

Polyurethane Dispersions Derived from Polycarbonatediols by a Solvent-Free Process

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ABSTRACT: Aqueous polyurethane dispersions derived from various polycarbonatediols, carboxylic diols, and *m*-di(2-isocyanatopropyl)benzene (TMXDI) were prepared by a solvent-free process. The dispersing procedure was investigated by Fourier transform infrared spectroscopy and it was found that the use of TMXDI could avoid the over hydrolysis of the isocyanate groups during dispersing in water. The molecular weight tends to reach a maximum around an NH₂/NCO ratio during chain extension of 0.8 : 1.0. The particle size, tensile properties, thermal properties, and dynamic mechanical properties of the

polyurethane dispersions were investigated. The properties were significantly influenced by the molecular weight of the polycarbonatediols and the chemical structure of the carboxylic diols, and described by the effects of the ionic content, miscibility between the polycarbonate soft segment and the polyurethane segment, and the soft segment content. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyurethanes; dispersions; polycarbonatediols; solvent-free process

INTRODUCTION

The emission of organic solvent is a severe problem for solvent-borne polyurethane coatings. It is an important target to decrease the level of volatile organic concentration recently. Aqueous polyurethane dispersion coating is an example compliant with such trend, and is expanding their applications in various fields.^{1–3} The incorporation of ionic groups into polyurethanes is a practical method to obtain aqueous polyurethane dispersions, and various polyurethane ionomers have been described in the literature.^{1–11} The presence of ionic groups not only provides dispersibility of polyurethanes in water, but also increases the intermolecular force and enhances the strength like other ionomers.^{12–16} Typically, an NCO-terminated prepolymer ionomer is first prepared, which is readily dispersible in water. After dispersion, a chain extender such as diamine is added to couple the NCO groups to enhance the molecular weight. Then the solvent is removed to obtain the desired aqueous polyurethane dispersion. The effects of various factors such as the structure and content of diisocyanates, polyols, carboxylic

diols, neutralizing agents, chain extenders on the preparation of polyurethane dispersions and their properties have been studied extensively.^{4–11,17–20}

Polycarbonatediols are recently commercialized polyols and are claimed to provide good hydrolysis resistance, heat aging resistance, oil resistance, weathering resistance, and fungi resistance.²¹ It is our recent effort to study the aqueous polyurethane dispersions derived from polycarbonatediols.^{22–25} As the mechanical strength is significantly affected by the molecular weight of the polyurethane ionomers, we found a practical method to prepare the aqueous polyurethane dispersions derived from various polycarbonatediols, various diisocyanates,^{22,24} and various carboxylic diols.^{22,23,25} As *m*-di(2-isocyanatopropyl)benzene (TMXDI) has been found to be lowly reactive with respect to water owing to the tertiary isocyanate nature, it has been used to prepare aqueous polyurethane dispersions by the solvent-free process.^{26,27} In this article, the aqueous polyurethane dispersions derived from TMXDI, various polycarbonatediols, and various carboxylic diols were prepared by a solvent-free process. The properties of the aqueous polyurethane dispersions were characterized.

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EXPERIMENTAL

Materials

Three polycarbonatediols (L4672, L6002, and L5652) with a molecular weight of 2000 and another three polycarbonatediols (L4671, L6001, and L5651) with a

TABLE I
Formulation of the Polyurethane Dispersions

	TMXDI (g)	Polyol (g)	Carboxylic diol ^a (g)	TEA (g)	EDA (g)	Free NCO (%)	Water (g)
T4672PF	36.6	100	6.7	6.1	2.34	2.81	354.3
T6002PF	36.6	100	6.7	6.1	2.34	2.79	354.3
T5652PF	36.6	100	6.7	6.1	2.34	2.72	354.3
T4672BF	36.6	100	7.4	6.1	2.34	2.73	356.0
T6002BF	36.6	100	7.4	6.1	2.34	2.75	356.0
T5652BF	36.6	100	7.4	6.1	2.34	2.77	356.0
T4672PCLF	36.6	100	25.0	6.1	2.34	2.38	397.0
T6002PCLF	36.6	100	25.0	6.1	2.34	2.41	397.0
T5652PCLF	36.6	100	25.0	6.1	2.34	2.35	397.0
T4671PF	36.6	50	6.7	6.1	2.34	4.15	237.7
T6001PF	36.6	50	6.7	6.1	2.34	4.11	237.7
T5651PF	36.6	50	6.7	6.1	2.34	4.16	237.7
T4671BF	36.6	50	7.4	6.1	2.34	4.05	239.3
T6001BF	36.6	50	7.4	6.1	2.34	4.07	239.3
T5651BF	36.6	50	7.4	6.1	2.34	4.07	239.3
T4671PCLF	36.6	50	25.0	6.1	2.34	3.48	280.0
T6001PCLF	36.6	50	25.0	6.1	2.34	3.53	280.0
T5651PCLF	36.6	50	25.0	6.1	2.34	3.54	280.0

^a Notation: P for dimethylol propionic acid (DMPA), B for dimethylol butyric acid (DMBA), and PCL for the carboxylic polycaprolactonediol (Placel 205BA).

molecular weight of 1000 were supplied by Asahi Kasei, Tokyo, Japan. The polycarbonatediols are derived from 1,6-hexanediol and another diol of either 1,4-butanediol or 1,5-pentanediol and ethylene carbonate. The molar ratio of 1,4-butanediol to 1,6-hexanediol in L4672 and L4671 is 70 : 30. The molar ratio of 1,5-pentanediol to 1,6-hexanediol in L6002 and L6001 is 5 : 95 and that in L5652 and L5651 is 50 : 50, respectively.

m-Di(2-isocyanatopropyl)benzene(*m*-tetramethylxylene diisocyanate; TMXDI) was obtained from Cytec Industries, New Jersey, USA and used as received. 2,2-Di(hydroxymethyl)propanoic acid (dimethylolpropionic acid; DMPA) was Aldrich reagent grade and 2,2-di(hydroxymethyl)butanoic acid (dimethylol butyric acid; DMBA) was obtained from Nippon Kasei, Tokyo, Japan. A carboxylic polycaprolactonediol, Placel 205BA with a molecular weight of 500 was supplied by Daicel Corporation, Tokyo, Japan. Triethylamine (TEA) and ethylene diamine (EDA) were Merck reagent grade and treated with molecular sieve before use.

Preparation of the polyurethane dispersions

The polyurethane dispersions were prepared by forming an NCO-terminated prepolymer followed by directly dispersing of the prepolymer in water. No solvent was used. A typical procedure is as follows.

Into a 1-L glass reaction kettle, 36.6 g (0.15 mol) of TMXDI, 100 g (0.05 mol) of L4672, 7.4 g (0.05 mol) of DMBA, and 6.1 g (0.05 mol) of TEA were reacted at 120°C at a speed of 100 rpm for 2.5 h to obtain an NCO-terminated prepolymer. Its NCO content was

determined by a di-*n*-butylamine back titration method² to be 2.73%. The polyurethane prepolymer is cooled down to below 90°, and then mixed enough cooled deionized water (<5°C) under vigorous stirring (500 rpm) to obtain a prepolymer dispersion. A solution of 2.4 g (0.004 mol) of EDA in 2.0 g of deionized water was added to the prepolymer dispersion and stirred at 30°C for an hour to obtain an aqueous polyurethane dispersion with a solid content of 30%. The polyurethane dispersion is denoted as T4672BF, wherein T represents TMXDI, 4672 represents L4672 polycarbonatediol, B means that DMBA is used as the anionomer, and F represents that the solvent-free process was used. The formulations in the preparation of other polyurethane dispersions are summarized in Table I.

Measurements

The IR spectra of the prepolymer or dried dispersion coated onto a quartz plate were measured by a Perkin Elmer 1600 series Fourier transform infrared spectroscopy (FTIR). The IR spectra of the cast films were also measured. The characteristic peaks are at 3375 cm⁻¹(N-H), 2950 cm⁻¹(C=H), and 1745 cm⁻¹(C=O). The ¹H NMR spectra of the polyurethanes in *d*-chloroform were determined by a Bruker AM 400 NMR. The resonance peaks are at about δ (chemical shift) = 7.2–7.4 (aromatic protons of TMXDI unit), δ = 3.9–4.1 (carboxylated or carbonated α -methylene protons of polycarbonatediol unit and DMBA unit), about δ = 2.1 (methylene protons of TEA unit and EDA unit), δ = 1.1–1.8 (methylene protons of polycarbonatediol unit and DMBA unit),

about $\delta = 0.9$ (methyl protons of TMXDI unit, DMBA unit, and TEA unit).

The molecular weight and molecular weight distribution of the polyurethane dispersions were determined by the gel permeation chromatography (GPC) performed on a Tosoh HLC-8220 GPC equipped with a TSK gel Super HM-H*4 column and a RI detector. The eluent was dimethyl formamide, the flow rate was 0.5 mL/min, the operation temperature was set to be 40°C, and the molecular weight was calibrated with polystyrene standards.

The particle size of the polyurethane dispersions was measured by a Photal Par-III's Photon Correlator (Otsuka Electronics) at 25°C.

The polyurethane dispersions were casted into films and dried. The tensile stress-strain data of dumb-bell-shaped film specimens were determined by an Instron 4469 Universal Testing Machine at an extension rate of 100 mm/min at 23°C, and the gauge length used was 25 mm.

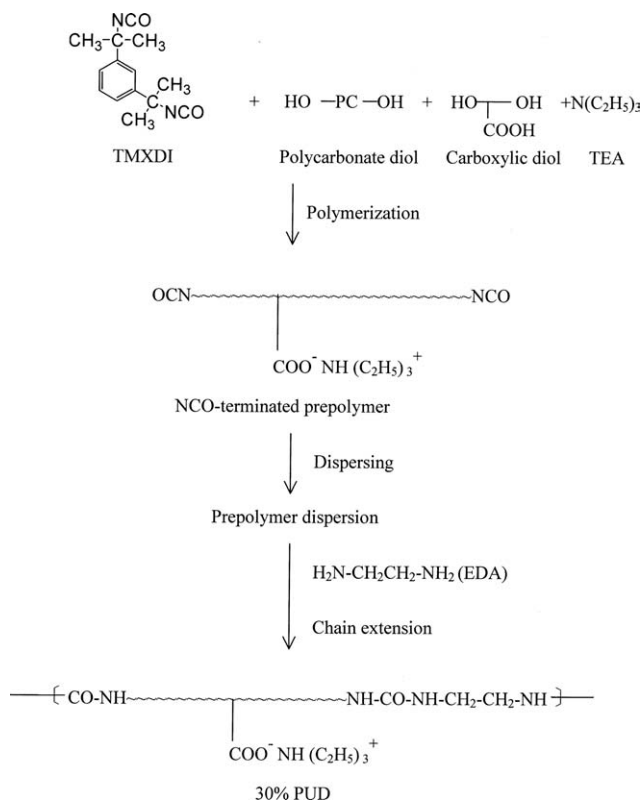
The DSC heating curves of the cast film samples from -100 to 250°C were determined by a DSC-Q10 of TA Instruments at a heating rate of 20°C/min under nitrogen.

The dynamic mechanical properties of strip specimens (20 × 5 × 1 mm) were measured by a Perkin Elmer Dynamic Mechanical Analysis, DMA7 (DMA, dynamic mechanical analysis) with a tensile mode at a forced vibration frequency of 1 Hz and a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The preparation procedure of the polyurethane dispersions is shown in Scheme 1. The molar ratio of TMXDI:polycarbonatediol:carboxylic diol:TEA was held as 3.0 : 1.0 : 1.0 : 1.0. The reaction of TMXDI, polycarbonatediol, carboxylic diol, and TEA gave polyurethane prepolymers with isocyanate end groups. Theoretically, one third of isocyanate groups would remain unreacted. The NCO content values determined by the di-*n*-butylamine back titration method listed in Table I can confirm this. For example, the NCO content of the prepolymer of T4672BF was found to be 2.73%, which is very close to the theoretic value of 2.71%. The prepolymer was then dispersed in enough water, and water-soluble EDA was added to couple the NCO end group for chain extension.

As TMXDI is lowly reactive with respect to water,^{26,27} the remained isocyanate groups would not be over hydrolyzed during dispersing. This can be verified by IR analysis. The IR spectrum of the prepolymer coated onto a quartz plate of T4672BF was recorded referred to a background scanning of the quartz plate. The use of the quartz plate instead of a KBr salt plate was to avoid the interference of water, especially for the dispersions. The C=H absorption



Scheme 1 Reaction procedure of the preparation of the polyurethane dispersions.

peak at about 2950 cm^{-1} is taken as the reference peak, the relative absorbance of NCO group (peak at 2260 cm^{-1}) to C=H group, $A_r (=A_{2260}/A_{2950})$, of the prepolymer was found to be about 0.6. It should be mentioned that the relative absorbance can be related more directly to the NCO content. The prepolymer was mixed with water and directly dispersed in water. A portion of the dispersion was taken out immediately and coated onto to a quartz plate to be dried and the IR spectrum was determined. The IR spectrum of the dried dispersion taken out just after mixing with water is shown in Figure 1(a). The relative absorbance of NCO to C=H was about 0.7. It seems that little isocyanate group was consumed after mixing with water. The dispersion was continued to be stirred vigorously for 2 h. Then, a portion of the dispersion was taken out to be dried, and the IR spectrum was determined. The IR spectrum of the dried dispersion taken out after stirring in water for 2 h is shown in Figure 1(b). The relative absorbance of NCO to C=H was about 0.7. This means that little fraction of the isocyanate group of the prepolymers was hydrolyzed during dispersing.

The dispersion was chain extended with ethylene diamine for 1 h. Then, a portion of the dispersion was taken out to be dried, and the IR spectrum was determined. The obtained IR spectrum is shown in Figure 1(c). It can be seen that the NCO absorption

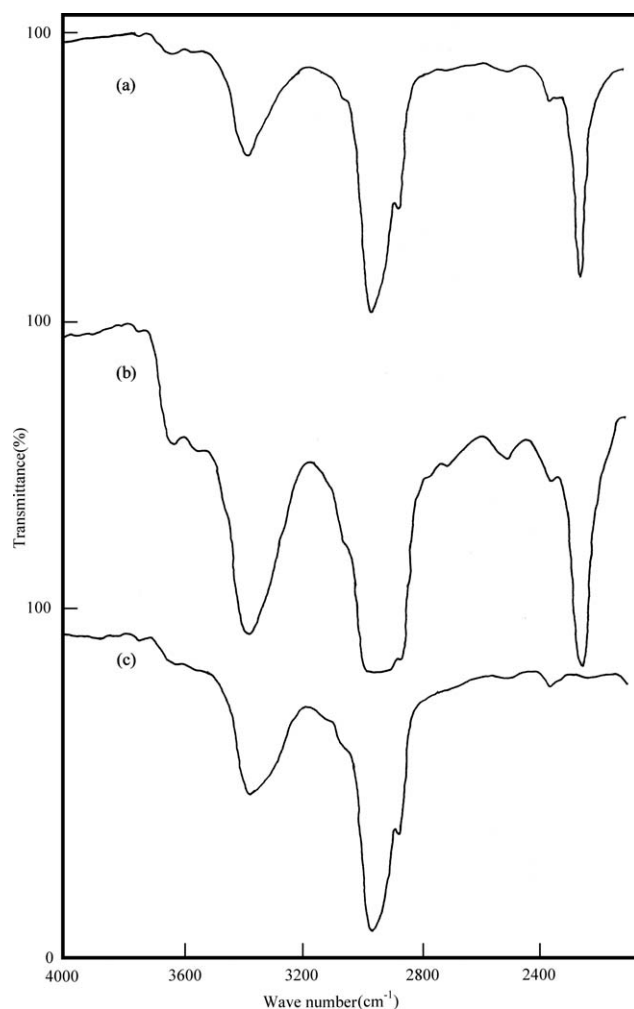


Figure 1 The IR spectrum of the dried dispersions taken out (a) just after mixing with water, (b) after mixing and stirring for 2 h, and (c) after chain extension for 1 h.

peak decreases considerably. The relative absorbance of NCO to C=H was smaller than 0.03. This indicates that the chain extension by ethylene diamine was effective.

It can be seen from IR analysis that the use of TMXDI could avoid the hydrolysis of the isocyanate groups during dispersing, but the chain extension was still effective.

During chain extension, the molar amount of isocyanate group used was set to be stoichiometrically greater than that of hydroxy group and amine groups ($\text{OH} + \text{NH}_2$) owing to the hydrolysis of the NCO groups by water during dispersing. Fortunately, the hydrolytic reaction formed amine groups which reacted with isocyanate groups to enhance the molecular weight. When the NH_2/NCO ratio during chain extension was 0.5 : 1.0 as used previously,^{22,23} the M_n values of the obtained polyurethane dispersions were always below 10,000. It has been found that the NH_2/NCO ratio during chain extension was one of the important factors govern-

ing the molecular weight of the polyurethanes. Thus, the NH_2/NCO ratio during chain extension was varied to obtain polyurethane dispersions for comparison. Figure 2 shows the effect of the NH_2/NCO ratio during chain extension on the M_n of a typical polyurethane dispersion (T6002B). It can be seen that the molecular weight tends to reach a maximum around an NH_2/NCO ratio during chain extension of 0.8 : 1.0. This value is greater than the previous composition for the isophorone diisocyanate (IPDI) and di(4-isocyanatocyclohexyl)methane (HMDI) system.^{22,24} This should be owing to the lower reactivity of TMXDI with respect to water as compared with IPDI and HMDI.^{26,27} Thus, this NH_2/NCO ratio was used for the preparation of other TMXDI-based polyurethane dispersions. After chain extension, polyurethane dispersions with a solid content of 30% were obtained.

The formulations in the preparation of the polyurethane dispersions are summarized in Table I. The molecular weight data determined by GPC are summarized in Table II. The M_n values are all around or $>20,000$. This indicates that the use of an NH_2/NCO ratio during chain extension of 0.8 : 1.0 was also effective in enhancing the molecular weight for this TMXDI system. The molecular weight distribution index (M_w/M_n) is close to 2, which seems to be a result of the step polymerization conducted in a homogeneous system.²⁸ This might be also owing to the low reactivity of TMXDI.

The average particle size data of the polyurethane dispersions are summarized in Table II. The particle

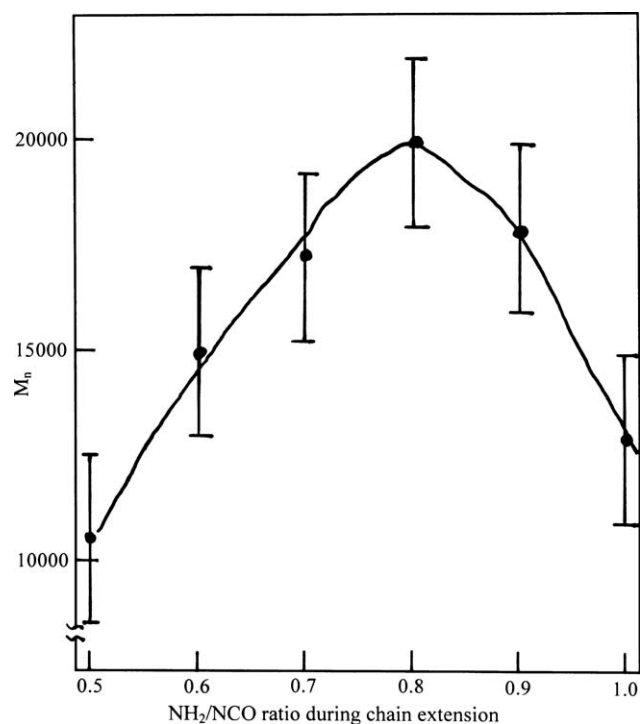


Figure 2 Effect of NH_2/NCO ratio during chain extension on the molecular weight of the polyurethane dispersions (T6002BF).

TABLE II
GPC Data and Particle Size of Polyurethane Dispersions

Sample	M_n	M_w	M_w/M_n	Particle size (nm)
T4672PF	19,500	34,600	1.8	80
T6002PF	19,200	37,600	2.0	94
T5652PF	19,700	34,800	1.8	69
T4672BF	19,200	36,500	1.9	71
T6002BF	19,400	37,500	1.9	71
T5652BF	28,000	50,500	1.8	68
T4672PCLF	23,600	46,600	2.0	54
T6002PCLF	21,500	45,500	2.1	59
T5652PCLF	20,200	38,400	1.9	56
T4671PF	19,100	35,600	1.9	31
T6001PF	21,200	37,600	1.8	44
T5651PF	20,900	36,200	1.7	39
T4671BF	25,100	44,800	1.8	36
T6001BF	19,200	35,800	1.9	43
T5651BF	18,600	39,000	2.1	33
T4671PCLF	30,600	67,100	2.2	24
T6001PCLF	20,400	40,600	2.0	16
T5651PCLF	30,000	64,300	2.0	18

size of the dispersion may be affected by the ionic content of the resin, the chemical structure of the resin, and the dispersing procedure.²⁵ It seems that the effect of the chemical structure of the polycarbonatediol on the particle size of the polyurethane dispersions shows no obvious trend, as summarized in Table II. For example, the ionic content of the polyurethane dispersions derived from the polycarbonatediols with molecular weight of 2000 and DMPA or DMBA (the first six polyurethane dispersions in Table II) is similar, they exhibit particle size range of 60–90 nm, but no trend can be found by the effect of chemical structure of the polycarbonatediols. Hence, do the other series. The ionic content of the resin seems to be a major factor. As the molecular weight of the polycarbonatediols is 1000 rather than 2000, the ionic content of the resin is higher, and the polyurethane dispersions tend to display smaller particle size, as expected. A special case is the series derived from the carboxylic polycaprolactonediol (Placel 205BA). The polyurethane dispersions derived from the carboxylic polycaprolactonediol exhibit significantly smaller particle size than those derived from DMPA and DMBA for the series of the same molecular weight of the polycarbonatediols, as summarized in Table II. This might be owing to the more flexible nature of the carboxylic polycaprolactonediol unit which might enhance the penetration of water molecule into polyurethane ionomers, and finer dispersions were obtained, similar to the cases described previously.^{23,24}

The aqueous polyurethane dispersions were cast into films and their tensile properties were determined. Typical stress versus strain curves are shown in Figure 3. The tensile properties of the aqueous polyurethane dispersions are summarized in Table III. The elongation at break of the films is rather high,

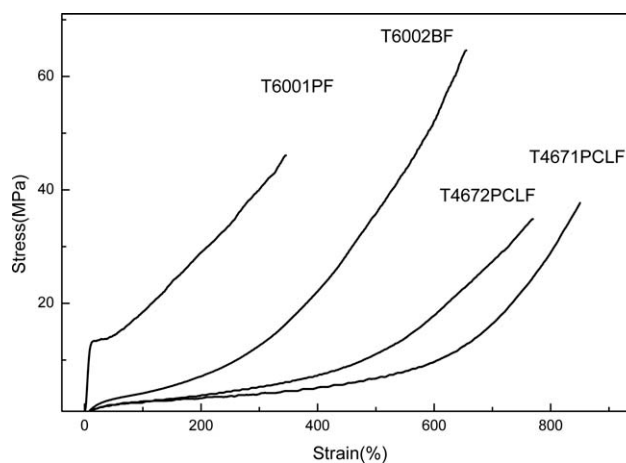


Figure 3 Tensile stress–strain curves of T6002BF, T4672PCLF, T6001PF, and T4671PCLF.

indicating that the films are ductile. It seems that the difference in the chemical structure of the polycarbonatediols does not affect the tensile properties greatly, as the molecular weight of the polycarbonatediols is the same. However, the chemical structure of the carboxylic diols and the molecular weight of the polycarbonatediols affect the tensile properties significantly. The chemical structure of DMPA is more or less similar to that of DMBA, and it is reasonable that a polyurethane dispersion-derived DMPA exhibits tensile properties similar to those of the corresponding polyurethane dispersion-derived DMBA for the same molecular weight of the polycarbonatediol. On the other hand, the films of the polyurethane dispersions derived from the carboxylic polycaprolactonediol behave significantly softer for the same molecular

TABLE III
Tensile Properties of Casted Films of Polyurethane Dispersions

Sample	100% Modulus (MPa)	300% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
T4672PF	5.2	11.2	55	640
T6002PF	4.1	10.8	53	660
T5652PF	4.5	9.7	48	690
T4672BF	6.4	14.8	63	620
T6002BF	4.2	12.6	65	660
T5652BF	4.2	9.5	63	710
T4672PCLF	2.8	4.2	38	850
T6002PCLF	2.2	4.8	44	730
T5652PCLF	2.2	3.7	34	840
T4671PF	19	37	44	370
T6001PF	19	40	46	350
T5651PF	14	31	41	390
T4671BF	13	28	48	480
T6001BF	19	38	46	380
T5651BF	14	31	41	390
T4671PCLF	2.7	5.3	35	770
T6001PCLF	3.1	4.1	33	760
T5651PCLF	3.0	5.6	34	790

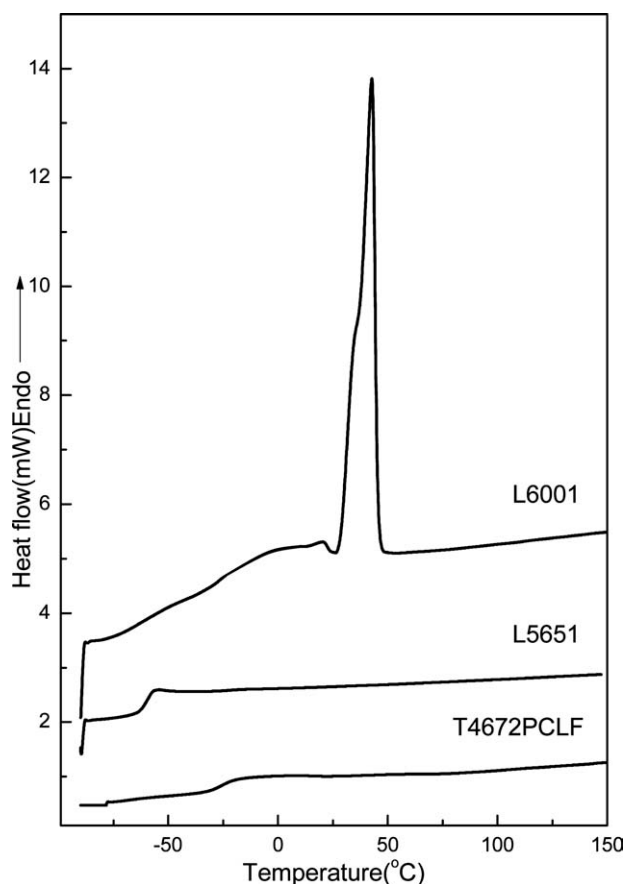


Figure 4 DSC heating curves of L6001, L5651, and T4672PCLF.

weight of the polycarbonatediol, and their tensile strength and tensile moduli are also significantly lower as compared with the polyurethane dispersion derived from DMPA and DMBA and summarized in Table III. This is ascribed to the more flexible nature of the carboxylic polycaprolactonediol. Thus, it is easy to design softer products with high elongation through the use of the carboxylic polycaprolactonediol. The molecular weight of the polycarbonatediols also affects the tensile properties significantly. As the molecular weight of the polycarbonatediols increased, the soft segment content increases, the polyurethane dispersion films tend to behave softer and higher elongation as expected, as summarized in Table III.

Typical second-run DSC heating curves of the polycarbonatediols and the casted films of the polyurethane dispersions are shown in Figure 4. The DSC heating curves of L6002 and L6001 exhibit a step inflection and a melting endotherm. The mid-point of the step inflection is taken as the glass transition temperature (T_g) and the peak temperature of the melting endotherm is taken as the melting point (T_m). The heat of fusion (ΔH_m) of L6002 and L6001 is rather high as summarized in Table IV. This indicates that L6002 and L6001 can crystallize signifi-

cantly after cooling from the molten state at a slow cooling rate. The DSC heating curves of L4672 and L5652 show only a T_g , but no T_m . All the second-run DSC heating curves of the cast films of the polyurethane dispersions exhibit only a step inflection corresponding to the glass transition temperature of the soft segments (T_{gs}). The results are summarized in Table IV. It can be seen that the T_{gs} values of the polyurethane dispersions are about 20–40 °C higher than those of the corresponding polycarbonatediols as summarized in Table IV. This may be owing to the presence of the ionic groups which hinder the motion of polycarbonate soft segments and better miscibility between the polycarbonate soft segment and the polyurethane hard segment.²⁹ The presence of the ionic groups might also hinder the crystallization of the polycarbonate soft segments in the polyurethane dispersions derived from L6002 and L6001, and thus no T_{ms} was found. No obvious trend can be found in each series of the polyurethane dispersions derived from the polycarbonatediols of the same molecular weight. As the ionic content of the polyurethane dispersions derived from the polycarbonatediols with a molecular weight of 1000 is higher than that of 2000, they exhibit slightly higher T_{gs} values as compared to the polyurethane dispersions derived from the polycarbonatediols with a molecular weight of 2000, as expected.

Typical DMA curves of the cast films of the polyurethane dispersions are shown in Figure 5. The

TABLE IV
Thermal Transitions of Polycarbonatediols and Cast Films by DSC and DMA

Sample	T_{gs} (°C) (DSC)	T_{ms} (°C) (DSC)	ΔH_{ms} (J/g) (DSC)	T_{gs} (°C) (DMA)
L4672	-50	-	-	-
L6002	-52	49	48.9	-
L5652	-55	-	-	-
L4671	-56	-	-	-
L6001	-60	43	41.8	-
L5651	-60	-	-	-
T4672PF	-23	-	-	-10
T6002PF	-33	-	-	-23
T5652PF	-29	-	-	-13
T4672BF	-25	-	-	-14
T6002BF	-31	-	-	-20
T5652BF	-27	-	-	-18
T4672PCLF	-26	-	-	-10
T6002PCLF	-35	-	-	-22
T5652PCLF	-29	-	-	-20
T4671PF	-10	-	-	-
T6001PF	-16	-	-	-
T5651PF	-13	-	-	-
T4671BF	-9	-	-	-
T6001BF	-12	-	-	-
T5651BF	-19	-	-	-
T4671PCLF	-10	-	-	14
T6001PCLF	-16	-	-	12
T5651PCLF	-11	-	-	15

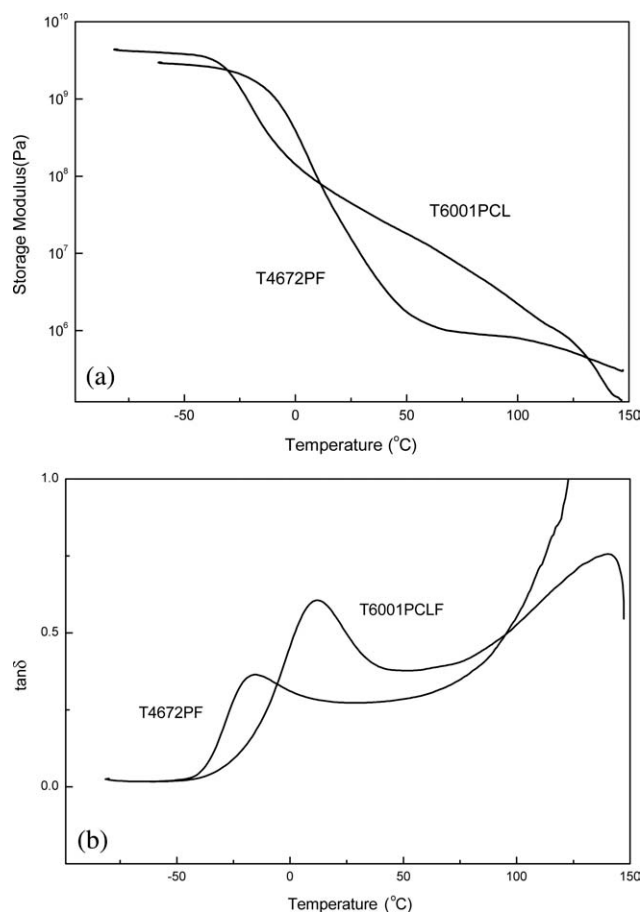


Figure 5 DMA curves of T6001PCLF and T4672PF: (a) E' versus temperature curves, and (b) $\tan\delta$ versus temperature curves.

$\tan\delta$ versus temperature curves of the polyurethane films derived from the polycarbonatediols with a molecular weight of 2000 exhibit a major damping peak around -20°C corresponding to the glass transition temperature of the soft segments (T_{gs}). The polyurethane films derived from the polycarbonatediols with a molecular weight of 1000 and DMPA or DMBA show no clearly observable damping peak; however, the polyurethane films derived from the polycarbonatediols with a molecular weight of 1000 and the carboxylic polycaprolactonediol exhibit a major damping peak around 10°C corresponding to the glass transition temperature of the soft segments (T_{gs}). The results are summarized in Table IV. Comparing with the DSC data, The T_{gs} values of the polyurethane films derived from the polycarbonatediols with a molecular weight of 1000 and the carboxylic polycaprolactonediol are higher than those of the polyurethane films derived from the polycarbonatediols with a molecular weight of 2000 to a greater extent. This might be owing to the higher ionic content of the former, and the ionic force might play stronger restriction contribution of chain motion in a dynamic mode than in a static one.

The polyurethane films show similar real modulus (E') versus temperature curves in each own series. Above -40°C , $\log E'$ continues to drop up to a point of testing interruption, and there is a greater drop in $\log E'$ around T_{gs} as shown in Figure 5. The real modulus data indicate that the polyurethane films derived from the polycarbonatediols with a molecular weight of 2000 are significantly softer than those of 1000, and the polyurethane films derived from the carboxylic polycaprolactonediol (PCL series) are also softer than those derived from DMBA and DMPA. This trend is consistent with the tensile modulus data.

CONCLUSION

The solvent-free process can be used to prepare the aqueous polyurethane dispersions by using TMXDI. FTIR analyses of the samples during dispersing show interesting results. It can be seen that the use of TMXDI could avoid the over hydrolysis of the isocyanate groups during dispersing, but the chain extension was still effective. The molecular weight tends to reach a maximum around an NH_2/NCO ratio during chain extension of 0.8 : 1.0 and this optimum ratio was used in preparations. As the molecular weight of the polycarbonatediols is 1000 rather than 2000, the ionic content of the resin is higher, and the polyurethane dispersions tend to display smaller particle size. The polyurethane dispersions derived from the carboxylic polycaprolactonediol exhibit significantly smaller particle size than those derived from DMPA and DMBA. As the molecular weight of the polycarbonatediols increases, the soft segment content increases, the polyurethane dispersion films tend to behave softer as expected. Hence, the series was derived from the carboxylic polycaprolactonediol. The effect of the composition on the thermal transitions can be described as the cause of ionic content, better miscibility between the polycarbonate soft segment and the polyurethane hard segment, and the soft segment content.

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