

Aqueous Dispersion of Polyurethanes Containing Ionic and Nonionic Hydrophilic Segments

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SYNOPSIS

Aqueous polyurethane (PU) dispersions were prepared from isophorone diisocyanate (IPDI), polytetramethylene glycol (PTMG), polypropylene glycol (PPG), polyethylene glycol (PEG), and dimethylol propionic acid (DMPA) as anionic center. The effects of the PEG/PTAd mixing ratio, type of polyether polyols, and hard segment content on the state of dispersion, surface, dynamic, and tensile properties of emulsion-cast film were determined. With more incorporation of nonionic hydrophilic PEG, particle size of the emulsion and tensile strength of the emulsion-cast film decreased, while the emulsion viscosity and elongation at break increased. Among ether type polyols, PTMG-based PU generally showed superior mechanical properties. With increasing hard segment content, particle size, storage modulus (E'), and tensile strength increased. At the lowest hard segment content (36 wt %) tested in this experiment, soft segments crystallized and water swell decreased. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Aqueous polyurethane (PU) dispersions are steadily expanding their usage in textile coatings, sizing, and adhesives for a number of polymeric materials, glass surface, etc.¹⁻³ The development of these aqueous PU applications has been motivated primarily by environmental considerations to reduce solvent emissions into the atmosphere. In addition, the quality of these PU dispersions, notably excellent adhesion to many polymeric and glass surfaces, and film-forming ability at ambient make them suitable for a myriad of applications.⁴ However, most work with aqueous PU has been done in industrial laboratories, and basic structure/property data are sparse in the open literature.

Aqueous PU dispersions can be formulated into ionic and nonionic type. Ionic and nonionic types of PU dispersion mutually have certain advantages and disadvantages. Namely, nonionic PU dispersions have important advantages over the ionic ones in terms of stability against electrolyte, freezing, and strong shear forces. On the other hand, they have

the disadvantage of being heat sensitive due to the decrease of polyether solubility in water with increasing temperature.⁴ Recently, combinations of ionic and nonionic hydrophilic segments in the same PU have been attempted, and desirable synergistic effects in terms of dispersion stability and fine particle size at an overall reduced hydrophilic group content have been reported.^{2,4,5}

This article describes the preparations of PU ionomer dispersions from polytetramethylene adipate glycol (PTAd), polypropylene glycol (PPG), polyethylene glycol (PEG), polytetramethylene ether glycol (PTMG), and dimethylol propionic acid (DMPA) as anionic centers. Chain extensions of prepolymers were formed by diamines leading to linear PUs. Effects of PEG/PTAd ratio, type of polyether polyols, and hard segment content, on the state of dispersion and physical properties of emulsion-cast film, were examined.

EXPERIMENTAL

Materials

PTAd (Mn = 1000, Songwon), PEG (Mn = 1000, Korea Polyol), PPG (Mn = 1000, Korea Polyol) and

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PTMG ($M_n = 1000$, Hodogaya) were dried and degassed for 5 h at 80°C, 1–2 mmHg before use. DMPA (Aldrich) was dried at 100°C for 2 h in an oven. Extra pure grades of IPDI (Scholven), and dibutyltin dilaurate (DBT) were used as received. Dimethyl formamide (DMF), ethylene diamine (EDA), triethylamine (TEA), and solvents used in titration were dried over a 3 Å molecular sieve before use.

Prepolymer Synthesis

The basic formulations are given in Table I. 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 a reactor. Reaction was carried out in a constant temperature oil bath. Polyols and DBT (0.03% based on the total solid), and DMPA dissolved in DMF (5% based on the total reaction mass) were charged into the dried flask. While stirring, the mixture was heated to 90°C for ca. 30 min, followed by adding IPDI to the homogenized mixture. The mixture was heated to 90°C for ca. 3 h to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined using a standard dibutylamine back titration method.⁶ Upon obtaining the theoretical NCO value, calculated from the $[NCO]/[OH]$ index of feed, the prepolymers were cooled to 60°C, and the neutralizing solution [i.e., TEA dissolved in DMF (5% based on total reaction mass)], was added and stirred for 1 h while maintaining the temperature at 60°C. The 1 : 1 stoichiometry was obtained by adding EDA at the chain extension step, and PU obtained in these experiments is linear.

Emulsification and Chain Extension

Aqueous dispersion of PU was obtained by adding water (35°C) to the mixture (60°C). Since the rate of water addition to the mixture is a critical parameter to obtain stable dispersion, a tubing pump was used to add water at a constant flow rate. The phenomena of phase inversion, viscosity, and conductivity change during the emulsification process are well documented by Dieterich¹ and in our earlier work.^{7,8} Upon completing the phase inversion, EDA dissolved in water was fed to the emulsion for a period of 40 min, and chain extension was carried out for the next 2 h. The resulting product was a stable (over 6 months at room temperature), urea-urethane dispersion with a solids content of about 35%.

Tests

Particle size and its distribution were measured with an Autosizer (Malvern IIC), and the state of dispersion was observed by transmission electron microscopy (TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO_4 for 1 week. Using the emulsion-cast film of PU, surface tension and contact angle with water at room temperature were measured on a Tensiometer (Kruss-K10T) and a contact angle meter (Goniometer, G-1), respectively. The viscosity of emulsions was measured at 20°C using a Brookfield viscometer. The degree of swell in water was measured at room temperature by $\% \text{ swell} = 100 \times (w - w_0)/w_0$, where w_0 and w are the weight of dried film, and that of equilibrium (24 h) swell, respectively. Tensile prop-

Table I Basic Formulations of the Feed (g)

	PEG	PTAd	DMPA	IPDI	TEA (mL)	EDA
Variation of PEG (wt %) Content						
0	0.0	16.4	3.00	10.16	0.94	0.29
5	0.8	15.5	3.00	10.16	0.94	0.29
10	1.6	14.7	3.00	10.16	0.94	0.29
15	2.5	13.9	3.00	10.16	0.94	0.29
20	3.3	13.1	3.00	10.16	0.94	0.29
Variation of Hard Segment Content (wt %)						
36	3.9	15.7	1.50	8.31	0.94	0.29
42	3.6	14.4	2.25	9.23	0.94	0.29
47	3.3	13.1	3.00	10.16	0.94	0.29
53	2.9	11.8	3.75	11.08	0.94	0.29
58	2.6	10.5	4.50	12.01	0.94	0.29

* PEG (%) = PEG weight/(PEG + PTAd) weight \times 100

erties of the emulsion-cast films were measured using an Instron tensile tester at a crosshead speed of 100 mm/min, and an average of at least five measurements was taken to 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 mechanical tests were performed with a Rheovibron (Toyo Baldwin DDV-II) from –100 to 50°C at 11 Hz with the sample, 0.03 × 0.2 × 3 cm in size.

RESULTS AND DISCUSSION

Effect of PEG Content

Effect of PEG content on average particle size and emulsion viscosity is shown in Figure 1 (Table I). It is seen that average particle size decreases asymptotically and the emulsion viscosity increases almost linearly with the PEG content. Decrease in particle size with increasing PEG is shown with TEM (Fig. 2). In a self-emulsified dispersion, particle size is governed mainly by the hydrophilicity of the dispersed phase both in ionic and nonionic type dispersion.^{1,6} Since the concentration of anionic species is fixed in this series of experiments, the decrease of particle size with PEG content is due primarily to the more hydrophilic nature of PEG over PTAd.

Emulsion viscosity increases linearly with PEG content. It is generally accepted that the ionomer dispersion is stabilized by an electrical double layer,

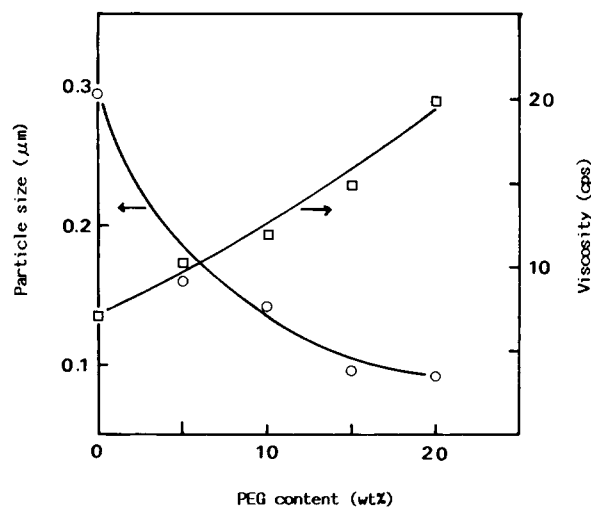


Figure 1 Particle size and emulsion viscosity vs. PEG content.

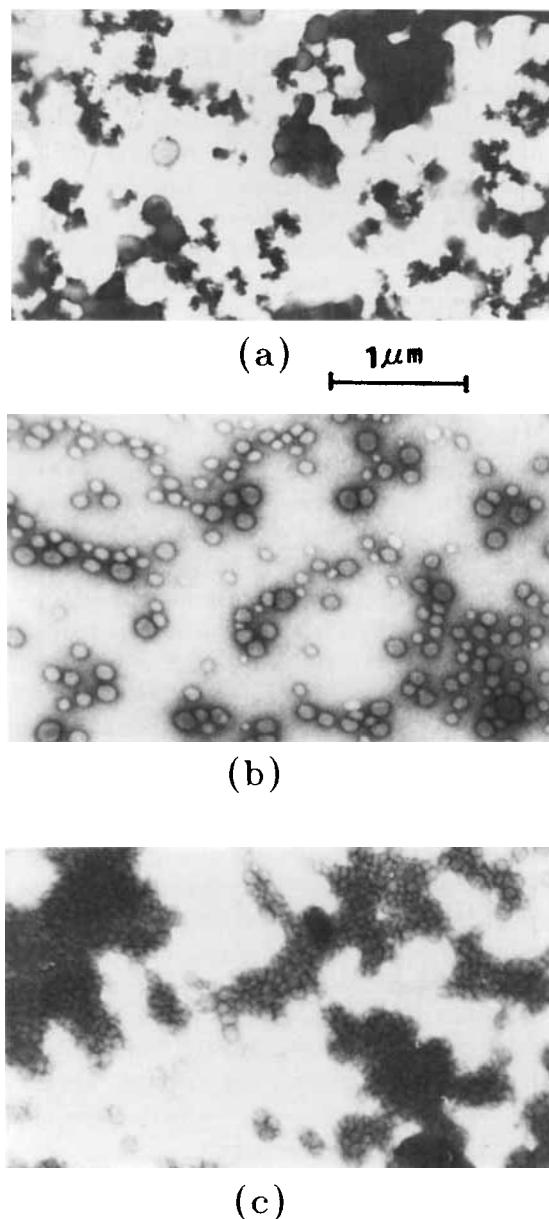


Figure 2 TEM micrographs of the emulsion with different PEG contents: (a) 0%, (b) 10%, and (c) 20%.

and the nonionomer by enthalpy repulsion.^{1,9} Therefore, at fixed ionic content, the effective volume increase due to the formation of an electrical double layer should be practically fixed, and the increase of viscosity with PEG content should come from the augmented hydrophilicity of PU. At low PEG content, the increase of hydrophilicity due to PEG incorporation leads directly to a decrease of particle size. However, at relatively high PEG content, the decrease of particle size due to the increased hydrophilicity is largely offset by the effective vol-

ume increase from the movement of water into the particle. The overall effect would be an asymptotic decrease of particle size as our results indicate. On the other hand, the emulsion viscosity is directly related to the effective volume fraction of the dispersed phase,¹⁰ which increases with water swell.

Figure 3 shows that when the 20% of PTAd is replaced by PEG, the degree of swell in water increased over four times (50 → 220%) (Fig. 3). As expected, the contact angle with water decreased, and surface tension increased from about 41 to 45 mN/m (not shown).

The relaxation behavior of the PU was studied with loss modulus (E'') (Fig. 4). The peak temperature decreases at 10 and 15% and increases at 20% PEG content, as compared to 100% PTAd PU. The present relaxation should correspond to the glass transition temperature (T_g) of the soft segment or soft segment-rich phase. In segmented PU, phase mixing is generally greater in ester-based PU than in ether-based PU and with shorter segment of comparable soft and hard segment lengths. With 100% PTAd of $M_n = 1000$, a relatively high degree of phase mixing is obtained. Addition of 10–15% PEG may disturb the phase mixing, and simply contribute to the decreased T_g of the soft segment-rich phase following basic rule of copolymers.¹¹ Further introduction of PEG to the soft segment seems to augment the soft-hard phase mixing due to the internal repulsions between PTAd and PEG segments, leading to an increase of soft segment-rich phase T_g . The increase of phase miscibility due to the internal repulsion is sometimes reported in blends of copolymer with homopolymers. For example, blends of

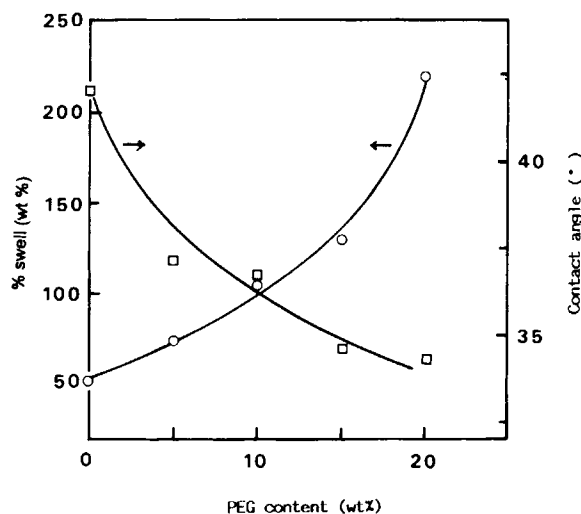


Figure 3 Water swell and contact angle of the emulsion cast film vs. PEG content.

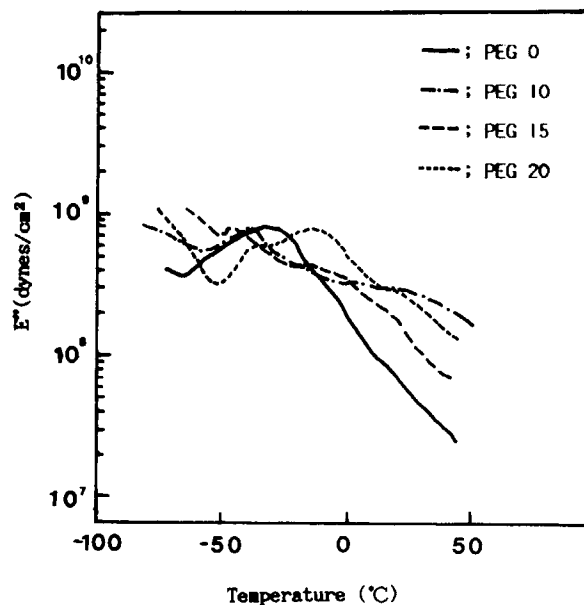


Figure 4 Dynamic mechanical properties of the emulsion cast film vs. PEG content at 11 Hz.

styrene-acrylonitrile copolymer (SAN) with poly(methyl methacrylate) are miscible when the acrylonitrile content of SAN is about 7–27%, and are immiscible beyond this composition range.^{12,13} This phenomenon is properly explained in terms of miscibility driven by the internal (within the SAN) repulsion. With the increase of phase mixing the hard segments in the soft segment would hinder the motion of soft segment and broaden the distribution of their relaxation times.¹⁴

Hardness, tensile modulus (Fig. 5), and strength (Fig. 6) decrease, and elongation at break (Fig. 6)

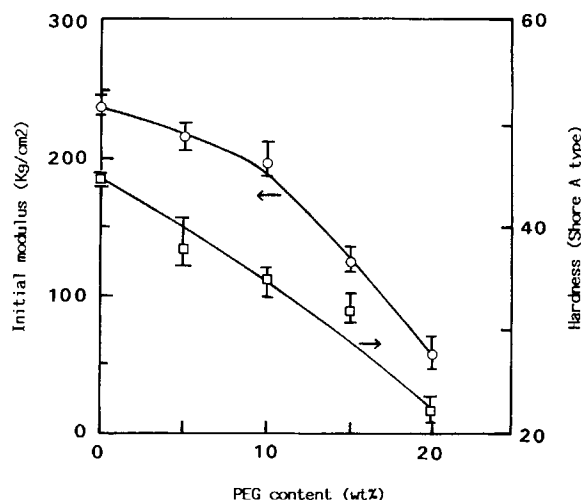


Figure 5 Hardness and tensile modulus of the emulsion cast film vs. PEG content (20°C).

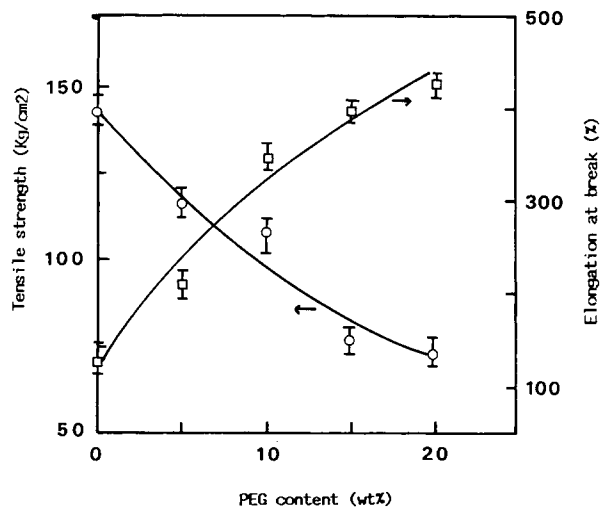


Figure 6 Tensile strength and ultimate elongation of the emulsion cast film vs. PEG content (20°C).

increases with increasing PEG content, as expected. The weaker interchain forces, caused by the incorporation of ether polyol, should be the prime reason for the decreased modulus and strength. However, due to the decrease of soft segment T_g , elongation ductility increased over four times when 20% of the PTAd is replaced by PEG.

Effect of the Type of Ether Polyol

These experiments were formulated at a fixed polyol composition (PTAd/PEG = 4/1 by weight) and at a hard segment content of 48% (corresponds to run 5 of Table I), and the results are given in Table II. Particle size, surface tension, and water swell are highest with PEG and lowest with PTMG, the order being consistent with the hydrophilicity of the polyols. PEG is not used unless in the form of a copolymer due to its water swellability (220%) and

Table II Effect of the Polyol Type on Emulsion Characteristics and Film Properties

Properties	Type of Polyol 20%		
	PEG	PPG	PTMG
Particle size (μm)	0.092	0.198	0.231
Viscosity (cP)	20	7	6
Tensile strength (kg/cm^2)	52	22	68
Elongation at break (%)	430	208	412
Hardness (shore A)	22	35	67
Water swell (wt %)	220	39	32
Surface tension (mN/m)	45.2	39.1	35.6

the water sensitivity of the derived PU.¹⁵ Hardness of PTMG-based PU is two- or threefold that of PEG or PPG, due mainly to the higher T_g of PTMG. Highest tensile properties (strength and elongation) are obtained with PTMG-based PU, whereas the lowest ones were from PPG-based PU. In PPG, the side chain methyl group prevents crystallization and increases interchain separation resulting in inferior mechanical properties.

Effect of Hard Segment Content

This series of experiments was formulated at a fixed polyol composition (PTAd/PEG = 4/1 by weight, Table I). The DMPA content was varied 5–15% (numbers in the table are weights in grams); however, a constant amount of it was neutralized to give the same ionic content of the PU.

Particle size increases and emulsion viscosity decreases with increasing hard content, slowly at low and rapidly at high content. This is essentially due to the increased chain rigidity of the PU (Fig. 7). The increased chain rigidity gives higher prepolymer solution viscosity,⁸ and coarse breakup during the emulsification, leading to a large particle size.¹⁶

DSC thermograms (Fig. 8) show that the soft segment of PU containing 36% hard segment is the only one which crystallizes. With the increase of hard segment, soft-hard phase mixing is enhanced and soft segments do not crystallize.

Water swell (Fig. 9) as a function of hard segment content shows a spike at 42% hard content, and decreases with further increase of hard content, im-

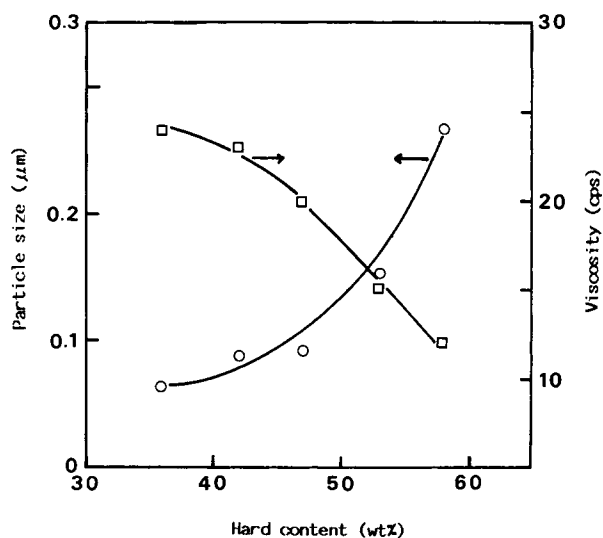


Figure 7 Particle size and viscosity of emulsion (20°C) vs. hard content.

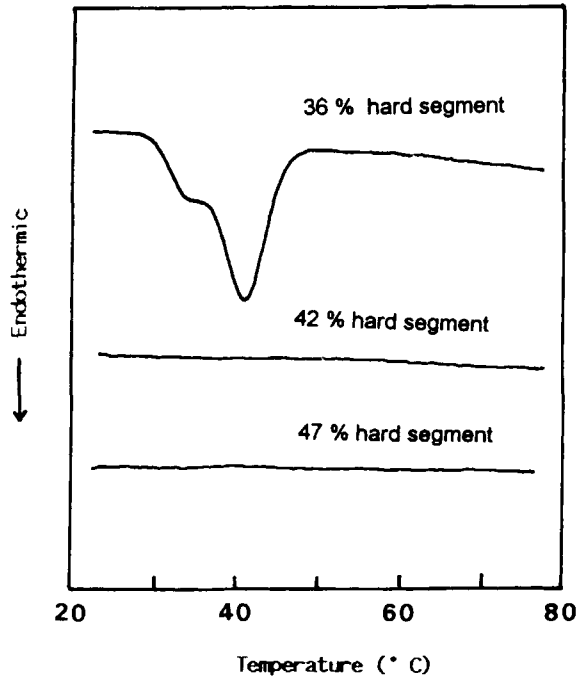


Figure 8 DSC thermograms of the emulsion-cast film vs. hard content.

plying that water preferentially penetrates into the soft segments. When the hard segment content is 36%, soft segments crystallize and hence water swell in the soft segment domains is decreased. Contact angle (Fig. 9) with water increases asymptotically with hard segment content due to the decreased average hydrophilicity of the film.

Elastic modulus (E') increases, and the loss modulus peak (Fig. 10) moves toward higher tempera-

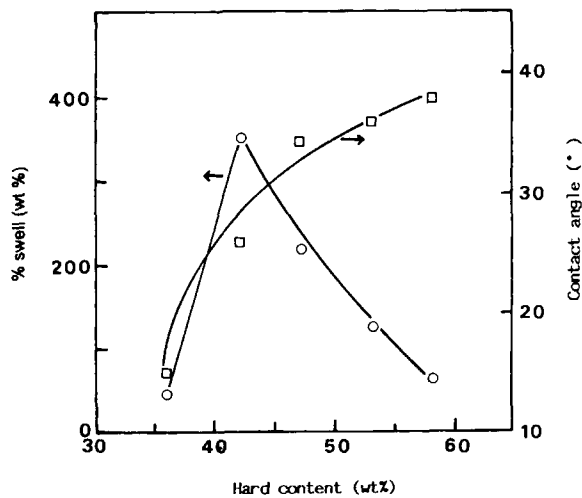


Figure 9 Water swell and contact angle of the emulsion-cast film vs. hard segment content.

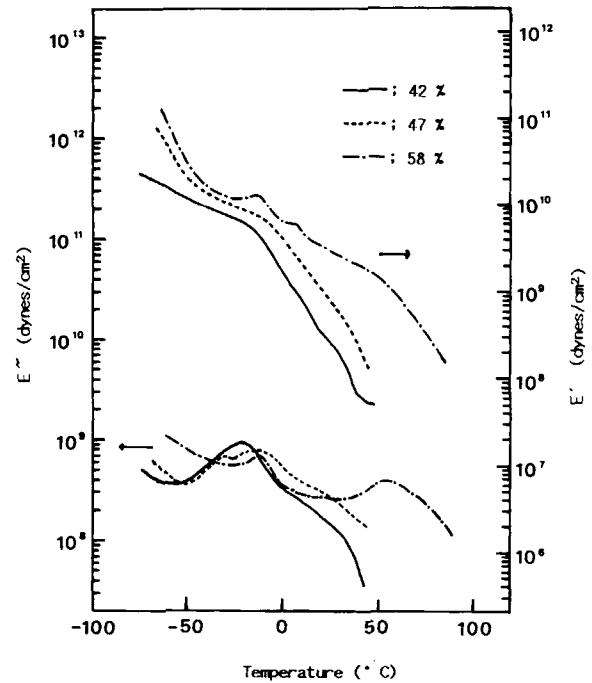


Figure 10 Dynamic mechanical properties of the emulsion-cast film vs. hard segment content at 11 Hz.

tures as the hard segment content increases. The loss peak appearing below 0°C should correspond to the T_g of the soft segment-rich phase, and its increase is caused by the increased hard segment content and phase mixing as well. The T_g of the hard segment-rich phase is not seen for 42 and 47% hard content, but is observed at about 70°C when the hard content is 58%.

Hardness and tensile properties are shown in

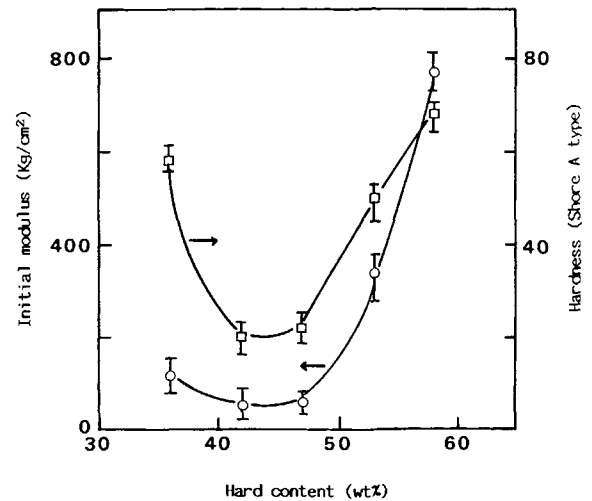


Figure 11 Hardness and initial modulus of the emulsion-cast film vs. hard segment content (20°C).

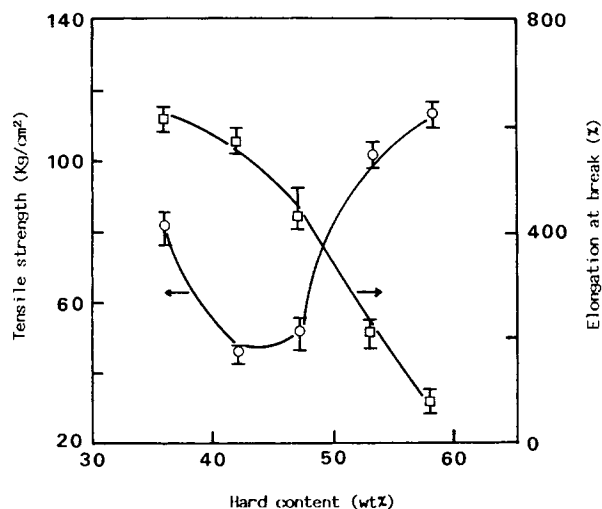


Figure 12 Tensile strength and ultimate elongation of the emulsion-cast film vs. hard segment content (20°C).

Figures 11 and 12. Hardness shows a deep minimum at 42% hard segment content, while a shallow minimum for tensile modulus is obtained. Our DSC thermogram showed that soft segments do not crystallize when the hard content is large ($\geq 42\%$). With noncrystallizable soft segment, modulus and strength (Fig. 12) should be governed mainly by the hard fraction,¹⁷ as our results of high hard segment content ($\geq 42\%$) indicate. At 36% hard segment content, crystallization of soft segments contributes to the enhanced mechanical properties. It seems that, for the particular composition with 42% hard segment content, soft segments do not crystallize, and hard content is insufficient to give strong physical properties. The progressive decrease of elongation with increasing hard segment content would be caused by increased soft-hard phase mixing. With intimate phase mixing, hard segments do not act as effective crosslinks to induce elasticity.

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