

The Effect of Diamine Extender on the Properties of Polyurethane Dispersions

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Abstract: Polyurethanes dispersion (PUD) containing carboxylate anion as the hydrophilic pendant group were prepared by prepolymer mixing process based on isophorone diisocyanate (IPDI), poly(oxytetramethylene) glycol (PTMG), dimethylol propionic acid (DMPA), toluene diisocyanate (TDI), triol (trade name FA-703) and different chain extender. IR spectroscopy was used to check the end of polymerization reaction and characterization of polymer. The mechanical properties of the emulsion-cast films were studied using tensile strength, tear, elongation, hardness testes, DSC and TGA. Tensile strength, tear strength and hardness increase with decrease the number of carbons in chain extenders from 6 to 2 carbons. The increase tensile strength, tear strength and elongation at break properties are interpreted in terms of increasing hard segments, in PUD.

Key words: Polyurethanes • Dispersions • Mechanical properties • Physical properties • Ionomers

INTRODUCTION

Aqueous polyurethane dispersions (PUDs) are widely appreciated for their versatility, high performance and low environmental impact and because they enable formulators to customize precise properties, such as durability, hardness and flexibility, for each specific application such as fibers, elastomers, foams, coatings and adhesives [1, 2]. Polyurethanes are a family of block copolymers, which are composed of alternating blocks of soft and hard segment units linked together by a urethane or urea group [3-6]. The soft segments are typically long chain polyols with low glass transition temperature (T_g), such as polyester, polyether or polyalkyldiol. The hard segments have high glass transition temperatures and are typically diisocyanates with low molecular chain extenders [7-18].

Chain extenders are low molecular weight, multifunctional compound that react with the NCO groups of diisocyanates. Chain extenders are categorized as either alcohols or amines. Amines contain the reactive NH group, which, upon reaction with the NCO group, yield a

urea. Polyureas are typically thermoset polymers; however, in some cases, the combination of an aliphatic diisocyanate with a hindered aliphatic amine will yield a melt processable polyurea. The effect of varying the chain extender on the final properties of PUD is documented in literature [19-24]. This study focuses on preparation of PUD by prepolymer mixing process avoids the use of large amounts of solvent. In this process, NCO-terminated prepolymer containing pendant acid group, i.e. dimethylol or 2,2-bis(hydroxymethyl) propionic acid (DMPA) is neutralized with base to form an aqueous dispersion. The chain extension step is accomplished by the addition of diamine to aqueous dispersion. Chain extenders used in this study are Ethylenediamine, butanediamine and hexamethyldiamine.

This article describes the preparation of (PUDs) from poly (oxytetramethylene) glycol (PTMG), triol (FA-703), dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI). The influence of the different types of chain extenders on mechanical properties of emulsion-cast films was studied.

MATERIALS AND METHODS

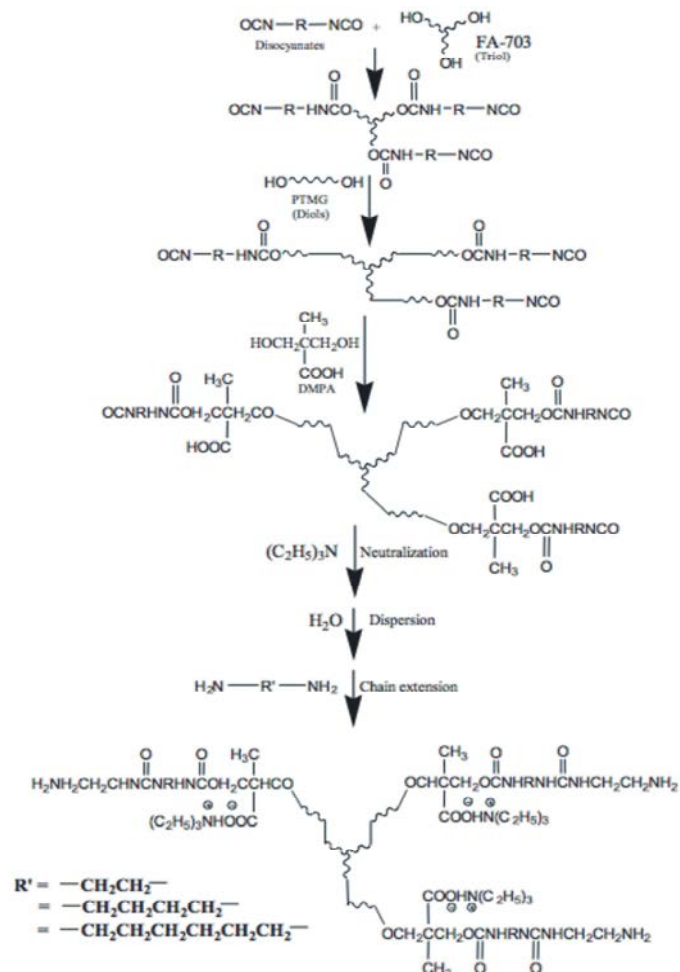
Materials: Poly (oxytetramethylene) glycol (PTMG, $M_w = 2000$, OH number = 55 mg/g, Korea PTG, Korea), triol trade name (FA-703, $M_w = 3200$, OH number = 33 mg/g, Korea Polyols, Korea) were dried and degassed at 80°C, 1 – 2 mm Hg for 2 h before use. Dimethylol propionic acid (DMPA, $M_w = 134.13$, Aldrich) was dried at 50°C for 48 h, while isophorone diisocyanate (IPDI, $M_w = 222.29$, Bayer) were used as received. Triethylamine (TEA, $M_w = 101.19$, Merck) was dried over molecular sieves (Å).

Chain extenders are ethylenediamine (EDA), butanediamine (BDA) and hexamethyldiamine (HMDA), supplied from Merck. The chain extenders (Table 1) were used as received without further purification.

Synthesis and Characterization of Copolymers: The preparation of the PUDs and the methods of analysis (FT-IR, mass spectroscopy as well as viscosity) have been previously described [25-28]. The general method of synthesis shown in Scheme 1. The mix proportions of PUDs are shown in Table 2.

Table 1: Structure of chain extenders

Chain extender	Symbol	Structure
Ethylenediamine	EDA	
Butanediamine	BDA	
Hexamethyldiamine	HMDA	



Scheme 1: Formation of PU dispersion having anionic center

Table 2: Feed compositions of dispersion polyurethanes synthesized with variable contents of polyol and isocyanate

	M1		M2		M3	
	Polyols, OH					
Samples	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)
PTMG	102.198	89.7	102.198	89.7	102.198	89.7
FA-703	2.2775	2.0	2.2775	2.0	2.2775	2.0
DMPA	9.403	8.3	9.403	8.3	9.403	8.3
Total	113.879	100	113.879	100	113.879	100
	Isocyanates, NCO					
TDI	2.4088	5	2.4088	5	2.4088	5
IPDI	45.767	95	45.767	95	45.767	95
Total	48.176	100	48.176	100	48.176	100
NCO/OH	1.8					
NMP	18.806		18.806		18.806	
TEA	7.094		7.094		7.094	
EDA	5.852		----		-----	
BDA	----		5.852		-----	
HMDA	----		-----		5.852	
Water	306.193		306.193		306.193	

Film Preparation: Films were prepared by casting the aqueous dispersions on leveled surfaces and allowing them to dry at room temperature for 7 days and then at 60°C, for 12 h [29-31]. The films were stored in a desiccator at room temperature for further characterization and measurements.

Measurements: FTIR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer. The tensile properties of the emulsion cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least 4 measurements was taken and the 1-kN load cell was used. Shore A hardness was measured using an indentation hardness tester according to ASTM D2240-75. Thermogravimetric analysis (TGA) was recorded on a TGA/SDTA851e, METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N₂ flow at 20 mL min⁻¹. The measurements were carried out between -50°C and 200°C at a heating rate of 10°C Min⁻¹.

RESULTS AND DISCUSSIONS

FT-IR Analysis: IR spectrum analysis was used to check the end of polymerization reaction, verifying the disappearance of the ν NCO at 2265 cm⁻¹ and the appearance of ν N – H at 3291 cm⁻¹ as shown in Figure 1. The N – H group in polyurethane could form hard segment H – bonding with the carbonyl oxygen and hard-soft H – bonding with the ether oxygen.

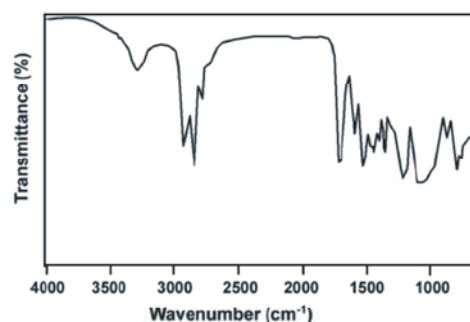


Fig. 1: IR spectrum of polyurethane dispersion

Table 3: Mechanical properties of the PU emulsion cast films

Samples	M1	M2	M3
Tensile strength (kgf/cm ²)	200.34	150	105
Elongation (%)	610.57	730	800
Tear strength (kgf/cm ²)	86.89	60.7	55.8
Hardness	75.5	71	68
T _g , °C	-27.3	-30.8	-36.1

The stronger hard-hard segment H – bonding acts as physical cross-links leading to difficult segmental motion of the polymer chain that results in a more significant phase separation between the hard and soft segments. The phase separation improves the mechanical properties of polyurethanes but reduces the flexibility and solubility [32, 33].

Mechanical Properties: The mechanical properties of the PUD films were affected by type of extenders as shown in Table 3. Films of PUDs with shorter chain extender (M1) has higher tensile and tear strength as compared to films

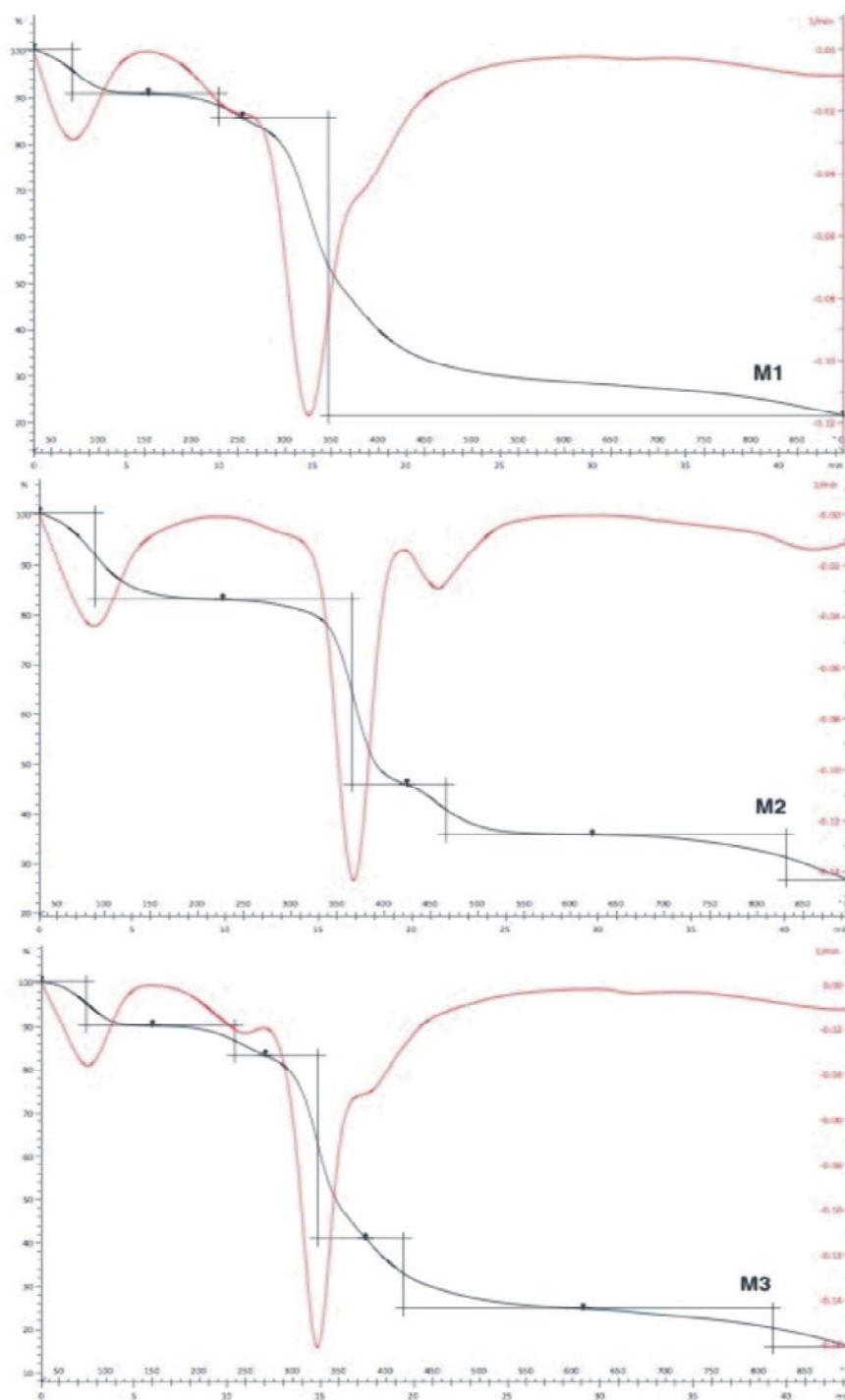


Fig. 2: TGA curves for PUD films at different diamine extenders

of PUDs with longer chain straight (M2 & M3). It may be due to the higher hard segment contents for the same NCO/OH ratio and highest hydrogen bonding density. The elongation at break was increased with chain extender (EDA) and decreased with BDA and HMDA. It may be

due to the decreased in chain flexibility and phase separation. The variation of hardness for the studied PUDs in different chain extenders can be arranged according to the following decreasing order, EDA > BDA > HMDA.

Table 4: Thermal properties of PUD films at different chain extenders

PUDs	Temperature range, °C	Weight lost, wt. %	Residue, wt. %
M1	29.6 – 152.75	9.7	90.74
	152.75 – 252.35	5.13	85.6
	252.35 – 894.66	64.25	21.34
M2	29.44 – 225.54	17.46	82.91
	225.54 – 422.65	37.13	45.78
	422.65 – 617.88	10.1	35.72
	617.88 – 894.71	9.05	26.66
M3	29.66 – 148.22	10.14	89.93
	148.22 – 268.79	6.84	83.10
	268.79 – 377.58	42.39	40.69
	377.58 – 607.66	16.14	24.55
	607.66 – 894.85	8.70	15.80

Thermal Properties: The thermal behaviour of PUD films with different extenders was evaluated with TGA, DTG in air at a heating rate of 10°C/min and DSC at the same heating rate under nitrogen atmosphere. The TGA thermogram for PUD films is given in Figure 2. The temperatures for various percentages of weight loss for all formulations are shown in Table 4.

The TGA curves show a small weight loss in the range 9.7-17.46 % starting at 29.6°C until temperature in the ranging of 148.22 to 225.54°C, which may be attributed to loss of moisture and entrapped solvents. TGA curves also indicate that, PUD (M1) follows three-step degradation process, while all the other formulations follow 4 and 5 steps depending upon the kind of extender chain. The first step ranging between 29.6 and 152.75°C, the second step of degradation occurs between 152.75 and 252.35°C and the third step of degradation occurs between 252.35 and 894.66°C. The rate of degradation in the third step is slightly faster than that in the other stages and is considered as rate determining step. The first degradation step involves the scission of adduct weak links with the liberation of free linear chains. The second and the third steps involve a random scission of the free linear chains into smaller fragments.

On the other hand, four major weight losses were observed in PUD (M2). The second major weight loss was observed in the range 225.54-422.65°C in step 2 of degradation, which corresponds to the loss of H₂O. Upon heating M2 above the decomposition temperature the polymer begins a rapid chain-stripping elimination of H₂O (24, 26). The third major weight loss was observed in between 422.65 and 617.88°C in step 3 of degradation and the fourth weight loss was between 617.88 and 894.71 in step 4 corresponds to the side chain decomposition of PUD. The decomposition steps of (M3) are as the follows: the first step has between 29.66 to 148.22°C, which are due

to moisture vaporization. In the second, third, fourth and fifth steps, in the range of 148.22-894.85°C and weight loss (6.84-42.39%) are attributed to the decomposition of PUD.

The initial decomposition temperature (IDT) corresponds to the temperature at which the initial degradation may occur. IDT for pure PUD occurs at 320 °C is considered to be the polymer decomposition temperature (PDT). Therefore, the data in Table 4 indicate that the thermal stabilities are in the order M1> M2> M3 which increase with decreasing chain length of extender.

Glass transition temperatures (T_g) for PUDs with different chain extenders were calculated from the corresponding typical DSC traces as given in Table 4. The reported T_g has one values, -27.3, -30.8 and -36.1°C for M1, M2 and M3 respectively, which are probably dependant on the thermal history and water content of the tested sample [34]. From the DSC curves, it can be seen that, the increase of chain length of extender from EDA to HMDA shifts the glass transition of different phases to lower temperatures. PUD(M1) has higher T_g value due to the higher hard segment contents.

CONCLUSION

Aqueous polyurethane dispersions were synthesized from TDI, IPDI, PTMG and FA-703 with different chain extenders EDA, BDA and HMDA. The effect of types of chain extenders mechanical properties is studied. Tensile strength, tear strength, hardness increase with the decreasing chain straight of extenders. The increase in tensile properties is interpreted in terms of increasing hard segments of PUD.

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