

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Aqueous Dispersion of Polyurethane Anionomer from Aliphatic Diisocyanates and Poly(Hexamethylene Carbonate) Diol

B. K. Kim^a; C. K. Kim^a; H. M. Jeong^b

^a Department of Polymer and Science Engineering, Pusan National University, Pusan, Korea ^b Department of Chemistry, University of Ulsan, Ulsan, Korea

To cite this Article Kim, B. K. , Kim, C. K. and Jeong, H. M.(1995) 'Aqueous Dispersion of Polyurethane Anionomer from Aliphatic Diisocyanates and Poly(Hexamethylene Carbonate) Diol', *Journal of Macromolecular Science, Part A*, 32: 11, 1903 – 1913

To link to this Article: DOI: 10.1080/10601329508009369

URL: <http://dx.doi.org/10.1080/10601329508009369>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

AQUEOUS DISPERSION OF POLYURETHANE ANIONOMER FROM ALIPHATIC DIISOCYANATES AND POLY(HEXAMETHYLENE CARBONATE) DIOL

B. K. KIM* and C. K. KIM

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

H. M. JEONG

Department of Chemistry
University of Ulsan
Ulsan 680-749, Korea

ABSTRACT

Water dispersible polyurethanes (PUs) were prepared from poly-(hexamethylene carbonate) (PHC) diol, isophorone diisocyanates (IPDI), hexamethylene diisocyanate (HDI), and dimethylolpropionic acid (DMPA) as latent anionic sites. After neutralization of the carboxyl group from the DMPA unit with triethylamine (TEA), the PU anionomers were dispersed by adding water, following by crosslinking using triethylenetetramine (TETA). The particle size of the dispersion decreased with the content of DMPA and increased with HDI in the HDI-IPDI system, and it exhibited a minimum when the number-average molecular weight (M_n) of the prepolymer was 3000 and 4500, respectively. PUs with a higher content of hard segments from DMPA or TETA, or with a higher content of IPDI rather than HDI, had higher tensile moduli and storage moduli at room temperature. Ultimate tensile properties increased with an increase of the prepolymer molecular weight and the DMPA and HDI content.

INTRODUCTION

Polyurethanes (PUs) are unique polymeric materials which exhibit a wide range of physical and chemical properties. Extensive investigations have been devoted to the structure-property relationship of PUs, not only from the academic point of view but also for valuable commercial applications [1-3].

Important applications of PUs are coatings and adhesives, where waterborne types have recently been in demand to replace solventborne types due to environmental regulations. Research in PU dispersions were pioneered by industrial laboratories, and basic structure-property data are rare in the open literature.

Water-dispersible PUs can be prepared by various methods which commonly incorporate ionic and/or nonionic hydrophilic segments in their structures [4-6]. The basic structure-property relationship of PU anionomer dispersions prepared by the acetone process and the prepolymer mixing process was discussed in our previous reports [7-10].

In this research, PU anionomers were synthesized through chain extension of NCO-terminated prepolymers by triethylenetetramine (TETA) in water. The prepolymers were obtained by the reaction of poly(hexamethylene carbonate) (PHC) diol, isophorone diisocyanate (IPDI), or hexamethylene diisocyanate (HDI), with dimethylolpropionic acid (DMPA) as a latent anionic site. Upon neutralization of the carboxyl group from DMPA with triethylamine (TEA) [8-10], a PU anionomer was obtained. The particle size of the emulsion and the mechanical properties of the emulsion-cast film, together with the effect of a mixed isocyanate, were discussed in terms of chemical structure, including the effect of mixed isocyanates. Polycarbonate diols lead to dyeable PUs [11, 12], although these materials, especially ionomer dispersions, have not been extensively studied.

EXPERIMENTAL

Materials

PHCs with number-average molecular weights (M_n) of 1000 and 2000 (hereafter called PHC 1000 and PHC 2000, respectively) were dried at 80°C with 0.1 mmHg for 3 hours. TEA (Junsei) was used after treatment with a 3 Å molecular sieve overnight. First grades of the other reagents, i.e., IPDI (Huls), HDI (Wako), DMPA (Aldrich), *N*-methyl-2-pyrrolidinone (NMP, Fluka), dibutyltin dilaurate (T-12, Junsei), and TETA (Junsei), were used without further purification.

Preparation Procedure

Formulations are given in Table 1. A 500-mL round-bottom, 4-necked separable glass reactor with a mechanical stirrer, thermometer, and a condenser with drying tube was used. Reactions were carried out in N_2 atmosphere in a constant temperature oil bath. PHC, DMPA, NMP, and T-12 were charged into the dried reactor, and the mixture was heated to 90°C with agitation. After adding IPDI and HDI to the homogenized mixtures, reactions proceeded for about 3 hours at 90°C to obtain NCO-terminated prepolymer, followed by cooling to 60°C. TEA dissolved in NMP was then added and stirred for 10 minutes to neutralize the carboxyl groups

TABLE 1. Formulations for PU Synthesis

Run number	M_n of prepolymer ^a	PHC		DMPA		IPDI, g	HDI, g	TEA, mL	TETA, g
		M_n	g	wt% ^b	g				
P-1	1500	1000	23.0	3.5	1.300	12.730	—	0.980	1.806
P-2	3000	1000	26.0	3.5	1.332	10.784	—	1.006	0.928
P-3	4500	1000	26.9	3.5	1.342	10.092	—	1.013	0.624
P-4	6000	1000	27.4	3.5	1.349	9.750	—	1.018	0.469
P-5	1500	2000	25.4	3.5	1.302	10.488	—	0.983	1.815
P-6	3000	2000	28.6	3.5	1.336	8.222	—	1.009	0.934
P-7	4500	2000	29.6	3.5	1.343	7.393	—	1.014	0.620
P-8	6000	2000	30.2	3.5	1.350	7.016	—	1.020	0.470
P-9	4500	2000	29.8	3.5	1.342	6.690	0.563	1.014	0.628
P-10	4500	2000	30.1	3.5	1.344	5.218	1.692	1.014	0.621
P-11	4500	2000	30.4	3.5	1.342	3.751	2.838	1.013	0.627
P-12	4500	2000	28.5	4.5	1.714	7.880	—	1.294	0.619
P-13	4500	2000	27.4	5.5	2.082	8.355	—	1.571	0.614

$${}^a M_n = X_n \times \frac{(n_{\text{PHC}} \times M_{\text{PHC}}) + (n_{\text{DMPA}} \times M_{\text{DMPA}}) + (n_1 \times M_{\text{isocyanate}})}{n_{\text{PHC}} + n_{\text{DMPA}} + n_1}$$

where $X_n = (1 + r)/(1 - r)$ and $r = (n_{\text{PHC}} + n_{\text{DMPA}})/n_1$.

$${}^b \text{wt}\% = \frac{n_{\text{DMPA}} \times M_{\text{DMPA}}}{(n_{\text{PHC}} \times M_{\text{PHC}}) + (n_{\text{DMPA}} \times M_{\text{DMPA}}) + (n_1 \times M_{\text{isocyanate}})} \times 100$$

NMP = 11.5 g, H₂O = 63 g, T-12 = 200 ppm.

of DMPA. NMP was charged in several steps to reduce the increase in viscosity with the progress of the urethane-forming reaction.

Emulsification was accomplished by adding demineralized water to the solution at 60°C. The rate of water addition was carefully controlled by using a tubing pump. TETA dissolved in NMP, and then water, were then fed to the emulsion for a period of 10 minutes, and chain extension was done for the next 2 hours at 60°C. The resulting product, a PU anionomer dispersion with a solid content of about 35 wt%, was stable for over 6 months at room temperature.

In Table 1 the M_n of prepolymer was controlled by the stoichiometric imbalance of the reactants, i.e., an excess amount of diisocyanate over diol was used. The mole ratio of prepolymer to TETA was kept at 2.0 in order to form crosslinking by TETA.

Characterizations

Average particle size and particle size distribution of the dispersion were determined by an Autosizer (Malvern IIC) instrument. Tensile and viscoelastic properties of the emulsion-cast films were determined by Instron and Rheovibron (Tokyo Baldwin DDV-II) instruments. Films were prepared by casting the emulsion on a glass plate, followed by drying at 40°C for 24 hours. The remaining moisture was dried off at 30°C and 20 mmHg for the next 24 hours. Rheovibron tests were

performed from -150 to 80°C at 11 Hz. Tensile tests were made at room temperature by following ASTM D-412 with a type C specimen.

RESULTS AND DISCUSSION

Effect of Prepolymer Molecular Weight

Table 2 (same run number as Table 1) suggests that particle size could be minimum at an intermediate M_n of prepolymer, viz., 3000 and 4500, rather than a monotonic variation. This is probably due to the two opposite effects of prepolymer molecular weight on particle size, i.e., the increased hydrophilicity of the hard segment and increased viscosity of the prepolymer solution with increasing prepolymer molecular weight. With increasing M_n of prepolymer, the content of hydrophilic DMPA in the hard segment (DMPA + IPDI) increases (see Table 1) to give a smaller particle size. Water enters more easily into the hard segment domains of high ionic content [4, 13]. On the other hand, during the dispersion process the higher viscosity of prepolymer solution of higher M_n of prepolymer should make the breakup of the organic phase more difficult [14], leading to increased particle size. These two opposite effects would lead to minimum particle size at an intermediate M_n of prepolymer. We observed that the emulsification proceeded faster with smaller particles (P-1 to P-4 and P-5 to P-8), i.e., a smaller amount of water was added before phase inversion was observed by turbidity [4, 13].

The DMPA unit more probably lies at the mid position of the prepolymer chain when the M_n of PHC is 1000 rather than 2000. This seems to be a reason why PU dispersions from PHC 1000 (P-1 to P-4) have better dispersions than those from PHC 2000 (P-5 to P-8) in Table 1. Lower molecular weight PHC is expected to have enhanced mixing with the hard segment of the DMPA-IPDI unit, and this also seems a cause of better dispersion.

Figure 1(b) shows that the glass-rubber transition occurs at higher temperature as the M_n of the prepolymer decreases, i.e., as the TETA-IPDI unit content increases. This increase seems to be due to partial phase mixing of the soft segment of the PHC unit and the hard segment of the TETA-IPDI unit [11, 15]. At the glassy state, P-1 has the lowest storage modulus value, but at the rubbery state the order is reversed (Fig. 1). When the soft segment domain, which is the major

TABLE 2. Particle Size of PU Dispersion

Run number	Particle size, μm
P-1	0.14
P-2	0.11
P-3	0.11
P-4	0.15
P-5	0.21
P-6	0.13
P-7	0.13
P-8	0.15

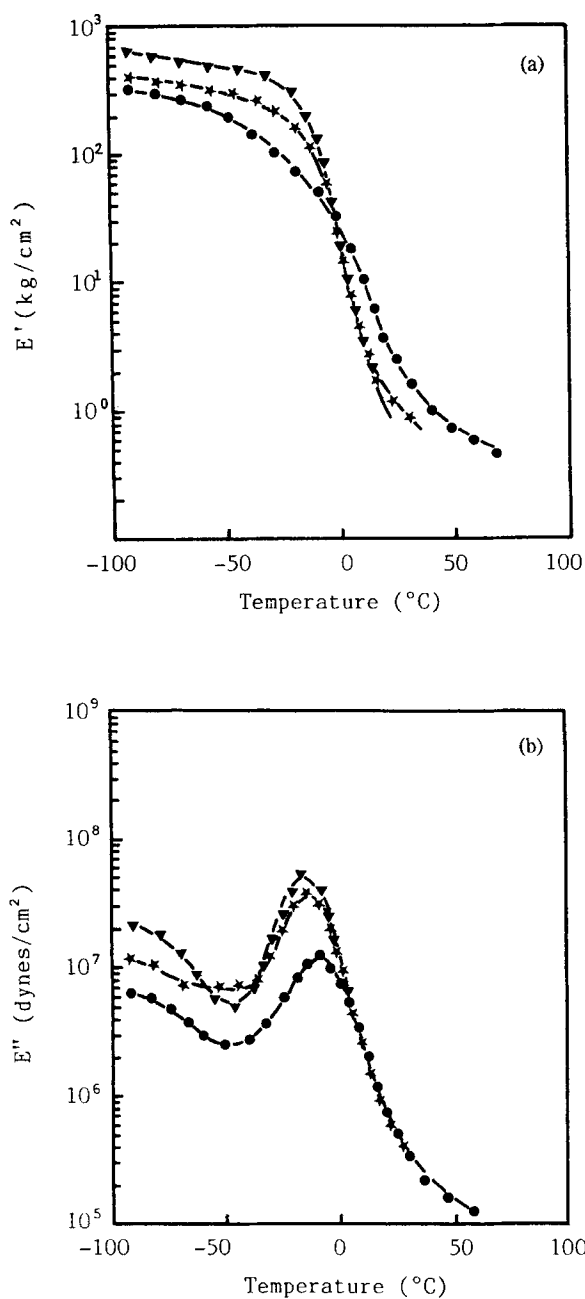


FIG. 1. Effect of prepolymer molecular weight on storage (a) and loss (b) moduli: (●) P-1, (★) P-3, and (▼) P-4.

component and likely to be a continuous matrix, is in the rubbery state, the hard segment is totally responsible for resistance against the external force [16, 17]. Therefore, the higher storage modulus at the rubbery state with a higher content of the TETA-IPDI unit can be explained by its effective role as a filler or crosslinker, but in the glassy state the matrix of the soft segment is rigid enough to resist the external force. So the regular close packing in the soft segment domain becomes important and results in a higher storage modulus value. The decrease in storage modulus with the TETA-IPDI unit content in the glassy state shows that this unit disrupts the ordering of the soft segment.

At low deformation of the rubbery sample, the hard segment acts as an effective filler. Therefore, PUs with higher content of the TETA-IPDI unit, i.e., those from prepolymers of lower M_n and those from PHC 1000 rather than PHC 2000, are expected to have higher modulus values.

Figure 2 shows these trends except at high M_n of the prepolymer, where PUs from PHC 2000 have rather higher modulus values than those from PHC 1000. When the TETA-IPDI unit content is not sufficient for discrete domain formation, soft-hard segment mixing will be more evident in PUs from a soft segment of lower molecular weight [15], yielding a lower modulus. This seems to be the reason for the above reversal at high M_n of the prepolymer.

When PUs are highly deformed, both hard and soft segments orient toward the direction of elongation in order to have the maximum intermolecular interaction [1, 18]. However, when PUs have chemical crosslinks introduced, for example, by TETA in our case, this arrangement will be restricted and the results shown in Fig. 3 may be obtained, i.e., deteriorated tensile properties at high deformation at a higher TETA-IPDI unit content.

Effect of DMPA

As the content of DMPA increases, average particle size decreases and polydispersity increases (P-7, P-12, and P-13 in Table 1). Decreased particle size might be due to the increased hydrophilicity of a PU with more ionic sites. During the experiment it was observed that turbidity due to phase inversion was seen with a smaller amount of water when the ionic content was high [4]. So, higher polydispersity can be ascribed to fast phase inversion in the dispersion process. DMPA provides anionic centers which enhance intermolecular forces as well as increasing the hard fraction; it also increases the tensile properties as shown in Fig. 4 [19, 20].

Effect of Diisocyanate

Figure 5 shows that the glass-rubber transition temperature decreases with increasing HDI content. This comes from enhanced ordering of hard segment domains with HDI incorporation, and consequently enhanced soft-hard segment phase separation [21-23]. HDI gives hard domains much stronger cohesion compared to IPDI due to its symmetric structure, and the increased segment cohesion augments soft-hard phase separation.

As aliphatic HDI replaces alicyclic IPDI, the stiffness of the polymer chain itself is decreased, but the conformation for stronger intermolecular interaction can be more easily obtained. The decrease of the rubbery plateau modulus with increas-

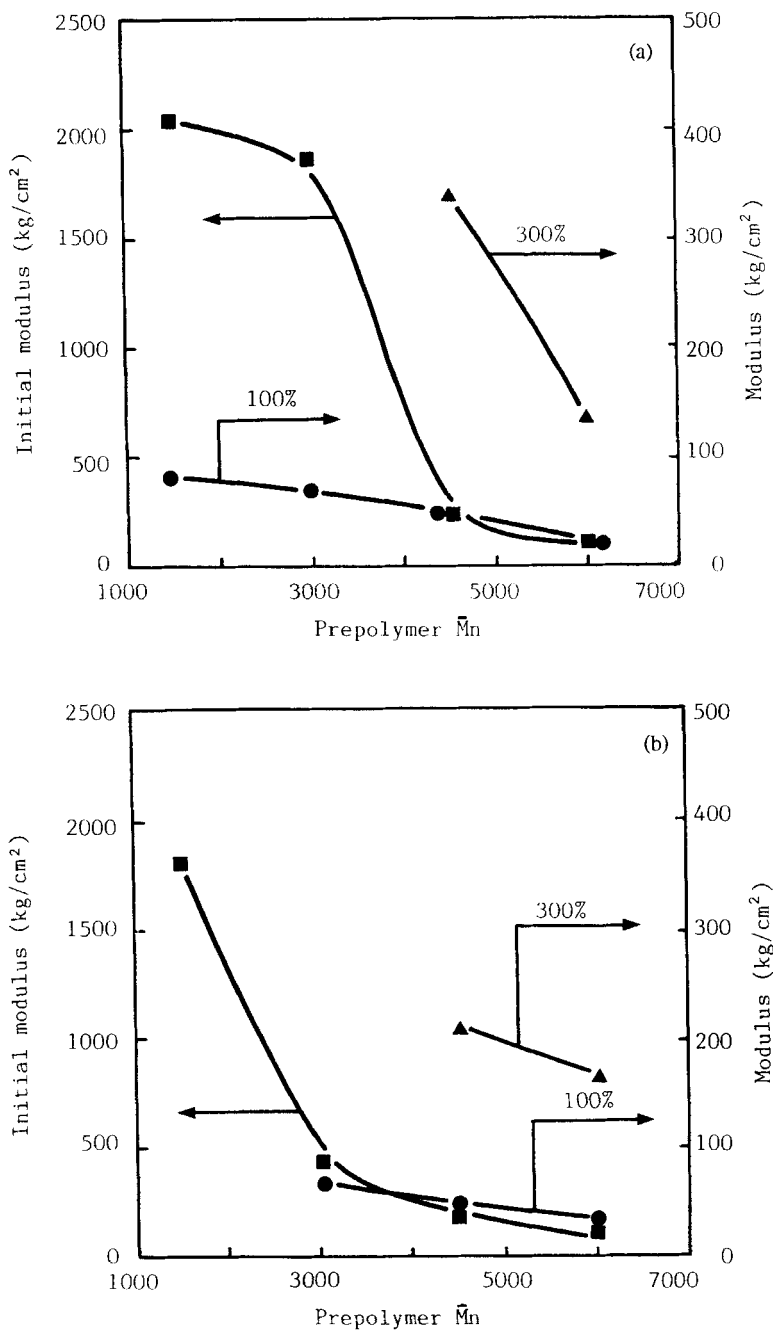


FIG. 2. Effect of prepolymer molecular weight on initial, 100%, and 300% modulus of PUs from PHC 1000 (a) and PHC 2000 (b).

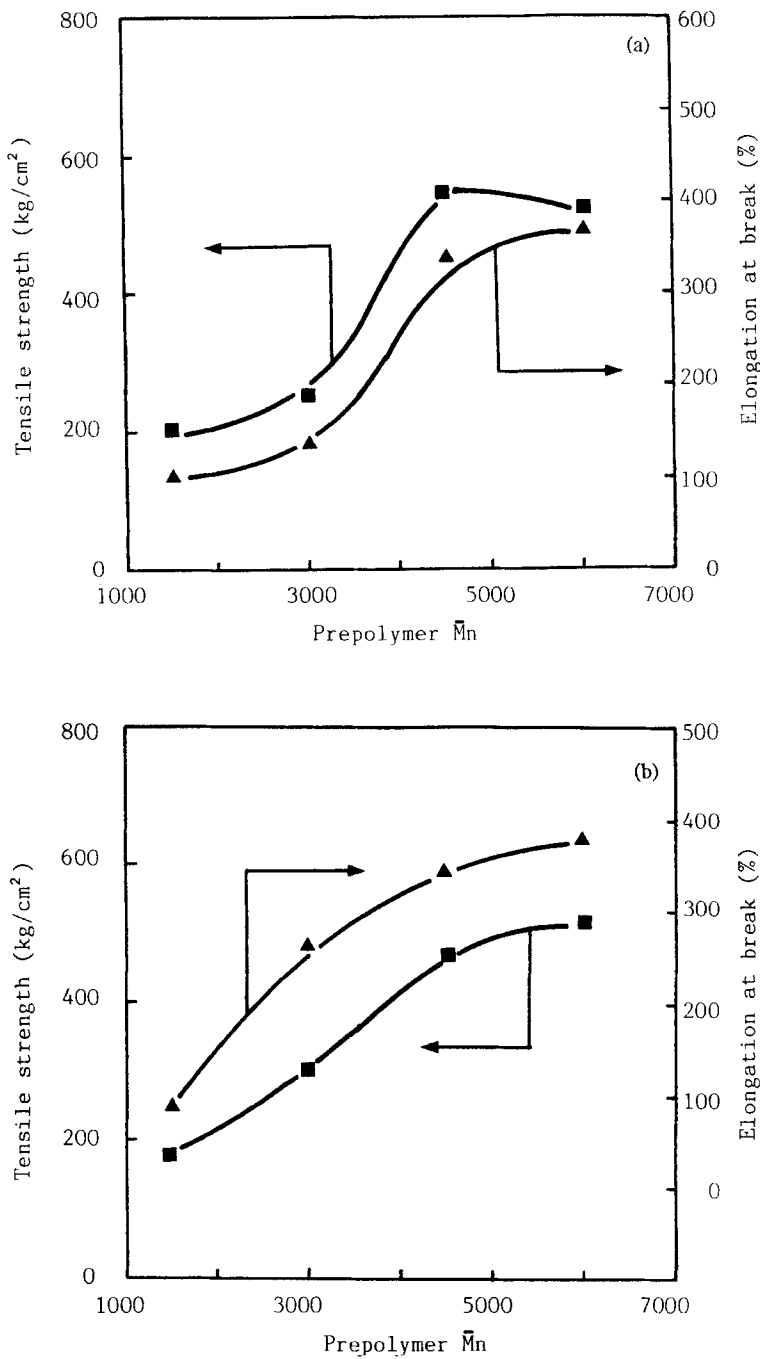


FIG. 3. Effect of prepolymer molecular weight on tensile strength and elongation at break of PUs from PHC 1000 (a) and PHC 2000 (b).

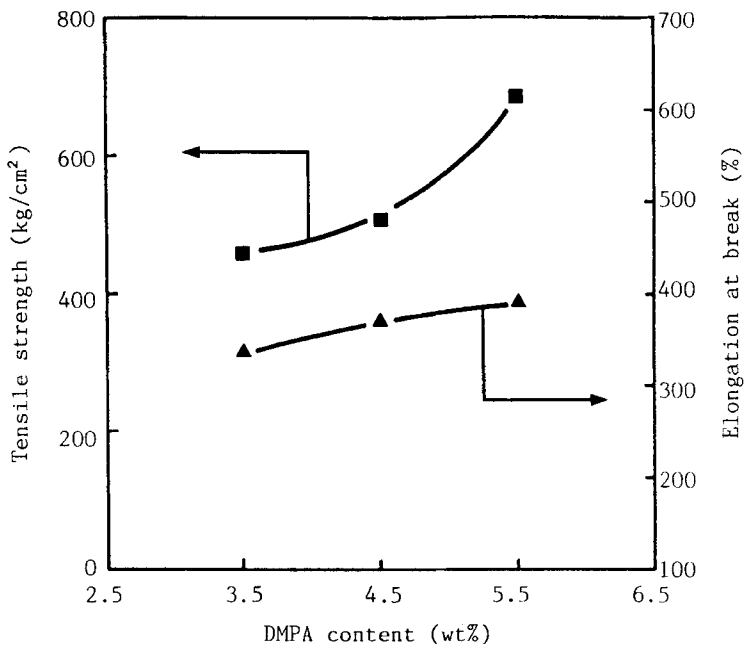


FIG. 4. Effect of DMPA content on tensile strength and elongation at break of PU from PHC 2000 (Mn of prepolymer = 4500).

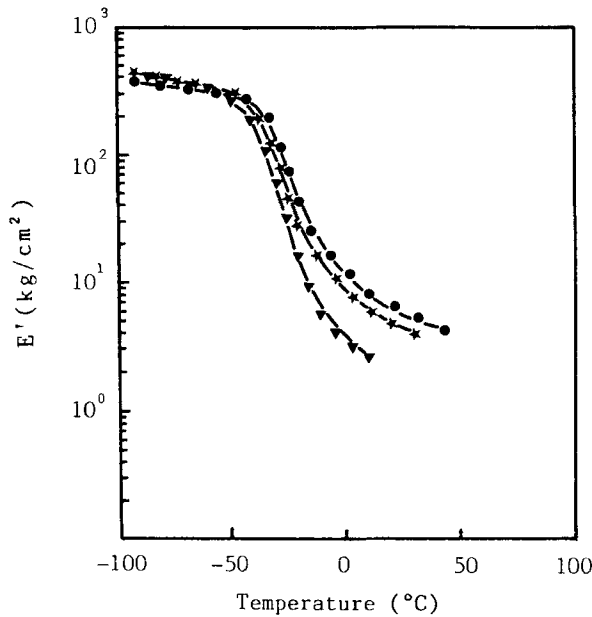


FIG. 5. Effect of diisocyanate structure on storage modulus: (●) P-7, (★) P-10, and (▼) P-11.

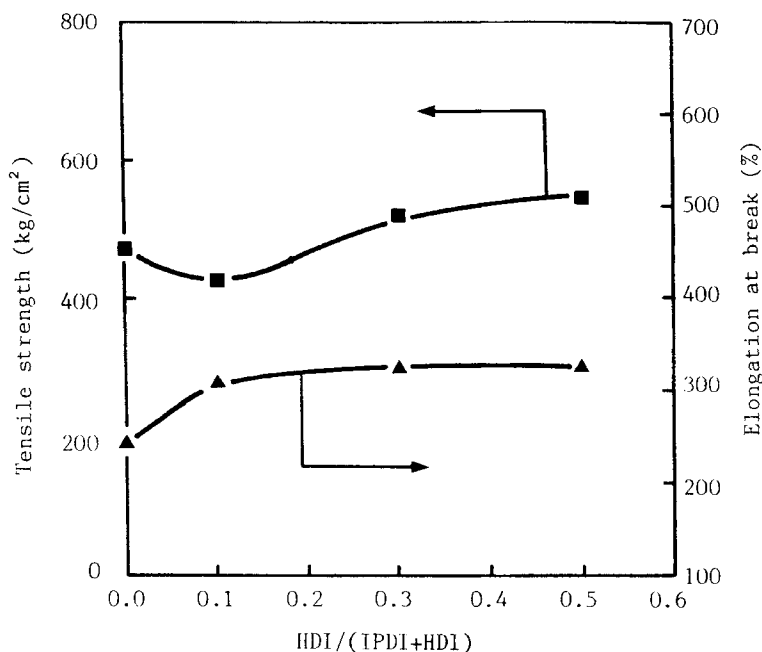


FIG. 6. Effect of diisocyanate structure on tensile strength and elongation at break of PU (P7, P9–P11).

ing HDI (Fig. 5) is probably due to the reduced stiffness of the hard segment. Tensile strength (Fig. 6) shows that reduced stiffness and regular structure predominate at lower and higher contents of HDI, respectively.

CONCLUSIONS

The particle size of a PU dispersion was minimum at an intermediate M_n of a prepolymer. This is probably due to the opposite effects of prepolymer molecular weight on particle size, i.e., increased hydrophilicity of prepolymer and increased viscosity of prepolymer solution. In addition, the particle size increased as HDI replaced IPDI, probably due to enhanced phase separation of the soft–hard segment.

Higher room temperature tensile and storage moduli were observed for PUs with higher stiffness, i.e., those with a higher content of hard segments from DMPA or TETA, or with a higher content of IPDI than of HDI.

Ultimate tensile properties were improved with decreasing M_n of the prepolymer, i.e., with high contents of DMPA and HDI. This is seemingly due to increased intermolecular forces caused by increased ionic sites and/or in addition to the increased hard content of PU.

REFERENCES

- [1] S. Gogolewski, *Colloid Polym. Sci.*, **267**, 757 (1989).
- [2] J. Foks and H. Janik, *Polym. Eng. Sci.*, **29**, 113 (1989).
- [3] T. M. Chapman and R. Benrashid, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 3685 (1990).
- [4] S.-A. Chen and W.-C. Chan, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 1515 (1990).
- [5] B. Chattopadyay, K. Balasubramanian, D. Ramaswamy, and K. S. V. Srinivasan, *Polym. Commun.*, **31**, 15 (1990).
- [6] H. A. Al-Salah, K. C. Frisch, H. X. Xiao, and J. A. McLean Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2127 (1987).
- [7] C. K. Kim, B. K. Kim, and H. M. Jeong, *Colloid Polym. Sci.*, **269**, 895 (1991).
- [8] T. K. Kim and B. K. Kim, *Ibid.*, **269**, 889 (1991).
- [9] B. K. Kim and T. K. Kim, *J. Appl. Polym. Sci.*, **43**, 393 (1991).
- [10] B. K. Kim and Y. M. Lee, *J. Macromol. Sci. – Pure Appl. Chem.*, **A29**(12), 1207 (1992).
- [11] R. F. Harris, M. D. Joseph, C. Davidson, C. D. Deporter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 487 (1990).
- [12] R. F. Harris, M. D. Joseph, C. Davidson, C. D. Deporter, and V. A. Dais, *Ibid.*, **41**, 509 (1990).
- [13] D. Dieterich, *Prog. Org. Coatings*, **9**, 281 (1981).
- [14] US Patent 4,408,008 (1983).
- [15] C. S. Paik Sung, C. B. Hu, and C. S. Wu, *Macromolecules*, **13**, 111 (1980).
- [16] S. Abouzahr and G. L. Wilkes, *J. Appl. Polym. Sci.*, **29**, 2695 (1984).
- [17] L. M. Leung and J. T. Koberstein, *Macromolecules*, **19**, 706 (1986).
- [18] M. Shibayama, T. Kawauchi, T. Kotani, S. Nomura, and T. Matsuda, *Polym. J.*, **18**, 719 (1986).
- [19] S.-A. Chen and W.-C. Chan, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 1499 (1990).
- [20] S. L. Hsu, H. X. Xiao, H. H. Szmant, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
- [21] N. S. Schneider, C. S. Paik Sung, R. W. Matton, and J. L. Illinger, *Macromolecules*, **8**, 62 (1975).
- [22] J. W. C. Van Bogart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 65 (1983).
- [23] M. N. Pandya, D. D. Deshpande, and D. G. Hundiwale, *J. Appl. Polym. Sci.*, **32**, 4959 (1986).

Received August 18, 1994

Revision received January 20, 1995