

IPDI-Based Polyurethane Ionomer Dispersions: Effects of Ionic, Nonionic Hydrophilic Segments, and Extender on Particle Size and Physical Properties of Emulsion Cast Film

CHANG KEE KIM and BYUNG KYU KIM*

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

SYNOPSIS

Isophoron diisocyanate (IPDI)-based polyester polyurethane (PU) dispersion in water was prepared in a prepolymer mixing process. Dimethylol propionic acid (DMPA), triethylamine (TEA), and triethyl tetramine (TETA) were used, respectively, as potential anionic center, neutralizing agent, and chain extender in aqueous phase. The effects of DMPA, butanediol (BD), and nonionic hydrophilic segment, viz. monofunctional ethylene-propylene oxide ether polyol, on the particle size of dispersion and the mechanical and viscoelastic properties of the emulsion cast films were systematically analyzed.

INTRODUCTION

Due mainly to environmental considerations, aqueous polyurethane (PU) dispersion has recently been widely encountered in coatings and adhesives to textiles, leather, and many of the polymeric substrates.¹⁻³ Conventional PU is insoluble in aqueous media, and forms phase separations into large domains. For PU to be dispersible in water, ionic and/or nonionic hydrophilic segments should be incorporated in PU structure.⁴⁻⁶ Advantages and disadvantages of ionic and nonionic type PU are well documented in the literature.^{7,8}

Pioneer work on aqueous PU dispersions has in the past been performed by industry laboratories,^{3,9-11} and detailed data on particle size and physical properties of emulsion cast films are rarely available in open literature.¹²

We describe the preparations of aqueous PU dispersion from isophoron diisocyanate (IPDI), poly(tetramethylene adipate) glycol (PTAd), and α,α' -dimethylolpropionic acid (DMPA) as anionic centers. Nonionic hydrophilic segment, that is, monofunctional ethylene-propylene oxide ether (EOE), was also incorporated. Effects of DMPA,

EOE, and BD contents were systematically analyzed in terms of particle size, mechanical, and viscoelastic properties of emulsion cast films.

EXPERIMENTAL

Materials

EOE ($M_n = 1930$) used in this study was synthesized from 1-butanol, ethylene oxide (EO), and propylene oxide (PO) following the standard procedure described elsewhere.¹³ Molar ratio of EO to PO was 83 : 17. PTAd ($M_n = 1016$, Dongsung Chemicals) and EOE were dried at 80°C, 0.1 mmHg until no bubbling was observed. Triethylamine (TEA) was used after treating over 3 Å molecular sieve for 3 d before use. Other extra pure grades of DMPA (Aldrich), triethylene tetramine (TETA, Junsei Chemical), N-methyl-2-pyrrolidone (NMP), and isophoron diisocyanate (IPDI, Huls AG) were used without further purifications. Extra pure grade of dibutyltin dilaurate (DBT, T-12) was employed as catalyst (Table I).

Procedure

A 500 mL round-bottom, 4-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pipette outlet was used as

* To whom correspondence should be addressed.

Table I Feed Compositions (Unit: g)

Sample #	PTAd	DMPA	EOE	BD	IPDI	TEA	TETA
PU-D1	27.31	0.937 (2.4) ^a	0.0 (0)	0.0 (0)	10.304	0.707	0.773
PU-D2	26.92	1.050 (2.7)	0.0 (0)	0.0 (0)	10.444	0.792	0.783
PU-D3	26.65	1.171 (3.0)	0.0 (0)	0.0 (0)	10.640	0.884	0.798
PU-D4	25.57	1.475 (3.7)	0.0 (0)	0.0 (0)	11.004	1.113	0.826
PU-D5	25.21	1.608 (4.2)	0.0 (0)	0.0 (0)	11.200	1.214	0.840
PU-E1	26.92	1.050 (2.7)	0.8 (2)	0.0 (0)	10.444	0.792	0.783
PU-E2	26.92	1.050 (2.7)	1.6 (4)	0.0 (0)	10.444	0.792	0.783
PU-E3	26.92	1.050 (2.7)	2.4 (6)	0.0 (0)	10.444	0.792	0.783
PU-E4	26.92	1.050 (2.7)	3.2 (8)	0.0 (0)	10.444	0.792	0.783
PU-E5	26.92	1.050 (2.7)	4.0 (10)	0.0 (0)	10.444	0.792	0.783
PU-B1	25.34	1.033 (2.7)	0.0 (0)	0.46 (1.2)	11.480	0.780	0.861
PU-B2	24.94	1.083 (2.7)	0.0 (0)	0.98 (2.4)	13.160	0.820	0.987
PU-B3	22.18	1.031 (2.7)	0.0 (0)	1.38 (3.6)	13.636	0.778	1.023
PU-B4	21.58	1.076 (2.7)	0.0 (0)	1.92 (4.8)	15.400	0.821	1.155

^a Wt % on total solid base.

NMP: 11.5 g, DBT: 200 ppm, H₂O: 63 g.

reactor. Reaction was carried out in a constant temperature oil bath, with $\pm 0.5^\circ\text{C}$ precision. PTAd, DMPA, NMP, EOE, and DBT were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30 min, followed by adding IPDI to the homogenized mixtures. However, when BD was used, the homogenized mixture was lowered to 65°C and IPDI was added. The mixture was heated to 90°C for about 3 h to obtain NCO terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration.¹⁴ Upon obtaining the theoretical NCO value, the prepolymers were cooled to 60°C , and TEA/NMP neutralizing solution was added and stirred for 10 min maintaining a temperature of 60°C .

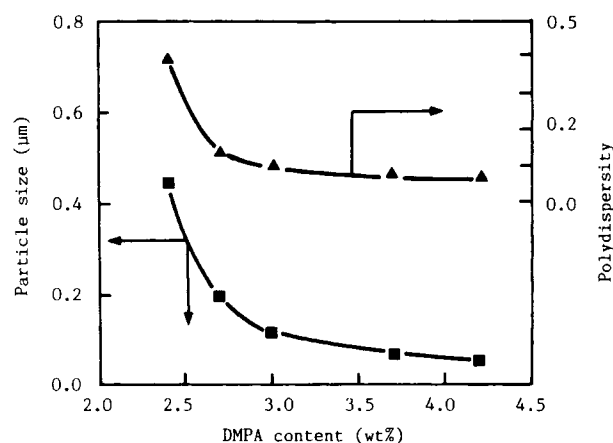


Figure 1 Average particle size and distribution as a function of DMPA content (PU-D).

While stirring rapidly, demineralized water was added to the solution to form water dispersion. TETA solution, dissolved in NMP and water, were then fed to the emulsion for a period of 10 min, and chain extension was carried out for the next 2 h. The resulting product was urea-urethane dispersion with a solid content of about 35%, which was stable over six months at room temperature.

Characterizations

Particle size of the dispersion was measured using an Autosizer (Malvern II C) after treating the samples with ultrasonic waves. State of dispersion was also viewed from transmission electron microscopy (TEM, Hitachi H300). TEM samples were stained with OsO₄ for 1 week. Mechanical and viscoelastic

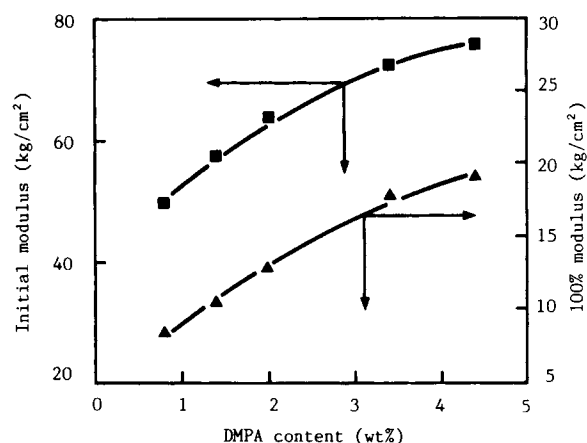


Figure 2 Initial and 100% modulus as a function of DMPA content (PU-D).

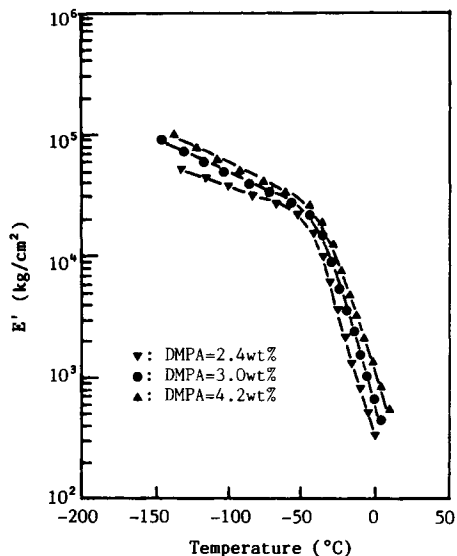


Figure 3 Effect of DMPA on storage moduli of films (PU-D).

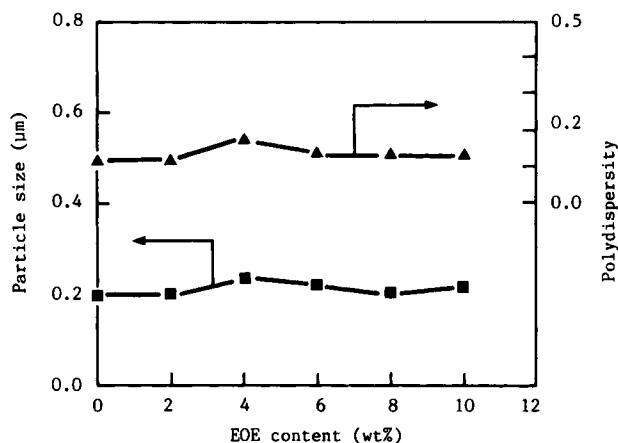


Figure 4 Average particle size and distribution as a function of EOE content (PU-D2, PU-E).

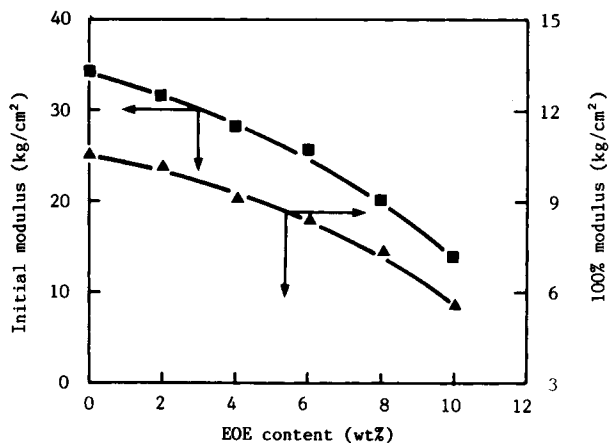


Figure 5 Initial and 100% modulus as a function of EOE content (PU-D2, PU-E).

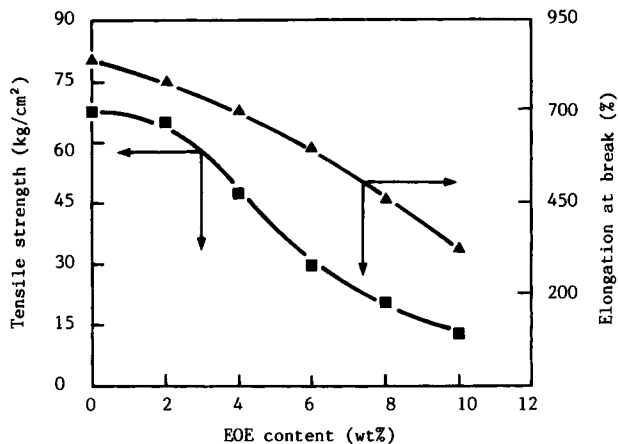


Figure 6 Tensile strength and elongation at break as a function of EOE content (PU-D2, PU-E).

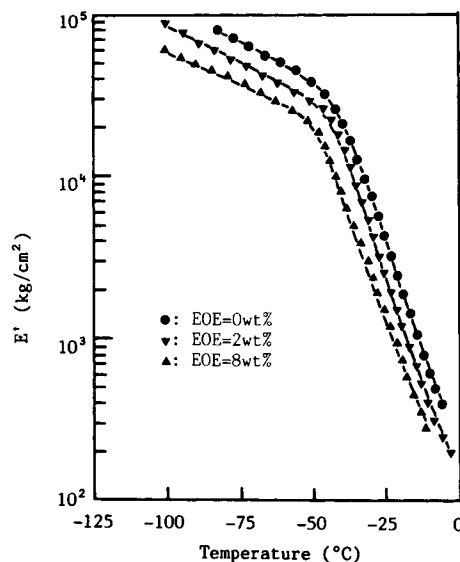


Figure 7 Effect of EOE on storage moduli of films (PU-D2, PU-E).

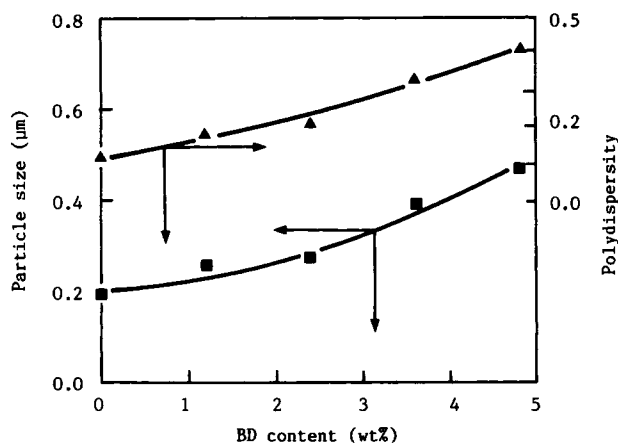
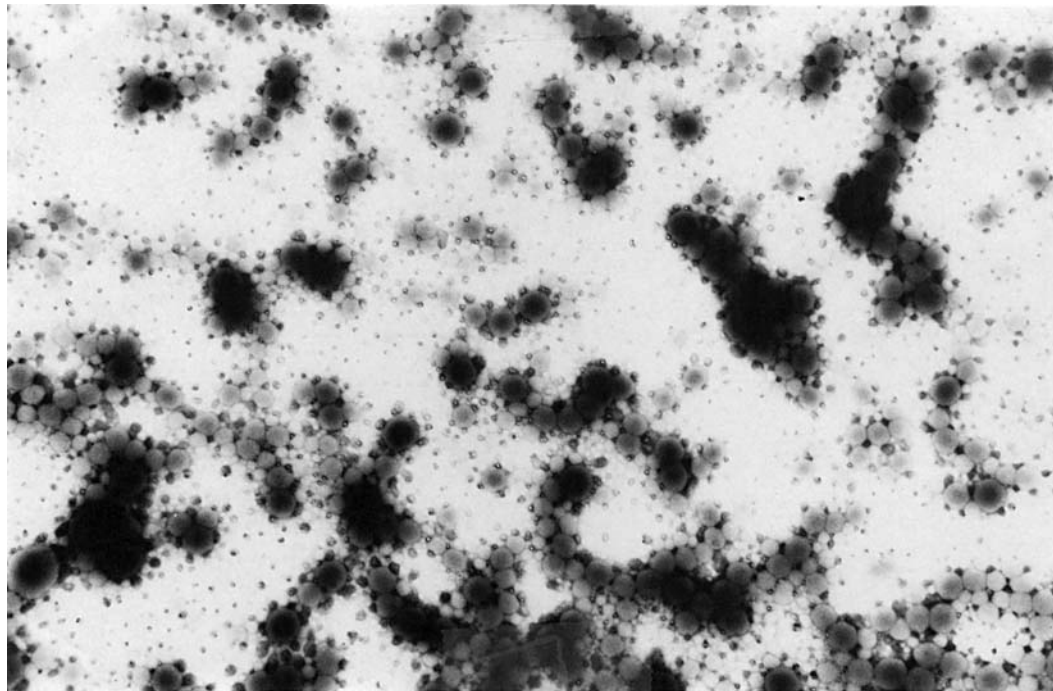
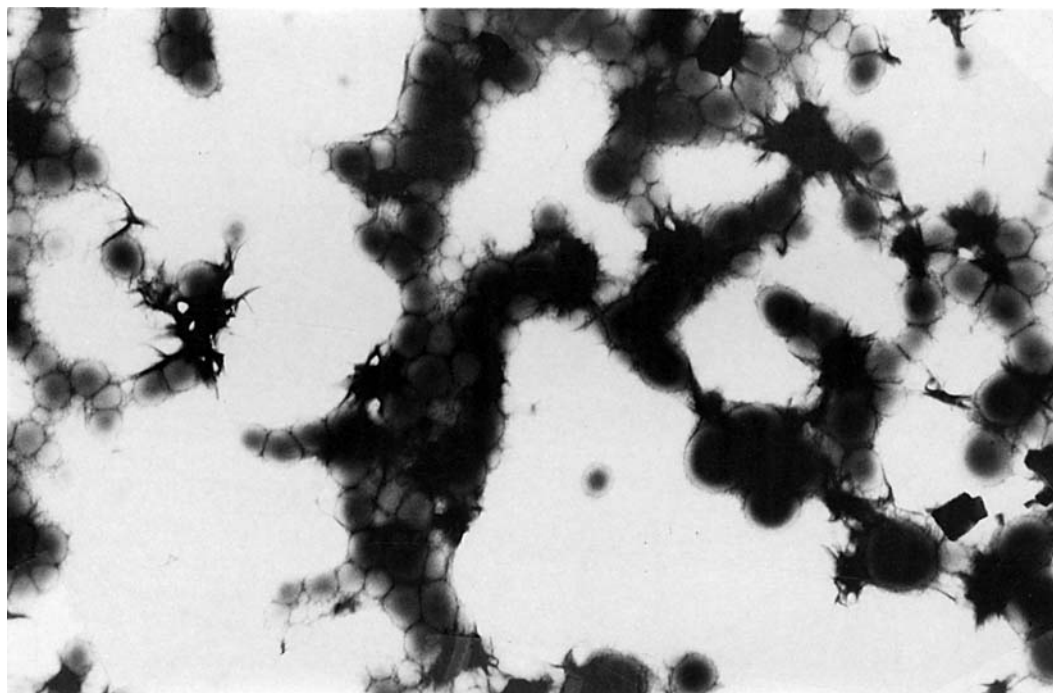


Figure 8 Average particle size and distribution as a function of BD content (PU-D2, PU-B).

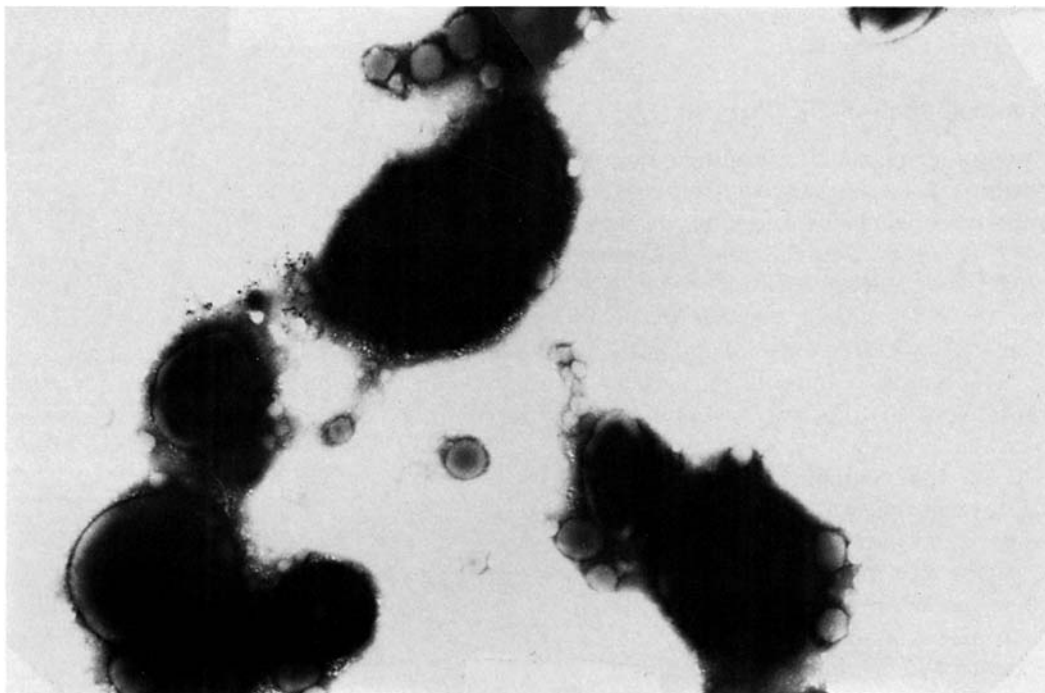


(a)



(b)

Figure 9 TEM micrographs of the emulsion with different BD content at DMPA = 2.7 wt %: (a) 0.0 (b) 2.4 (c) 4.8 wt % (20,000 \times).



(c)

Figure 9 (Continued from the previous page)

properties of the emulsion cast films were respectively measured from Instron tensile tester, and Rheovibron (Tokyo Baldwin DDV-II). Tensile tests were made at room temperature following ASTM D-412 with type C specimens. Rheovibron tests were performed from -150 to 80°C at 11 Hz. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at 40°C for 12 h. Moisture was further dried off at 30°C , 20 mmHg for the next 24 h.

RESULTS AND DISCUSSION

Effects of DMPA

Effects of DMPA content on particle size and its distribution are shown in Figure 1. In self-emulsified dispersions with no external emulsifiers, particle size decreases with increasing hydrophilicity of dispersed phases, both in anionic and nonionic type dispersions.^{7,15} Anionic centers, viz. DMPA, are essentially hydrophilic in nature, and it is expected that the particle size decreases with increasing DMPA content, as our results indicate. It is, however, noted that the particle size decreases rapidly at low DMPA

content (≤ 3.0 wt % on total solid), and shows an asymptotic decrease to about $0.1\ \mu\text{m}$. It seems that there is a critical concentration of DMPA content on particle size reduction. It is also seen that the particle size distribution with DMPA content shows basically identical dependence with average particle size, i.e., a smaller particle size is accompanied by a narrower particle size distribution. Particle sizes determined from Autosizer, as a function of DMPA content, were again confirmed from TEM micrographs (not shown).

Moduli (initial and 100%) of emulsion cast films are shown in Figure 2. Moduli increase with DMPA content of the PU. Effect of DMPA on mechanical property can be viewed from several points of view. First, DMPAs provide anionic centers of PU ionomers. With increased ionic centers, more Coulombic forces are expected.^{9,15} This gives increased inter-chain interactions, resulting in enhanced stiffness. Second, with more DMPA incorporations in PU structure, less long chain polyols are incorporated, and more of urethane linkages result. Urethane linkages, together with isocyanate segments, form hard domains in PU as our results indicate.¹⁶⁻¹⁸ Viscoelastic properties of the films (Fig. 3) show that

the elastic modulus (E') increases with DMPA, consistent with the Instron data.

Effects of Nonionic Hydrophilic Segment (EOE)

Effects of nonionic hydrophilic segment content (EOE) on the particle size, viscoelastic, and mechanical properties of emulsion cast films are shown in Figures 4–7. It is seen that the particle size and its distributions are independent of, or slightly increasing with, the EOE content. Apparently the results are opposite to what we expect from EOE hydrophilicity. The reason is most likely because of the temperature sensitivity of polyoxyethylene hydrophilicity, which is completely lost at about 65°C and above.^{4,5} At the emulsification temperature (60°C), EOE is expected to lose its solubility in water, and does not affect particle size. In fact, nonionic hydrophilic segment is incorporated primarily to improve the salt resistance of aqueous PU, which, with ionic type alone, is not obtained.¹⁵

The effects of EOE on rigidity and strength are rather negative. Modulus (Fig. 5) and strength (Fig. 6) decrease with EOE content. This in part is due to the weak interchain interactions of ether type polyol (EOE) compared to those of ester type polyol (PTAd). It should be also noted that the elongation at break also decreases with EOE content. PO side chains should be, at least in part, responsible for the reduced elongation, in addition to reduced interchain interactions between EOE's. However, the simultaneous decrease of strength and ductility is most likely due to the decreased molecular weight of PU. As the content of monofunctional polyol is increased, the extent of TETA chain extension should be decreased. The decrease of elastic modulus with EOE content was also clear from dynamic test

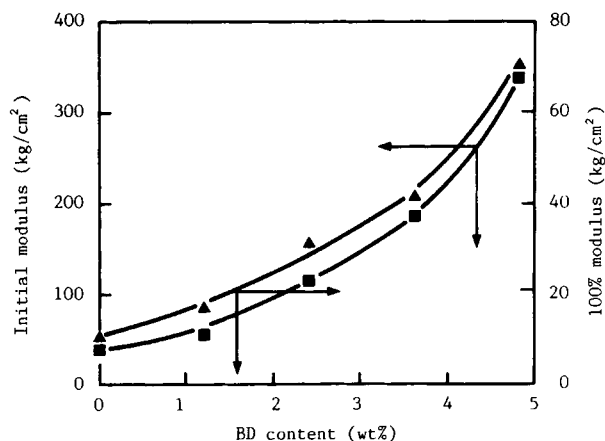


Figure 10 Initial and 100% modulus as a function of BD content (PU-D2, PU-B).

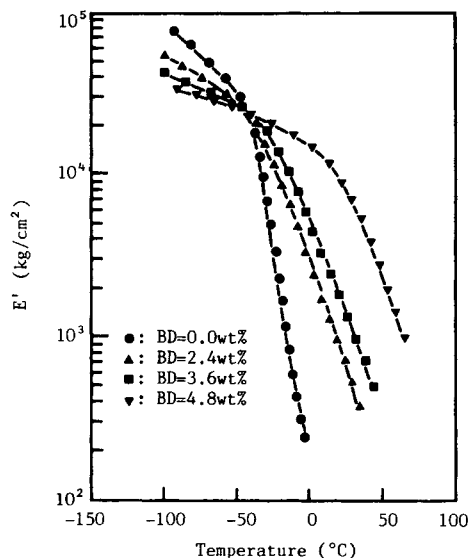


Figure 11 Effect of BD on storage moduli of films (PU-D2, PU-B).

(Fig. 7). The value of E' decreases, and the point of inflection moves toward lower temperature as the EOE content increases.

Effects of Butanediol (BD)

Effect of BD on particle size and its distribution are shown in Figure 8. It is seen from the figure that the average particle size increases with BD content, and that the particle size distribution becomes broader. Typically in PU, diisocyanates and chain extenders form hard segments and polyols form soft segments.^{16,19} As more chain extenders are incorporated in PU structure, PU backbones should become rigid with the increased number of urethane linkages. Also, it is reasonably presumed that the nonionic hydrophilic segments, as well as anionic centers, are predominantly located on the surfaces of PU particles in aqueous media.²⁰ However, with increased chain rigidity of PU, conformational changes from homogeneous solution in NMP to hydrophobic–hydrophilic spherical structure in water may be less plausible. In addition, rigid particles are less deformable in shear field, and this should lead to larger particle size at the stage of emulsification under shear. The increase of particle size with BD content is also seen in TEM micrographs (Fig. 9).

As expected, moduli (Fig. 10) increase with BD content. Basic structure–property relationships in PU state that hard segments affect hardness and strength, and are controlled by the total NCO content.¹⁹ With the increase of BD, NCO content is increased proportionally in stoichiometric reactions.

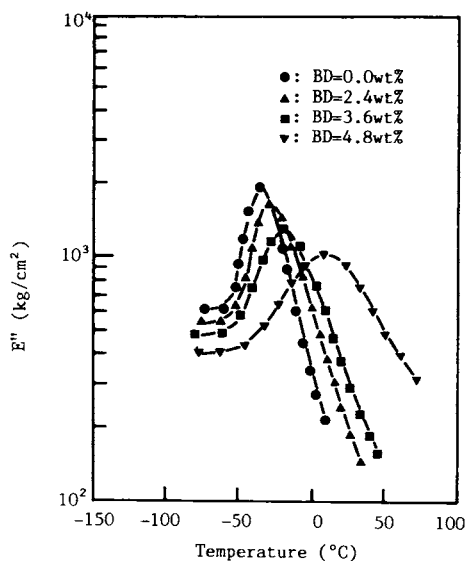


Figure 12 Effect of BD on loss moduli of films (PU-D2, PU-B).

Viscoelastic properties of the PU as a function of BD are shown in Figures 11 and 12. Elastic moduli of the present PUs (Fig. 11) are typical of linear amorphous polymers, and the value at room temperature increases as the BD content increases. The trend is consistent with our Instron data. Temperature characteristics of PU are, more or less, governed by the hard/soft segment morphology, which often is obtained by X-ray data. It is seen that the loss peak (Fig. 12) moves toward the higher temperature as the BD content increases, indicative of increased chain rigidity. It may be noted that the peak area also increases with BD contents. Since the loss peak mainly corresponds to amorphous interactions, increased amorphous interactions are also indicated, probably via the increased number of urethane linkages.

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