Aqueous Dispersion of Polyurethane Anionomers from H₁₂MDI/IPDI, PCL, BD, and DMPA

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SYNOPSIS

Polyurethane anionomer dispersions were prepared from hydrogenated diphenylmethane diisocyanate (H_{12}MDI) or isophorone diisocyanate (IPDI), poly(caprolactone) (PCL) diol, 1,4-butane diol (BD), and dimethylolpropionic acid (DMPA). Upon neutralization of the DMPA with triethylamine (TEA), the NCO-terminated polyurethane (PU) ionomers were self-emulsified by adding water, followed by chain extension using triethylenetetramine (TETA) in aqueous media. Polyurethanes from H_{12}MDI showed coarser dispersion and better tensile properties over those from IPDI. Polyurethanes prepared by the one-shot method had better dispersion and tensile properties over those by the two-shot method. When some of the PCL diol was replaced by DMPA or BD, tensile strength increased and ductility decreased due mainly to the increased chain rigidity and intermolecular forces. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane (PU) ionomers contain a relatively small number of ionic sites in the polymer backbone or side chains. These materials are dispersible in aqueous medium and nowadays are widely used in industries such as coatings or adhesives instead of solvent-borne PUs.[1-7] Beside the environmental regulation imposed on solvent emission into the atmosphere in many countries, the superior quality of waterborne PUs over solvent-borne ones, e.g., enhanced mechanical properties and excellent adhesion to many surfaces such as glass and polymeric fibers due to the existence of Coulombic forces of the ionic centers, is the cause of this substitution.[1]

Dimethylolpropionic acid (DMPA) units incorporated in a PU backbone can be converted into effective anionic sites for water dispersion by the subsequent neutralization reaction with triethylamine (TEA).[1,8-10] Poly(caprolactone) (PCL) diol shows improved hydrolytic stability and better

properties at low temperature over other polyester-type diols.[11-13] In a prepolymer mixing process, chain extension by triethylenetetramine (TETA) is performed with isocyanate-terminated prepolymer in water. This reduces solvent usage compared with other processes like the acetone process where water dispersion is performed after chain extension.[1,8-10,14] Prepolymers made from cycloaliphatic diisocyanates are most commonly used due to their stability in water in the prepolymer mixing process.

In this research PU anionomers were obtained from PCL diol, hydrogenated diphenylmethane diisocyanate (H_{12}MDI), isophorone diisocyanate (IPDI), and DMPA. The DMPAs in PU prepolymers were neutralized by TEA to give PU anionomers,[8-10] which subsequently were emulsified by adding water. Chain extension between NCO-terminated prepolymers (PU anionomers) was done with TETA in water. The effect of DMPA, and the difference between one-shot and two-shot procedures are discussed in terms of particle size of emulsion and tensile properties of emulsion cast films. In addition, the effect of BD was determined with regard to the crystallization of soft segments using X-ray diffraction profile and thermal analysis.

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EXPERIMENTAL

Materials

PCL diol with the number-average molecular weight of 2000 (Daicel) was dried at 80°C, 0.1 mmHg for 3 h. TEA (Junsei) and BD (Junsei) were used after treating with a molecular sieve. Other first grade reagents, i.e., H_{12}MDI (Mobay), IPDI (Huls), DMPA (Aldrich), N-methyl-2-pyrrolidinone (NMP, Fluka), dibutyltin dilaurate (T-12, Junsei), and TETA (Junsei) were used without further purification.

Preparation Procedure

Formulations for PU synthesis are given in Table I. A 500-mL round-bottom, 4-necked separable glass reactor with a mechanical stirrer, thermometer, and condenser with drying tube, was used in preparation. Reaction was carried out in a N_2 atmosphere in a constant-temperature oil bath.

In the one-shot method, PCL, DMPA, T-12, NMP, and BD were charged simultaneously into the dried reactor and the mixture was heated to 90°C with stirring. After adding H_{12}MDI or IPDI to the homogenized mixtures, reaction proceeded 3 h to obtain NCO-terminated prepolymer, followed by cooling to 60°C, where TEA/NMP solution was added and stirred 10 min for neutralization. NMP was charged in several steps to reduce the viscosity rise with the progress of the urethane-forming reaction.

In the two-shot method PCL, T-12, and NMP were charged first and reacted with H_{12}MDI at 90°C for about 2 h. DMPA was subsequently charged and reaction proceeded for another 1 h at 90°C. Emulsification was done by adding demineralized water to the prepolymer solution at 60°C. The rate of water addition was carefully controlled by a tubing pump. TETA dissolved in NMP and water was then fed to the emulsion for a period of 10 min, and chain extension was done for the next 2 h at 60°C. The product was a stable PU anionomer dispersion with a solid content of about 35 wt %.

Characterization

Average particle size of dispersion was determined by the Autosizer (Malvern IIC). Approximately 0.15

Table I Recipe for PU Synthesis and Particle Diameter

Designation	PCL g	DMPA g	DMPA wt %	BD g	BD wt %	H_{12} MDI g	IPDI g	TEA mL	TETA g	Particle Dia. (μm)
H101	31.38	0.6	1.5	—	—	7.1145	—	0.62	0.4539	1.08
H201										1.65
H102	29.85	1.0	2.5	—	—	7.8927	—	1.04	0.5036	0.36
H202										1.25
H103	28.32	1.4	3.5	—	—	8.6783	—	1.45	0.5537	0.15
H203										0.88
H104	26.77	1.8	4.5	—	—	9.4668	—	1.87	0.6040	0.07
H204										0.50
H105	25.25	2.2	5.5	—	—	10.2424	—	2.28	0.6535	0.05
H205										0.15
H106	26.22	1.4	3.5	0.48	1.2	10.1870	—	1.45	0.6500	0.10
H107	24.15	1.4	3.5	0.96	2.4	11.6869	—	1.45	0.7457	0.10
H108	22.04	1.4	3.5	1.44	3.6	13.2170	—	1.45	0.8433	0.11
H109	22.40	1.4	3.5	1.92	4.8	14.7378	—	1.45	0.9404	0.12
I101	32.31	0.6	1.5	—	—	—	6.1725	0.63	0.4648	0.85
I102	30.88	1.0	2.5	—	—	—	6.8511	1.04	0.5159	0.21
I103	29.47	1.4	3.5	—	—	—	7.5130	1.45	0.5658	0.10
I104	28.04	1.8	4.5	—	—	—	8.1907	1.87	0.6168	0.08
I105	26.60	2.2	5.5	—	—	—	8.8803	2.28	0.6687	0.07
I016	27.57	1.4	3.5	0.48	1.2	—	8.8271	1.45	0.6647	
I107	25.71	1.4	3.5	0.96	2.4	—	10.1273	1.45	0.7626	
I108	23.81	1.4	3.5	1.44	3.6	—	11.4351	1.45	0.8611	
I109	21.87	1.4	3.5	1.92	4.8	—	12.7862	1.45	0.9624	

mL of emulsion was diluted with deionized water to an appropriate concentration in the cell, followed by setting the pin hole to 200 μm. The z-average mean diameters were measured at 25°C.

Films were prepared by casting the emulsion on a glass plate, followed by drying at 40°C for 24 h. Remaining moisture was evaporated off at 30°C, 20 mmHg, for the next 24 h.

Thermal properties of the samples were measured using differential scanning calorimetry (DSC, Du Pont 1090). Thermal history of the sample was erased through the first run. Melting temperature (T_m) and heat of fusion (ΔH_f) were measured during the second heating (20°C/min) scan.

The crystalline structures of the films were examined with an X-ray diffractometer (Rigaku) using copper K_α radiation (30 kV, 20 mA).

Tensile properties of the emulsion-cast films were determined by an Instron. Tests were performed at room temperature following ASTM D-412 with type C specimen. At least five runs were made to report.

RESULTS AND DISCUSSION

The basic formulations are given in Table I. Throughout the runs, the number-average degree of polymerization (X_n) of prepolymer, calculated by Eq. (1),[15] and the mole ratio of prepolymer–TETA was kept at 2.2 to ensure crosslinking by TETA. In the designation of run, H and I denote $H_{12}MDI$ and IPDI, respectively, and the first digit 1 and 2, following H or I, indicates the one- and two-shot method, respectively.

$$X_n = \frac{1 + r}{1 - r} \qquad (1)$$

where

$$r = \frac{\text{mole of diols } (PCL + DMPA + BD)}{\text{mole of diisocyanate } (H_{12}MDI \text{ or IPDI}) \text{ in feed}}$$

In series H101–H105, H201–H205, and I101–I106, part of PCL was replaced by DMPA while maintaining X_n of prepolymer about 7 by adjusting the amount of diisocyanate used. PCL was replaced by BD at fixed content (3.5 wt %) of DMPA in series H103, H106–H109 and I103, I106–I109.

Particle Size of PU Dispersion

Average particle size of PU dispersion is given in the last column of Table I. It is seen that the particle size decreases with the increase of DMPA in series H101–H105, H201–H205, and I101–I105, and this is due to the enhanced hydrophilicity of PU, as anticipated.[9,10]

I101–I105 series shows better dispersion than H101–H105 series. This probably is due to the unsymmetric structure of IPDI relative to $H_{12}MDI$, because in the dispersion process, water can diffuse into a hard segment domain more easily when the domain has a less ordered structure.[4]

Polyurethanes dispersions from the one-shot method (H101–H105 series) have better dispersions than those from the two-shot method (H201–H205 series) (last column of Table I). Because DMPA has higher reactivity, in the urethane-forming reaction with $H_{12}MDI$ than PCL diol, the DMPA units are more likely to be linked in series by $H_{12}MDI$ in the one-shot method, whereas in the two-shot method DMPA units are more likely to be separated by PCL units in the prepolymer because the prereacted product of $H_{12}MDI$ and PCL diol is chain extended with DMPA.[16] So, the results would explain why hydrophilic ionic sites linked in series are favorable for better dispersion than those located with regular spacing. Enhanced association of ionic sites seems to promote the diffusion of water into hard segment domains in the dispersion process.[1,4]

As the content of BD increases, dispersions become slightly coarser (H106–H109 in Table I), however, the effect is marginal as compared to the significant reduction of average number of DMPA per prepolymer. The number of DMPA unit per prepolymer is reduced from 1.0(H106) to 0.8(H109) by Eq. (1) and Table I. This shows that the average weight percentage of hydrophilic ionic site, rather than the average number of DMPA per prepolymer, is the critical factor for good dispersion. In prepolymer from the one-shot method, the ionic sites are presumably localized, and some prepolymers may not have ionic site in their structure. But, these showed rather better dispersions than those from the two-shot method. This also supports the observation that regular distribution of ionic site in prepolymer is not a critical factor for good dispersion.

Melting of Soft Segment

When two polymers are miscible at the molecular level in the amorphous phase, T_m decreases in blends.[17,18] The variations of T_m, ΔT_m (width of melting endotherm, $T_{final} - T_{initial}$), and the heat of fusion (ΔH_f) (Table II) show that the small amount of BD unit incorporated in PU structure enhances the soft (PCL)–hard (DMPA + BD + IPDI

Table II Melting Behavior of Emulsion Cast Films

Designation	T_m (°C)	ΔT_m (°C)	ΔH (J/g-PCL)
I103	51.4	50	66
I106	53.4	41	67
I107	52.3	36	56
I108	—	—	—
I109	—	—	—

+ TETA) segments phase segregation. Increased T_m and ΔH_f, and a narrower melting endotherm suggest diminished dissolution of hard segments into soft segment domains.[19,20] However, at a higher content of BD, no melting endothermic peak was observed.

The DSC results are confirmed by the X-ray diffraction profile (Fig. 1). Up to 2.4 wt % BD in PU (I103, 106, 107), two sharp crystalline peaks at 2θ = 21° and 23° are clear. As the content of BD increases further (I108, 109), the crystalline peaks disappear and instead an amorphous shoulder around 2θ = 19° becomes evident. This shows that the crystallization of a soft segment is inhibited by the increased rigidity of polymer chains caused by the higher content of BD and accompanied by a higher content of other hard segments (IPDI + TETA).

Tensile Properties

Moduli (Fig. 2) and tensile strengths (Fig. 3) increase with the content of DMPA in PU, whereas
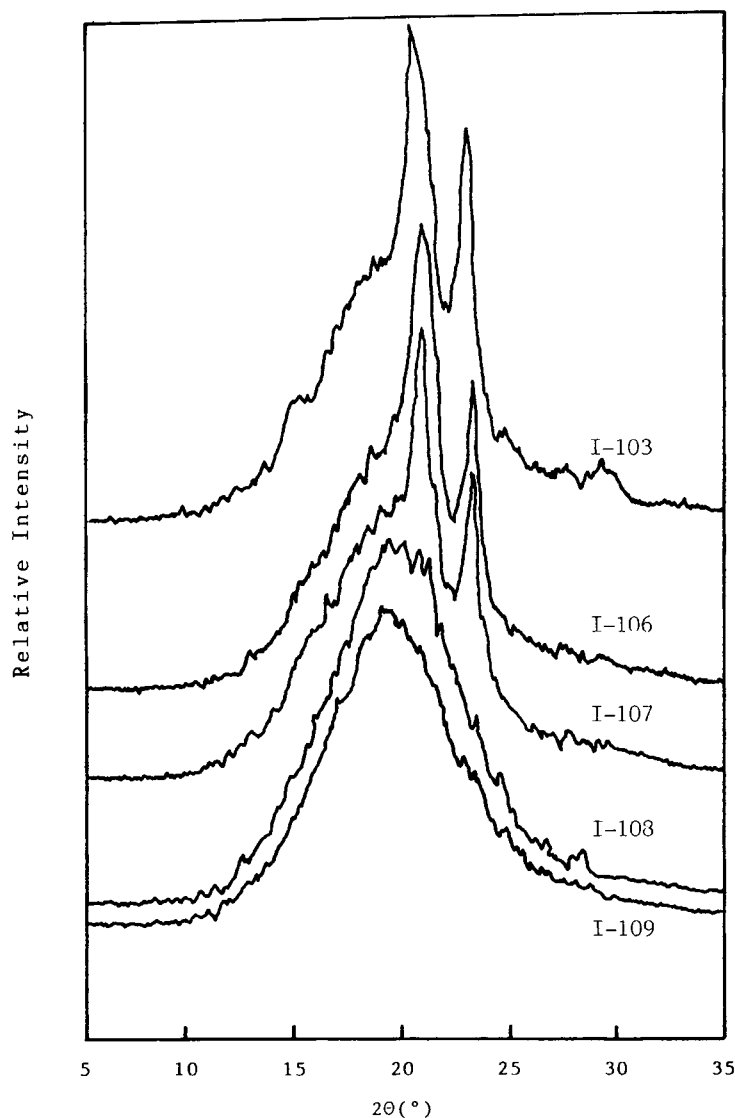

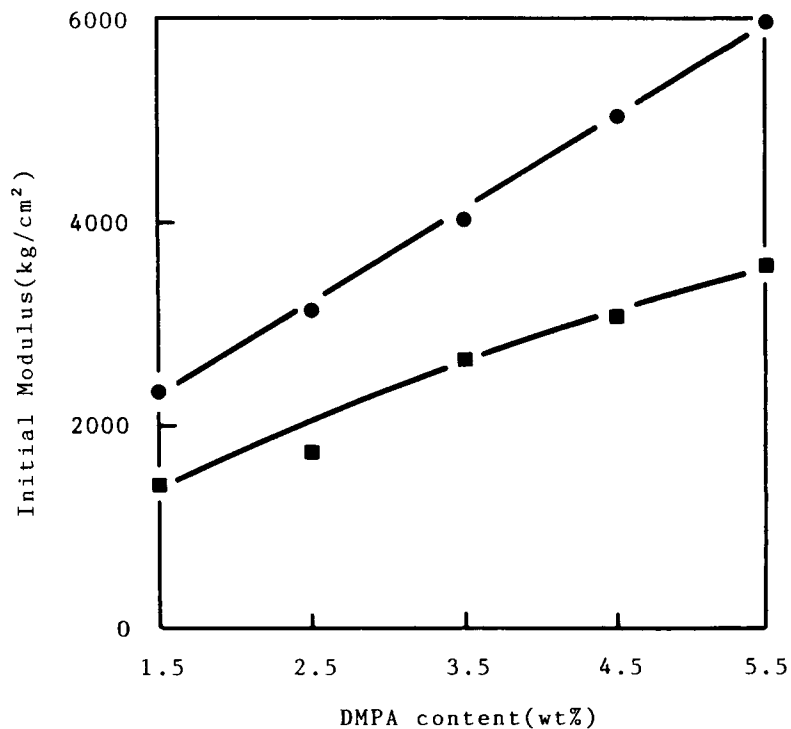**Figure 1** X-ray diffraction profile of series I103, I106–I109.

Figure 2   Effect of DMPA on initial modulus for series (●) H101–H105 and (■) I101–I105.
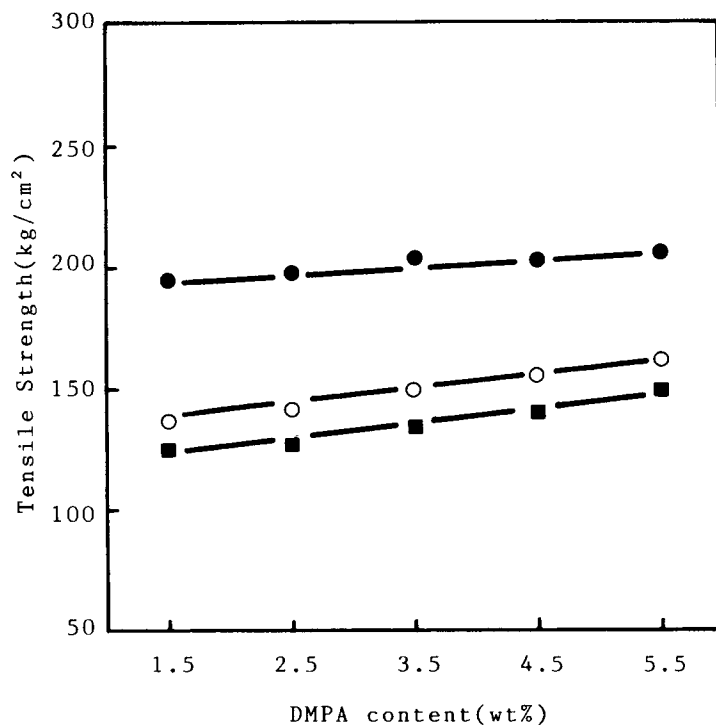

Figure 3   Effect of DMPA on tensile strength for series (●) H101–H105, (○) H201–H205, and (■) I101–I105.

elongation at break (Fig. 4) decreases. In all of the series in Figures 2 and 3, the increase of DMPA is accompanied by increases of other hard segments ($H_{12}MDI$ or IPDI, TETA). Consequently, the increases of moduli and tensile strengths with DMPA might be due to increased intermolecular Coulombic force and hydrogen bonding, augmented by the increased hard segment content.[2,3,21-24] At high deformation, soft and hard segments of PU chains orient toward the direction of external force.[11,25] This rearrangement will be possible when PU chains have a larger amount of hard segments, having stronger Coulombic force and hydrogen bonding, and larger amount of crosslinker such as TETA. This would give decreases of elongation at break at high contents of DMPA.[2,3,21]

Polyurethanes from $H_{12}MDI$ generally have higher moduli, tensile strengths, and elongations at break than those from IPDI (Figs. 2-4). This should come from the enhanced ordering of hard segment domains and consequently enhanced soft-hard segments phase segregation caused by the more symmetric structure of $H_{12}MDI$ relative to IPDI.[2,16,19]

Polyurethanes from the one-shot method show better ultimate tensile properties than those from the two-shot method (Figs. 3 and 4). As mentioned before, PUs from the one-shot method are more

likely to have ionic sites linked in series. This seems to promote aggregation of ionic sites and consequently soft-hard segments phase segregation, resulting in better ultimate tensile properties.

As the content of BD in PU increases (Figs. 5 and 6), moduli at low deformation increases followed by a decrease, and tensile strength decreases followed by an increase. When the amorphous phase of a soft segment is in the rubbery state, the hard segment and the crystalline soft segment domains will resist external force. The first increase of modulus at low deformation seems to be due to the increased content of hard segment (BD, $H_{12}MDI$ or IPDI, and TETA) and the enhanced soft-hard segment phase segregation (Table II), which will improve the role of hard segment as filler.[16] The decrease of modulus at low deformation observed at a higher content of BD is presumably due to the decreased crystallinity of soft segment domains (Table II and Fig. 1).

CONCLUSION

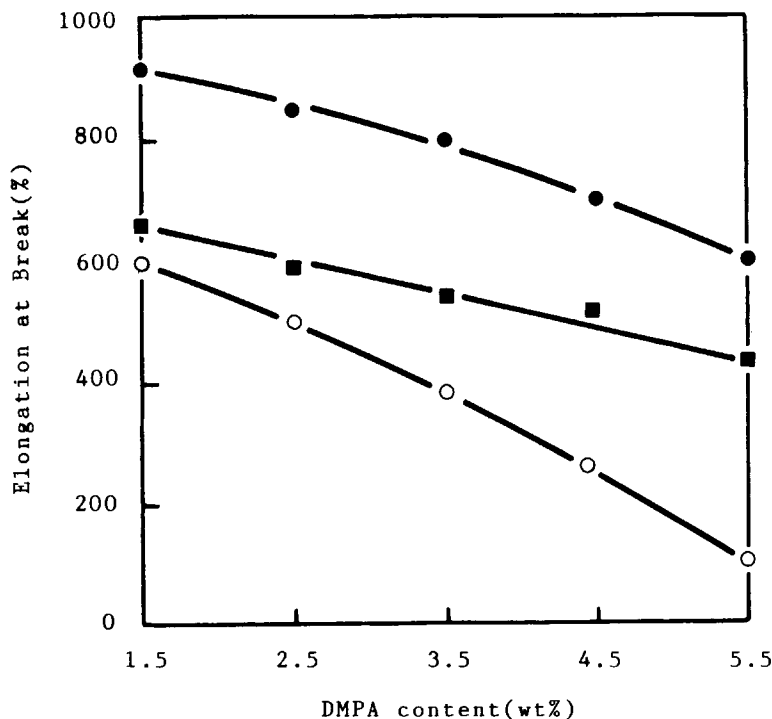Polyurethane ionomers showed finer dispersion when the hard segment domain (DMPA, BD,

Figure 4   Effect of DMPA on elongation at break for series (●) H101–H105, (○) H201–H205, and (■) I101–I105.
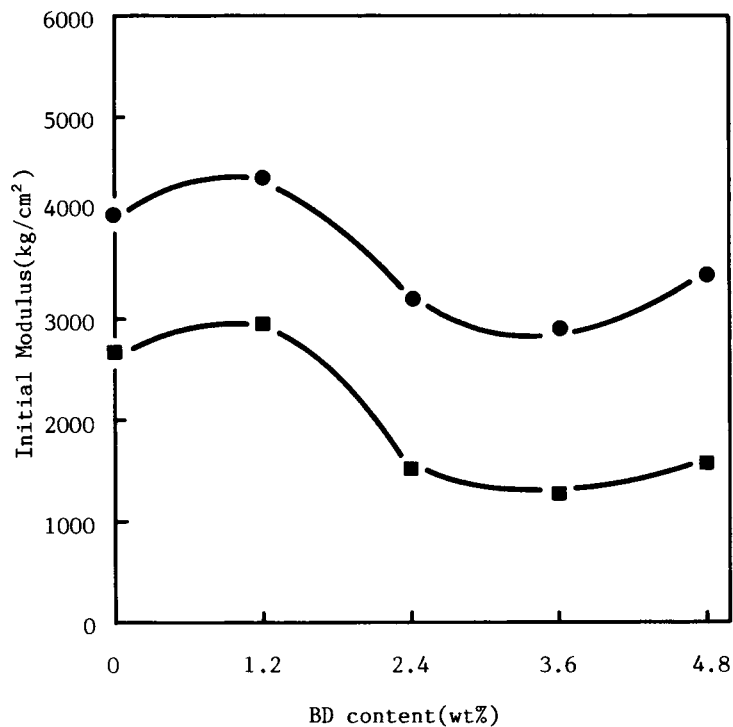
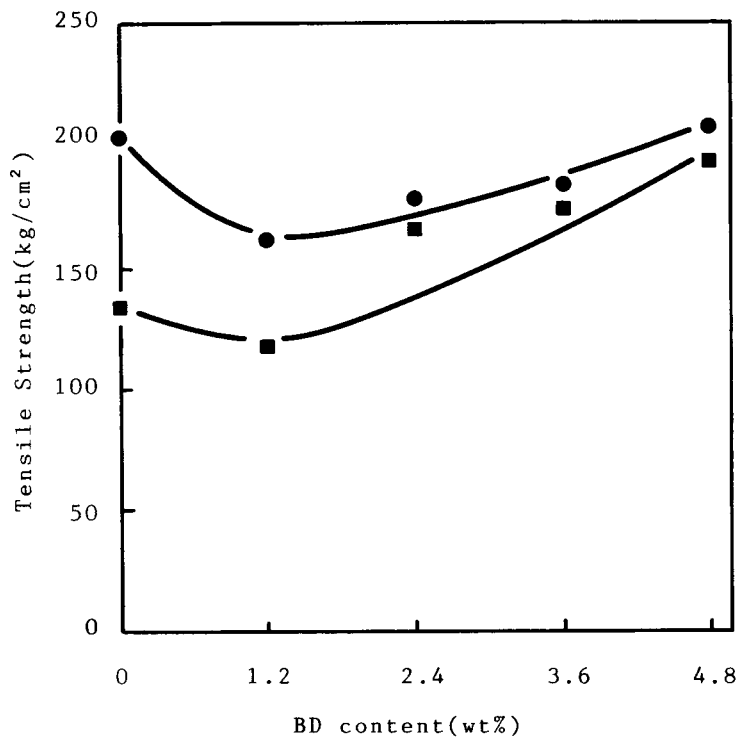**Figure 5** Effect of BD on initial modulus for series (●) H103, H106–H109 and (■) I103, I106–I109.

Figure 6 Effect of BD on tensile strength for series (●) H103, H106–H109 and (■) I103, I106–I109.

$H_{12}MDI$, or IPDI) has a structure enabling easier diffusion of water into hard segment domain in the dispersion process, i.e., when hard segment domain has higher hydrophilicity, when DMPA units are linked in series by diisocyanate, or when IPDI, with its unsymmetric structure, rather than $H_{12}MDI$, is used.

Polyurethanes prepared by the one-shot procedure and from $H_{12}MDI$ had better tensile properties over those by the two-shot method or from IPDI. Upon replacing part of PCL diol by DMPA or BD, tensile strength generally increased and elongation at break decreased, and this was interpreted in terms of increased intermolecular force, and decreased chain flexibility for rearrangement at high deformation.

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