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POLYURETHANE IONOMERS FROM CYCLOALIPHATIC DIISOCYANATE AND POLYTETRAMETHYLENE GLYCOL

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ABSTRACT

Segmented polyurethane (PU) ionomers were prepared from cycloaliphatic diisocyanate [methylene bis(4-cyclohexyl isocyanate) (H_{12} MDI) and isophoron diisocyanate (IPDI)] and polytetramethylene glycol (PTMG) by using an anionic-type chain extender, viz., dimethylol propionic acid (DMPA). The effect of ionic content and butanediol (BD) on the state of dispersion and physical properties of emulsion-cast film was determined using Autosizer, transmission electron microscopy (TEM), Instron, and Rheovibron. With increased incorporations of DMPA in PU, particle size of emulsion decreased asymptotically, tensile modulus and strength increased, and the glass transition temperature (T_g) moved toward the higher temperature. On the other hand, with increased incorporation of BD in PU, particle size of emulsion, tensile modulus, and strength of the emulsion cast film increased, and the major transition of soft segment moved toward higher temperature. With regard to the structural effect of the isocyanate, H_{12} MDI gave finer dispersion and better mechanical properties over IPDI.

INTRODUCTION

Aqueous polyurethane (PU) is nontoxic, nonflammable, and does not pollute the air. Ideally, only water evaporates during the drying process. In addition, chain extension between NCO-terminated prepolymers occurs in aqueous PU in the form

of a dispersion. Consequently, it is possible to set the mole mass to practically any level without the viscosity being impaired.

PU dispersion can be prepared with or without the aid of an external emulsifier depending on the structure of PU [1, 2]. For PU to be self-emulsifiable, it should contain hydrophilic segments in its structure. A number of ionic and non-ionic compounds have been widely encountered [3–5]. In general, the ionic type is stable at high temperatures whereas the nonionic type is stable against electrolytes and freezing. Among ionic types, the anionic type is preferred over the cationic one, especially for textile applications. Usually 1 wt% of the salt group in the PU proved sufficient to obtain a stable dispersion [6]. Most work with aqueous PU has been done in industrial laboratories [7–10], and basic data concerning the structure–property relationship are sparse in the open literature [11]. This paper describes the preparation of PU ionomers in a prepolymer mixing process. Two types of cycloaliphatic diisocyanate, i.e., isophoron diisocyanate (IPDI) and methylene bis(4-cyclohexyl isocyanate) (H_{12} MDI), were used with poly(oxytetramethylene) glycol (PTMG) and dimethylol propionic acid (DMPA) (potential ionic center). The effects of DMPA, BD, and isocyanate structure on the state of dispersion and the mechanical and viscoelastic properties of emulsion-cast film were analyzed.

EXPERIMENTAL

Materials

PTMG ($M_n = 1000$, Hodogaya) and butanediol (BD) were dried and degassed at 80°C, 1–2 mmHg for 5 h before use. DMPA (Aldrich) was dried at 100°C for 2 h in a drying oven. Extra pure grade H_{12} MDI (Mobay), IPDI (Scholven), and dibutyltin dilaurate (DBT) were used as received. *N*-Methyl-2-pyrrolidone (NMP), triethylene tetramine (TETA), triethylamine (TEA), and solvents used in the titrations were dried over a 3-Å molecular sieve before use.

Prepolymer Synthesis

The basic formulations are given in Tables 1 and 2. A 500-mL round-bottom, 4-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pipet outlet was used as the reactor. The reaction was carried out in a constant temperature oil bath. PTMG, DBT (0.03 wt% based on the total solid weight), and DMPA dissolved in NMP (5 wt% based on the total weight) were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30 min, followed by adding isocyanate (H_{12} MDI or IPDI) to the homogenized mixtures. The mixture was heated to 90°C for about 3 h to obtain NCO-terminated prepolymers. The change of the NCO value during the reaction was determined by using a standard dibutylamine backtitration method [12]. Upon obtaining the theoretical NCO value calculated from the $[NCO]/[OH]$ index of feed, which was fixed at 1.37, the prepolymers were cooled to 60°C, and the neutralizing solution, i.e., triethylamine (TEA) dissolved in NMP (5 wt% based on the total weight), was added and stirred for 1 h while maintaining the temperature at 60°C. The 1:1 stoichiometry was obtained by adding TETA at the chain extension step. The

TABLE 1. Feed Compositions with the Variation of DMPA (unit: g)^a

Sample	DMPA (wt%)	Hard segment content (wt%)	IPDI	H ₁₂ MDI	PTMG	DMPA	TEA	TETA
PU-I1	1.5	30	9.888	0.000	28.209	0.580	0.421	0.877
PU-I2	2.5	33	10.378	"	27.001	0.957	0.722	0.921
PU-I3	3.5	35	10.881	"	25.830	1.333	1.001	0.965
PU-I4	4.5	38	11.343	"	24.654	1.697	1.279	1.006
PU-I5	5.5	41	11.832	"	23.519	2.058	1.553	1.050
PU-H1	1.5	33	0.000	11.221	26.920	0.581	0.437	0.884
PU-H2	2.5	36	"	11.769	25.639	0.959	0.723	0.884
PU-H3	3.5	39	"	12.327	24.413	1.332	1.004	0.927
PU-H4	4.5	42	"	12.868	23.185	1.696	1.281	0.967
PU-H5	5.5	45	"	13.401	21.978	2.059	1.552	1.008

^a MPA wt%, prepolymer base; DBT, 300 ppm; NMP, 11.5 g; H₂O, 63 g.

amount of NMP used in each step, i.e., to dissolve the DMPA and to reduce the solution viscosity, was approximately the same (see the total amount in the tables).

Emulsification and Chain Extension

Aqueous dispersion of PU was obtained by adding water (35°C) to the mixture (60°C) at 900 rpm. Since the water addition rate, in addition to the viscosity ratio between prepolymer solution and water, is a critical parameter to obtain stable

TABLE 2. Feed Compositions with the Variation of BD (unit: g)^a

Sample	BD (wt%)	Hard segment content (wt%)	IPDI	H ₁₂ MDI	PTMG	DMPA	BD	TEA	TETA
PU-I3	0.0	35	10.881	0.000	25.830	1.333	0.000	1.001	0.965
PU-I6	1.2	40	11.930	"	24.225	1.329	0.455	1.002	1.059
PU-I7	2.4	43	12.945	"	22.677	1.323	0.906	0.997	1.149
PU-I8	3.6	46	13.546	"	21.459	1.320	1.379	0.996	1.262
PU-I9	4.8	51	15.021	"	19.547	1.318	1.808	0.995	1.330
PU-H3	0.0	39	0.000	12.327	24.413	1.332	0.000	1.004	0.927
PU-H6	1.2	43	"	13.515	22.681	1.330	0.455	1.002	1.016
PU-H7	2.4	48	"	14.690	20.951	1.325	0.909	0.999	1.104
PU-H8	3.6	52	"	15.878	19.250	1.324	1.361	0.998	1.194
PU-H9	4.8	56	"	17.051	17.540	1.320	1.811	0.995	1.282

^aAs described in Table 1.

dispersion, a tubing pump was used, and water was added for 6 min at constant flow rate. The phenomena of phase inversion, viscosity, and conductivity change during the emulsification process are well documented in Dieterich [13] and our earlier papers [14, 15]. TETA dissolved in water was then fed to the emulsion for a period of 40 min, and chain extension was carried out for the next 2 h. The resulting product, a urea-urethane dispersion with a solid content of about 35%, was stable over 6 months at room temperature.

Tests

Particle size and distribution were measured with an Autosizer (Malvern IIC), and the state of dispersion was investigated by transmission electron microscopy (TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO_4 for 1 week. The tensile properties of the emulsion-cast films were measured by using an Instron Tensile Tester at a crosshead speed of 100 mm/min, and an average of at least five measurements was taken for our report. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at 80°C for 5 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg. Microtensile test specimens were prepared according to ASTM D-1822. Dynamic tests were performed with a Rheovibron (Toyo Baldwin DDV-II) from –100 to 50°C at 11 Hz with a sample size of $0.03 \times 0.2 \times 3$ cm.

RESULTS AND DISCUSSION

Effect of DMPA

It is of practical importance to be able to control the average particle size and its distribution of PU dispersion. For example, relatively large particles are preferred in many surface coatings to facilitate rapid drying, and relatively small particles are desirable when deep penetration of the dispersion into the substrate is an essential step. Figure 1 shows the average particle size and its distribution as a function of DMPA content. It is seen that the particle size decreases with increasing DMPA in both the IPDI and H_{12} MDI systems. The Autosizer result was visually confirmed from TEM (Fig. 2). In PU dispersion, the average size of particle is more or less controlled by such mixing conditions as rpm and temperature. However, it is mostly governed by the hydrophilicity of the PU. DMPA is hydrophilic in nature, and it reduces the particle size effectively at low content and asymptotically at high content. The asymptotic behavior is probably due to the increase of viscosity with DMPA. An ionic-type PU dispersion is stabilized by diffusing electrical double-layer formation by the salt groups [16]. The reduction of particle size with more DMPA should augment the total double-layer and hydrodynamic volume of the particle as well, leading to an increase in viscosity [17]. Moreover, an increase of the hard fraction increases the viscosity ratio between the dispersed and continuous phases [18]. This makes the breakup of the dispersed phase more difficult, and the asymptotic behavior shown in Fig. 1 is expected.

The mechanical properties of emulsion-cast films are shown in Figs. 3 and 4. While the modulus and tensile strength increase, elongation at break decreases as the DMPA content increases. Typically in PU, polyols form a soft domain and isocyanates and urethane linkages form a hard domain. As the content of DMPA

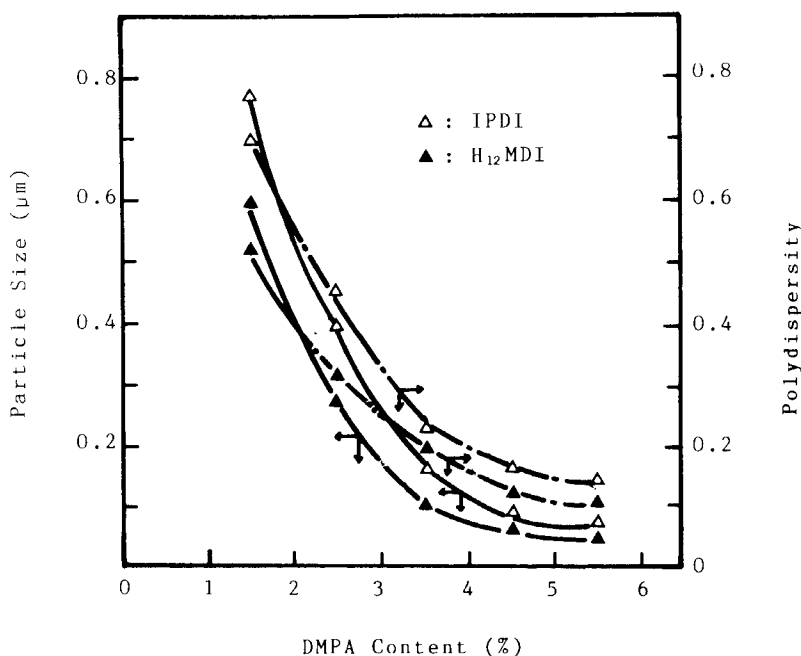


FIG. 1. Average particle size and its distribution as a function of DMPA.

increases, there is a smaller amount of polyol soft segment, and a larger amount of urethane linkages are incorporated in the PU structure, leading to an increased hard fraction and a decreased molecular weight. The increase of modulus and strength comes mainly from the increased hard fraction (see Table 1). Moreover, the ionic centers are the source of Coulombic force and hydrogen bonding, which together contribute to the increased interchain interactions [19–21]. This, at least in part, should support an increase in the modulus and tensile strength with an increasing amount of DMPA. The decreased ductility of the PU with DMPA is mainly due to increased rigidity as the soft domain fraction decreases.

The viscoelastic properties of the PU are shown in Figs. 5(a) and 5(b). The storage modulus (E') increased with DMPA, below and above T_g (Fig. 5a). It is also seen that the effect of DMPA is much more pronounced in the rubbery state than in the glassy state. This is an indication that the ionic force, in addition to the increased number of urethane linkages, significantly contribute to the elastic properties of the PU. With more DMPA incorporation, the glass transition temperature (T_g) also increases (Fig. 5b), a result consistent with a modulus increase. An increase in T_g may be caused mainly from a hard fraction increase. However, when the area of loss peak is considered as a unit, it may be concluded that the increased number of ionic centers gave more amorphous interactions, as expected.

Effect of BD

In this series of experiments the content of DMPA was fixed at 3.5 wt% based on the prepolymer. With more incorporation of BD, as with DMPA, less polyol is incorporated in the PU structure. This leads directly to an increase of the hard

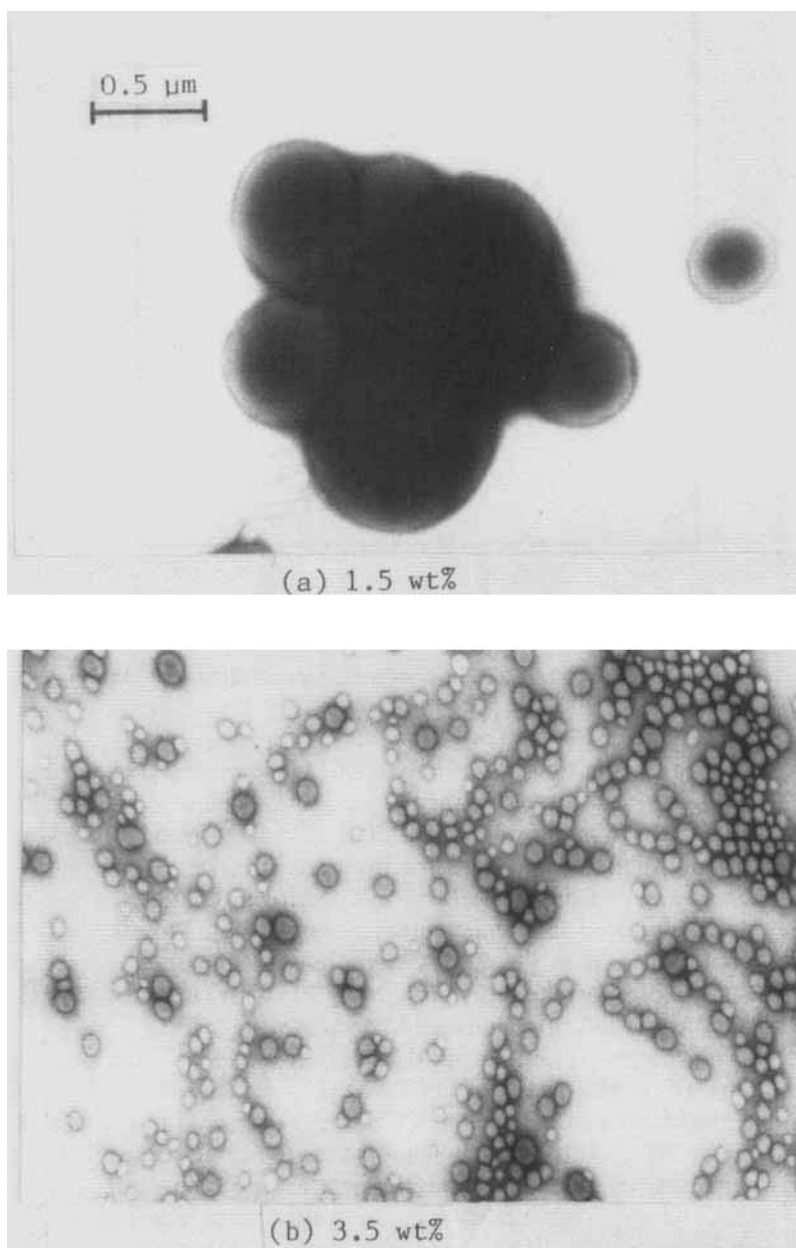


FIG. 2. TEM micrographs of the emulsion with different DMPA contents for the $\text{H}_{12}\text{MDI-PTMG}$ system. $30,000\times$.

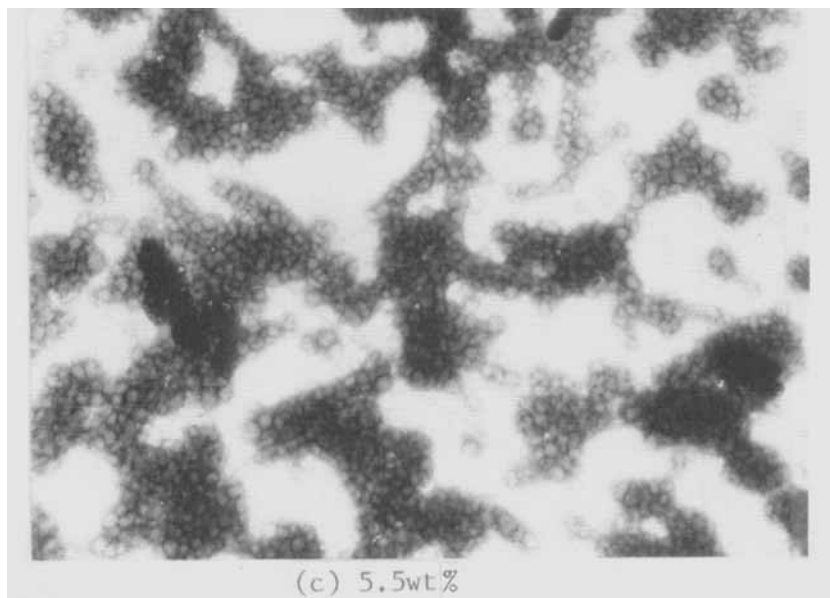


FIG. 2 (continued).

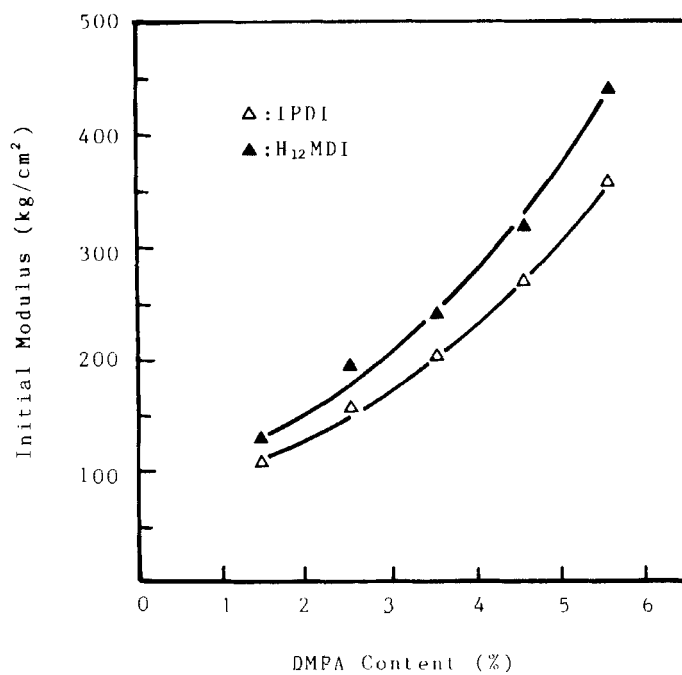


FIG. 3. Initial modulus as a function of DMPA.

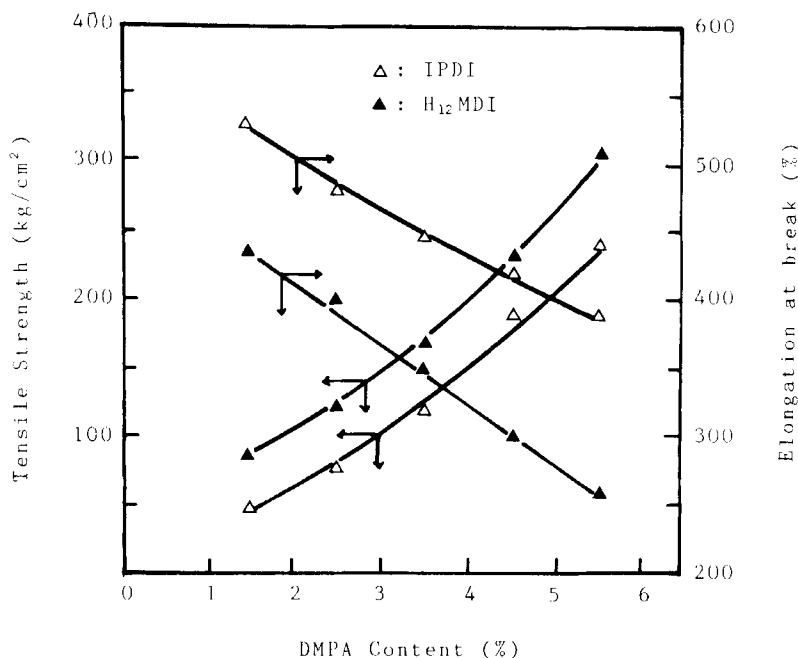


FIG. 4. Tensile strength and elongation at break as a function of DMPA.

fraction in PU (see Table 2) and more urethane linkages. The urethane linkages are capable of hydrogen bonding with the oxygen of the polyether soft segment, and they augment interchain interactions, leading to improved phase mixing.

Figure 6 shows the effect of BD on emulsion size and distribution. As noted in the figure, particle size increases linearly with BD. As mentioned earlier, the size of the PU emulsion is primarily governed by the hydrophilicity of PU, and it is believed that the BDs do not contribute to the hydrophilicity, as does DMPA. Therefore, it might be reasonable to consider the effect in terms of PU structure, i.e., the increased chain rigidity and interchain interactions with BD. It is generally accepted that the ionic centers are predominantly located on the surface of PU particles in water. With the increase of chain rigidity of PU prepolymer, a conformational change from a homogeneous solution in an organic solvent (NMP) to a micelle structure in water may be less plausible. In addition, rigid particles are less deformable in a shear field, and this should give larger particles at the stage of emulsification under shear. Also, the increased interchain interactions between prepolymers should provide the PU with a more cohesive structure and a higher viscosity. Fine breakup should be difficult with a higher viscosity of the dispersed phase. In fact, rod climbing was observed with high BD content at the early stage of emulsification. (See Fig. 7.)

Alternatively, the increase of particle size with more BD incorporation could be due to the increased prepolymer solution viscosity (before emulsification). During the experiment it was observed that the solution viscosity significantly increased with rod climbing at higher BD content. The increased solution viscosity would augment the dispersion size because of the difficulty of breakup. An essentially

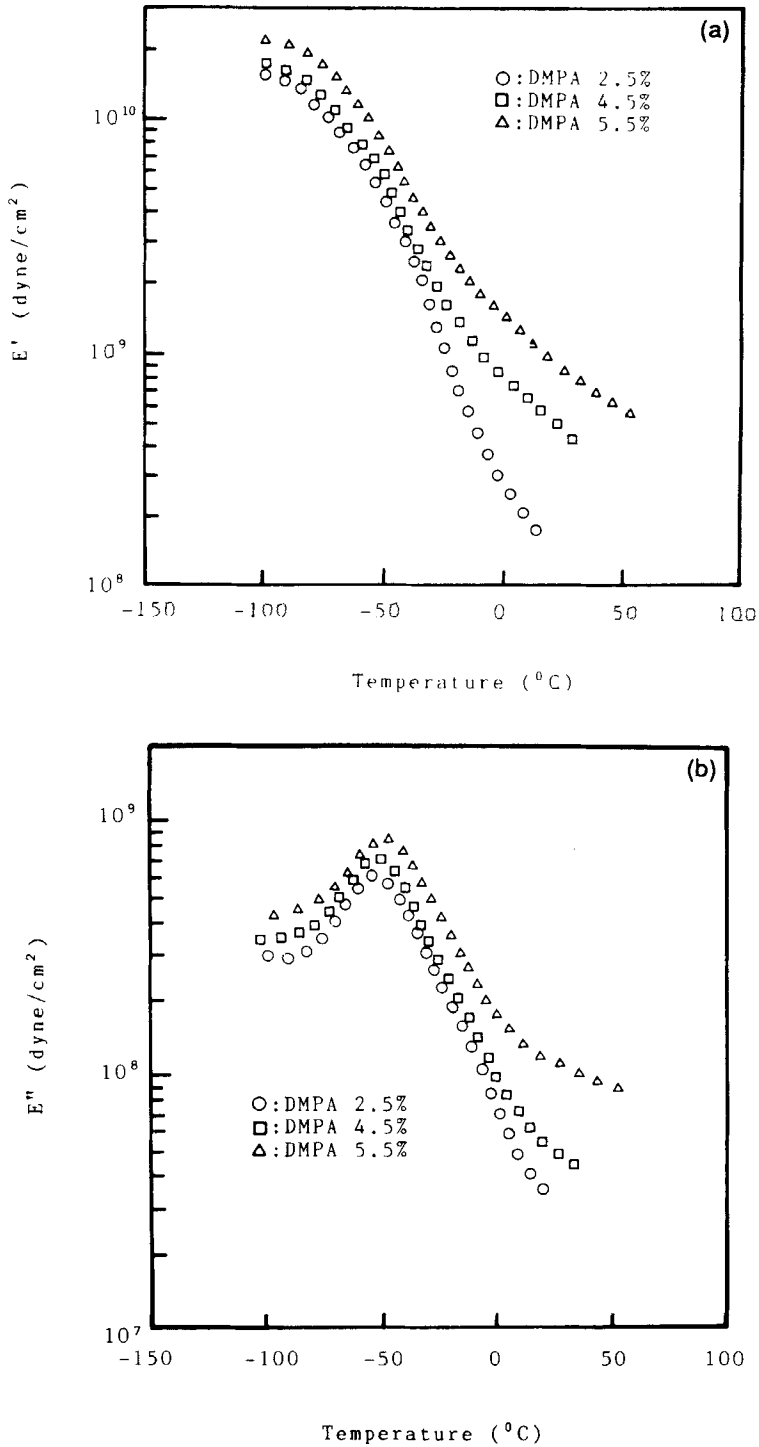


FIG. 5. Effect of DMPA on storage moduli (a) and loss moduli (b) of the PTMG- H_{12} MDI system.

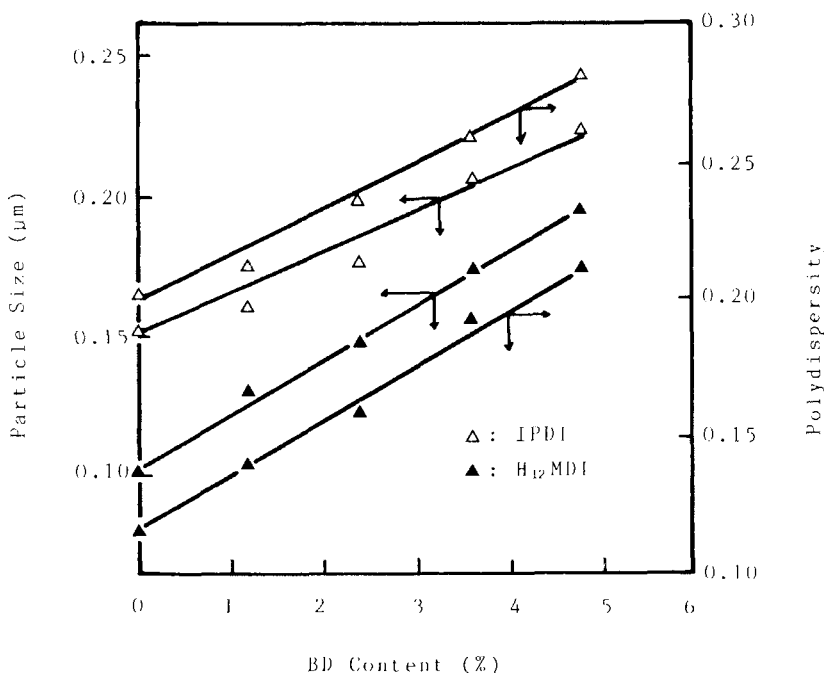


FIG. 6. Average particle size and its distribution as a function of BD.

identical argument may be applied for DMPA. However, the increase of hydrophilicity with DMPA should have a dominant effect on controlling the particle size.

With an increase of BD, the modulus (Fig. 8) and strength (Fig. 9) of the PU film increase, and the elongation at break (Fig. 9) decreases. The results are similar to those of DMPA. BD provides PU with augmented hard fractions and urethane linkages, whereas DMPA gives hydrophilicity and Coulombic force in addition to the above effects. However, the increase of modulus and strength with BD is apparently more prominent than with DMPA. This is probably due to the synergistic effect of DMPA (3.5 wt%) and BD.

Regardless of the type of isocyanate, the elastic modulus (E' , Fig. 10a) increases, and the major transition temperature (Fig. 10b) moves toward the higher temperature with BD, a direct indication of increased chain rigidity due primarily to the increased hard fraction. In addition, with an increase of BD accompanied by an increase of hard domains, hard-soft phase mixing should be more plausible. With intimate phase mixing, the T_g of the soft domain should increase.

Effect of Isocyanate Type

Both IPDI and H₁₂MDI have been described for use in PU dispersion [7, 8]. This is primarily due to their nonyellowing upon exposure to UV. In addition, the stability of cycloaliphatic-type diisocyanate toward water during processing is also of significance for its use in PU dispersion. Particle size and its distribution are smaller and narrower with H₁₂MDI than with IPDI (Figs. 1 and 6). Tensile modulus

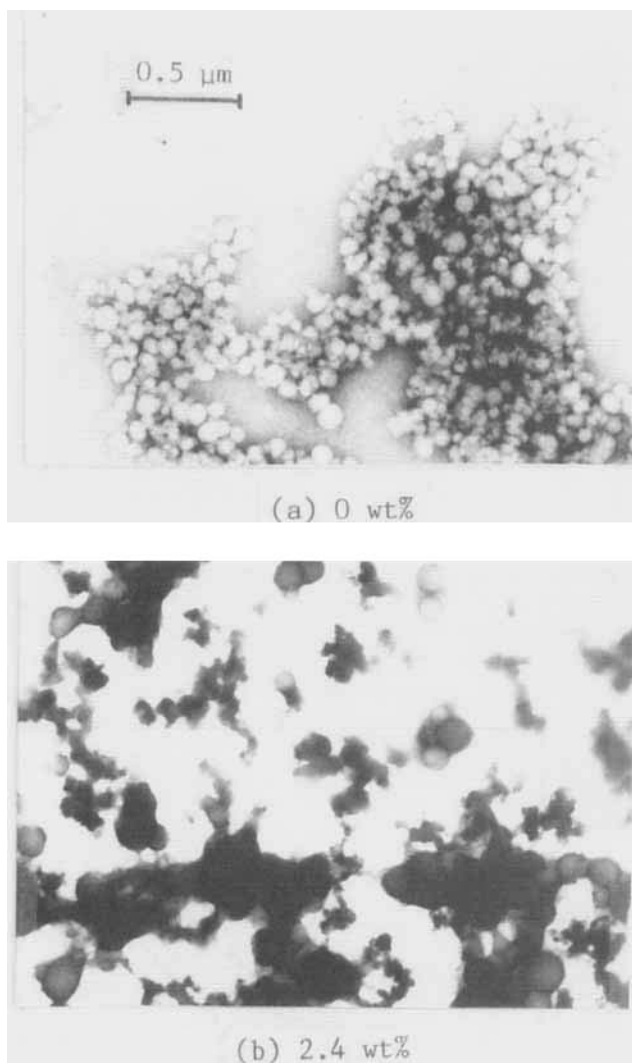


FIG. 7. TEM micrographs of the emulsion with different BD contents for the IPDI-PTMG system. 30,000 \times .

(Figs. 3 and 8) and strength (Figs. 4 and 9) are higher, and elongation at break (Figs. 4 and 9) is lower with H_{12} MDI than with IPDI when they are compared at the same DMPA content. However, the effect of DMPA gives essentially identical trends in both the PUs containing different types of isocyanates. This suggests that the difference in properties between the two types of PUs essentially comes from structural differences of the isocyanates. Hard domains containing IPDI as well as H_{12} MDI do not crystallize due to the existence of isomers [22, 23]. However, H_{12} MDI is symmetric and IPDI is asymmetric. In addition, two NCO groups of H_{12} MDI are directly attached to the cyclohexane ring, and this gives a very cohesive

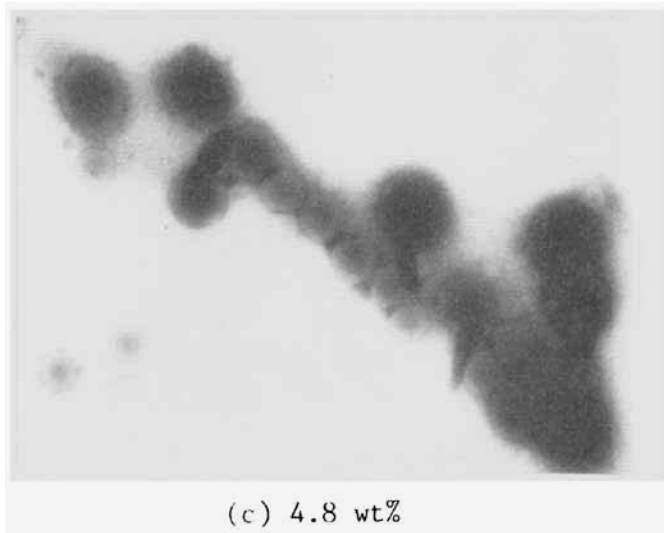


FIG. 7 (continued).

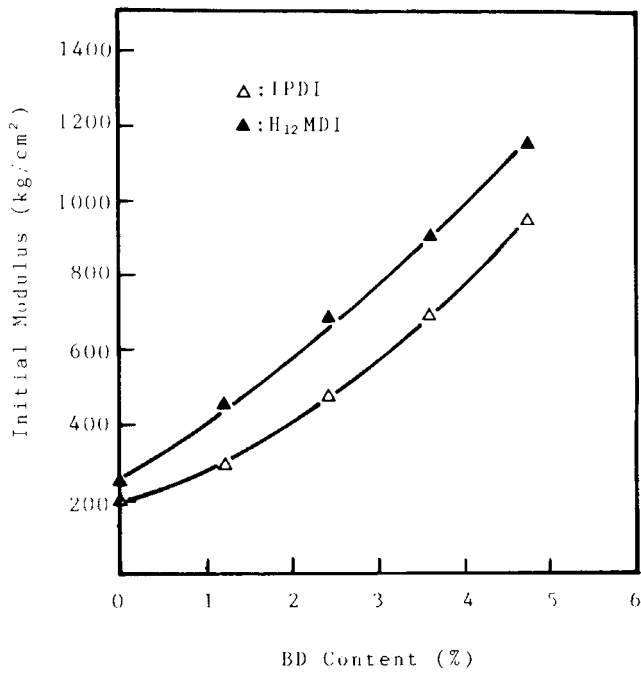


FIG. 8. Initial modulus as a function of BD.

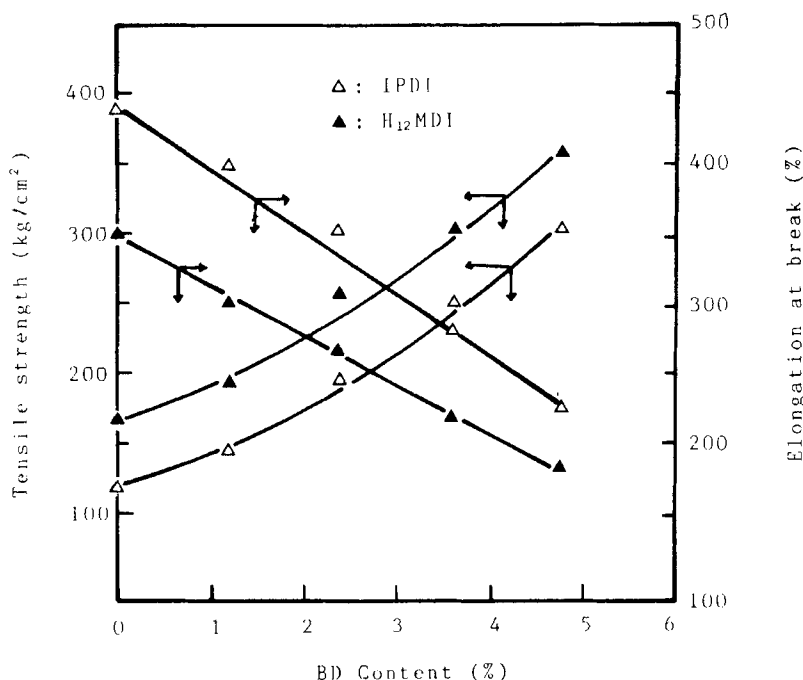


FIG. 9. Tensile strength and elongation at break as a function of BD.

structure of hard segments. On the contrary, only one of the NCO groups of IPDI is directly attached to the ring, and the other is connected via a methylene linkage. The asymmetry and less cohesive structure of IPDI should provide PUs with more flexibility and less rigidity, as our results indicate.

The solubility parameters of water, IPDI, and H₁₂MDI, as calculated from group contribution theory [24], were 24.41, 17.75, and 13.27, respectively. The slightly closer value of PU based on H₁₂MDI with water over IPDI with water may imply better mixing.

CONCLUSIONS

With regard to PU ionomers from cycloaliphatic diisocyanates and PTMG with DMPA as the ionic center, the following conclusions were reached.

The average particle size decreased with DMPA and increased with BD at approximately the same hard content. Since the viscosity of prepolymer solution increases with extender content regardless of its type, the breakup of prepolymer solution during emulsification becomes difficult, leading to larger particle size, as in BD. The reduction of particle size with DMPA should therefore come from the increased hydrophilicity of PU.

The modulus, strength, and glass transition temperature (T_g) of the soft segment increased with DMPA as well as with BD due primarily to the increased hard fraction of the PU. With an increasing hard fraction, soft-hard phase mixing is favored to augment the soft segment T_g .

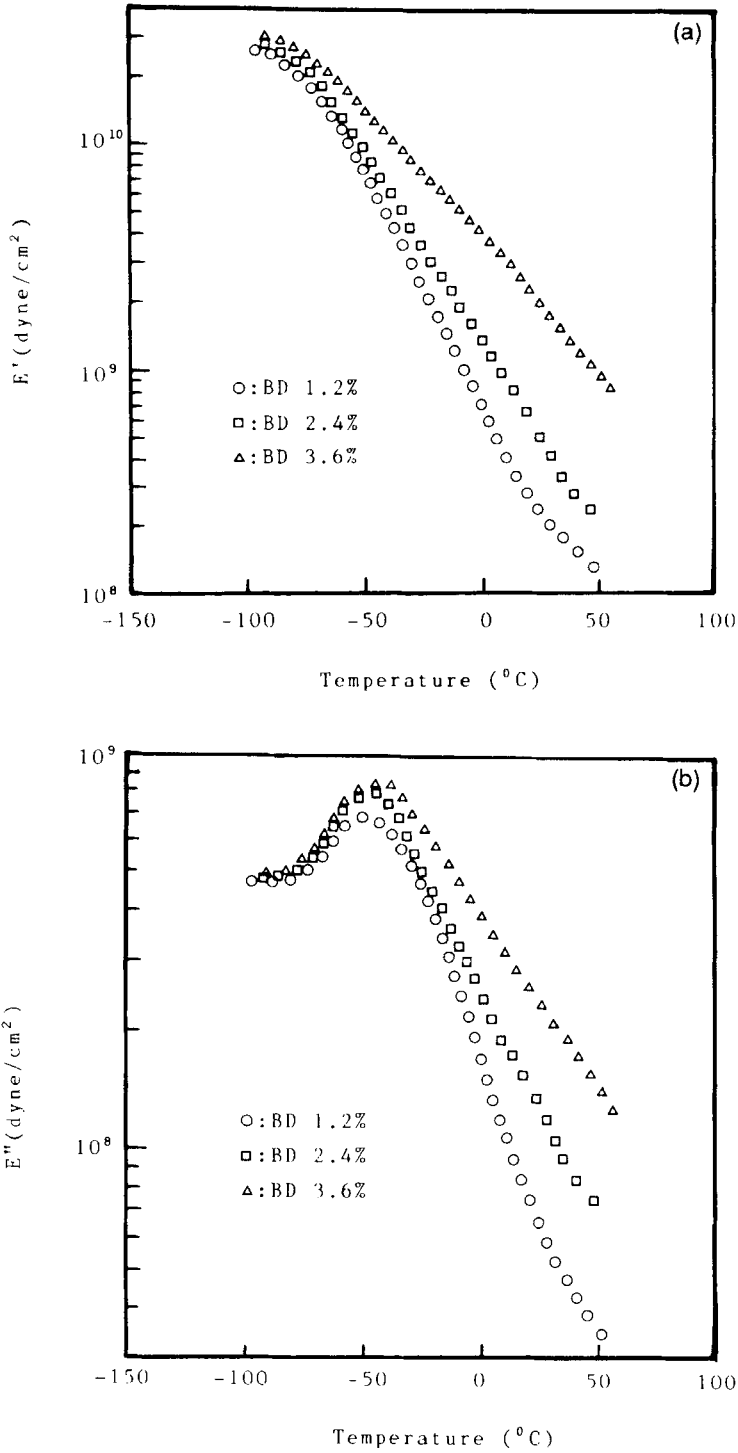


FIG. 10. Effect of Bd on storage moduli (a) and loss moduli (b) of the PTMG- H_{12} MDI system.

With regard to the structural effect of isocyanate H₁₂MDI, which has a solubility parameter closer to water, the more cohesive structure gave finer dispersion and better mechanical properties than IPDI.

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