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Polyurethane ionomer dispersions from poly(neopentylene phthalate) glycol and isophorone diisocyanate

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Polyurethane (PU) anionomers were synthesized from phthalic anhydride, neopentyl glycol, isophorone diisocyanate and dimethylolpropionic acid (DMPA) according to a prepolymer-mixing process. Emulsion characteristics and basic structure–property relationships of the emulsion-cast film were studied with regard to the DMPA concentration, degree of neutralization (*DN*), prepolymer molecular weight (M_{pre}) and the extender functionality (f). Average particle size decreased and emulsion viscosity increased with increasing DMPA concentration and *DN*. The major glass transition temperature of the PU (transition of the phase rich in soft segments (T_{gs})) increased with increasing DMPA concentration and f and decreased with increasing M_{pre} and *DN*. The increase was interpreted in terms of soft segment–hard segment phase mixing, due to the increased hard fraction (DMPA) and increased cohesion of PU (f), whereas the decrease was interpreted in terms of increased phase separation (M_{pre}) and increased hard segment cohesion (*DN*).

(Keywords: polyurethane; anionomer; dispersion)

INTRODUCTION

Since aqueous dispersions of polyurethane (PU) are non-toxic, non-flammable and do not pollute the air, they are widely encountered in coatings and adhesives for flexible substrates (textiles, leather, paper and rubber), wood and glass fibres[1–5]. In addition, the chain extension reaction between NCO-terminated prepolymers is carried out in the form of a dispersion. Therefore it is possible to set the molecular weight to any level without the viscosity being impaired.

PU dispersions can be prepared in ionomeric and non-ionomeric form. The advantages and disadvantages of these two types of dispersions are well documented in the literature[1,6,7]. Synergistic effects in ionic and non-ionic dispersions have also been obtained by combining ionic and non-ionic hydrophilic groups in one and the same PU[6].

As for solvent-borne PU, the properties of PU ionomers are largely governed by soft segment–hard segment phase separation[8–10]. Factors influencing behaviour include segmental polarity difference, segment length, crystallizability of each segment, intra- and intersegment interactions and overall composition. The existence of hard segments may give PU ionomers their excellent mechanical properties. An elevation of the soft segment glass transition temperature (T_g) is observed as a result of the presence of dissolved hard segments[11,12]. It is generally known that polyester soft segments contribute to phase mixing through hydrogen bonding between the oxygen of the ester group and the NH group of the urethane linkage[13]. Many previous investigations have reported on the microdomain structure in segmented PU[14–17]. However, work on PU ionomers in the past has mainly been done in industrial laboratories[18], and systematic data on structure–property relationships are sparse in the open literature.

The work in this paper is part of our continuing efforts[13,19–23] to elucidate the structure–property relationships of PU ionomers dispersions. Owing to the diverse variables required to determine phase morphology and properties, no straightforward approach seems to exist.

We have prepared PU anionomers from phthalic anhydride, neopentyl glycol, isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA) according to a prepolymer-mixing process. The concentration of ionic groups, degree of neutralization, prepolymer molecular weight and extender functionality were the design variables used to control the property response. In our earlier experiments we noted that the dynamic mechanical response was most sensitive to the phase morphology. We have intensively measured the dynamic mechanical response using a rheovibron.

EXPERIMENTAL

Materials

Polyols with molecular weights of approximately 700 g mol^{-1} were synthesized from phthalic anhydride and neopentyl glycol, and were subsequently dried and degassed at 80°C and 1–2 mm Hg until no bubbling was observed. DMPA (Aldrich) was dried at 100°C for

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2h in a drying oven. Dimethylformamide (DMF), ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) were dried over 3Å molecular sieves before use. An extra-pure grade of triethylamine (TEA) was used without further treatment.

Prepolymer synthesis

Detailed procedures are available elsewhere[1–3]. A 500ml four-necked flask equipped with mechanical stirrer, nitrogen inlet, condenser with drying tube and a pipette outlet was charged with the polyols, and the reactants were heated to 60°C in a constant temperature water bath. Since urethane-forming reactions with aliphatic diisocyanates are slow, approximately 0.03wt% of dibutyltin dilaurate was added as a catalyst. In the presence of a catalyst, the reaction between an isocyanate and a primary alcohol follows second-order kinetics[24]. IPDI was then dissolved in a substantial amount of DMF (5wt% based on the total reaction mass) and added to the mixture and the reaction was allowed to proceed for 3h at 80°C. The change in NCO content during the reaction was determined using a standard dibutylamine back-titration. Upon obtaining the theoretical NCO content, the reaction mixture was cooled to 50°C and neutralized with TEA over about 1h.

Emulsification and chain extension

A PU emulsion was obtained by adding water to the prepolymer solution at 60°C. The rate of water addition to the mixture was carefully controlled using a tubing pump to obtain a stable inversion. The phenomenon of phase inversion and the viscosity and conductivity changes that occur during the emulsification process have been well documented by Dieterich[1] and in our earlier papers[13,19–21]. Upon completing the phase inversion, an amine chain extender dissolved in water was fed to the emulsion for a period of 40min, and chain extension was carried out over the next 2h. The resulting product was a stable (over six months at room temperature) urea–urethane dispersion with a solids content of about 30wt%.

Tests

Particle size and its distribution were measured using a Malvern Autosizer II C. The viscosity of the emulsion was measured using a Brookfield viscometer at 20°C. The contact angle at room temperature was measured by dropping a drop of water onto a film (Erma G-1 type). Dynamic mechanical properties were measured using an Orientec DDV 01-FP rheovibron at 11Hz for a sample size of 0.03 × 0.2 × 3cm. Tensile properties of the emulsion-cast films were measured using a Tinius Olsen 1000 tensile tester at a crosshead speed of 50mm min^{-1} and the average of at least five measurements was taken. Films for the above tests were prepared by casting the emulsion on to a Teflon plate, followed by drying at 80°C for 5h. The resulting films were then heated overnight in an oven at 60°C under 2–3mmHg. Microtensile test specimens were prepared according to ASTM D-1822 using a punch.

RESULTS AND DISCUSSION

Unless otherwise stated, the concentration of DMPA was 6wt% which was completely neutralized. The NCO-terminated prepolymer molecular weight was 5000g mol^{-1}, and the prepolymer was chain extended with TETA.

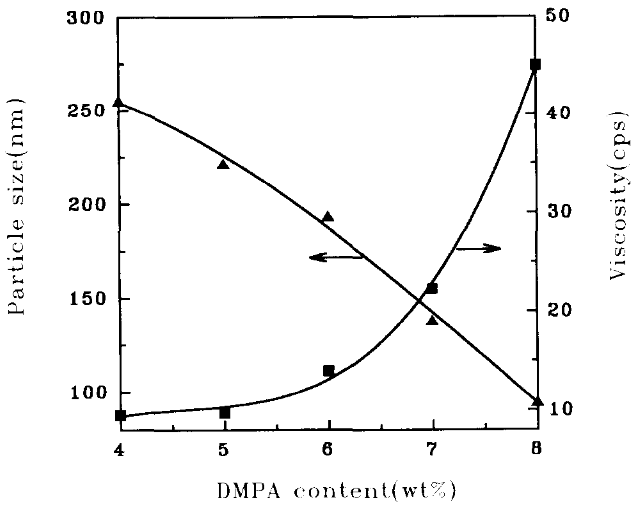

Figure 1 Particle size and emulsion viscosity versus DMPA concentration

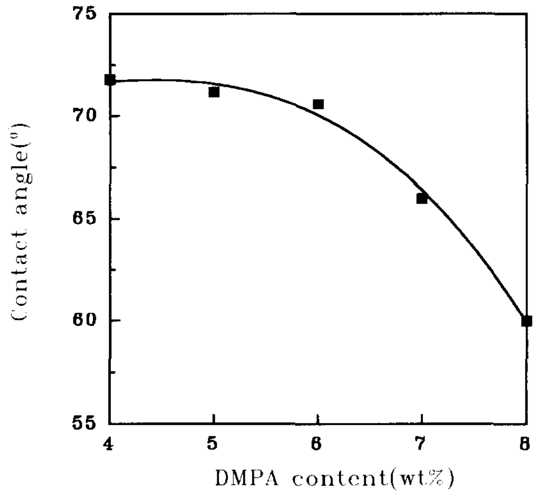

Figure 2 Contact angle of emulsion-cast film versus DMPA concentration

Effect of ionic content

In these experiments, the DMPA concentration was varied in the range 4–8wt% based on total solid. In PU dispersions, the average particle size is of practical importance. 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 essential. *Figure 1* shows the average particle size and the emulsion viscosity as a function of DMPA concentration. It can be seen that the particle size decreases almost linearly, whereas the emulsion viscosity increases slowly at low and rapidly at high DMPA concentration. In PU dispersions, the average particle size can be controlled to some extent by such emulsification conditions as the revolutions per minute of the mixer and temperature. However, it is mostly governed by the concentration of

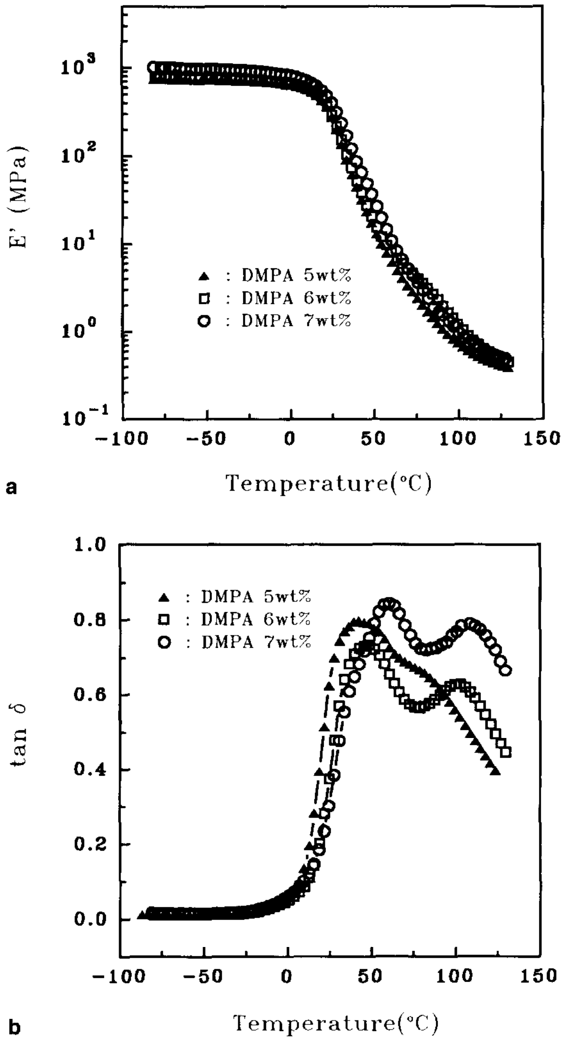

Figure 3 Dynamic mechanical properties of emulsion-cast films prepared with different DMPA concentrations: (a) storage modulus (E'); (b) tan δ (1 dyn = 10^{-5} N)

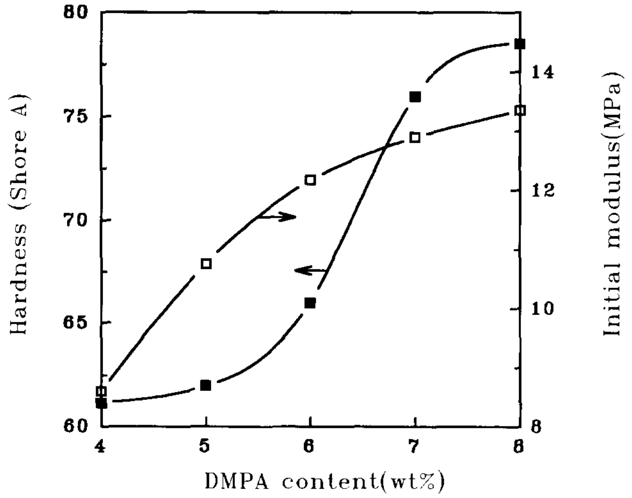

Figure 4 Hardness and initial modulus of emulsion-cast films prepared with different DMPA concentrations

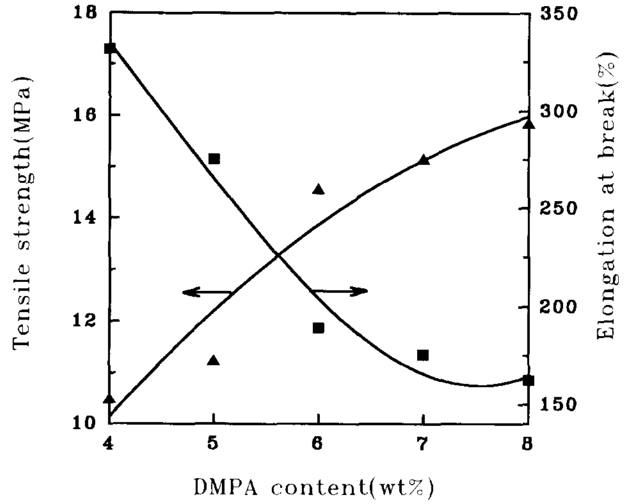

Figure 5 Tensile properties of emulsion-cast films prepared with different DMPA concentrations

solubilizing groups[1,25]. The solubilizing groups in ionomer dispersion are the ionic groups, viz. the carboxylate anions. Therefore, average particle size should decrease with increasing DMPA concentration.

On the other hand, an ionic PU dispersion is stabilized by diffusing electrical double layers which grow with increasing ionic concentration[26]. In addition, the absorption of water into the particle is also increased with increasing hydrophilicity of the PU. These together augment the hydrodynamic volume of the particles under motion, to which the emulsion viscosity is proportional, linearly at low and non-linearly at high particle concentration[27]. It seems that as the DMPA concentration increases, non-linear terms become significant owing to the increased hydrodynamic volume of the particles.

Figure 2 shows the contact angle of the emulsion-cast film against DMPA content. The contact angle should decrease with increasing hydrophilicity of the film since spreading of a drop of water on a more hydrophilic substrate is more likely. The decrease in contact angle with DMPA content, at low concentration ($\leq$ 6 wt%) is insignificant, but it becomes significant at relatively high DMPA content, and the tendency basically agrees with the particle size decrease and viscosity increase with increasing DMPA concentration.

Figure 3 shows the dynamic mechanical properties of the emulsion-cast films. Elastic modulus generally increases with DMPA concentration (*Figure 3a*) and the major transition corresponding to the glass transition of the phase rich in soft segments (at T_{gs}) moves towards higher temperature (*Figure 3b*). The glass transition of the phase rich in hard segments (at T_{gh}) is simply a shoulder at 5 wt% DMPA, but it becomes a well-defined peak and moves towards higher temperature as the DMPA concentration increases. In the segmented PU where high molecular weight polyols are incorporated, soft segment–hard segment phase mixing increases with increasing hard fraction and decreases with increasing cohesion between hard domains[28]. It seems that the property response towards DMPA is two-fold, i.e. augmentation of phase mixing by increasing the hard fraction and augmentation of the cohesion between hard domains through ionic interactions[29], resulting in simultaneous increase of T_{gs} and T_{gh}. Soft segment–hard segment phase separation seems minimal at 5 wt%

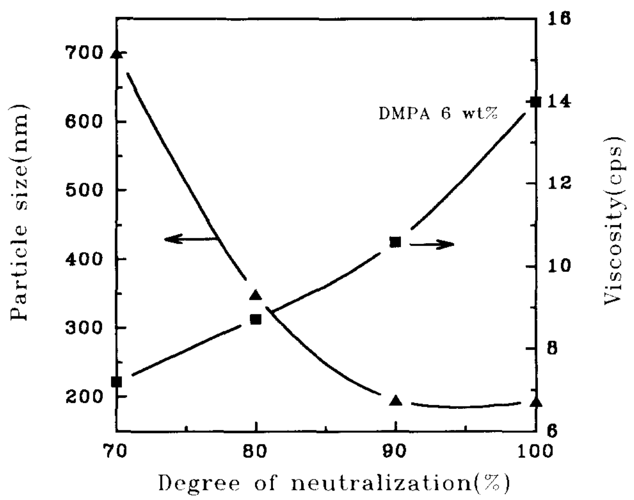

Figure 6 Particle size and emulsion viscosity versus *DN*

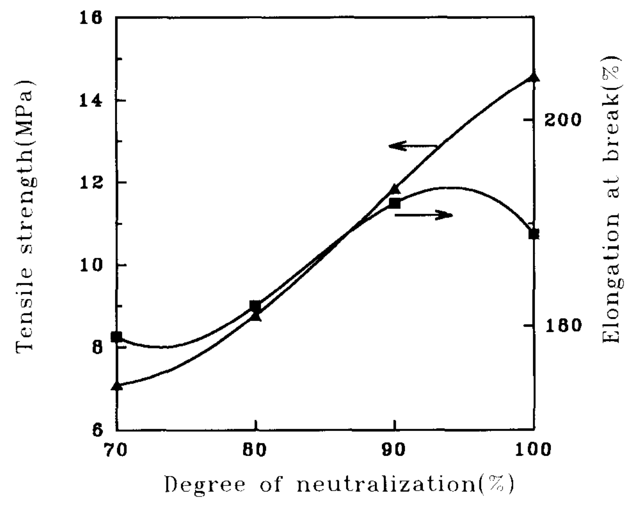

Figure 8 Tensile properties of emulsion-cast films prepared with different *DN*s

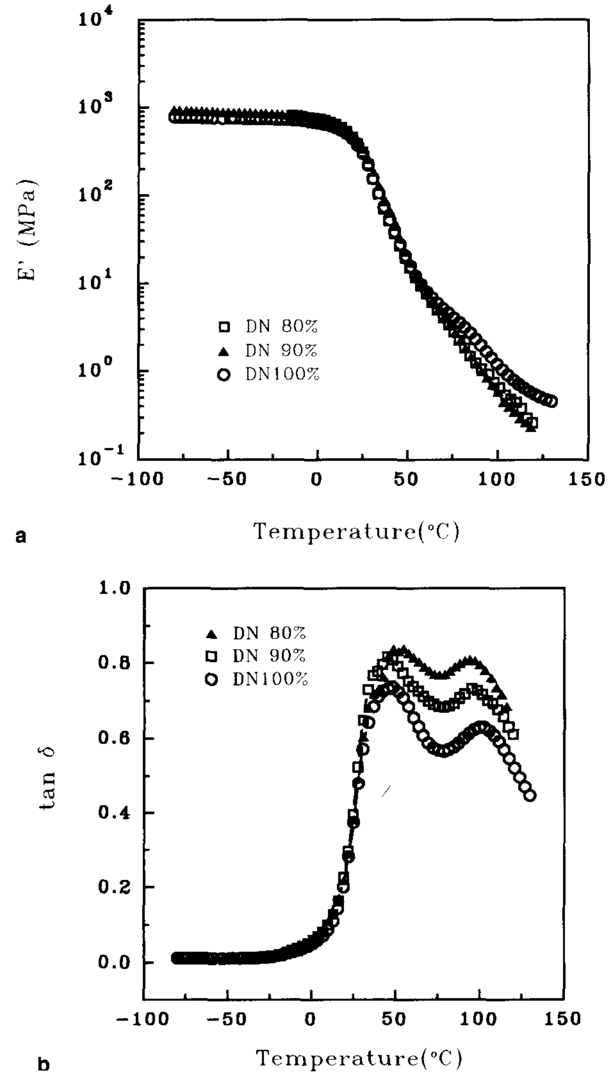

Figure 7 Dynamic mechanical properties of emulsion-cast films prepared with different *DN*s: (a) storage modulus (E'); (b) tan δ

DMPA (a shoulder), owing to the insufficient hard fraction.

The hardness and initial modulus of the emulsion-cast films as a function of DMPA concentration are shown in *Figure 4*, where S-shaped (hardness) and asymptotic (initial modulus) increases with DMPA concentration are shown. Within the DMPA concentration range (4–8 wt%), modulus increase is more pronounced than hardness increase. This is perhaps because hardness is a bulk property, whereas modulus should depend on the phase morphology as well. With increased phase mixing, the resistance to initial deformation should effectively increase, unless the phase-separated soft segments resist initially[30].

Tensile strength increases with DMPA concentration owing to the increased hard fraction and hard domain cohesion, whereas elongation at break decreases owing to the decreased soft fraction (*Figure 5*).

Effect of degree of neutralization (DN)

In this series of experiments, the *DN* was varied in the range 70–100%. *Figure 6* shows that particle size decreases asymptotically and emulsion viscosity increases almost linearly with increasing *DN*. Since the *DN* is the only variable in these experiments, the variation in particle size with increasing *DN* is due to the increased hydrophilicity, endowed by the increased ionic content. At low *DN* the particle size decreases rapidly with increasing *DN*, but at high *DN* the particle size decrease is seemingly offset by the increased absorption of water, and an equilibrium particle diameter is obtained to give an asymptotic decrease at high *DN*. On the other hand, emulsion viscosity increases in proportion to the effective particle volume[31], and its dependence on *DN* should be more or less direct or accelerated with the increase in dispersed volume, as our results indicate. In accordance with the increased hydrophilicity, the contact angle of water on the film decreased from about 80° at 70% *DN* to 70° at 100% *DN* (not shown).

The effects of the *DN* on the dynamic mechanical properties of the emulsion-cast films are shown in *Figure 7*. With increasing *DN* at fixed overall composition, storage modulus increases above room temperature and T_{gs} decreases, whereas T_{gh} increases. The outward migration of the two T_gs is an indication of increased phase separation[22]. It seems that the increased cohesion between hard domains via ionic interactions augments

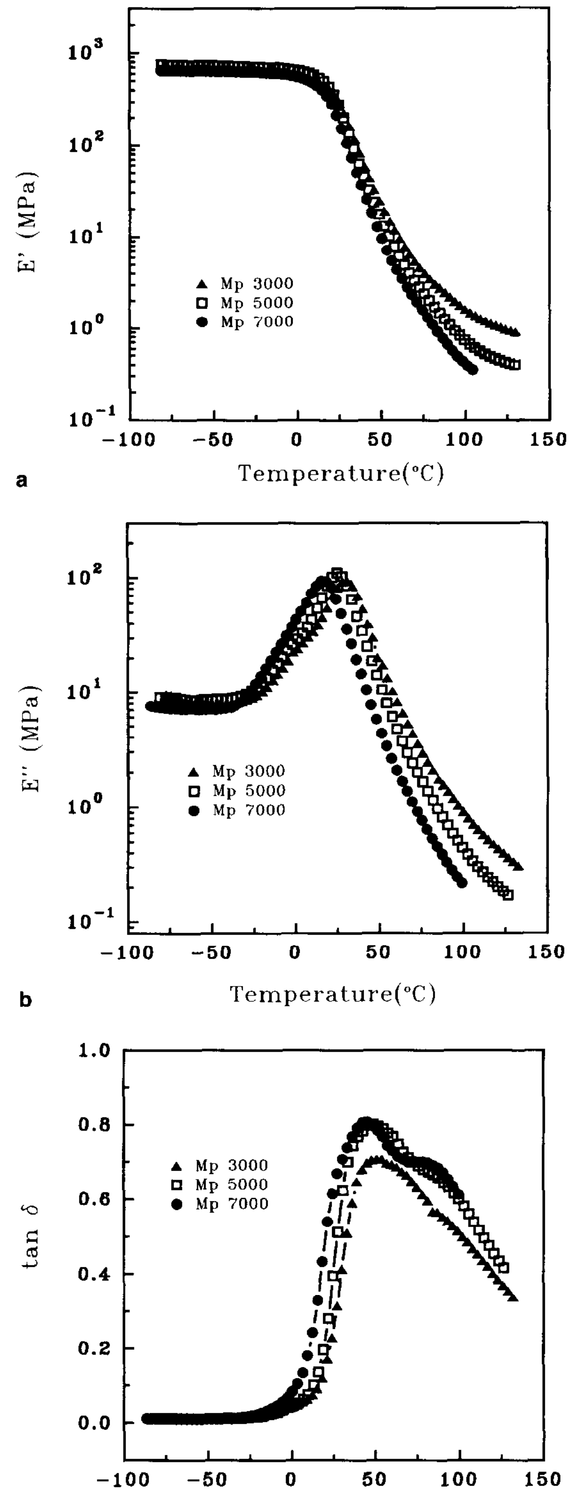

Figure 9 Dynamic mechanical properties of emulsion-cast films prepared with different prepolymer molecular weights: (a) storage modulus (E'); (b) loss modulus (E''); (c) tan δ

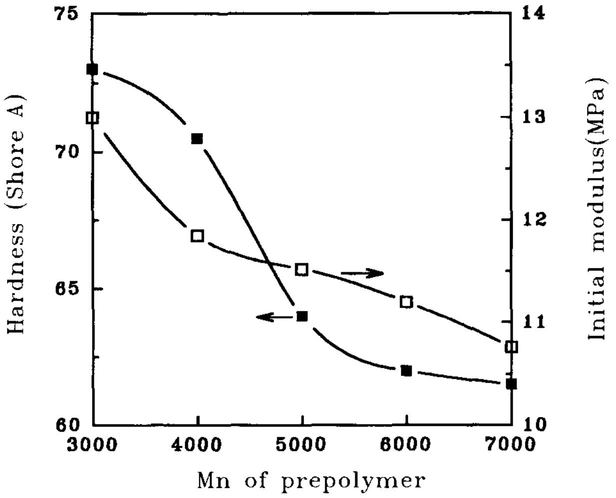

Figure 10 Hardness and initial modulus of emulsion-cast films prepared with different prepolymer molecular weights

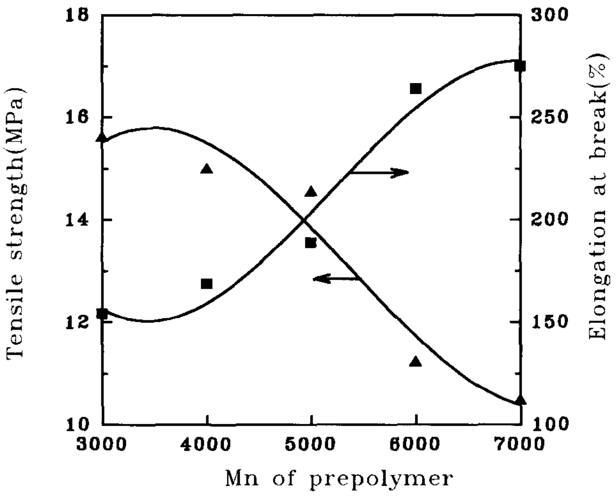

Figure 11 Tensile properties of emulsion-cast films prepared with different prepolymer molecular weights

the phase separation[32,33]. With increased phase separation, the tan δ peaks become better resolved and well defined.

Hardness (not shown) increased almost linearly with *DN*, from 62 (Shore A) at 70% to 75 at 100% *DN*, mainly owing to the increased hard segment cohesion. As expected, tensile strength and elongation at break increase with *DN* (*Figure 8*). The increased elongation again confirms that phase separation is increased with increasing *DN*.

Effect of prepolymer molecular weight (M_{pre})

In these experiments, $M_{\rm pre}$ was varied in the range 3000–7000 g mol^{-1}. The effect of prepolymer molecular weight $M_{\rm pre}$ on the viscoelastic properties of the emulsion-cast films are shown in *Figure 9*. As $M_{\rm pre}$ increases, the storage modulus (*Figure 9a*) decreases above the temperature at which the PUs are no longer glassy. The effect is more pronounced at higher temperature, and the plateau modulus, though not well defined, at $M_{\rm pre} = 7000$ g mol^{-1} is less than half that at $M_{\rm pre} = 3000$ g mol^{-1}.

The loss peak (*Figure 9b*) corresponding to $T_{\rm gs}$ moves towards lower temperature as $M_{\rm pre}$ increases. The subsidiary transition at $T_{\rm gh}$ can be seen in the loss tangent (*Figure 9c*). It is a mere shoulder for $M_{\rm pre} = 3000$ g mol^{-1} and a relatively well-defined peak for $M_{\rm pre} = 7000$ g mol^{-1}. It should be noted that the $T_{\rm g}$ determined from the tan δ peak is higher than the one determined from the loss modulus peak by several

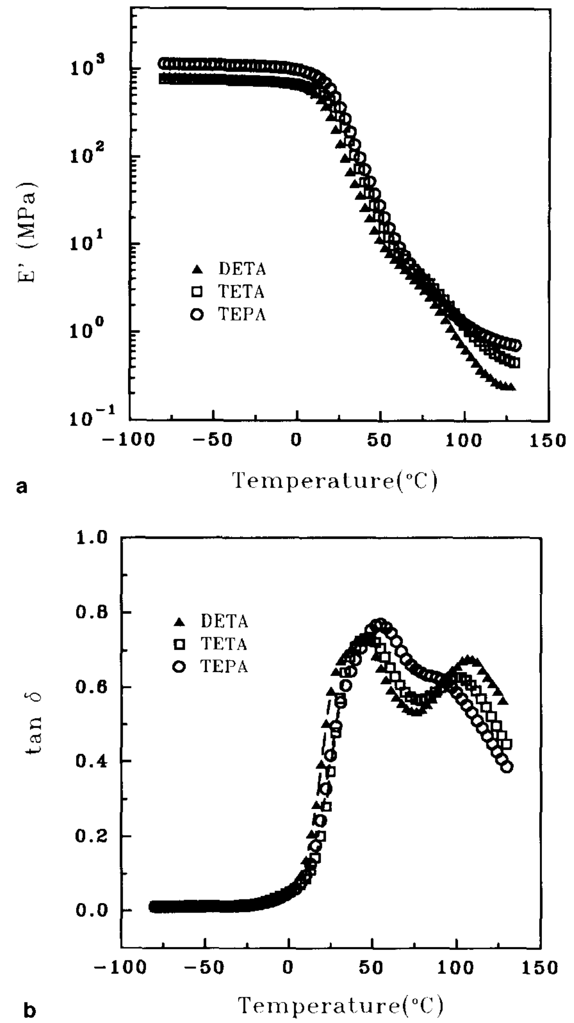

Figure 12 Dynamic mechanical properties of emulsion-cast films prepared with different types of chain extender: (a) storage modulus (E'); (b) tan δ

degrees. More importantly, T_{gh} is more sensitive to tan δ than to the loss modulus.

The decreased storage modulus, especially the plateau value, and lowered T_{gs} with increased M_{pre} can be interpreted as follows. The NCO-terminated prepolymers were chain extended with TETA, giving a crosslinked PU structure. Therefore M_{pre} corresponds to the molecular weight between crosslinks (M_c). With decreasing M_c, the plateau modulus should increase with rubber elasticity, which has proved applicable to crosslinked PUs[34]. On the other hand, phase separation is favoured when there are fewer restrictions (crosslinks) on segment conformations, and hence larger phase separation is obtained with larger M_{pre}. As the degree of phase separation increases, more of the hard segments dissolved in soft segments and acting as reinforcing fillers are extruded, and the major transition temperature decreases[22].

Hardness and initial modulus (*Figure 10*) decrease with increasing M_{pre}, mainly because of the decreased crosslinking density. Tensile strength decreased because of the decreased number of crosslinks, and elongation at break increases because of the increased phase separation (*Figure 11*).

Effect of extender functionality (f)

These experiments were performed with 6 wt% DMPA, which was completely neutralized. The only variable was functionality (f) of the chain extender, which varied in the range 2–5. The elastic modulus (*Figure 12*) generally increases with increasing f. Since M_{pre} is the same regardless of f, M_c is the same. However, with increasing f the PUs become more tightly packed since more isocyanate termini are anchored on one extender. This is, soft segments and hard segments are packed tightly together since the freedom of segment conformation is restricted. This picture may be compared with increased hard segment cohesion as the *DN* increases, where phase separation increased with *DN* to result in a decreased T_{gs}. The increased cohesion of the PUs would give an increased modulus, even in the glassy state, because of the increased rigidity.

As expected, T_{gs} increases and the higher T_{gh} decreases with increasing f, indicative of increased phase mixing. Increased phase mixing is evident from the shape of the peak, i.e. the hard segment transition is a well-defined peak with $f = 3$ and 4, but it is merely a shoulder with $f = 5$.

As expected the hardness and initial modulus of the films increase with increasing f (*Figure 13*). The increased

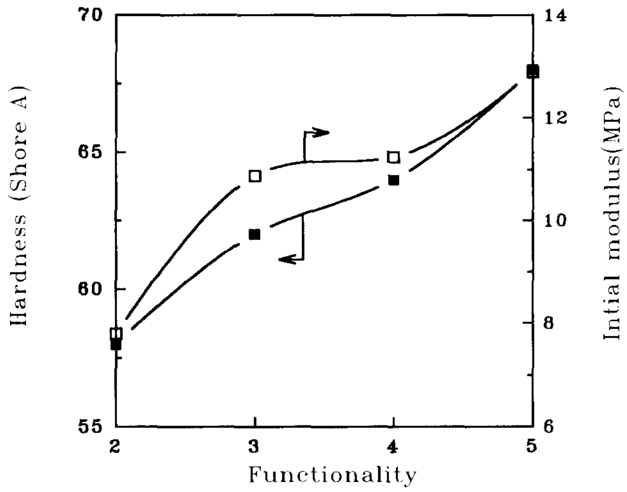

Figure 13 Hardness and initial modulus of emulsion-cast films prepared with different types of chain extender

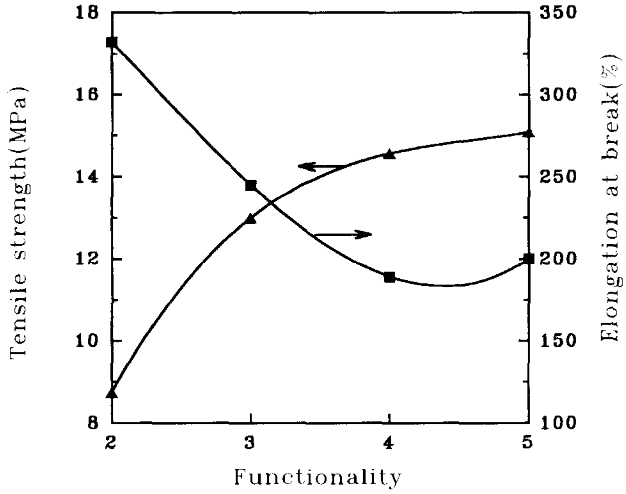

Figure 14 Tensile properties of emulsion-cast films prepared with different types of chain extender

tensile strength and decreased elongation at break with increasing *f* are other indirect verifications of the increased cohesion between PU segments and increased phase mixing (*Figure 14*).

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