Enhancement of Hydrolytic Stability and Adhesion of Waterborne Polyurethanes

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ABSTRACT: A new type of polyester polyol, with alkyl side groups, viz. poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAd) was synthesized and used to improve the hydrolytic stability of waterborne polyurethanes (PU). The results compared favorably with poly(tetramethylene adipate) glycol (PTAd)–based PU and blends of the two types of PU in terms of particle size, thermal, XRD, mechanical, dynamic mechanical, and swell behavior of the dispersion cast films in addition to hydrolytic stability and adhesion properties. Blends of PTAd-based PU and PDPAd-based PU gave significantly improved green (immediate) adhesion and hydrolytic stability due to the synergistic effects of crystallinity (heat of crystallization, high density) and amorphous regions (tack, high thermal stability). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1961–1969, 2005

Key words: adhesion; polyurethanes; polyesters; blends

INTRODUCTION

Polyurethanes (PUs) are versatile polymers and can be easily prepared by a simple polyaddition reaction of polyol, isocyanate, and chain extender. They are utilized in a wide variety of industrial products, including industrial parts, building materials, sports goods, medical equipment, adhesives, and coatings. Properties of PUs depend not only on chemical structure but also on their superstructure.[1–3]

Conventional solvent-based PUs are being restricted in their traditional applications, in many countries due to safety and environmental regulations, hence, aqueous-based PUs should replace the solvent-based ones. Such environmental advantages, coupled with increasing solvent price, has steadily expanded their usage in a number of applications in textile coatings, fiber sizings, and adhesives of many polymeric and glassy surfaces.[4–6]

Depending on the field of application, polyester polyols (PEPO) or polyether polyols have generally been chosen as the soft segment.[7] The PEPO is synthesized from a dibasic acid and a diol. Both end groups of PEPO are designed to be hydroxyl groups.

The PUs, which are derived from PEPO as soft segment, have excellent heat stability, adhesive properties, and oil resistance. Moreover, because the manufacturing cost is comparatively low, polyester-type PUs have been widely used as a representative PU. However, this type of PUs is vulnerable to the gradual hydrolysis of the ester group, resulting in molecular weight decreases and deterioration of physical properties.[8]

With regard to this problem, Schollenberger et al.[8] reported that PUs using PEPO derived from a linear diol with a high concentration of methylene groups, such as 1,6-hexanediol, had good hydrolysis resistance. Furukawa et al.[9] also reported that PUs derived from a branched diol, such as 3-methyl-1,5-pentanediol, showed improved hydrolysis resistance. Recently, Murata et al.[10] and Furukawa et al.[11] reported that the PEPO derived from a branched diol having two ethyl groups, such as 2,4-diethyl-1,5-pentane diol, had enough practical hydrolysis resistance.
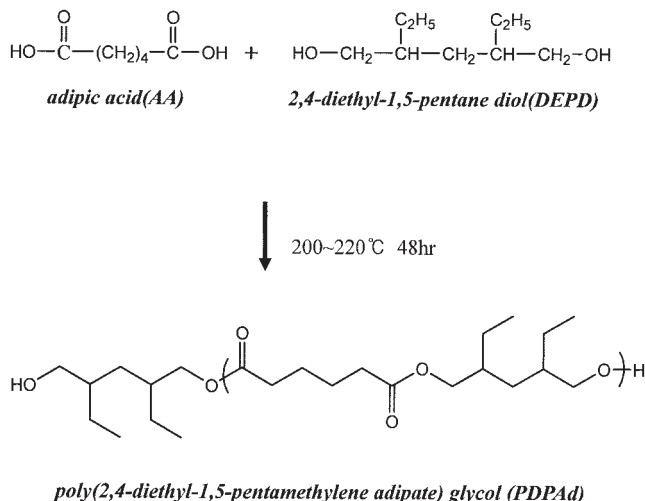
In this work, poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAd), having two ethyl groups as side chains, was synthesized and used to prepare waterborne PUs. A second type of waterborne PU, based on poly(tetramethylene adipate) glycol (PTAd), was synthesized and blended with PDPAd-based PU with expected synergies of high hydrolytic stability and adhesion properties.

EXPERIMENTAL

Materials

Poly(tetramethylene adipate) glycol (M_n = 4,000 g/mol, Union Chemicals), 2,4-Diethyl-1,5-pentanediol (DEPD; TCI), and 1,4-butanediol (BD; Aldrich) were dried and degassed at 80°C, 1–2 mm Hg, for 3 h before use. Dimethylol butanoic acid (DMBA; Aldrich), adipic acid (AA; Junsei Chemicals) was dried at 50°C for 48 h *in vacuo*. 4,4'-Diphenylmethane diisocyanate (MDI, TCI), 1,6-hexamethylene diisocyanate (HDI; Al-

Scheme 1 Synthesis procedure of poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAd).

drich), and dibutyltin dilaurate (DBTDL; Aldrich) were used as received. Triethylamine (TEA; Aldrich) was dried over 4 Å molecular sieves before use.

Synthesis of poly(2,4-diethyl-1,5-pentamethylene adipate) glycol

PDPAd was prepared from AA and DEPD by direct esterification (Scheme 1), which is a reversible equilibrium reaction. As the reaction proceeds, *trans*-esterifications also occur, giving rise to a relatively broad molecular weight distribution.

1.37 mol of AA and 1.87 mol of DEPD were charged into a 1,000-mL round bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube and stirred at 500–600 rpm at 200–220°C in nitrogen atmosphere. The water produced with the progress of condensation reaction was distilled off through a column. When the acid value (AV) reached less than 0.2 and the desired hydroxyl value (OHV) was obtained, stirring was stopped and the reactant was taken out and cooled to room temperature.[10]
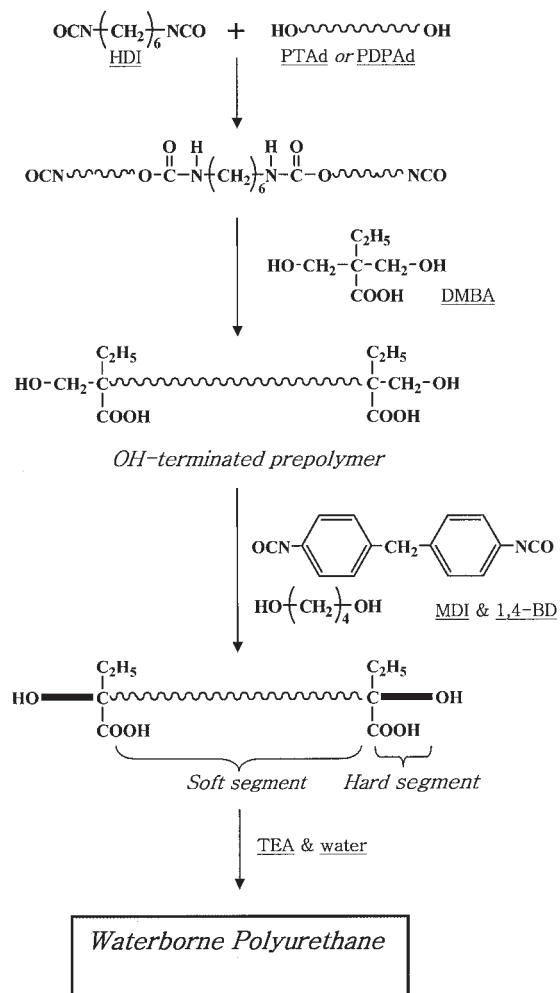
The molecular characteristics and the appearance of PDPAd are shown in Table I. The number average molecular weight (M_n) of PDPAd, calculated by OHV as follows, was approximately 1,078 g/mol.

$$M_n = 1/(OHV/1000/56.1/2) \tag{1}$$

TABLE I
Molecular Characteristics and Appearances of PDPAd

Name	$\bar{M}_n$	OHV	AV	Appearance
PDPAd	1078.8	104	0.17	Liquid

Scheme 2 Reaction scheme of waterborne polyurethanes.

The OHV was measured in accordance with ASTM D 4274–99, test method D: imidazole-catalyzed phthalic anhydride pressure bottle. Methanol and acetone were used as cosolvents with pyridine to completely dissolve the sample. The OHV was determined by titrating the sample with 0.5N potassium hydroxide/ethanol solution using phenolphthalein as indicator. Acid value is of particular importance because it is a measure of the residual amount of carboxyl end groups. It was measured by first diluting about 1 g of the samples with 50 mL of a neutralized methanol–ether mixture, followed by titration with 0.1M KOH in ethanol with phenolphthalein as indicator.[12] The residual carboxylic acid is known to have a strong influence on the hydrolysis resistance because acid is a catalyst for the hydrolysis of the ester group. The acid value of polyol synthesized in this work was less than 0.2 and is considered to be negligible.

Preparation of waterborne polyurethanes

The basic formulation and preparation procedure are given in Table II and Scheme 2, respectively. A 500-mL

TABLE II
Recipe for the Preparation of Waterborne Polyurethanes

| | Feed | | | | | | | | |
| | Soft segment | | | | Hard segment | | | | Neutralizer |
Sample designation	HDI (mol)	PTAd (mol)	PDPAd (mol)	Soft content (wt %)	MDI (mol)	BD (mol)	DMBA (mol)	Hard content (wt %)	TEA (mol)
PAD	4.798	3.798	—	80	10.576	7.576	5.219	20	3.653
DAD	13.695	—	12.695	80	10.576	7.576	5.219	20	3.653

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. Polyol (PTAd or PDPAd) and HDI were charged into the dried flask. While stirring, the mixture was maintained at 70°C for about 3 h to obtain NCO-terminated prepolymer. The change of NCO value during the reaction was determined using a standard dibutylamine back-titration method.[13] Upon obtaining the theoretical NCO value, DMBA was added and reacted to obtain OH-terminated prepolymer.

DMBA is indispensable for ionic dispersion but it deteriorates hydrolytic stability. Therefore, it is basic policy to minimize the content of DMBA so that the dispersion is stable. According to our earlier work,[14] ionic centers, when located in soft segments, gave a much finer dispersion. In this regard, DMBA was located between soft and hard segments in our present molecular design.

The OH-terminated prepolymer was reacted with MDI and chain extender to build up hard segments; then the prepolymers were cooled to 60°C, and a neutralizing agent, i.e., TEA, was added and stirred for 3 h while maintaining the temperature at 60°C. An aqueous dispersion of PUs was obtained by adding water (35°C) to the mixture (60°C) using a tubing pump. The resulting product was a stable urethane dispersion with a solid content of about 40%.

Emulsion blendings of PTAd-based PU (hereafter called PAD) and PDPAd-based PU (DAD) were prepared by mixing the two types of PU in a flask at 300 rpm for 3 h at room temperature and will be referred to as, for example, PD37, meaning PAD/DAD = 3/7 by weight.

Characterizations

^{1}H-NMR spectra were recorded at 25°C on a Varian Unity Plus 300 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were measured on a Mattson Saterllite Fourier transform infrared (FT-IR) spectrometer. The sample was obtained by casting films on the KBr pellet.

Particle size of emulsion was measure by a Coulter LS. A sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion.

Thermal properties of the emulsion-cast film were determined using differential scanning calorimetry (DSC, Seiko DSC 220). Samples were heated to 150°C to erase the thermal history and cooled to below –100°C at 5°C/min while recording crystallization behavior. Melting endotherm was recorded during the second heating cycle at 5°C/min.

Mechanical properties were measured with a universal testing machine (Tinius Olsen 1000) at a crosshead of 500 mm/min. Tests were made at room temperature and at least five runs were made to report the average.

Films were prepared by casting the emulsion onto a Teflon plate, followed by drying at 40°C for 12 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mm Hg. Microtensile test specimens were prepared according to ASTM D 1822.

Dynamic mechanical tests were performed with a dynamic mechanical thermal analyzer (Rheometric Scientific, DMTA MK-IV) from –100 to 130°C at 11 Hz. To measure the swelling in water, films were immersed in water at room temperature and the percentage of swelling was determined by measuring the weight increase as a function of time:

$$\text{Swelling (\%)} = \frac{(W_S - W_O)}{W_O} \times 100 \qquad (2)$$

where W_o is the weight of dried film and W_s is that of swelled film.

Shore A hardness was measured using an indentation hardness tester according to ASTM D 2240–75. Eight sheets with 1 mm thickness were stacked to about 8 mm thickness. The measurement was carried out by pressing the sample sheet on a type-A durometer at a load of 9.8 N.

X-ray diffraction (XRD) patterns were recorded in the symmetric reflection mode by using a Rigaku X-ray diffractometer (30 kV, 25 mA); monochromatic $CuK\alpha$ radiation was used. For each scanning interval of 2°/min, diffracted X-ray intensity was automatically recorded.

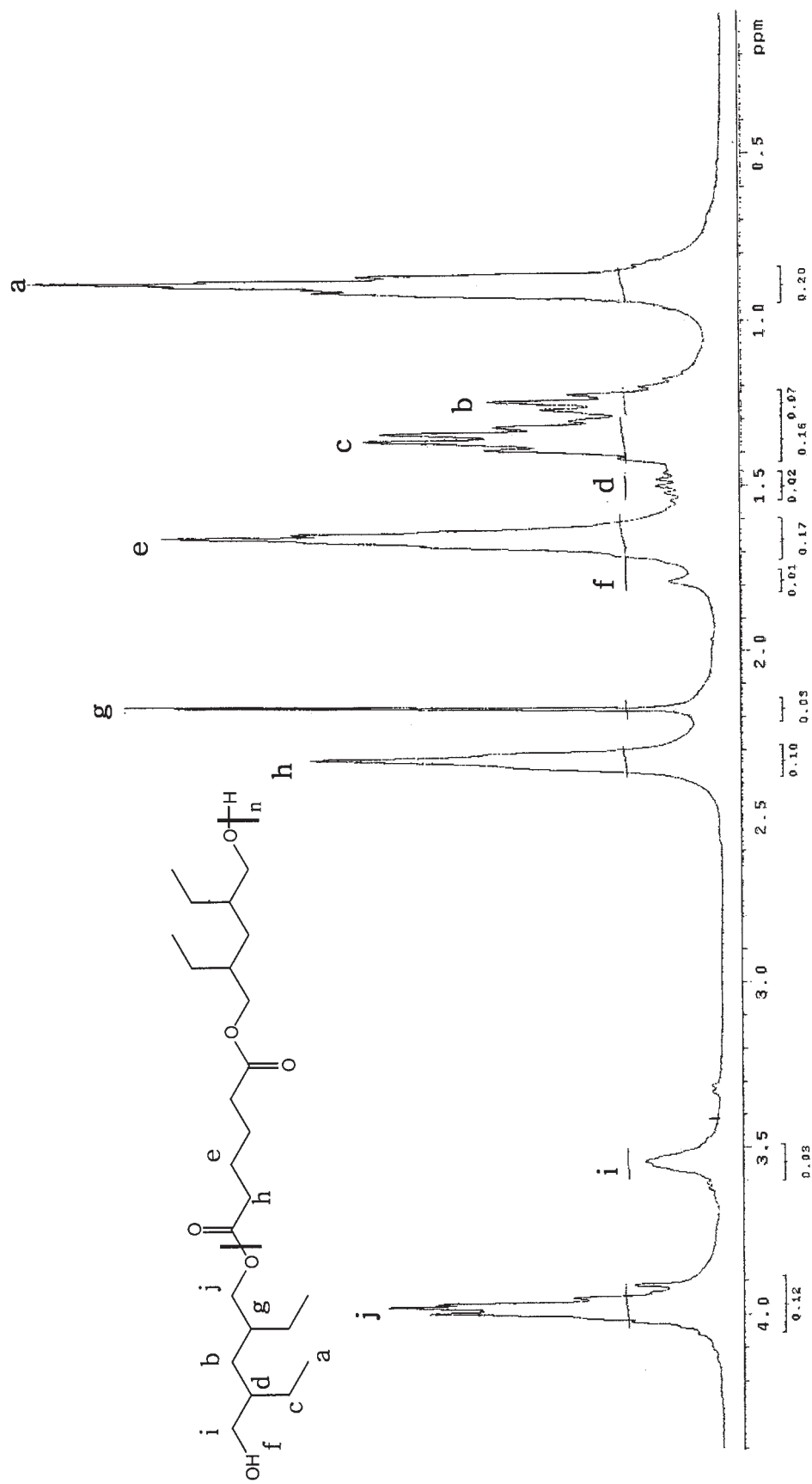T-peel strength of PUs was measured by using a tensile tester. A synthetic rubber (natural rubber 20%,

Figure 1 ^{1}H-NMR spectra of poly(2,4-diethyl-1,5-pentamethylene adipate) glycol (PDPAd).
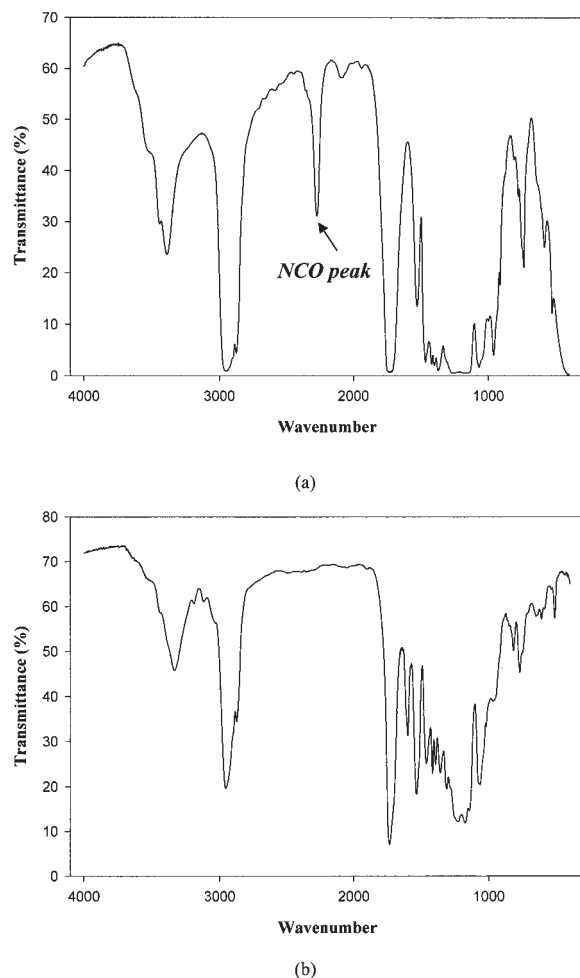
(a)

(b)

Figure 2 FT-IR spectra of PUs before DMBA was added (a) and after DMBA was added and reacted (b).

polybutadiene 80%) was selected as the substrate, because of its low polarity, which may be expected to give severe adhesion test conditions. Prior to the experiments, the synthetic rubber was washed in toluene and dried at 60°C to obtain a clean surface. This rubber was treated with a 0.3 wt % trichloroisocyanuric acid (TCIA) in acetone using a brush and dried at 60°C: halogenation with TCIA solutions is a common surface treatment for rubber materials to improve their adhesion to polyurethane adhesives in the footwear industry.[15,16]

Waterborne PUs and 0.45 wt % trifunctional NCO hardener were mixed at about 500 rpm. The mixture then was applied on the rubber using a brush and dried at 60°C for 10 min. After the water was evaporated, the two rubbers were brought into contact under a pressure of 0.8 MPa for 10 s to achieve a suitable joint. The rectangular sample (width: 20 mm) was used for the T-peel test at 500 mm/min at room temperature. The peel strength was obtained from the mean of five measurements.

RESULTS AND DISCUSSION

Structural analysis

The structure of PDPAd was determined by ^{1}H-NMR spectroscopy as shown Figure 1. The signals of PD-PAd are assigned as follows: 4.0 ppm ($-CH_2-O-CO-$esters), 3.55 ppm ($-CH_2-OH$ end groups), 2.35 ppm ($-O-CO-CH_2-$ esters), 2.2 and 1.56 ppm ($-CH-$ tertiary), 1.65 and 1.3 ppm ($-CH_2-$ secondary), and 0.9 ppm ($-CH_3$ primary).

FT-IR analysis was carried out to verify the progress of the reaction. The absorption peak of the NCO group (2270 cm^{-1}) decreased during the reaction and eventually disappeared. The results indicated the hydroxyl groups in the DMBA had completely reacted with the NCO group of NCO-terminated prepolymer as shown Figure 2.

Thermal properties

DSC thermograms of PUs and their blends are shown in Figure 3. PTAd-based PU, i.e., PAD, shows a sharp
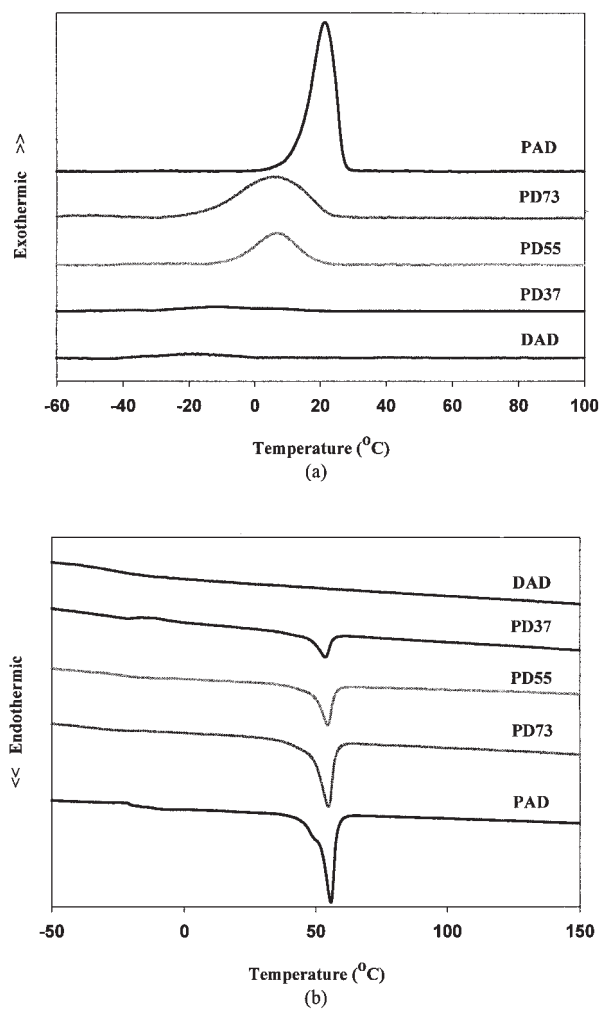

(a)

(b)

Figure 3 DSC thermograms of PAD, DAD, and their emulsion blends for heating (a) and cooling (b).
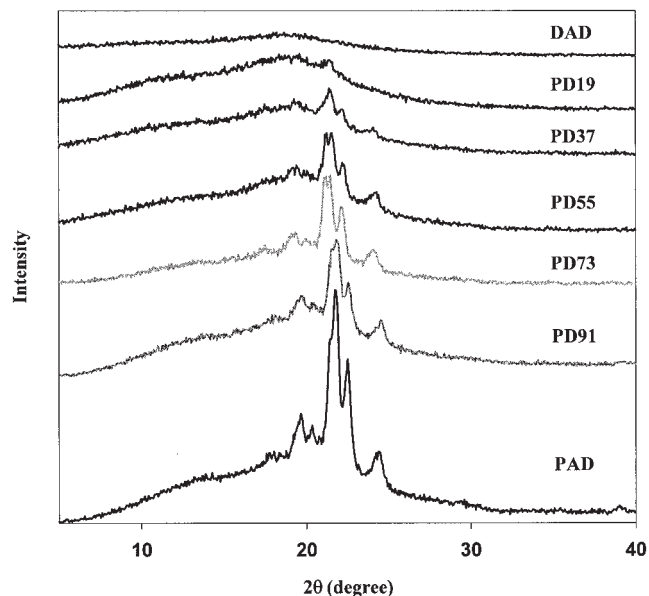
Figure 4 X-ray diffraction profiles of PAD, DAD, and their emulsion blends.

Figure 5 Particle sizes of PAD, DAD, and their emulsion blends.

melting peak at around 60°C corresponding to the crystalline melting temperature (T_m) of soft segment, whereas PU from PDPAd, i.e., DAD, shows no endothermic peaks, indicative of amorphous soft segment. As expected, peak area monotonically decreases with increasing amount of DAD in blends, although the peak temperature is not changed.

On the other hand, the crystallization peak temperature (T_c) and peak area significantly decrease in blends, resulting in significant decreases in the degree of super cooling (ΔT).

$$\Delta T = T_m - T_c \tag{3}$$

This implies that PDPAd-based soft segments provide the PTAd-based ones with a dilution effect. Interactions between the two types of soft segments are expected due to H-bonding between the different ester groups, and pendant diethyl groups of PDPAd should disturb the regular stacking of PTAd segments into crystalline lattices.
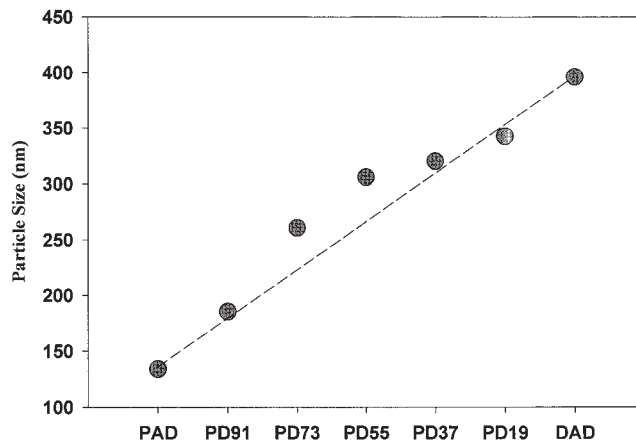
XRD profiles

The XRD profiles of PUs and their blends support the DSC data (Figure 4): a sharp diffraction peak is seen at about $2\theta = 25°$ for PAD, and it is a simple shoulder for DAD. Notably, the 2θ value of the major peak, as well as the peak area, decreases with increasing PAD content, implying that crystalline domains become coarse with increased d-spacing according to Bragg's law ($n\lambda = 2d\sin\theta$). This was again confirmed by the density measurement (Table III), where a monotonic decrease in density is seen with increasing amounts of DAD content in blends.

Particle size and water swell

Figure 5 shows the average particle size of PUs and PU emulsions. PAD dispersion gives the smallest particles, whereas DAD gives the largest, and blends show a small positive deviation from linear additivity. Since the molecular weight of PTAd is about four times greater than that of PDPAd, higher prepolymer molecular weight and viscosity are expected for PTAd-based PU, i.e., PAD. Assuming stress continuity at the interface during the breakup of prepolymer in

TABLE III
Mechanical Properties of Waterborne Polyurethanes

| Sample designation	100% secant modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Density (g/cm³)	Average particle size (nm)
PAD	41.99	64.16	495.25	97	1.207	134.0
PD91	39.69	56.96	516.15	93	1.177	185.3
PD73	28.97	48.98	580.53	90	1.164	260.7
PD55	19.48	27.31	606.05	86	1.154	306.0
PD37	12.29	20.77	718.95	76	1.130	320.3
PD19	6.05	14.26	851.26	67	1.112	342.5
DAD	4.27	13.10	993.85	53	1.101	396.0
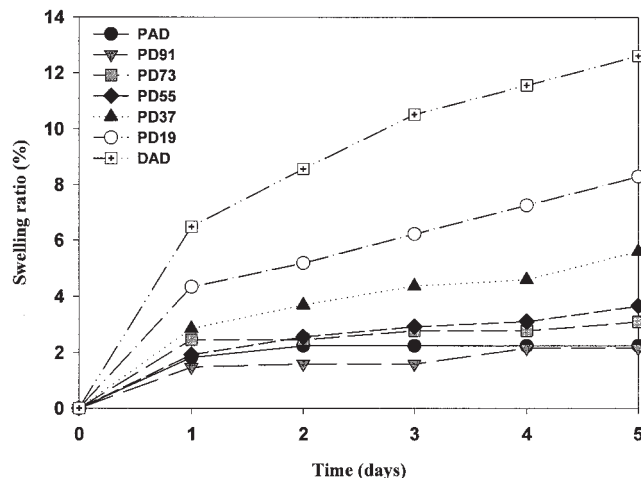
Figure 6 Water swell of PAD, DAD, and their emulsion blends.

water, finer breakup is expected with DAD according to

$$\eta_c \dot{\gamma}_c = \eta_d \dot{\gamma}_d \qquad (4)$$

where η and $\dot{\gamma}$ designate viscosity and shear rate, and subscripts c and d are the continuous (water) and dispersed phase, respectively. However, our results contradict this, implying that the DAD allows more water swelling compared with PAD due to its coarse structure. This was evidenced by the swell measurements (Figure 6). Water swell of dispersion cast film is low and marginally increased with immersion time for PAD. However, water swell is much greater for DAD compared with PAD, and the increase in 5 days of immersion is over 12%, approximately six times greater than PAD. Blends gave swelling a bit greater than the simple additivity prediction.
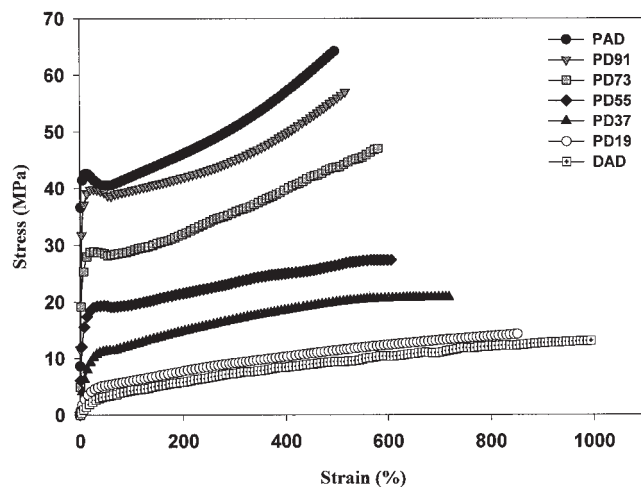

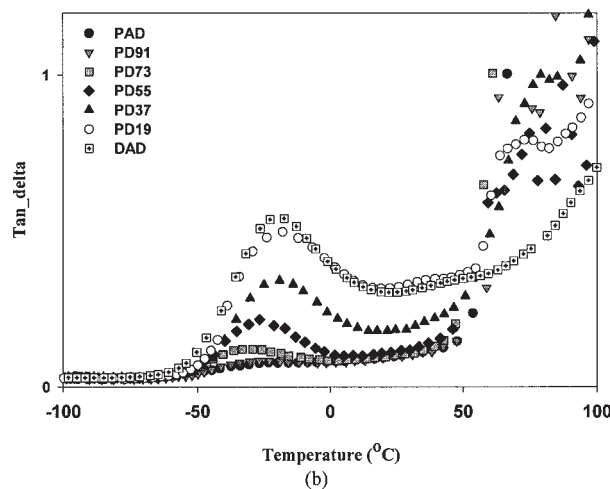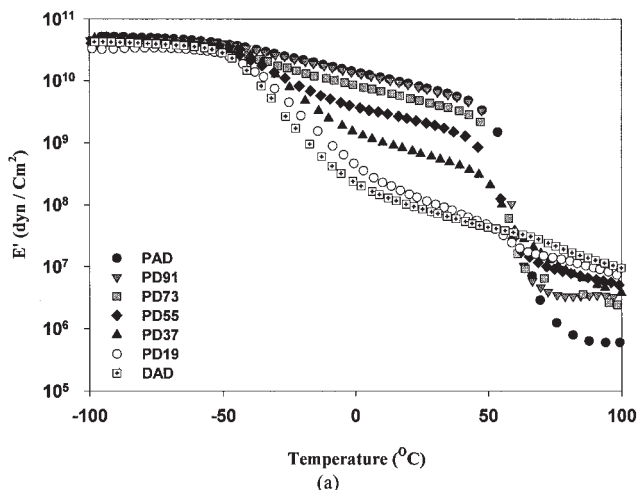Figure 7 Stress–strain properties of PAD, DAD, and their emulsion blends.

Figure 8 Dynamic mechanical properties of PAD, DAD, and their emulsion blends.

Mechanical and dynamic mechanical properties

Stress–strain behavior of PAD shows high initial modulus, positive yield and necking, followed by strain hardening, which are typical of semicrystalline polymers (Figure 7). On the contrary, the DAD shows typical elastomeric behavior with low modulus and high elongation at break of over 1000%. In blends, modulus and strength decrease and elongation at break increases with increasing DAD content. It is seen that a tailor-made stress–strain behavior would be obtained depending on the blend compositions.

Dynamic mechanical properties of the two types of PUs and their blends are shown in Figure 8. PAD shows a sharp melting transition at about 65°C [higher than the static measurement (DSC) by about 10°C due to the dynamic stimulus], followed by a rubbery plateau with a plateau modulus (G°_N) of the order of 10^5 (dyn/cm²). On the other hand, DAD shows a glass transition (instead of melting transition) at about −20°C, followed by a smoothly decreasing rubbery region, where the modulus is over one order of mag-
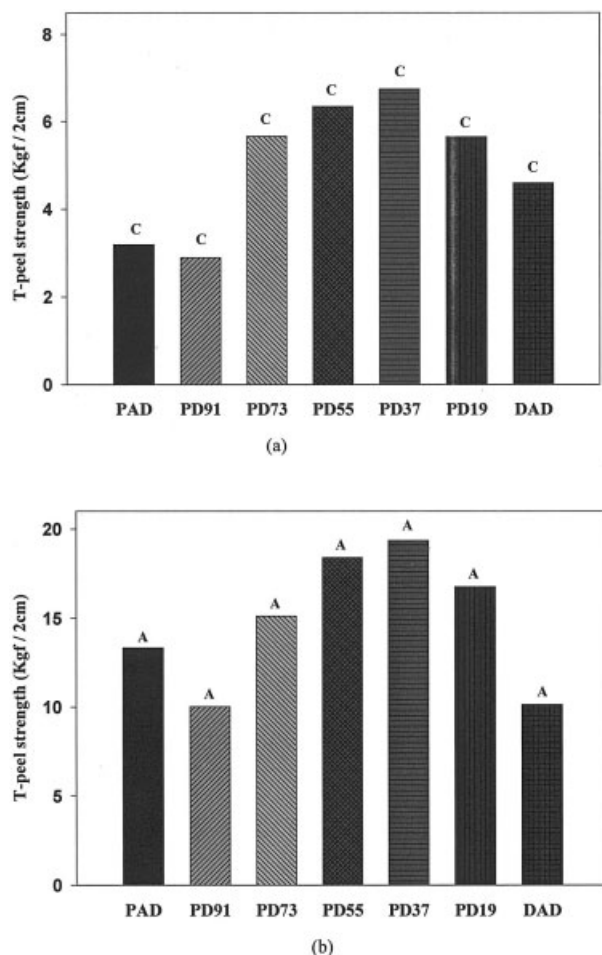
Figure 9 Green (a) and 24-h (b) T-peel strengths of PAD, DAD, and their emulsion blends. C, cohesive failure; A, adhesive failure.

nitude higher than that of PAD. This implies that DAD and blends give higher thermal stability above the T_m of PAD. Blends show both glass transition and melting transition, as expected from the DSC and X-ray measurements mentioned earlier. It is noted that blends show a single glass transition, which decreases with PAD content, indicative of strong interactions in amorphous domains.

Adhesion properties and hydrolytic stability

Figure 9 and Table IV shows the adhesion of the PUs and their blends measured from the T-peel test. It is seen that DAD gives higher instant and lower permanent adhesion compared with PAD. Notably, most of the blends, except PD91, gave instant as well as permanent adhesions greater than the base PUs (PAD and DAD), with a maximum for 3/7 (PAD/DAD), i.e., PD37. Higher instant (green) adhesion of DAD over PAD is mostly due to the higher tack of the former, whereas the higher permanent adhesion of PAD may be explained in terms of soft segment crystallization and the mechanical seal of these crystalline domains with the substrates. In blends, amorphous domains above T_g will induce flow of the blends on a molecular scale to grip the surface, and crystalline polymer will carry the load to give a synergistic effect and the balance is likely obtained at 7 : 3 (PD37).

Hydrolytic stabilities of the PUs and their blends were tested at 40°C (below T_m) and 60°C (above T_m) for a duration of 7 days. It is seen that results obtained at 40°C [Figure 10 (a)] are similar to that of permanent adhesion [Fig. 9 (b)]. It should be mentioned that the hydrolytic stability of PAD is high as long as the crystalline domains are not melted, thus not allowing swelling by water into the crystalline domains of PUs.

On the other hand, when the samples were immersed in hot water above T_m of soft segment, significant hydrolysis proceeded with PAD since its soft segment is in the molten state, whereas hydrolysis is effectively retarded with DAD due at least in part to its high rubbery modulus as well as its steric hinderence for hydrolysis. In blends, hydrolytic stability increases with PAD content increase, although the tendency is not monotonic.

Photographs of debonded surfaces, which were taken after bonded samples, were immersed in 10% NaOH solution at 70°C for 7 days, a condition more severe than the hydrolytic stability test, are shown in Figure 11. PD55 shows adhesive remained on the surface, whereas most of the adhesive was subject to hydrolysis leaving little on the surface for PAD.

TABLE IV
Adhesion Properties of Waterborne Polyurethanes

Sample designation	Instant T-peel strength (Kgf/2 cm)	T-peel strength after 24 h (kgf/2 cm)	T-peel strength after hydrolysis at 40 °C (kgf/2 cm)	T-peel strength after hydrolysis at 60 °C (kgf/2 cm)	Hydrolytic stability at 40°C (%)	Hydrolytic stability at 60°C (%)
PAD	3.1900	13.3350	7.3300	2.4400	54.97	18.30
PD91	2.8950	10.0225	4.4425	2.6425	44.33	26.37
PD73	5.6625	15.1250	8.7400	7.2450	57.79	47.90
PD55	6.3475	18.4050	9.8975	7.2725	53.78	39.51
PD37	6.7500	19.3600	10.2900	6.8750	53.15	35.51
PD19	5.6500	16.7650	10.3500	7.8275	61.74	46.69
DAD	4.5950	10.1400	7.3850	6.1700	72.83	60.85

CONCLUSIONS

Poly(2,4-diethyl-1,5-pentamethylene adipate) glycol was successfully synthesized from (adipic acid + 2,4-diethyl-1,5-pentanediol) and used to prepare waterborne Pus, which subsequently were blended with poly(tetramethylene adipate) glycol–based PU and tested for various properties.

It was found that PDPAd-based PU gave much higher hydrolytic stability due to its steric hindrance for hydrolysis of carbonyl groups, coupled with high temperature thermal stability, evidenced from the high rubbery state modulus. However, PDPAd segments provided the PTAd segments with a dilution effect, resulting in a high degree of super cooling (ΔT) and low crystallinity. PDPAd-based PU had an amor-
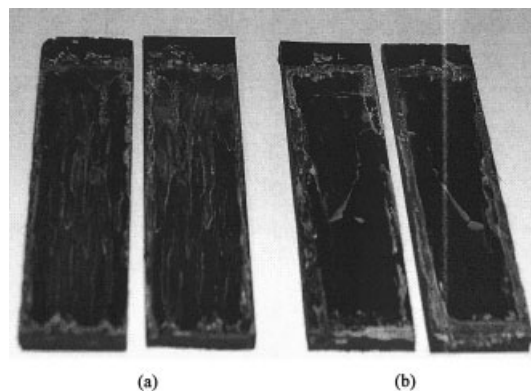

Figure 11 Photograph of T-peel tested surfaces for PD55 (a) and PAD (b) (immersed in 10 wt % NaOH solution at 70°C for 7 days).

phous nature with low T_g augmented tack and instant T-peel strength, whereas crystallization of PTAd-based PU augmented mechanical strength and permanent T-peel strength of the blend adhesives.
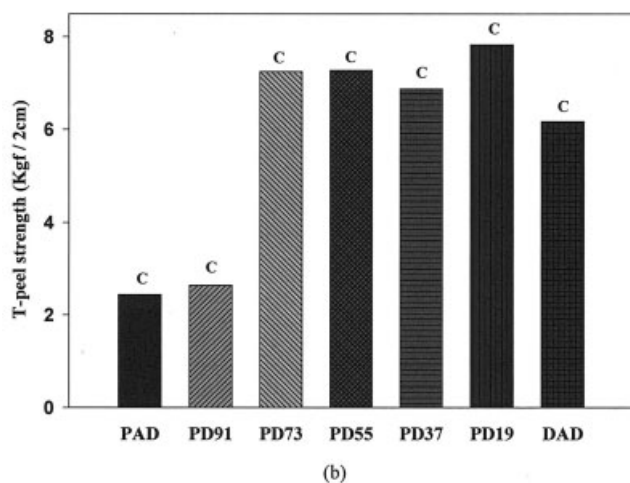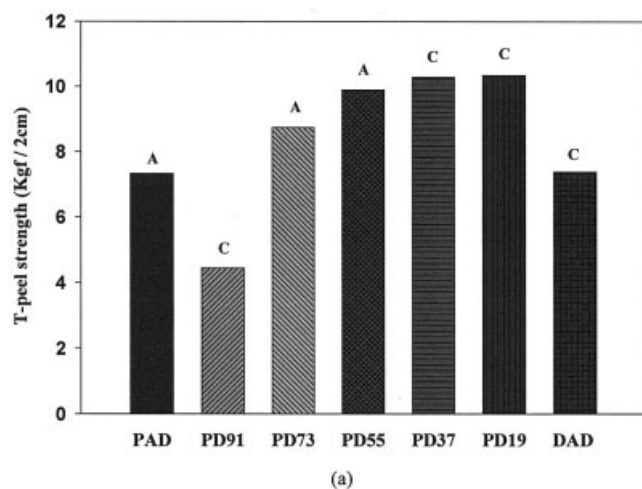
Figure 10 T-peel strengths of PAD, DAD, and their emulsion blends immersed in water at 40°C (a) and 60°C (b) for 7 days. "A" and "C" have the same meaning as in Figure 9.

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