment. The silanes having hydrophobic back bone and cross-linked network expected to render the desired solvent and water resistant properties. By keeping this in mind, it is attempted to prepare stable silane containing or end-capped PUDs by using blocked PU and aminosilanes and their properties are characterized and compared.

2. Experimental

2.1. Materials

The raw materials used in this study are presented in Table 1. The raw materials are laboratory grade chemicals and were used as received except polyols. The polyols (PTMGs) were dried in vacuum at 100 °C for 16 h before use. NMP and acetone were stored over well-dried molecular sieve.

2.2. Synthesis of aqueous anionic blocked PU dispersion

The reaction scheme shown outlines the synthetic process used to prepare water-dispersible blocked anionic polyurethane dispersion (BPUD) (Scheme 1). Poly(oxytetramethylene glycol) (PTMG, $\overline{M}_n = 1000$ and 2000 gmol^{-1}) and dimethylol propionic acid (DMPA) in N-methyl-2-pyrrolidone were firstly charged into the reaction kettle equipped with a reflux condenser. The reaction mixture was stirred at 75 °C under nitrogen atmosphere. After complete mixing, diisocyanate (MDI or TDI) was added to the reaction mixture. During the reaction, the change in isocyanate (NCO) content was determined by using a standard di-n-butylamine back titration until the theoretical end point was reached which was approximately about 2–3 h of reaction [17]. Then the reaction mixture was cooled down to 60 °C and the calculated amount of blocking agent diluted with 150 ml of acetone, was slowly added. The reaction was carried out until the NCO peak disappeared in the FT-IR spectrum. The obtained blocked PU prepolymers were cooled to 50 °C and the neutralizing agent (TEA) was added and allowed to react for 30 min. At the end, water was added to accomplish the dispersion under vigorous stirring. A uniform dispersion was obtained, from which the acetone was removed under low vacuum at 60 °C. All the experiments were carried out without catalyst to avoid side reactions. Compositions of each prepolymer (P1-P4) sample are given in Table 2.

In the above anionic blocked isocyanate prepolymers (BPUD), phenylaminopropyl trimethoxy silane (PAPTMS) was added in stoichiometric amounts, based on the isocyanate content, as end-capper/cross-linking agent to make one-package cross-linkable waterborne coating material.

2.3. Film formation and curing

The BPUD containing PAPTMS were coated using a silicone trough and dried in a convection oven at various de-blocking temperatures. The temperature was fixed above the de-blocking temperature to effect the reaction between aminosilane and blocked PU anionomer. After 30 min of baking, the films were removed from the oven and kept at room temperature for one week to effect moisture curing of the terminal alkoxysilane (methoxysilane) groups. The cured films were well dried in a vacuum oven and taken for characterization.

2.4. Characterizations

The particle size of the BPUD was measured using a BI- particle sizer ZPA (Brookhaven Inst. Co.). The viscosity of the BPUD was measured using a Brookfield LVDV-II viscometer at 25 °C. BPUDs in a sealed bottle were kept in a convection oven at 60 °C to examine their storage stability.

Fourier transition infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR analyzer in the range 400–4000 cm^{-1} at room temperature.

The average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity index (PDI, $\overline{M}_w/\overline{M}_n$) were measured by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a series of μ Styragel® columns (HR1, HR4, HR5 and HR5E), an Isocratic HLPC pump (Waters 1515), an Autosampler (Waters 717), a 2410 differential refractometer (RI detector) and integrator at 40 °C. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mlmin^{-1} and 1.0×10^3 Pa pump pressure. The molecular weight

Table 1
List of raw materials used in the preparation of anionic BPUDs

Designation	Chemical description	Suppliers
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
MDI	4,4′-methylene biphenyl isocyanae	Aldrich
TDI	Toluene 2,4-diisocyanate	Junsei Chemical Co., Ltd (Japan)
MEKO	Methyl ethyl ketoxime	Aldrich
PAPTMS	Phenylamino propyl trimethoxy silane	Aldrich
TEA	Triethylamine	Duksan Pharmaceutical Co., Korea
NMP	N-methyl-2-pyrrolidone	Lancaster
DBTDL	Di-butyl tin dilaurate	Aldrich
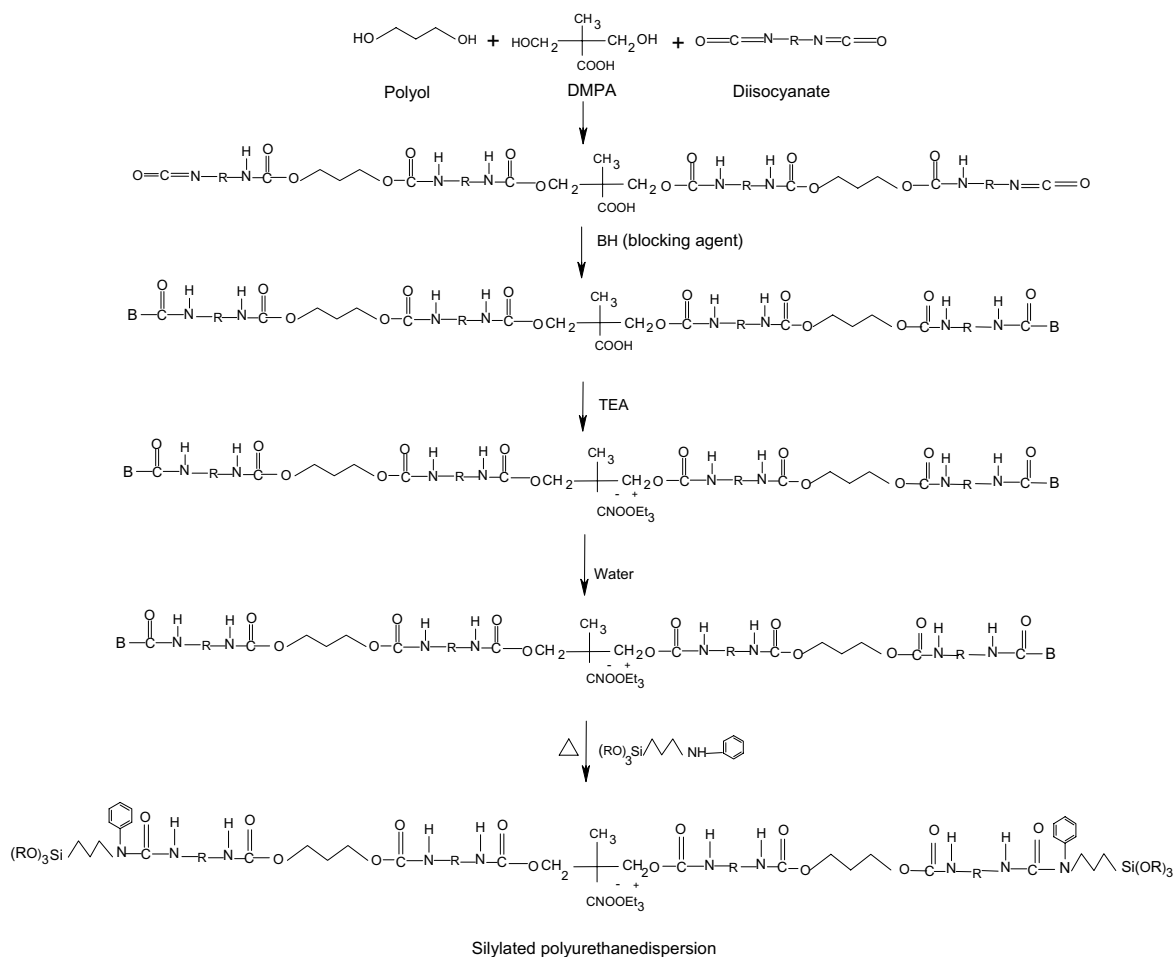
Scheme 1. Synthesis of anionically modified BPUD and its reaction with aminosilane (PAPTMS).

Table 2
Composition of anionic BPUDs (weight in grams)

Prepolymer dispersions	MDI	TDI	DMPA	NMP	TEA	PTMG-1000	PTMG-2000	MEKO	Storage stability (months)	
									RT	60 °C
P1	40.04	–	8.05	16.10	6.07	60.00	–	6.97	>6	>1
P2	30.03	–	6.04	12.08	4.56	–	90.00	5.23	>6	>1
P3	–	27.87	8.05	16.10	6.07	60.00	–	6.97	>6	>1
P4	–	20.88	6.04	12.08	4.56	–	90.00	5.23	>6	>1

calibration was carried out using polystyrene standards having molecular weights ($\overline{M}_w$) in the range of 1.024×10^3 to 3.9×10^6 g mol^{-1}. Molecular weight analysis was done before the neutralization process.

The tensile properties of the dispersion-cast films were measured using a universal tensile machine (IN-STRON) at a cross-head speed of 0.1 mmin^{-1}. Sample specimens were prepared from the films with a die of dimensions of 10 mm width and 40 mm length, the grip distance was set at 20 mm. The thickness of the film was 0.5–1.0 mm. For each film two specimens were tested and the average value is reported.

A differential scanning calorimeter (DSC), TA Instruments Model DSC Q10 was used to examine the

thermal properties of the blocked PU prepolymer obtained from aqueous dispersions with a heating rate of 20 °C min^{-1} under nitrogen purge of 30 ml min^{-1}. The sample size was 3–10 mg in a sealed aluminum pan.

Thermo-gravimetric analysis (TGA) was carried out with a TA Instruments Model TGA Q50 thermo-gravimetric analyzer. The sample weight was 5–10 mg. The experimental run was performed from 30 to 600 °C at a heating rate of 20 °C min^{-1} in nitrogen atmosphere with a gas flow rate of 30 ml min^{-1}. Samples obtained before the neutralization step were washed thoroughly with water for several times and well dried in a vacuum oven at room temperature for thermal analysis. Blocked and aminosilane endcapped/cross-linked samples were dried well in a vacuum oven before testing.

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

$$\text{Swelling ratio} = (W_S - W_D)/W_D \times 100\% \qquad (1)$$

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

The gel content was calculated as follows: A sample of approximately 0.1 g ($w1$) was wrapped in 300-mesh stainless steel mesh of known mass ($w2$) 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 ($w3$). The degree of cross-linking was measured in terms of the percent gel content, using the equation

$$\text{Gel content}(\%) = \{(w3 - w2)/w1\} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Synthesis

All the IR spectra of the silylated PUDs were identical and representative spectra of silylated PUD and pure BPUD are given in Fig. 1. The characteristic NCO absorption peak around 2270 cm^{-1} is absent which indicates the absence of free isocyanate groups. After deblocking the free isocyanate reacts with the aminosilane PAPTMS but due to the slower reactivity of PAPTMS the reaction may not go to completion. The absence of the NCO peak may be due to its reaction with inherent moisture or self-addition reaction. Strong absorptions at 1700 cm^{-1} (C=O stretching of urethane and carboxylic groups), 3250–3300 cm^{-1} (N–H stretching), 1530–1560 cm^{-1} (N–H bending) confirmed the formation of PUs.
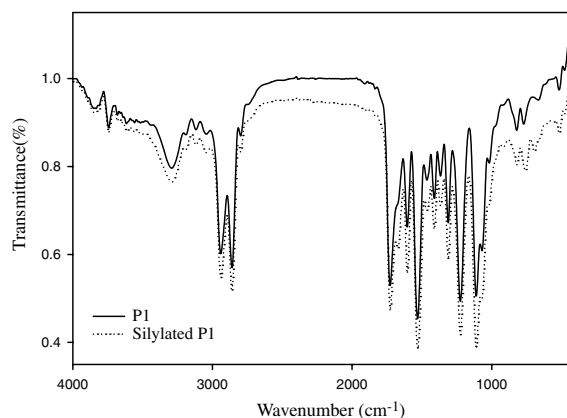

Fig. 1. FT-IR spectra of anionic MEKO-BPUD and PAPTMS cross-linked PU films.

Stretching vibrations of methyl protons of PTMG were absorbed around 2900 cm^{-1} and the C–O–C stretching vibration of PTMG was observed around 1100 cm^{-1}. Si–O–C stretching and Si–O–Si asymmetric stretching vibrations of PAPTMS were observed around 1100 cm^{-1}, which overlapped with the C–O–C absorption of PTMG. The stretching vibration of the C=O group of urea combined with the N–H group was observed around 1210–1240 cm^{-1} [18]. The absorption around 800 cm^{-1} (Si–C stretching and Si–O–C deformation) confirmed the formation of silylated PUs.

3.2. Molecular weight

Molecular weights of blocked PUDs were determined by GPC and are given in Table 3. The data showed that the weight-average molecular weight ($\overline{M}_w$) and the number–average molecular weight ($\overline{M}_n$) of MDI-BPUDs (P1 and P2) were higher than TDI-BPUDs (P3 and P4), which is due to the higher reactivity of MDI [19]. The low reactivity of TDI is attributed to the presence of methyl group in the molecule, which increases the electron density on the nitrogen atom and decreases the electrophilicity of the central carbon atom of the isocyanate bond. In general, electron-withdrawing groups increase the reactivity of the isocyanate while electron donor groups decrease it [20]. Polydispersity of MDI-BPUDs slightly higher than TDI-BPUDs which is also due to the high reactivity of MDI. Among the polyols, blocked prepolymers prepared from PTMG-2000 gave high molecular weight blocked PU.

3.3. Physical properties of the dispersions

Solid content of the obtained dispersions were adjusted to 28 wt%. Particle size, viscosity and pH of the BPUDs are presented in Table 3. The carboxylic groups

Table 3
Physical properties and thermal de-blocking temperature of anionic BPUDs

Prepolymer dispersions	Particle size (nm)	Viscosity (Cps)	pH	$\overline{M}_w$ (g mol^{-1})	$\overline{M}_n$ (g mol^{-1})	PDI	De-blocking temperature (°C)	
							DSC	TGA
P1	31	199	8.20	15194	6904	2.20	74–180	70
P2	52	60	8.48	20119	8749	2.30	75–180	85
P3	20	5	7.96	8492	4710	1.80	78–180	85
P4	26	3	7.70	12692	6207	2.05	60–180	80

$\overline{M}_w$: weight average molecular weight.
PDI: polydispersity index.

of DMPA were completely neutralized by TEA in all the experiments. The pH of the dispersions obtained by the neutralization of the weakly acidic pendant COOH groups of DMPA by a strong base, TEA, was weakly basic due to the remnant basicity of the internal salt groups. TDI-BPUDs were more basic in nature compared to MDI based dispersions. The high basicity of TDI-BPUDs was due to more DMPA-TEA content compared to MDI-BPUDs.

The viscosity of MDI-BPUDs was higher than the TDI-BPUDs. MDI-BPUDs have high molecular weight due to the high reactivity of MDI leading to high viscosity of the dispersions. This result is in accordance with the molecular weight. The viscosities of PTMG-2000-BPUDs were lower than PTMG-1000-BPUDs. It can be seen from Table 2 that in PTMG-2000-BPUDs, the DMPA content was lower than in PTMG-1000-BPUDs. This leads to lower ionic content in PTMG-2000-BPUDs. The lower the concentration of neutralized DMPA groups then lower the viscosity of the dispersions. Generally the average particle size of the dispersion increases with decreasing ionic content. When the particle size increases, the viscosity of the dispersion decreases due to smaller total effective volume of the particle. Moreover the ionomer dispersions are stabilized by formation of electrical double layer. When the ionic content decreases the thickness of the electrical double layer decreases and swelling of the particle in water also decreases. These collectively reduce the effective hydrodynamic volume of the dispersion and hence the viscosity of the dispersion decreases.

The particle size of PUD depends on many factors such as type of isocyanate, polyols, DMPA (hydrophilicity), blocking agents used, viscosity of the prepolymer and varies with ionic content and neutralization degree. In these experiments equimolar amount of TEA based on DMPA content was used to achieve 100% neutralization. Hence the amount of DMPA content directly corresponds to the ionic content of the PU. The particle size of TDI-based dispersions was smaller than the MDI-based ones. Polyurethanes from MDI have higher viscosity than the TDI based dispersion due to higher

reactivity of the former and it is well known that prepolymers with higher viscosity will give rise to larger particle size. In self-emulsification of ionomers, particle size increases with decreasing hydrophilicity, which is governed by the ionic content of the PU prepolymer. Dispersions prepared using PTMG-2000 (P2 and P4) showed larger particle size than those prepared using PTMG-1000 (P1 and P3). In the PTMG-2000-BPUD the DMPA content is lower than the PTMG-1000-BPUD, which resulted in larger particle size. Factor such as high prepolymer molecular weight also favors larger particle size in PTMG-2000-BPUDs [21]. It was reported that particle size decreases with the increase of molecular weight of polyol [21].

The storage stability of the BPUDs, which is an important parameter, depends on many functions like pH, solid content, particle size, and viscosity of the medium. Storage studies were performed at two conditions namely room temperature (25 °C) for six months and 60 °C for one month to evaluate the storage stability of dispersions and the results are tabulated in Table 3. The data reflect that all dispersions were stable. The stability clearly indicated that the de-blocking of the BPUD did not occur in the dispersion. The storage stability of the BPUDs containing PAPTMS stored at room temperature was stable for six months without any gelation. This is due to the low solids content of the dispersions. One might expect that the hydrolysis of silane groups in aqueous phase may destabilize the dispersions. The anionic PU dispersions are basic in nature. Aminosilanes are stable in basic conditions, which prevented the hydrolysis of silane groups leading to stable dispersions.

3.4. Tensile properties

The tensile properties of the films were evaluated and are presented in Table 4. In this test, BPUDs containing PAPTMS are de-blocked to regenerate free NCO groups and the regenerated NCO groups react further with PAPTMS to form aminosilylated PUD films. The silane end groups (trimethoxysilane) are hydrolyzed

Table 4
Tensile properties of pure and PAPTMS containing anionic BPUDs cross-linked at room temperature, 100, 125 and 150 °C

Curing temperature	Properties	Samples			
		P1	P2	P3	P4
Pure blocked PU	Tensile strength (N/mm^2)	2.7	1.4	2.1	1.1
	Elongation at break (%)	450	>500	>500	350
Room temperature	Tensile strength (N/mm^2)	11.7	5.5	12.5	8.4
	Elongation at break (%)	>500	>500	412	>500
100 °C	Tensile strength (N/mm^2)	14.2	8.4	15.0	9.3
	Elongation at break (%)	413	>500	488	>500
125 °C	Tensile strength (N/mm^2)	14.9	11.8	15.4	9.2
	Elongation at break (%)	225	360	413	428
150 °C	Tensile strength (N/mm^2)	14.7	11.4	12.7	9.2
	Elongation at break (%)	238	360	333	415

and cross-linked in the presence of moisture at room temperature by hydrolysis-condensation reaction leading to siloxane cross-linked network. For comparison, the tensile properties of pure BPUD films prepared under the same conditions were also measured. It was noted that the aminosilane containing and aminosilylated PUD films exhibited higher tensile properties compared to pure BPUDs. The variations in the tensile properties with diisocyanates (MDI and TDI) were also studied in terms of the molecular weight of polyol and curing temperature.

Generally, tensile strength increases with an increase in hard segment content and cross-linking density whereas elongation at break increases with increase in soft segment content. In the case of isocyanates, baked at different de-blocking temperatures, both MDI and TDI-BPUDs showed better tensile strength and percentage elongation with slight deviations. In the case of polyols, PTMG-1000-BPUDs have higher tensile strength and lower percentage elongation than PTMG-2000-BPUDs. This is because of the higher concentration of DMPA and the increase in hard segment content of PTMG-1000-BPUD [22,23]. The tensile strengths of samples cured at various de-blocking temperatures did not show much difference. This shows that variation of the baking temperature has no effect on de-blocking and formation of silylated PUD (urethane-urea bond) and this confirms that all samples de-block and end-capped with PAPTMS below 100 °C (initial de-blocking temperature of samples are lower than the baking temperature).

In the case of PAPTMS terminated PUD films after moisture curing, there is wide variation in the tensile properties compared to the pure BPUD films. The high tensile strength and decrease in elongation at break is mainly due to the self cross-linking of functional alkoxysilane present at prepolymer chain ends by moisture curing process at room temperature (hydrolysis–condensation mechanism). The result shows that the aminosilanes can be used as cross-linkers to impart

cross-linked networks in PU dispersions. The advantage of this method is that curing takes place after film formation, that is, after coating of the material hence the viscosity of the synthesized dispersion can be lower (non-crosslinked dispersion) and the curing process is also more convenient as it cures at room temperature. Moreover the cross-link density can be tailored by the choice of starting materials or building blocks according to the requirement.

3.5. Thermal properties

DSC technique was used to study the de-blocking properties because compounds synthesized contain different adduct structures and therefore, should exhibit significant energy variations (endothermic) when they de-block. The de-blocking temperature of the blocked isocyanates depends on the isocyanates and blocking agents. DSC results are given in Fig. 2. The DSC curves in Fig. 2 show broad endotherms around 74–180 °C of MEKO-blocked MDI-BPUD (P1) and 78–180 °C of
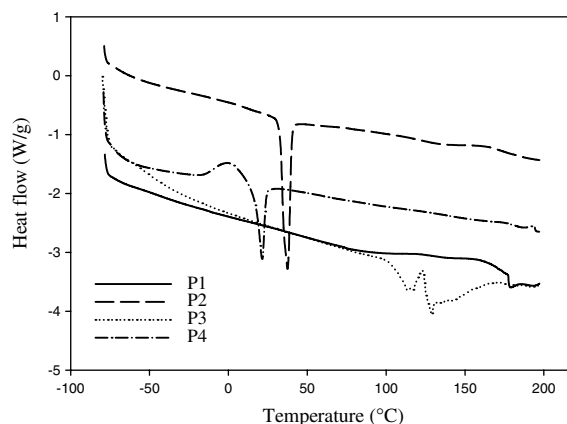

Fig. 2. DSC curves of anionic MEKO blocked-MDI and TDI PU dispersions.

MEKO-blocked TDI-BPUD (P3) samples. The de-blocking endotherm was clearly observed in the samples prepared using PTMG-1000. The de-blocking temperatures of MEKO-blocked MDI- and TDI-BPUDs were comparable and observed similar trend as that of the reported values of MEKO-blocked MDI- and TDI-BPUDs [24,25]. This is clearly due to the de-blocking phenomenon of blocked PU prepolymers and de-blocking temperatures were almost in the same range in all cases. The initial de-blocking temperatures of the above samples are lower than those of commercial MEKO-blocked TDI and MDI adducts. Similar behavior was observed in the DSC curves of BPUD samples P3 and P4. The de-blocking temperature of P4 was lower than that of P3. The molecular weight of polyols did not show any significant effect on the de-blocking behavior of blocked PU prepolymers prepared by using MDI while a difference was observed in de-blocking temperature of TDI-BPUD. The broad ranges of de-blocking temperatures of the BPUD samples may be due to slow and controlled release of blocking agents. Also, for anionic blocked urethane prepolymer samples, the melting of the short- and long-range order in the hard segment domains of the urethanes might take place at the same temperature range where de-blocking might occur [26]. This may also cause the broadening of the curve and interfere with the de-blocking temperature in the DSC measurement. The sharp endotherms at 40 °C of P2 and 20 °C of P4 were due to the melting of the soft segments of PTMG units. This soft segment melting is clearly observed in PTMG-2000 and it was not observed in PTMG-1000. This may resulted from favorable mixing condition with hard segment domain due to short soft segments of the polyol.

The experimental results of DSC of pure BPUD and PAPTMS endcapped PUD samples are summarized in Table 5. The T_g of pure BPUD samples of both MDI and TDI baked at 150 °C were observed at −55.6 and −51.8 °C, respectively. The T_g values of MDI-BPUD samples (P1 and P2) were lower compared to TDI-BPUD samples (P3 and P4). In the MDI-BPUD, the hard segments are more ordered which leads to hard segment cohesion and phase separation whereas in the TDI-BPUD the hard segments are less ordered that leads to low T_g of the soft segment. PAPTMS containing samples (P1 and P3) of the blocked PU dispersions dried at room temperature showed the T_g at −41 and −42 °C, respectively. This shows that the T_g of pure BPUD was lower than the T_g of samples containing PAPTMS and addition of PAPTMS increased the T_g of BPUD. The T_g values of the polyether soft segments of aminosilylated PU samples of P1 and P3 were found to be in the range of −41 to −43 °C and −38 to −42 °C, respectively. The T_g values of the soft segments of these samples were higher than those of pure poly (oxytetramethylene) glycol, which was reported as −86 °C. Baking temperature showed no significant effect on T_g while the molecular weight of the polyol showed more effect on the T_g of the obtained silylated PU from both MDI and TDI based dispersions as given in Table 5. The T_g values of aminosilylated PU prepared from polyol PTMG-1000 were higher than those prepared from PTMG-2000. When the molecular weight of polyol or prepolymer was increased, T_g decreased by about 25 °C, probably due to the decreased cross-linking density since the blocked PU prepolymers de-blocked and end-capped/cross-linked with PAPTMS [21]. DSC curves of selective silylated PUs baked at 125 °C are given in Fig. 3.

Thermo gravimetric analysis (TGA) is a very useful technique to observe the de-blocking temperature of blocked isocyanates, however, TGA could not be used for the compounds that did not exhibit volatility over the unblocking temperature range. The rate and extent of elimination reaction depend on several variables viz., the structure of the diisocyanates and blocking agents including substituents, solvents, the presence of catalysts and temperature. In order to obtain distinct

Table 5
Glass transition and initial decomposition temperatures of the pure, and PAPTMS containing anionic BPUDs cross-linked at room temperature, 100, 125 and 150 °C

| Samples	Baking temperature/time (°C/min)	T_g (°C)	Initial decomposition temperature (°C)
P1-PAPTMS	Room temperature	−41	175
P1-PAPTMS	De-blocked, 100/30	−43	188
P1-PAPTMS	De-blocked, 125/30	−42	261
P1-PAPTMS	De-blocked, 150/30	−43	263
P2-PAPTMS	De-blocked, 125/30	−67	272
P3-PAPTMS	Room temperature	−42	163
P3-PAPTMS	De-blocked, 100/30	−38	186
P3-PAPTMS	De-blocked, 125/30	−38	240
P3-PAPTMS	De-blocked, 150/30	−42	243
P4-PAPTMS	De-blocked, 125/30	−66	255
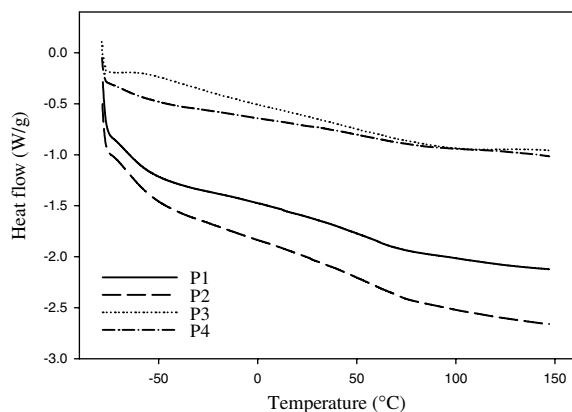
Fig. 3. DSC curves of anionic MEKO blocked-MDI and TDI PU dispersions containing PAPTMS baked at 125 °C.

differences for the de-blocking temperature, no catalyst was used for the de-blocking reaction.

The TGA curves of blocked PU prepolymers samples in Fig. 4 showed that the initial de-blocking of MEKO-blocked MDI based prepolymer samples (P1 and P2) occurred around 70–85 °C. The de-blocking of MEKO-blocked TDI (P3 and P4) samples was observed around 80–85 °C. These values were comparable to reported de-blocking values by TGA [24,25]. Similarly to the DSC results, the molecular weight of polyols did not show any significant effect on the de-blocking behavior of the blocked PU prepolymers and the de-blocking temperature of MEKO-blocked products was lower than that of commercial adducts. The samples, prepared using PTMG-2000 had higher retention in weight percent. The low de-blocking temperature of MEKO blocked PUs was also confirmed by our earlier report [27].
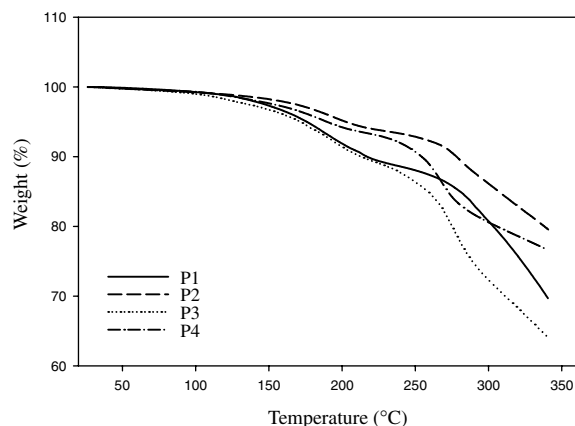
The TGA experimental results of the pure blocked PU prepolymer and PAPTMS-containing PU samples are summarized in Table 5. It was found that the thermal stability of the representative samples of P1 and P3 baked at different temperatures increased with increasing baking temperatures in both cases. The samples, baked at higher temperatures, had higher retention in weight percent. It indicated that the de-blocking was more complete at high baking temperature resulting in endcapping reaction/cross-linking and, thereby, higher thermal stability. The thermal stability of the samples showed that the high molecular weight polyol-PTMG-2000 (P2 and P4) produced aminosilylated PU with higher decomposition temperatures. The higher decomposition temperatures of PTMG-2000 based aminosilylated PUs were due to higher soft segment proportions [28]. The thermal stability of PAPTMS endcapped MDI based PU samples (P1and P2) were higher compared to the TDI based samples (P3 and P4), most likely because of the high reactivity of the MDI leading to higher molecular weight (soft segment) of the resulting aminosilylated PUs. The overall thermal stability of the aminosilylated samples was higher than the pure blocked PU prepolymers. The higher thermal stability of aminosilylated samples were due to the higher cross-linking density of the networks formed by hydrolysis-condensation of the alkoxysilane present at the chain ends at room temperature. Generally, silane compounds and silicones are thermally more stable and hydrophobic in nature. TGA curves of selective silylated PUs baked at various temperatures are given in Figs. 5–7.

3.6. Swelling (water and xylene) and gel content studies

As shown in Table 6, a representative sample (P4) was used to conduct this experiment and results were compared with other samples (P1, P2 and P3). It should be noted that the PAPTMS endcapped PU samples

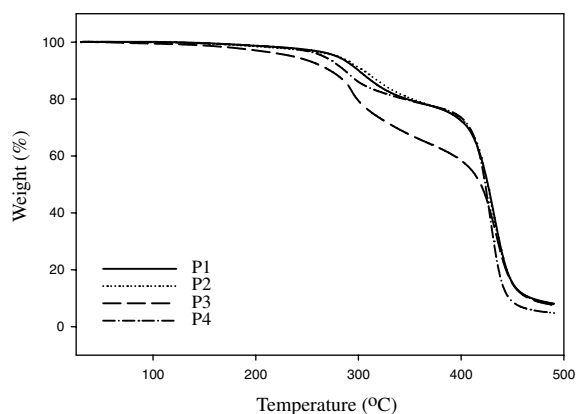Fig. 4. TGA curves of anionic MEKO blocked-MDI and TDI PU dispersions.

Fig. 5. TGA curves of anionic MEKO blocked-MDI and TDI PU dispersions containing PAPTMS baked at 125 °C.
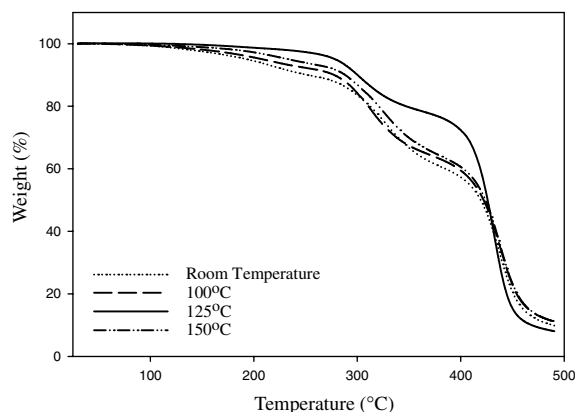
Fig. 6. TGA curves of anionic MEKO blocked-MDI PU dispersion (P1) containing PAPTMS baked at various temperatures.
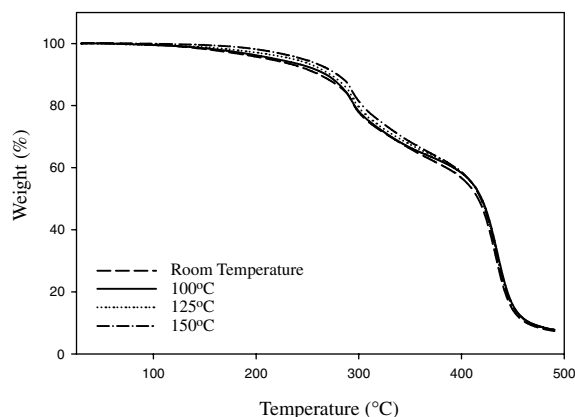

Fig. 7. TGA curves of anionic MEKO blocked-TDI PU dispersion (P3) containing PAPTMS baked at various temperatures.

Table 6
Swelling properties and gel content of pure and PAPTMS containing anionic BPUDs cross-linked at room temperature, 100, 125 and 150 °C

Samples	Percentage swelling (%)		Gel content (%)
	Water	Xylene	
P4-Pure	13.6	775	0
P4-RT	8.6	159	78.1
P4-100 °C	7.7	150	81.6
P4-125 °C	1.8	140	83.8
P4-150 °C	1.3	135	85.2
P1-100 °C	7.2	65	92.0
P2-100 °C	6.7	127	88.1
P3-100 °C	8.1	72	91.1

exhibited much lower swelling in both water and xylene than those of pure blocked PU. The detailed results were presented in Table 6. Swelling behavior of pure blocked PU sample increases to five-fold in xylene and two-fold in water compared to aminosilylated PU sample. The hydrophobic siloxane chains formed by hydrolyis and condensation of the trimethoxy silane with moisture migrate to the surface thus preventing the solvent (water or xylene) getting into the bulk and this might be the reason for less swelling of the samples. The swelling ratio of PAPTMS containing blocked PU sample baked at different de-blocking temperatures decreased with increasing baking temperature. With increase in baking temperature, the de-blocking reaction and the reaction with PAPTMS were complete which led to high cross-linking density. Hence the swelling ratio of the samples decreased. In the case of polyols, samples prepared using PTMG-2000 (P2) showed slightly lower swelling in water and more swelling in xylene than PTMG-1000 (P1) of MDI based samples. Generally, the hydrophobicity of PU based on PTMG-2000 was higher due to lower DMPA content leading to decrease in water swelling. The same trend was observed in the case of samples P3 and P4 prepared from TDI. In the case of isocyanates, MDI (P1 and P2) showed more resistance to water and xylene swelling compared to TDI (P3 and P4). The above results confirmed that the reduced swelling was due to the effective cross-linking of trimethoxysilane groups at the chain ends by moisture curing process. This result indicates that high cross-linking density via the siloxane bonds formation increases the solvent and water resistance which is highly required for coating materials. Hence silylation of PU by blocked PU process can be a viable alternate pathway for improving the properties of aqueous PU dispersions. From the percent gel content of silylated PUs it can be concluded that all PU samples cross-linked well after de-blocking and reacted with PAPTMS. The gel content of MDI and PTMG-1000 based PU was slightly higher than that of TDI and the PTMG-2000 based samples and also increased with increasing the de-blocking temperature. Disintegration of the pure BPUD film showed that the polymer was linear and non-crosslinked.

4. Conclusions

Stable aqueous anionomer-type MEKO-blocked aromatic PU (TDI and MDI) dispersions were prepared and characterized. The particle size and the viscosity of MDI based dispersions were higher compared to TDI based dispersions. Molecular weight ($\overline{M}_w$ and $\overline{M}_n$) of MDI based dispersions was higher than TDI based dispersions due to the high reactivity of MDI. These blocked PUs were de-blocked and end-capped with PAPTMS at different de-blocking temperatures. High tensile strength and

decrease in elongation of silylated PUs compared to pure anionic blocked PU dispersions confirmed that the blocked PU dispersions end-capped/cross-linked well with PAPTMS. The thermal studies of the dispersions confirmed that both MDI and TDI based dispersions de-block at about 60–85 °C. The thermal stability, water and solvent resistance of the silylated PUs was high. Gel content studies showed that silylated PUs were cross-linked well after silylation. The T_g values of the silylated PUs were higher than the blocked PU prepolymers and pure PTMG. The thermal studies confirmed that the blocked PUs were end-capped and cross-linked with PAPTMS. Storage stability results showed that all dispersions containing PAPTMS were stable for more than three months. Blocking of the isocyanate functionality allows making one-package compounds with required stability in aqueous medium. This study effectively describes the way to prepare anionic aqueous PU dispersions using aromatic isocyanates with remarkable storage stability. One-package silylated PU can be used as coating material. The physical properties of these coatings can be easily adjusted through formulation of the monomers used in the urethane polymerization. In addition, the cross-linking density of the prepolymer can be tailored to the requirement by changing and controlling the content of the functional silane derivatives that are end-capped with the prepolymer.

Acknowledgment

References

[1] Dieterich D, Schmelzer H, Oertel G. Polyurethane handbook. 2nd ed. Munich: Hanser Publishers; 1993. p. 25.

[2] Dieterich D. Prog Org Coat 1981;9:281.

[3] Noll K, Pedain J. US Patent No. 4,190,566 (1980).

[4] Lorenz O, Hick H. Angew Makromol Chem 1978;72:115.

[5] Kim BK, Lee JC. Polymer 1996;37:469.

[6] Chan WC, Chen SA. Polymer 1988;29:1995.

[7] Lee JS, Kim BK. Prog Org Coat 1995;25:311.

[8] Yang CZ, Hwang KKS, Cooper SL. Macromol Chem 1983;184:651.

[9] Kim BK. Colloid Polym Sci 1996;274:599.

[10] Tharanikkarasu K, Kim BK. Prog Rub Plast Technol 1997;13:26.

[11] Rosthauser JW, Nachtkamp K. In: Frisch KC, Klempner D, editors. Adv Urethane Sci Technol 1987;10:205. Technomic Publishing Co Inc.

[12] Kozakiewiez. J Adhesion (London) 1991;15:80.

[13] Sultan Nasar A, Jaisankar SN, Subramani S, Radha Krishnan G. J Macromol Sci: Pure Appl Chem 1997;A34:1237.

[14] Sultan Nasar A, Subramani S, Radhakrishnan G. Polym Int 1999;48:614.

[15] Sultan Nasar A, Subramani S, Radhakrishnan G. Polym Int 2000;49:546.

[16] Sultan Nasar A, Subramani S, Radhakrishnan G. J Polym Sci, Part A Polym Chem 1999;37:1815.

[17] David DJ, Staley HB. Analytical chemistry of polyurethanes, high polymer series. Part 3. New York: Wiley-Interscience; 1969.

[18] Hartz RE. J Appl Polym Sci 1975;19:795.

[19] Lee HT et al. Waterborne, High-Solids and Powder Coatings Symposium, New Orleans, LA, USA, PROCEEDS, 1995. p. 224–33.

[20] Kaplan J. J Chem Eng Data 1971;6:272.

[21] Kim BK, Lee JC. J Polym Sci, Part A Polym Chem 1996;34:1095.

[22] Hsu SL, Xiao HX, Szmant HH, Frisch KC. J Appl Polym Sci 1984;29:246.

[23] Lee JC, Kim BK. J Polym Sci, Part B 1994;32:1983.

[24] Subramani S, Park YJ, Lee YS, Kim JH. Prog Org Coat 2003;48:71–9.

[25] Subramani S, Park YJ, Cheong IW, Kim JH. Polym Int 2004;53:1145–52.

[26] Seymour RW, Cooper SL. Macromolecules 1973;6:48.

[27] Thomas P. Waterborne and solvent based surface coating resins and their applications—polyurethanes. London: Sita Technology Ltd; 1999. p. 141–58.

[28] Wang TL, Hsieh TH. Polym Degrad Stab 1997;55:95.