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POLYURETHANE ANIONOMER DISPERSION FROM ETHER-TYPE POLYOLS AND ISOPHORONE DIISOCYANATE

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ABSTRACT

Polyurethane (PU) anionomer dispersions were formulated from polytetramethylene ether glycol (PTMG), polypropylene glycol (PPG), dimethylol propionic acid (DMPA), and isophorone diisocyanate following a prepolymer mixing process. Effect of ionic content, mixing ratio of polyols (PPG/PTMG), and polyol molecular weight on the emulsion characteristics and the dynamic mechanical and tensile properties of the emulsion-cast films were studied. Particle size decreased with increasing DMPA, PPG content, and the molecular weight of PTMG. The glass transition temperature of the soft segment was almost independent of the DMPA content and the molecular weight of PTMG, but increased with PPG content in the mixed polyol system, due probably to the increased phase mixing between soft and hard segments.

INTRODUCTION

The usages of aqueous polyurethane (PU) dispersions are steadily expanding in textile coatings, sizing, and adhesives for a number of polymeric materials and glass surfaces [1–3]. The development of these aqueous PU applications has been motived primarily by environmental considerations to reduce solvent emissions into the atmosphere. In addition, the quality of these PU dispersions, notably their excellent adhesion to many polymeric and glass surfaces, and their film-forming ability at ambient temperature, has made them suitable for a myriad of applications [4].

The properties of PU ionomers are primarily due to the phase behavior of soft and hard segments as well as their ionic and counterionic character [5–8]. In general, soft–hard phase separation increases with increasing segment length, which is generally controlled by the molecular weight of the polyol [9–11]. The polyester soft segment was found to contribute to phase mixing by hydrogen bonding formation between the ester carbonyl of the soft segment and the urethane NH groups of the hard segment. This behavior also depends on the content, length, and polarity of the soft and hard segments. The existence of hard segment domains imparts mechanical strength to the PU ionomer and governs properties at high temperature, whereas soft segments control the elasticity of PU and properties at low temperature [6].

Aqueous PU dispersions can be formulated into ionic and nonionic types. Ionic and nonionic types of PU dispersion have certain advantages and disadvantages. Recently, combinations of ionic and nonionic hydrophilic segments in the same PU have been undertaken, and desirable synergistic effects in terms of dispersion stability and fine particle size at an overall reduced hydrophilic group content were reported [2, 4].

Most work with PU dispersions has been done in industrial laboratories, and basic structure/property behavior information is sparse in the literature. We here consider the preparation and structure/property behavior of polyurethane ionomer dispersions and their emulsion-cast films. Dispersions were formulated from polytetramethylene ether glycol (PTMG), polypropylene glycol (PPG), dimethylol propionic acid (DMPA), and isophorone diisocyanate (IPDI) according to the prepolymer process. The effects of ionic content, mixing ratio of polyols (PTMG with the more hydrophilic PPG), and molecular weight of PPG on the emulsion characteristics and the dynamic mechanical and tensile properties of the emulsion-cast films were studied.

EXPERIMENTAL

Materials

PTMG (M_n = 1000, 2000, Hodogaya) and PPG (M_n = 1000, Korea Polyol) were dried and degassed at 80°C and 1–2 mmHg for 5 hours prior to use. DMPA (Aldrich) was dried at 100°C for 2 hours in a drying oven. The extra-pure grade of IPDI (Scholven) and dibutyltin dilaurate (DBT) were used as received. Dimethylformamide (DMF), triethylenetetramine (TETA), triethylamine (TEA), and the solvents used in titration were dried over 3A molecular sieves before use.

Prepolymer Synthesis

The basic formulation is given in Table 1. A 500-mL round-bottom, four-necked 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, PPG, DBT (0.03 wt% based on the total solids), and DMPA dissolved in DMF (5 wt% based on the total reaction mass) were charged

TABLE 1. Basic Formulation of the PU Ionomers (in grams)[a]

A. Variation of DMPA Content [PTMG/PPG (100/0)]

Run	PTMG	IPDI	DMPA, wt%	TEA	TETA	Water	Hard content, %
A-1	42.11	15.13	2.5	1.55	0.848	140	29.82
A-2	41.28	15.45	3.0	1.87	0.845	140	31.20
A-3	40.46	15.77	3.5	2.18	0.842	140	32.58
A-4	39.63	16.09	4.0	2.49	0.838	140	33.95
A-5	38.81	16.41	4.5	2.80	0.835	140	35.32
A-6	37.98	16.72	5.0	3.11	0.832	140	36.70

B. Variation of PPG Content

Run	PTMG	PPG	IPDI	DMPA, wt%	TEA	TETA	Water	Hard content, %
B-1	40.46	0.00	15.77	3.5	2.18	0.842	140	32.58
B-2	36.41	4.05	15.77	3.5	2.18	0.842	140	32.58
B-3	32.37	8.09	15.77	3.5	2.18	0.842	140	32.58
B-4	28.32	12.14	15.77	3.5	2.18	0.842	140	32.58
B-5	24.27	16.18	15.77	3.5	2.18	0.842	140	32.58
B-6	20.23	20.23	15.77	3.5	2.18	0.842	140	32.58

C. Variation of Molecular Weight of PTMG (DMPA 3.5 wt%)

Run	PTMG(1)	PTMG(2)	IPDI	TEA	TETA	Water	Hard content, %
C-1	40.46	0.00	15.02	2.18	0.842	140	32.57
C-2	25.19	16.79	14.17	2.18	0.842	140	30.03
C-3	14.35	28.71	13.03	2.18	0.842	140	28.23
C-4	6.27	37.61	12.18	2.18	0.842	140	26.88
C-5	0.00	44.50	11.52	2.18	0.842	140	25.83

[a] PTMG(1): M_n = 1000. PTMG(2): M_n = 2000.

into the dried flask. The mixture was heated to 90°C with stirring for about 30 minutes, followed by the addition of IPDI to the homogenized mixture. The mixture was heated to 90°C for about 3 hours to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined by using a standard dibutylamine backtitration method [9]. Upon obtaining the theoretical NCO value, calculated from the [NCO]/[OH] index of the feed, the prepolymers were cooled to

60°C, and the neutralizing solution, i.e., TEA dissolved in DMF (5 wt% based on total reaction mass) was added and stirred for 1 hour while maintaining the temperature at 60°C. A 1:1 stoichiometry was obtained by adding TETA in the chain extension step.

Emulsification and Chain Extension

PU emulsion 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 obtaining a stable dispersion, a tubing pump was used to add water at a constant flow rate. The phenomenon of phase inversion, viscosity, and conductivity change during the emulsification process are well documented in Dieterich [1] and our earlier papers [12, 13]. Upon completing the phase inversion, TETA dissolved in water was fed to the emulsion for a period of 40 minutes, and chain extension was carried out for the next 2 hours. The resulting product, a urea-urethane dispersion with a solid content of about 35%, was stable over 6 months at room temperature. More detailed procedures are available in the literature [13].

Tests

Particle size and its distribution were measured with an Autosizer (Malvern II C), and the state of dispersion was observed from transmission electron microscopy (TEM, Hitachi H300). To obtain the micrographs, samples were stained with OsO_4 for 1 week. The viscosity of emulsion was measured using a Brookfield viscometer at 20°C. Tensile properties of the emulsion-cast films were measured using an Instron tensile tester at a crosshead speed of 50 mm/min, and an average of at least five measurements was taken. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at 80°C for 5 hours. The resulting films were then heated overnight in a drying 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 100°C at 11 Hz with a sample $0.03 \times 0.2 \times 3$ cm in size.

RESULTS AND DISCUSSION

Effect of DMPA Content

The effect of DMPA content was studied for PU prepared from PTMG 1000 (the number designates the molecular weight) and IPDI (Runs A1-A6). Figure 1 shows the variation of particle size and emulsion viscosity with DMPA content, where an asymptotic decrease of particle size and a linear increase of emulsion viscosity with increasing DMPA content were obtained. In self-emulsification of ionomer, particle size decreases with increasing hydrophilicity, which is governed by the ionic content of PU. Since in our system DMPA, upon neutralization by TEA, is the anionic center, hydrophilicity increases with DMPA content. In ionomer dispersion, particles are stabilized by electrical double-layer formation [1, 3]. Therefore, the effects of increasing DMPA content are to reduce the particle size due to the increased hydrophilicity, and to increase the particle size due to the

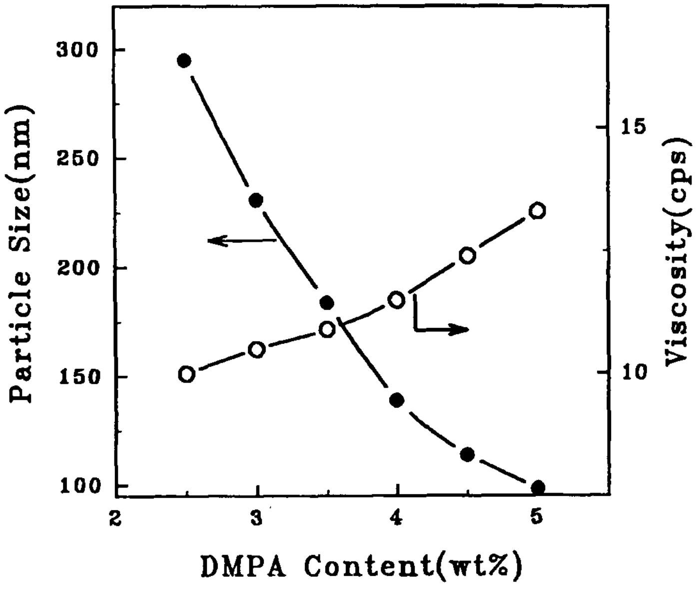


FIG. 1. Particle size and emulsion viscosity (20°C) vs DMPA content.

thickened electrical double-layer of counterions [14–16]. In addition, effective particle diameter is also increased by increased water swell due to the increased hydrophilicity of the PU. This effect should be more pronounced with increasing hydrophilicity. The overall effect would be an asymptotic decrease of particle size, i.e., rapid at low and slow at high DMPA content. On the other hand, emulsion viscosity increases with an increase of the effective volume of the dispersed particle, and a linear increase with increasing ionic group content can be obtained.

Figure 2 shows TEM micrographs of the emulsion at three DMPA contents, where a well-defined spherical particle is seen with 2.5 and 3.5 wt% DMPA. Relative particle size agrees with the Autosizer results (Fig. 1). However, with 4.5% DMPA the dispersed domains are generally very much swollen, as expected.

Dynamic mechanical and tensile properties of the emulsion-cast film are shown in Figs. 3 and 4. Around and above the glass transition temperature (T_g) of the soft segment, storage modulus (E', Fig. 3a) increases with increasing DMPA content. However, the T_g of the soft segment (Fig. 3b) does not vary with DMPA content. Due to the small content of hard segment (Table 1), its T_g is not seen in the figure. Tensile strength increases and elongation at break decreases asymptotically with an increase of DMPA.

The effects of DMPA on the physical properties of segmented PU are to increase the number of urethane linkage (also the hard content) and the interchain interactions caused by the ionic nature of neutralized DMPA [17–21]. Since the mechanical strength of PU is mainly governed by the hard domain [6], the above effects mainly contribute to the mechanical strength and modulus. On the other hand, T_g depends mainly on the degree of soft-hard phase mixing. As the degree of phase mixing increases, soft segment motion is restricted by the hard segments dissolved in soft segments, and hard segments are solubilized by the soft segment in

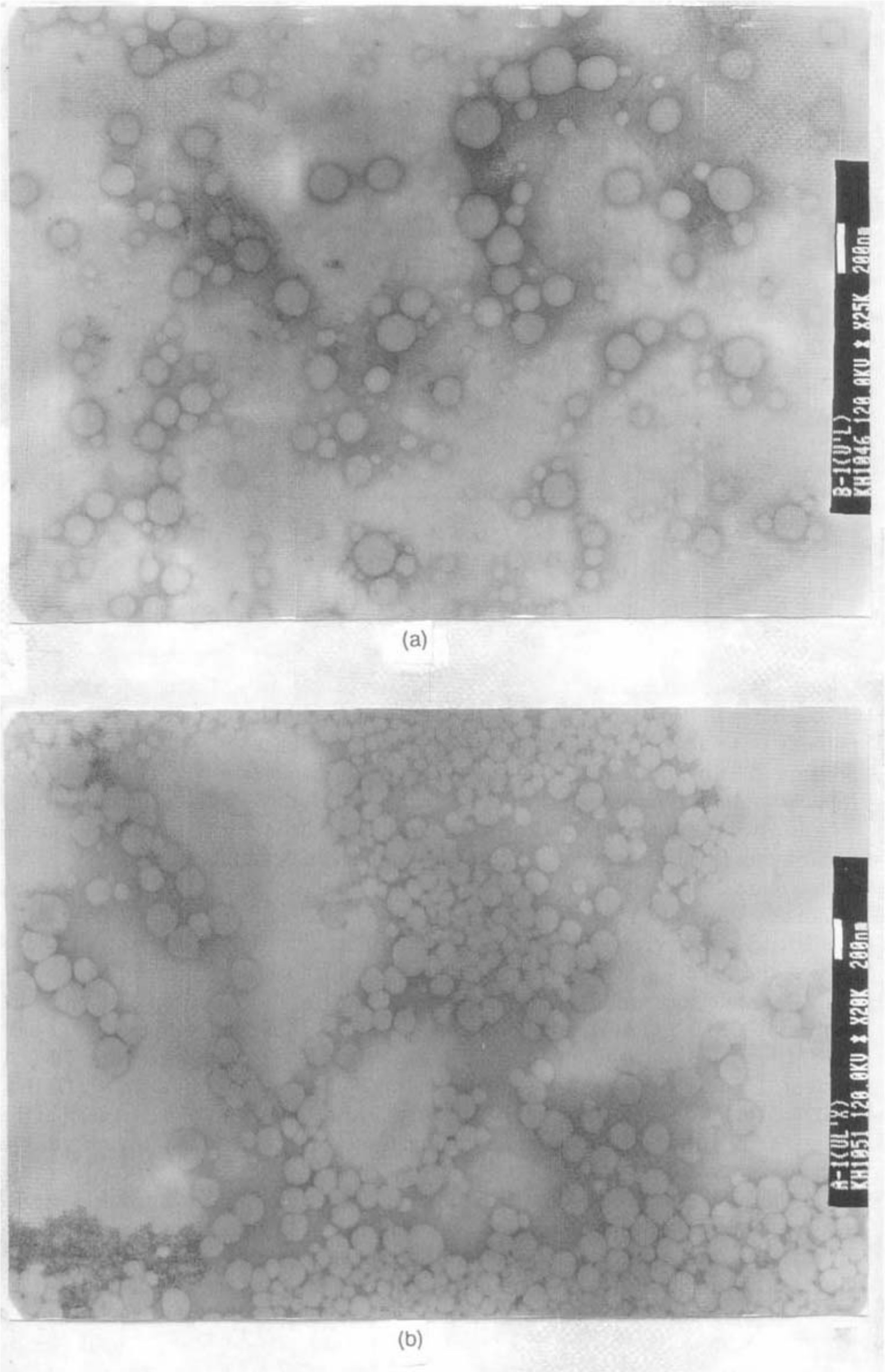


FIG. 2. TEM micrographs of the emulsions with different DMPA contents: (a) 2.5, (b) 3.5, and (c) 4.5%.

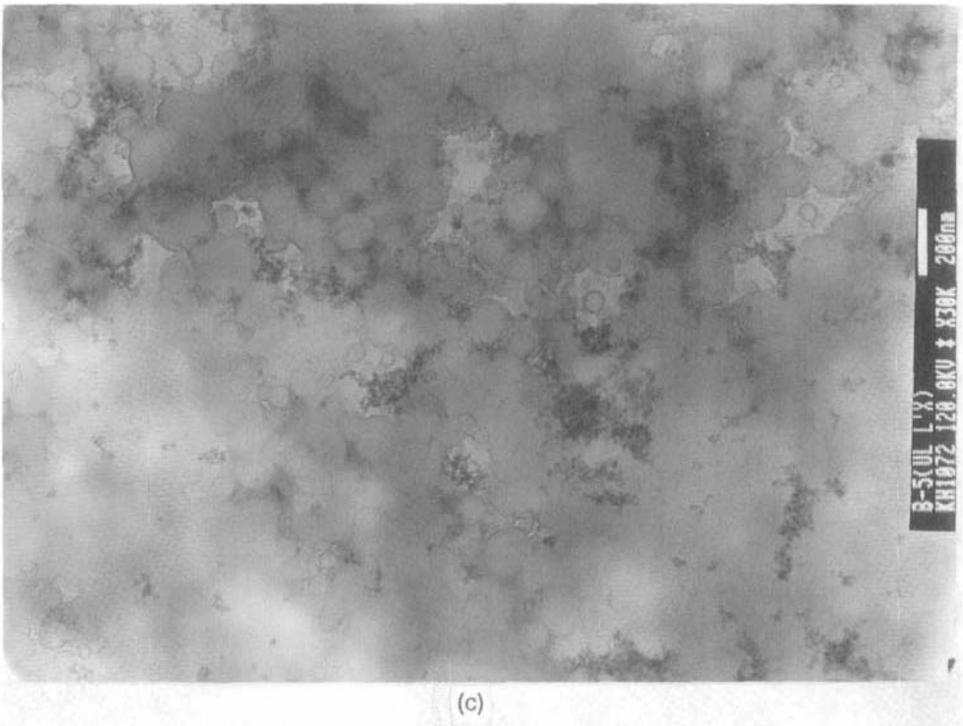


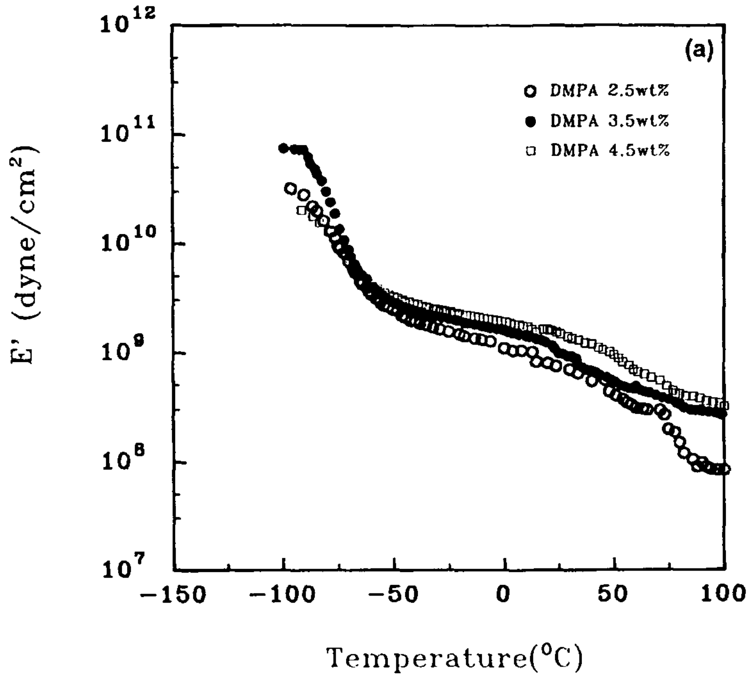
FIG. 2 (continued).

hard segments [11]. Therefore, phase mixing generally gives increased T_g for soft segment and decreased T_g for hard segment. Soft-hard phase mixing is favored with short segments and with ester-based PU rather than with ether-based PU due to the intensive hydrogen bonding formation between urethane NH and ester carbonyl than between urethane NH and ether oxygen. It seems that PTMG 1000 forms phase separation with hard segment, and the DMPA content does not exert an effect sufficient enough to alter the degree of phase mixing.

Effect of Mixed Polyols

In this series of experiments the DMPA content was fixed at 3.5 wt% (based on total solid), and up to 50% of the PTMG has been replaced by PPG (Runs B1–B6). PTMG and PPG having the same molecular weight were used to eliminate the effect of soft segment length.

Figure 5 shows emulsion size and viscosity as a function of PPG content. Particle size and emulsion viscosity show a minimum and a maximum, respectively, at 30% PPG. Since the concentration of the ionic center was fixed, the variation of particle sizes is mainly determined by the hydrophilicity of PU. At low PPG content, PPG simply provides PU with hydrophilicity, resulting in a decrease of particle size without bringing excessive swell. However, at higher PPG content, PPG in-



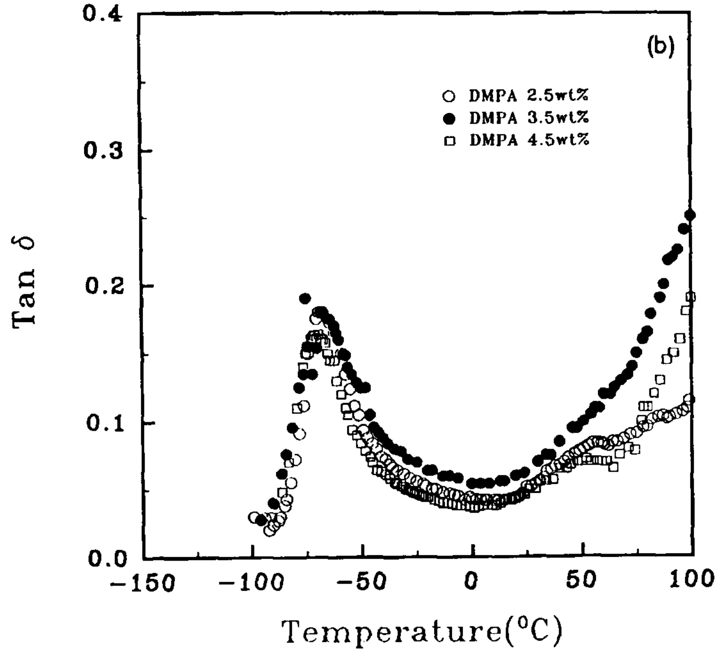


FIG. 3. Dynamic properties of the emulsion-cast films at 11 Hz: (a) storage modulus and (b) tan δ.

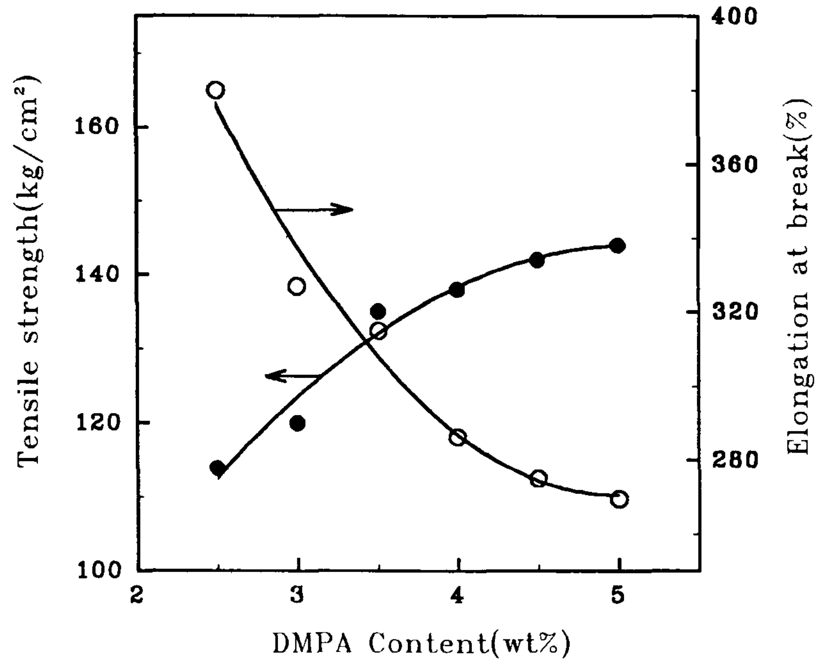


FIG. 4. Tensile strength and ultimate elongation of the emulsion-cast films vs DMPA content (20°C).

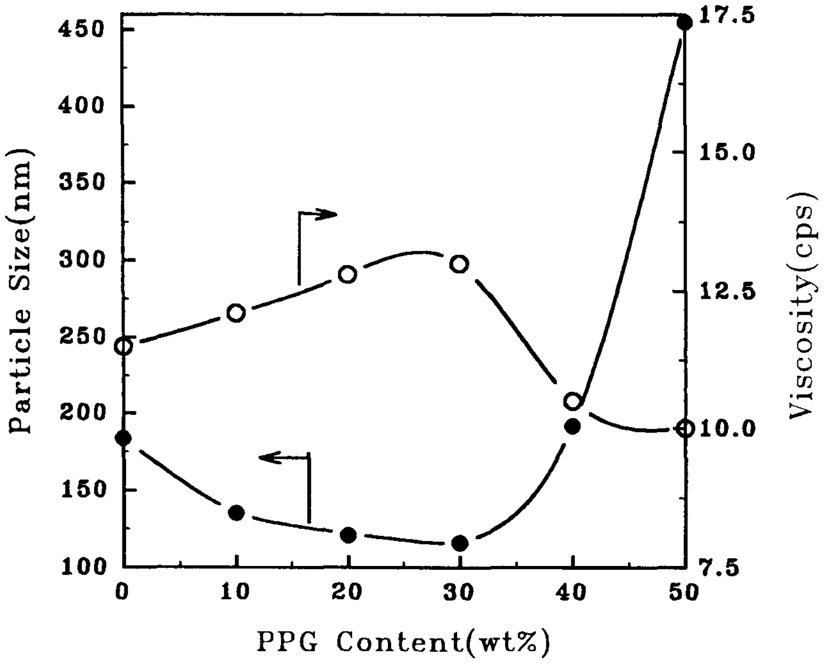
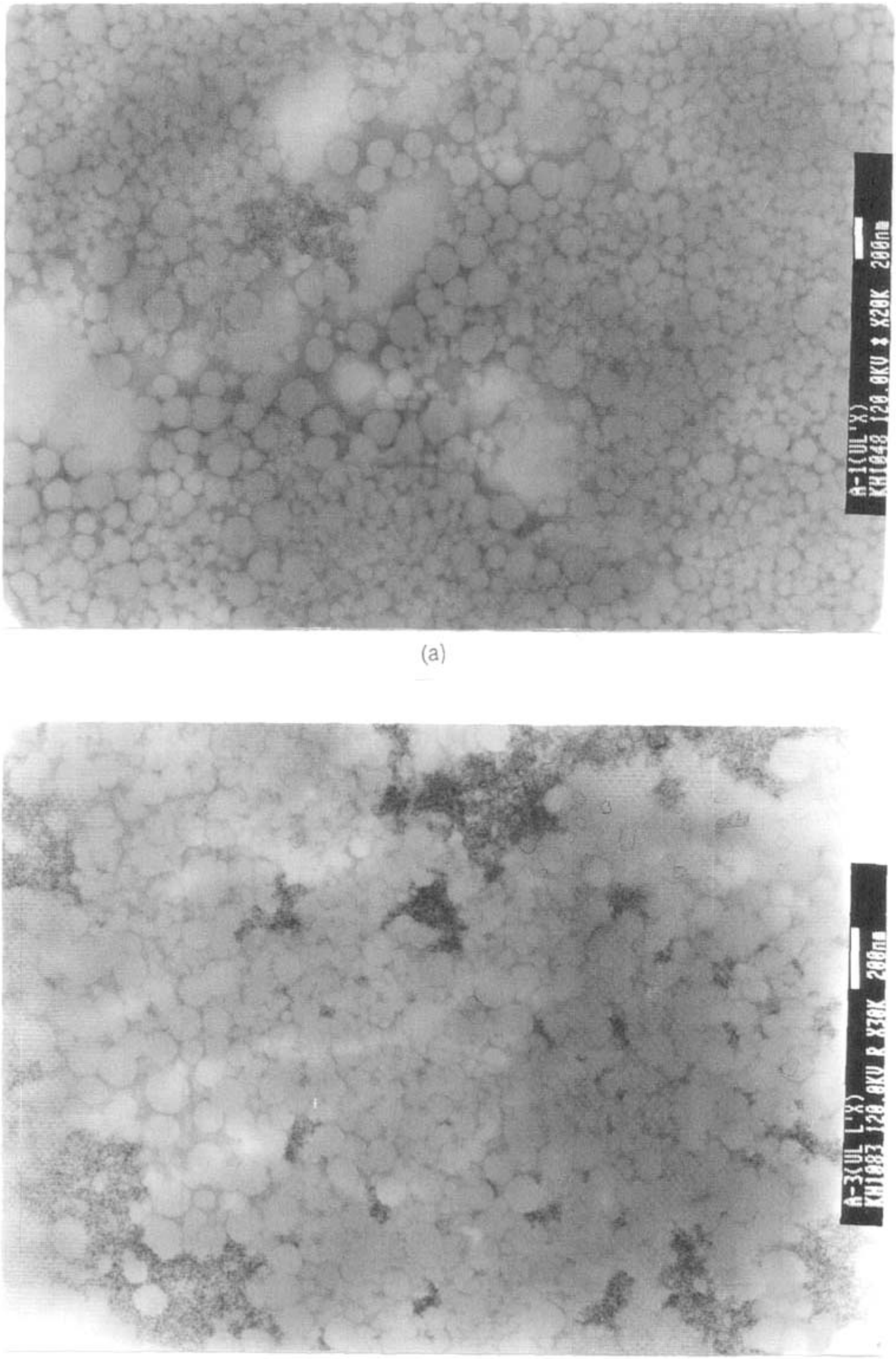


FIG. 5. Particle size and emulsion viscosity (20°C) vs PPG content.



(a)

(b)

FIG. 6. TEM micrographs of the emulsions with different PPG contents: (a) 0, (b) 20, and (c) 40%.

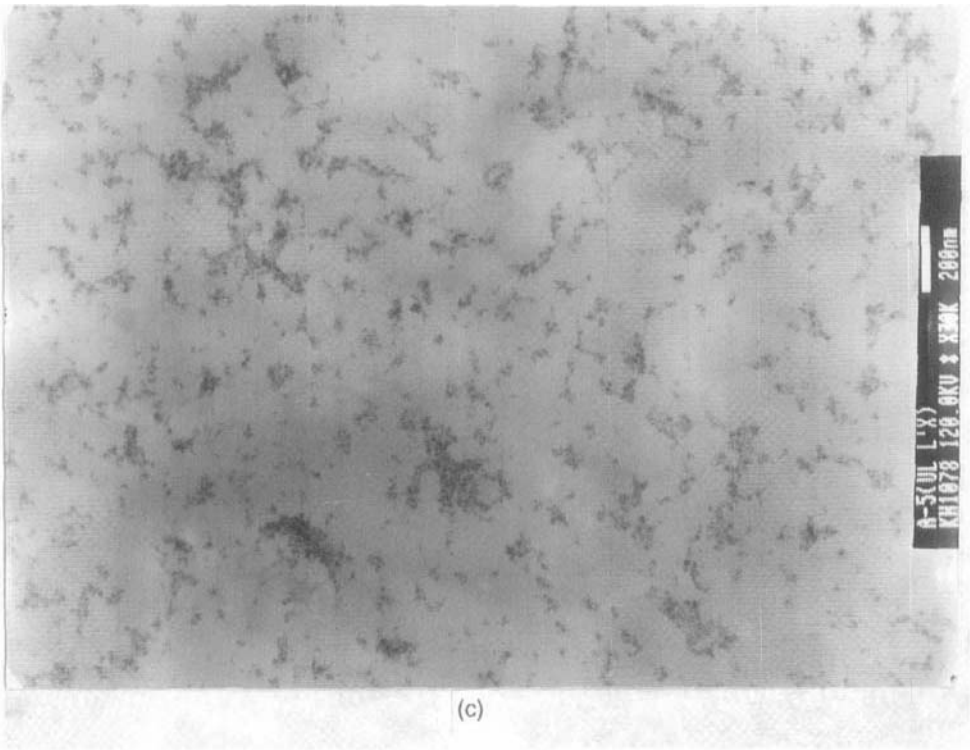


FIG. 6 (continued).

duces extensive water swell as a result of increased hydrophilicity, as was visualized from TEM micrographs (Fig. 6). With 0% (100% PTMG) and 20% PPG, the dispersed domains are well-defined spherical particles. However, at 40% PPG the dispersed domains are extensively swelled with water and isolated domains are not seen. It seems that the variation of viscosity follows particle size variation as determined by an Autosizer.

Dynamic mechanical and tensile properties of the emulsion-cast film of the PU ionomer are given in Figs. 7 and 8, respectively. Generally, at and above the T_g of the soft segment, storage modulus decreases with increasing PPG content. However, the tan δ peak (presumably corresponding to the T_g of the soft segment) moves toward a higher temperature as the PPG content increases. Tensile strength decreases and elongation at break increases with PPG content. It is generally believed that PTMG gives PU with superior physical properties due mainly to its regular chain structure and ability to crystallize upon extension. On the contrary, the side chain methyl group in PPG prevents crystallization of the soft segment and increases chain separation [6]. From this point of view, the decrease of dynamic modulus and tensile strength with PPG content is to be expected.

The increase of soft segment T_g with increasing PPG content should be caused by the increased soft-hard phase mixing with PPG incorporation. The addition of PPG to PTMG may disturb the chain regularity of PTMG soft segments and aug-

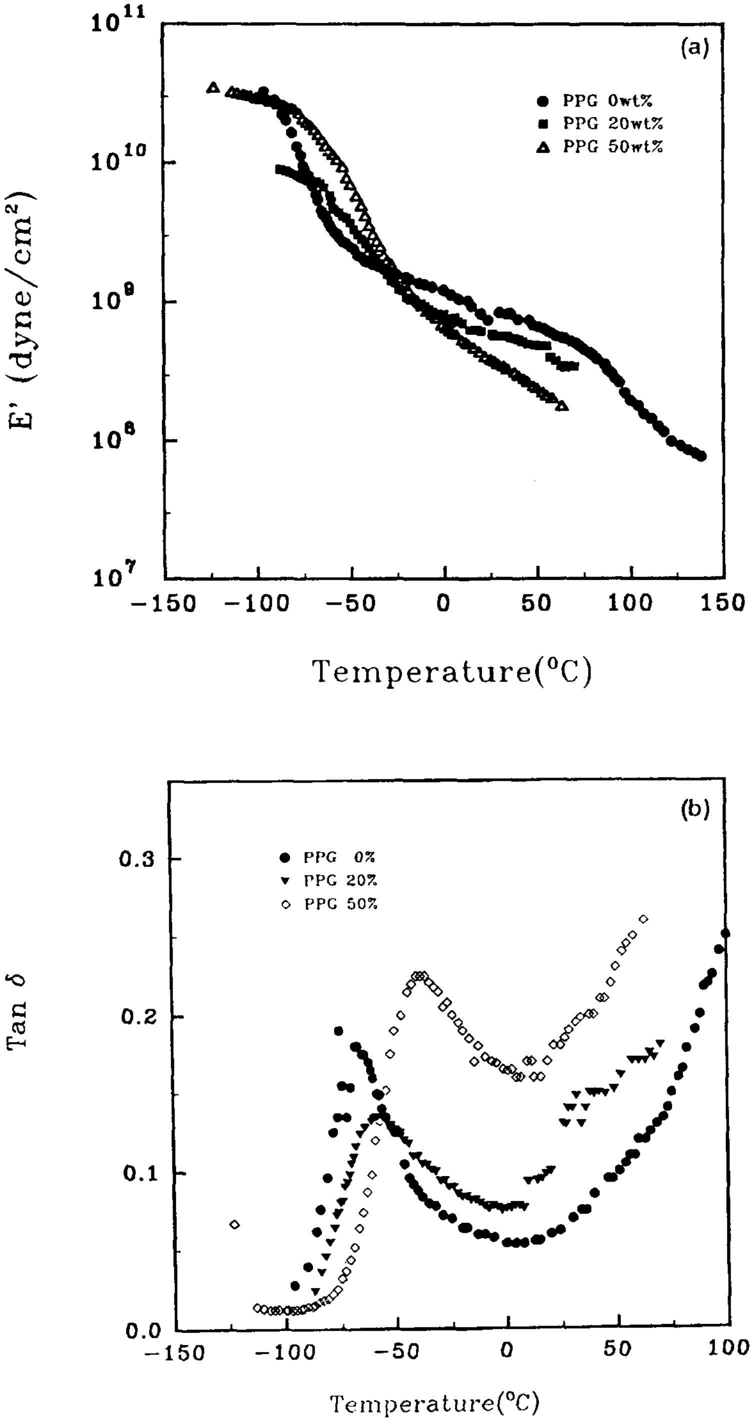


FIG. 7. Dynamic properties of the emulsion-cast films vs PPG content: (a) storage modulus and (b) tan δ.

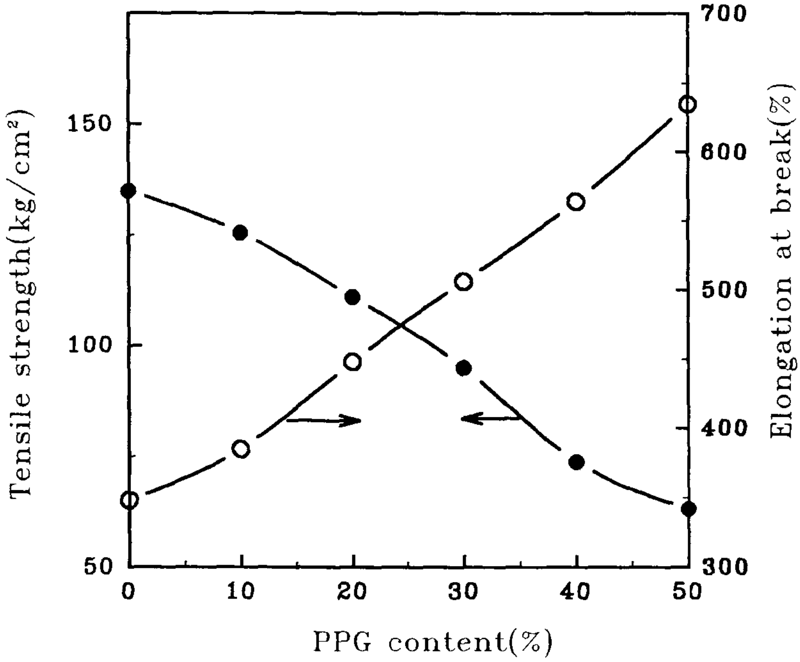


FIG. 8. Tensile strength and ultimate elongation of the emulsion-cast films vs PPG content (20°C).

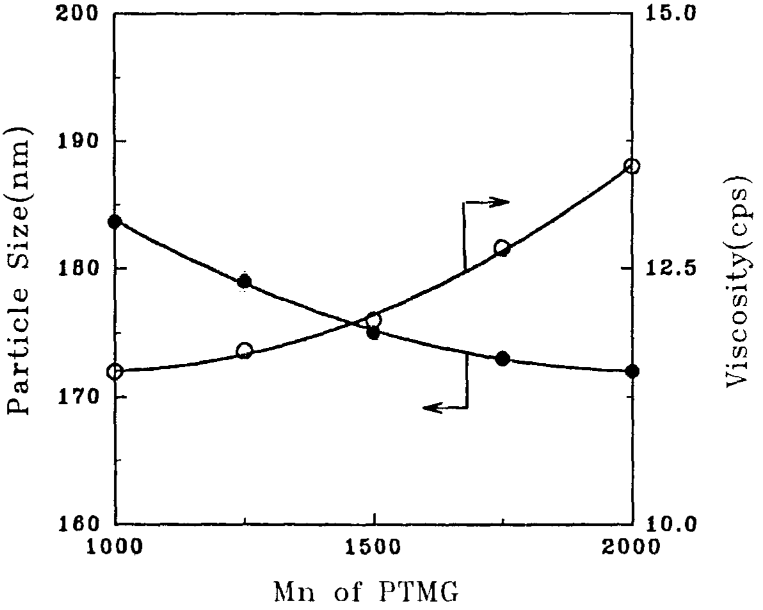


FIG. 9. Particle size and emulsion viscosity (20°C) vs molecular weight of PTMG.

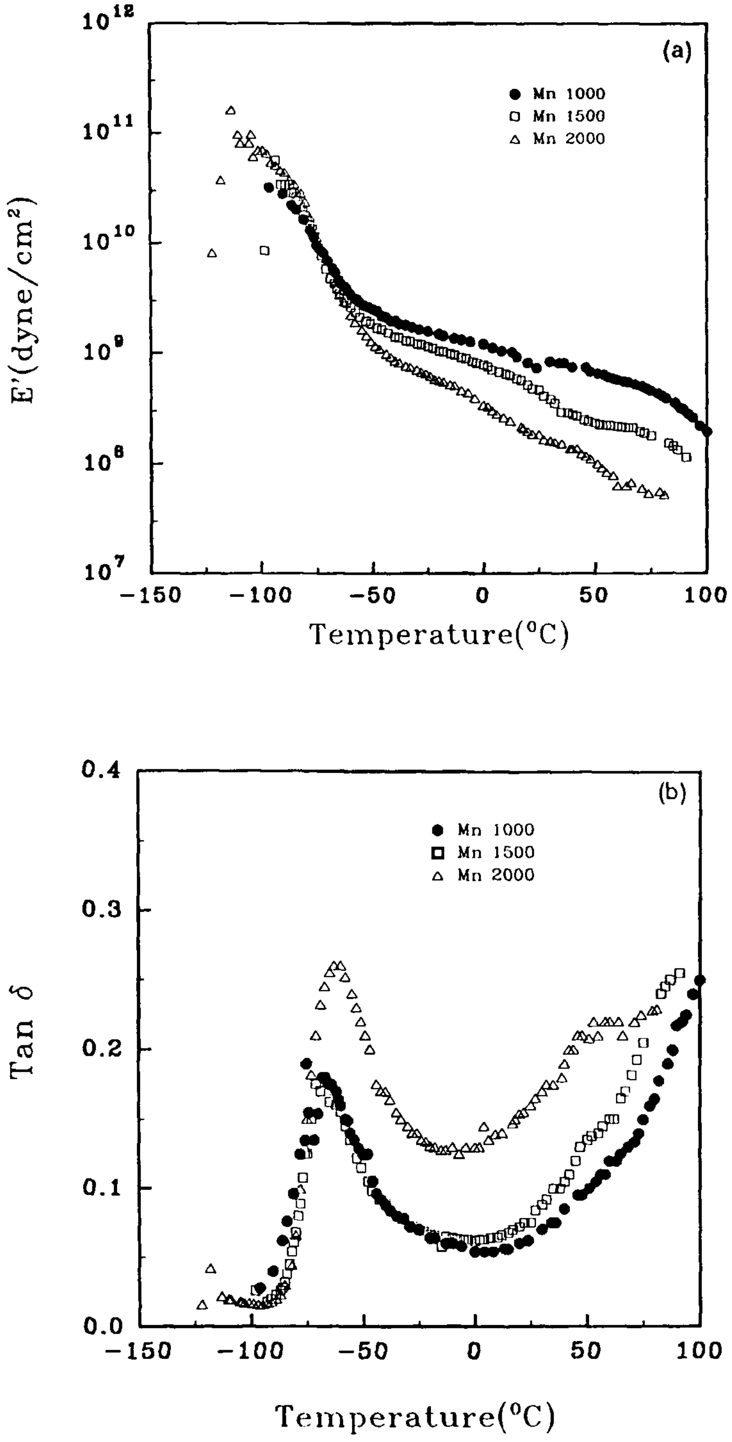


FIG. 10. Dynamic properties of the emulsion-cast films vs molecular weight of PTMG: (a) storage modulus and (b) tan δ.

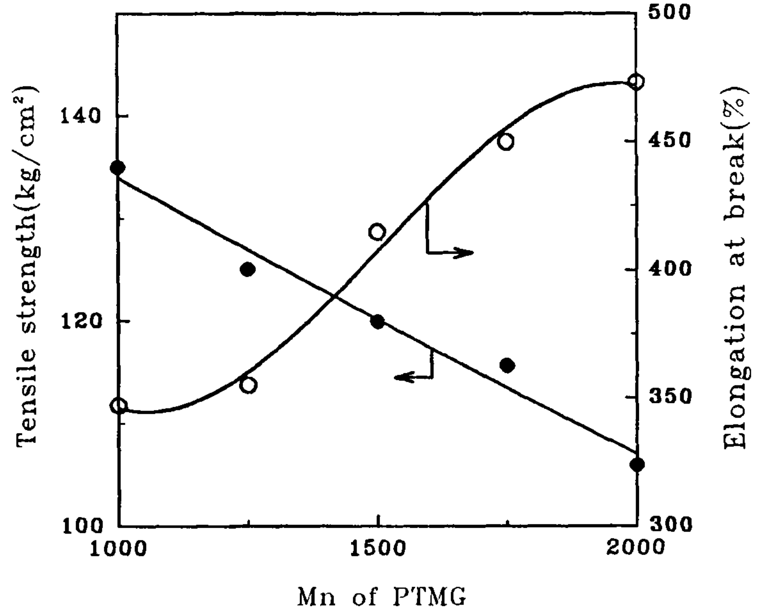


FIG. 11. Tensile strength and ultimate elongation of the emulsion-cast films vs molecular weight of PTMG.

ment soft–hard phase mixing, a phenomenon similar to the one observed in copolymer blends. For examples, blends of styrene-acrylonitrile copolymer (SAN) with poly(methyl methacrylate) are miscible when the acrylonitrile content of SAN is about 7–27%, and they are immiscible beyond the composition range [22, 23]. This phenomenon is properly explained in terms of miscibility driven by internal (within the SAN) repulsion. With an increase of phase mixing, the hard segments in soft segment hinder the motion of the soft segment and broaden the distribution of their relaxation times [11]. It is noted that the loss peak area becomes broad as the PPG content increases.

Effect of Polyol Molecular Weight

This series of experiments was formulated with PTMG 1000 and PTMG 2000 at a fixed DMPA content (Runs C1–C5). Upon mixing these two polyols, polyols of different molecular weight were obtained.

Figure 9 shows that the particle size decreases and the viscosity increases with increasing M_n of PTMG, but the variation is very small. The decrease of particle size in this case should be related to the increased flexibility of PU. As the flexibility of backbone PU is increased by the increased soft fraction, breakup of the dispersed phase into small drops and the formation of a micelle structure would be more feasible, leading to decreased particle size accompanied by a mild increase of viscosity [14].

Storage modulus decreases but the loss peak is unchanged or marginally increased with increasing M_n of PTMG (Fig. 10). Tensile strength decreases and elongation at break increases almost linearly with the M_n of PTMG (Fig. 11). The decreased modulus and strength are mainly due to the decreased hard fraction of PU. Since the soft segment of PTMG 1000 and PTMG 2000 are phase separated from hard domains, the increase of the soft segment molecular weight does not affect phase mixing, keeping the T_g of the soft segment almost unchanged (Fig. 10b).

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