

Modification of Waterborne Polyurethanes by Acrylate Incorporations

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SYNOPSIS

Waterborne polyurethanes (PUs) were hydrophobically modified using various types of acrylate monomers. PUs having hydroxy ethylacrylate (HEA) terminal groups were first obtained following a prepolymer mixing process. These PU base polymers were then chain extended with acrylate monomers via a radical polymerization mechanism. The effect of the overall composition, base polymer molecular weight, and type of acrylate were studied in terms of water swell and contact angle, as well as mechanical and dynamic mechanical properties of the emulsion cast film. It was found that water resistance, hardness, modulus, and tensile strength of the waterborne PU can be dramatically increased by acrylate incorporation. The reinforcing effect was more pronounced with multifunctional monomers, probably due to the crosslinking effect. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

As compared with solvent-borne polyurethanes (PUs), waterborne PUs are nontoxic, nonflammable, and do not pollute the air, and their film forming properties are generally good.¹⁻⁴ Typically, waterborne PUs are prepared in the form of ionomers which contain pendant acid or tertiary nitrogen groups. The potential ionic groups are neutralized or quarternized to form salts.^{5,6} These ionic centers positively contribute to the mechanical strength and elastomeric character of the materials.^{1,3} However, these ionic groups are hydrophilic in nature and provide the waterborne PUs with inferior solvent resistance and water resistance.⁴ Better solvent resistance could be obtained by higher crosslinking densities, which invariably lead to higher glass transition temperatures and hence particles will not coalesce to form films at normal drying temperature. Better water resistance could be obtained by incorporating a minimum amount of ionic groups, but this leads to unstable emulsions.

One method to resolve this problem is the post-treatment of waterborne PUs. That is, hydrophobic unsaturated monomers are grafted onto the PU backbone.⁷⁻⁹ Grafting is usually accomplished in aqueous media using emulsion polymerization techniques. Improved mechanical properties as well as water resistance and solvent resistance are generally obtained by grafting various acrylate monomers onto the PU. Interpenetrating polymer networks based on waterborne PU and polyacrylate have also been considered recently.¹⁰

This article considers modification of waterborne PUs using hydroxy acrylate and acrylate monomers. Ideally, hydroxyethyl acrylate (HEA) terminated PU base polymers are synthesized. These polymers are then dissolved in acrylate monomers, followed by self-emulsification by adding water to the PU base polymer solution. The acrylate monomers are subsequently polymerized via radical polymerization. Crosslinked PU acrylates, in addition to linear polyurethanes, and linear polyacrylate are produced. The effects of overall compositions, base polymer molecular weight, and type of acrylate monomers have been studied in terms of water resistance, as well as mechanical and dynamic mechanical properties of the emulsion cast films.

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Table I Feed Composition (in grams)

A. Variation of MMA Content								
Run #	PCL	H ₁₂ MDI	DMPA	HEA	TEA (mL)	MMA	DMF	H ₂ O
A1	28.65	10.328	2.025	1.882	2.10	0	9.0	126.0
A2	25.79	9.295	1.8225	1.694	1.90	4.5	8.1	126.9
A3	22.92	8.263	1.620	1.506	1.69	9.0	7.2	127.8
A4	20.06	7.230	1.4175	1.317	1.48	13.5	6.3	128.7
A5	17.19	6.197	1.215	1.129	1.27	18.0	5.4	129.6
B. Variation of Base Polymer Molecular Weight								
Run #	PCL	H ₁₂ MDI	DMPA	HEA	TEA (mL)	MMA	DMF	H ₂ O
B1	22.24	8.590	1.620	1.860	1.687	9.0	7.2	127.8
B2	22.92	8.263	1.620	1.506	1.687	9.0	7.2	127.8
B3	23.39	8.041	1.620	1.264	1.687	9.0	7.2	127.8
B4	23.72	7.880	1.620	1.090	1.687	9.0	7.2	127.8
C. Variation of Acrylate Type								
Run #	PCL	H ₁₂ MDI	DMPA	HEA	TEA (mL)	Acrylate	DMF	H ₂ O
C1	22.92	8.263	1.620	1.506	1.687	MMA(9.0)	7.2	127.8
C2	22.92	8.263	1.620	1.506	1.687	EMA(9.0)	7.2	127.8
C3	22.92	8.263	1.620	1.506	1.687	<i>t</i> -BMA(9.0)	7.2	127.8
C4	22.92	8.263	1.620	1.506	1.687	CHMA(9.0)	7.2	127.8
C5	22.92	8.263	1.620	1.506	1.687	TPGDA(9.0)	7.2	127.8
C6	22.92	8.263	1.620	1.506	1.687	TMPTA(9.0)	7.2	127.8

EXPERIMENTAL

Materials

Poly (caprolactone) glycol (PCL, $M_n = 2000$, Daicel) was dried and degassed at 80°C, 1 ~ 2 mm Hg, until no bubbling was observed. Dimethylol propionic acid (DMPA; Aldrich) was purified and dried at 100°C for 2 h in a drying oven. Extra-pure grades of dimethylformamide (DMF) and triethylamine (TEA) were dried over a 3-Å molecular sieve before use. The 2-hydroxy ethylacrylate (HEA), methyl methacrylate (MMA), ethyl methacrylate (EMA), *t*-butyl methacrylate (*t*-BMA), cyclohexyl methacrylate (CHMA), tripropylene glycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA) were purified and dried by fractional distillation in vacuum and stored under inert atmosphere. Extra-pure grades of methylene bis(4-cyclohexyl isocyanate) (H₁₂MDI), dibutyltin dilaurate (DBT), and potassium persulfate (KPS) were used as received.

Prepolymer Synthesis

The basic formulations are given in Table I. A 500-mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and pipet outlet was used as a reactor. Reaction was carried out in a constant-temperature oil bath. HEA and H₁₂MDI were first mixed and reacted at 45°C for 2 h to form HEA-H₁₂MDI dimeric units. Since H₁₂MDI was in excess, free H₁₂MDI also exists. Then PCL, DMPA, and DBT (0.03 wt % based on base polymer) were fed to the reaction mixture, and urethane forming reactions proceeded during the next 3 h at 80°C. The change of NCO value during the reaction was determined using a standard dibutylamine back-titration method.¹¹ Upon obtaining the theoretical NCO value, the base PUs were cooled to 60°C, and the neutralizing solution—TEA dissolved in DMF (5 wt % based on PU)—was added and stirred for 1 h while maintaining the temperature at 60°C, and acrylate monomers were then fed and thoroughly

mixed. Detailed procedures are available in our earlier articles.¹²⁻¹⁵

Emulsification and Radical Polymerization of Acrylate Monomer

PU emulsion was obtained by adding water (35°C) to the mixture (60°C). Since the water addition rate is a critical parameter to obtain a stable dispersion, a tubing pump was used and water was added for 6 min at a constant flow rate. The phenomenon of phase inversion, viscosity, and conductivity change during the emulsification process are well documented in Dieterich.¹ KPS (0.5 wt % based on total solid) dissolved in water was then fed to the emulsion dropwise for 30 min, and radical polymerization was carried out for the next 3 h. The resulting product was a stable emulsion with solid content of about 25%.

Tests

The swell of film in water was measured by immersing a film into a waterbath at room temperature until the film was in equilibrium with water. The percent of swell was calculated by

$$\% \text{ swell} = \frac{W - W_o}{W_o} \times 100$$

where W_o and W are the original and equilibrium weight of the films, respectively.

Contact angle at room temperature was measured by dropping water on the film (Erma G-1 type). Dynamic mechanical properties were measured using a Rheovibron (Orientec, DDV 01-FP) at 11 Hz, with a sample size of $0.03 \times 0.2 \times 3$ cm. Tensile properties of emulsion cast films were measured using a tensile tester (Tinius Olsen 1000) at a cross-head speed of 50 mm/min, and an average of at least five measurements was taken to report.

Films for the aforementioned tests 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 mm Hg. Microtensile test specimens were prepared according to ASTM D-412 using a punch. ASTM stands for "American Standards of Testing Materials. However, ASTM is so common and it is commonly used as it is.

RESULTS AND DISCUSSION

Effect of MMA Content

In these experiments, the composition of MMA in the feed varied from 0 to 40 wt % based on the total solid (Table IA). Figure 1 shows the effect of MMA composition on the water swell and contact angle of the emulsion cast films. As expected, water swell and contact angle of the film, respectively, decreases and increases significantly with the increase of MMA composition. This implies that the waterborne PUs have been hydrophobically modified with MMA incorporations.

Mechanical properties (hardness, modulus, and tensile strength) have also been greatly improved by the present method of modification (Fig. 2). The increase is mild up to 20 wt % MMA and is much more pronounced beyond this composition. The earlier mild increase may be due to the dilution effect often observed in fiber-reinforced elastomer.^{16,17}

Figure 3 shows the dynamic mechanical properties of the emulsion cast films. As expected, the glassy state extends to higher temperature and the rubbery plateau modulus is generally higher as the MMA content increases [Fig. 3(a)]. A single loss peak (E'') is defined regardless of the MMA content [Fig. 3(b)]. However, the peak temperature moves toward the higher temperature, and the peak becomes broader as the MMA content increases. The broadening of the loss peak may indicate that the relaxation is not a single one and comprises of several consecutive ones. The increased peak temperature would mean the mean relaxation occurs at

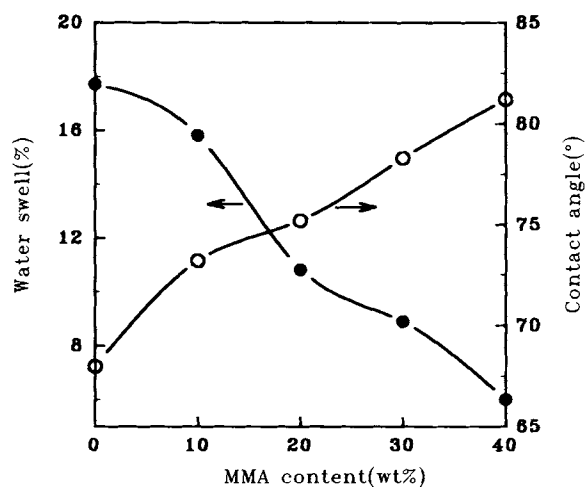


Figure 1 Water swell and contact angle of the emulsion cast films with water as a function of MMA content.

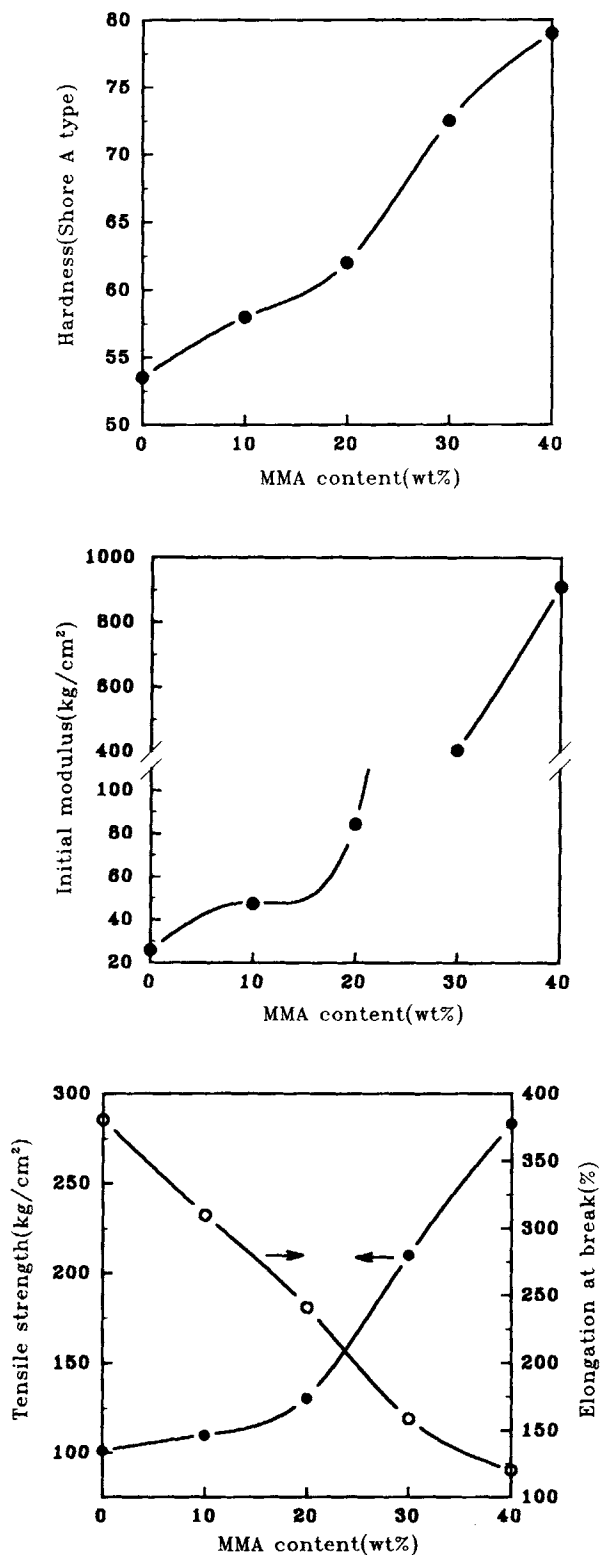


Figure 2 Mechanical properties of emulsion cast films as function of MMA content: hardness, modulus, and tensile strength and elongation at break.

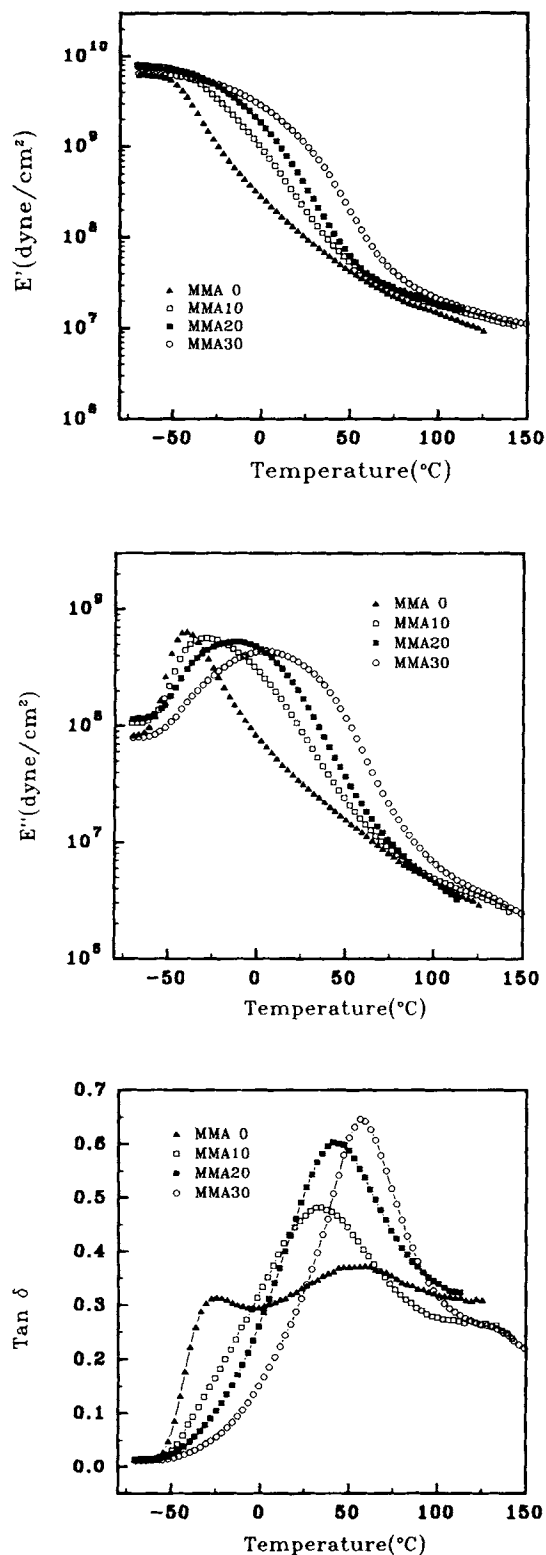


Figure 3 Dynamic mechanical properties of emulsion cast films as a function of MMA content: storage modulus (E'), loss modulus (E''), and $\tan \delta$.

higher temperature, indicative of increased film rigidity with MMA incorporation. The $\tan \delta$ [Fig. 3(c)] peak of PU shows two peaks which are not clearly resolved, one around -25° and the other around 55°C , each corresponding to the soft domain and hard domain glass transition temperature (T_g). It seems that $\tan \delta$ is much more sensitive to the relaxation of PUs than loss modulus. Compared with PU containing no HEA termini, both soft and hard domain T_g of the HEA encapsulated PU are higher by several degrees.¹⁸ On the other hand, the MMA modified PUs show one single peak for PU domains with its temperature increasing with MMA content, and another ridge at around 130°C . It seems that the ridge around 130°C corresponds to the sequence of MMA units, or polymethyl methacrylate homopolymers.

Effect of Base PU Molecular Weight

These experiments were done at a fixed MMA composition (20 wt %) in feed, and the molecular weight of base polymer (PU) was varied from 4000 to 7000 (Table IB).

Figure 4 shows that hardness, modulus, and tensile strength decrease and elongation at break increases with increasing base polymer molecular weight. The base polymers are PUs having HEA, hydroxy, or isocyanate termini. When the base polymers have HEA termini, which are extended by acrylate monomer, the base polymer molecular weight corresponds to the molecular weight between crosslinks (M_c). However, this idea is not quantitatively implemented in our system because not all of the acrylate monomers add to the HEA termini and there exist acrylate homopolymers and PUs that have no HEA terminal. However, the decrease of hardness, modulus, and tensile strength with base polymer molecular weight is qualitatively in agreement with increasing base polymer molecular weight. In amorphous polymers, hardness, tensile modulus, and strength are inversely proportional to the molecular weight between crosslinks—namely, the base PU molecular weight.

Effect of Acrylate Type

These experiments were done at a fixed acrylate composition (20 wt %) and base PU molecular weight (5000) (Table IC). Four types of monoacrylate, one diacrylate, and one triacrylate were used.

Generally, water swell is decreased and contact angle is increased with increasing functionality of

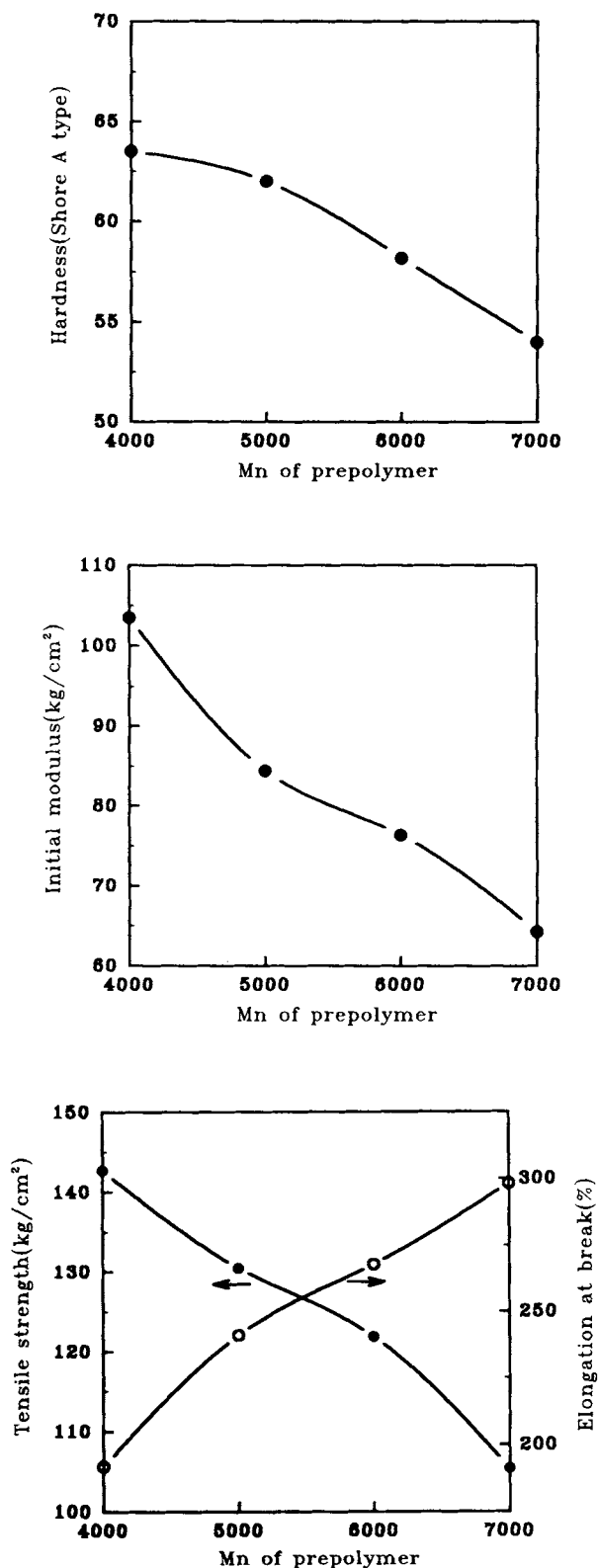


Figure 4 Mechanical properties of emulsion cast films as a function of base polymer molecular weight: hardness, modulus, and tensile strength and elongation at break.

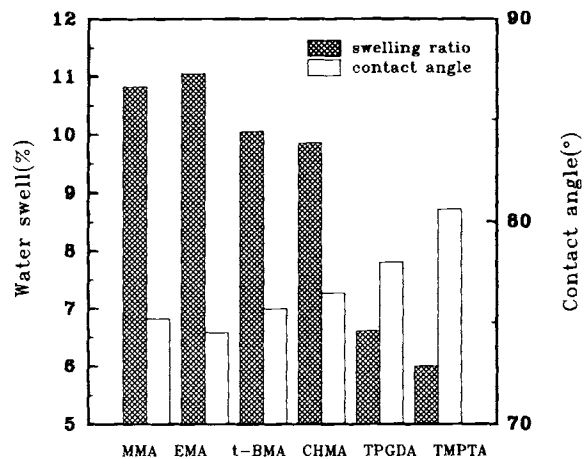


Figure 5 Water swell and contact angle of the emulsion cast films as a function of acrylate type.

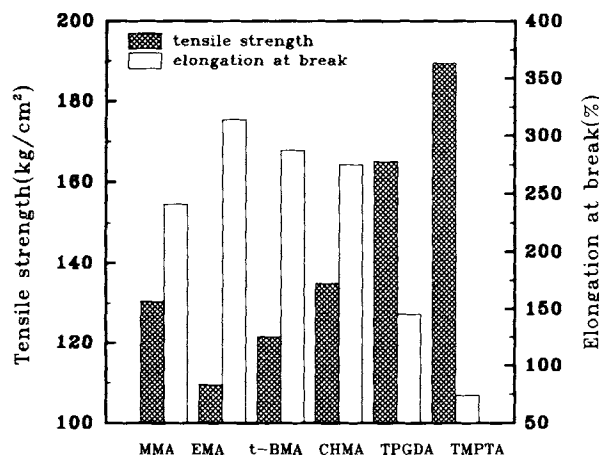
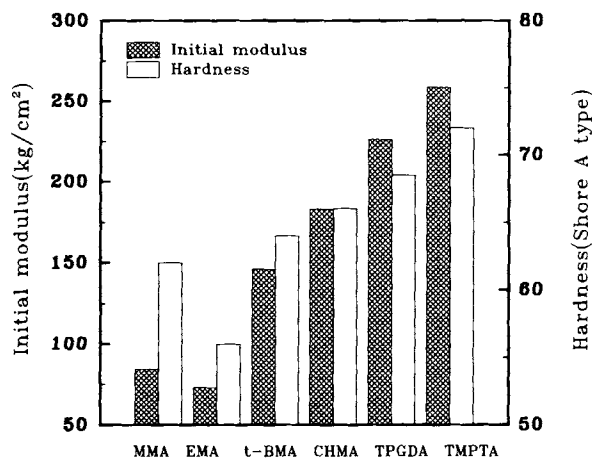


Figure 6 Mechanical properties of emulsion cast films as function of acrylate type: hardness and modulus, and tensile strength and elongation at break.

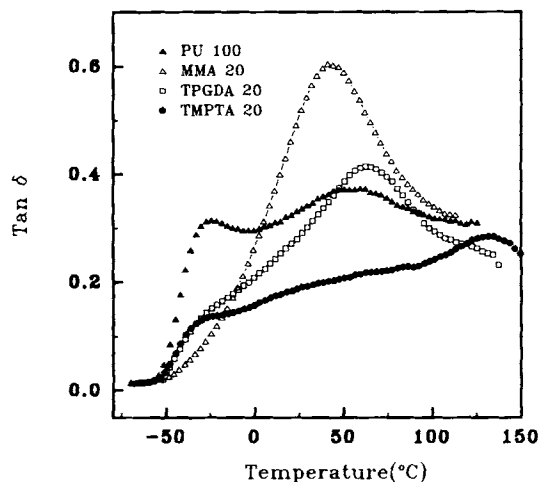
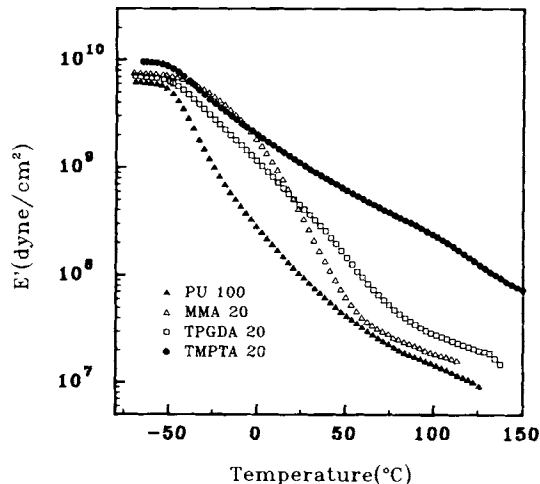


Figure 7 Dynamic mechanical properties of emulsion cast films as a function of monomer functionality: storage modulus (E') and $\tan \delta$.

the acrylate (Fig. 5). This is presumably due to the increased crosslinking density with multifunctional monomer. Regarding the monoacrylate type, monomer with a larger substituent generally shows relatively little swell and a larger contact angle. It seems that larger alkyl substituents add hydrophobicity to the monomer, leading to the increased contact angle with water and decreased swell in water.

Hardness, modulus, and tensile strength (Fig. 6) also increase with the increase of monomer functionality, due mainly to the increased crosslinks. Among monofunctional acrylates, a larger substituent generally gives higher hardness and modulus. MMA gives better mechanical properties than EMA, presumably by a different mechanism. MMA has the smallest substituent among the methacrylates being used; hence it gives minimum main chain dis-

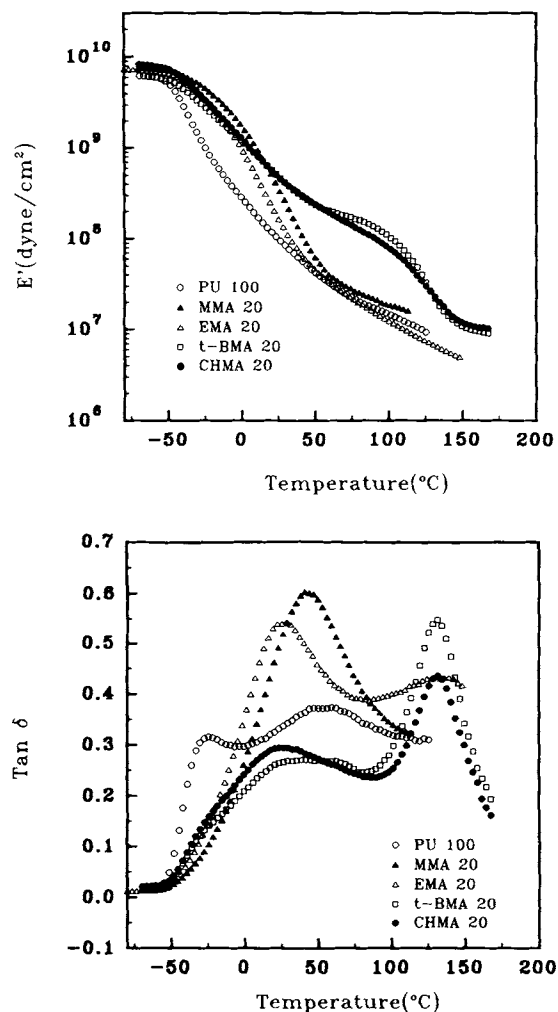


Figure 8 Dynamic mechanical properties of emulsion cast films as a function of monoacrylate type: (a) storage modulus (E') and (b) $\tan \delta$.

turbance leading to close chain packing. Substituents larger than ethyl group (EMA) may provide the polymers with sufficient rigidity and strength over the close packing effect of MMA.

The effects of monomer functionality on dynamic mechanical properties of the films are shown in Figure 7. The incorporation of acrylate gives PU significantly higher storage modulus, in proportion to its functionality due to the increased crosslinking density (i.e., TMPTA is by far the highest). The glassy state of MMA modified PU extends to a higher temperature than the other monomers, indicative of close packing due to the relatively small pendant methyl groups. The $\tan \delta$ curve of PU shows two broad peaks, although they are not sharply resolved. With MMA incorporation, the lower temperature peak (soft domain T_g) completely disappears and a well-defined single

peak appears at about 40°C, which is lower than the higher temperature peak of PU (hard domain T_g) by about 10°C. With TPGDA and TMPTA incorporations, the lower temperature peak becomes a mere shoulder and the higher temperature one becomes a mere ridge and moves toward a still higher temperature. It seems that monoacrylates contribute to the microphase mixing of PU acrylates, whereas the multifunctional extenders do not since the penetration of PU soft segment into the crosslinked hard domains is less plausible.

Substituent effects of monoacrylate on the dynamic mechanical properties are shown in Figure 8. In general, larger alkyl substituents (i.e., *t*-BMA and CHMA) give higher storage moduli. MMA extends the glassy state up to the highest temperature, and this gives a higher storage modulus at below-transition temperatures. Regardless of the type of monoacrylates, two $\tan \delta$ peaks are defined. The lower temperature peak should correspond to the T_g of the PU-rich phase and the higher one to the T_g of the acrylate phase. It is seen that the T_g of the PU-rich phase generally decreases with increasing substituent size, whereas the T_g of the acrylate phase is independent of the type of substituents. It is generally accepted that the acrylate phase is more compatible with the hard segment of PU, rather than the soft segment, due to the similar polarity and hydrogen bonding formation between urethane NH and acrylate carbonyls.¹⁹ Consequently, larger alkyl substituents would lead to a relatively poor phase mixing between PU and the acrylate phase, resulting in the decreased T_g of PU-rich phases. Relatively higher and independent T_g of the acrylate phase, as compared with T_g of acrylate homopolymers [85° (EMA) ~ 115°C (*t*-BMA)], should in part be due to the crosslinkings. Further studies on product characterizations and morphology should follow to clarify the dynamic behavior.

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