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Structure–property relationships of polyurethane anionomer acrylates

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Polyurethane (PU) ionomer acrylates and non-ionomer acrylates were synthesized from poly(propylene glycol) (PPG), isophorone diisocyanate (IPDI), dimethylolpropionic acid (DMPA), 2-hydroxyethylacrylate (HEA), and *N*-vinylpyrrolidone (NVP), tripropyleneglycol triacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), and were characterized in terms of water swell, mechanical, and dynamic mechanical properties in response to their structure. At fixed DMPA content (PPG/DMPA 8/2), neutralization caused an inward migration of soft segment glass transition (T_{gs}) and hard segment glass transition (T_{gh}) in PU acrylate without diluent. However, with increasing DMPA (ionized) content, T_{gh} increased keeping T_{gs} constant, together with an increase in equilibrium swell, tensile modulus, tensile strength, and the rubbery plateau modulus. At a fixed diluent level (20%), tensile strength and T_{gh} increased in the order of no diluent < TPGDA < TMPTA < NVP, and the tensile modulus, no diluent < TPGDA < TMPTA ≈ NVP. The rubbery plateau modulus ($E_N{}^{\circ}$) was well defined increasing in the order of no diluent < TPGDA < TMPTA. However, $E_N{}^{\circ}$ was not defined with NVP. Regarding the effect of TPGDA level, $E_N{}^{\circ}$ increased in magnitude, and T_{gh} shifted to the higher temperature with increasing TPGDA level. Copyright © 1996 Elsevier Science Ltd.

(Keywords: structure; mechanical properties; polyurethane)

INTRODUCTION

Polyurethane (PU) ionomers are segmented copolymers that consist of alternating soft and hard segments, with a minority of repeat unit carrying pendent acid or tertiary nitrogen groups which are neutralized to form salts[1-3]. The presence of ionic species in PU ionomers has a considerable impact on physical properties[4-9]. PU ionomers are of considerable scientific and commercial interest due to their unique structure–property relationships and the fact that they can be utilized in the form of water dispersions for coatings and adhesives[10].

U.v. curing saves energy, and reduces or eliminates solvent emission compared to solvent-based system. This technique has become commercially important in applications ranging from protective coatings[11-13] to photoresists[14,15] for fabrication of microelectronic devices. Recently, u.v. curing has also been used in photolithography[16] and polymer-dispersed liquid crystals (PDLC)[17]. In photolithographic applications, a u.v. beam is repeatedly projected onto photocurable resin along every layer of the sliced image of the model, and creates a complex structure which is not possible with any conventional manufacturing method. In PDLC composite, u.v. curing modifies the polymer–liquid crystal interfaces, thereby enhancing the electro-optic performance of the composite films.

U.v.-curable systems are typically composed of reactive urethane oligomers, reactive diluents, and photoinitiators. The reactive urethane oligomer is typically segmented polyurethane oligomers which are end-capped with hydroxyalkyl acrylate or methacrylate such as 2-hydroxyethylacrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA). The microphase separation of the urethane segments, which is mainly governed by the soft segment length and type, is a key parameter in controlling the dynamic mechanical properties of the PU acrylates[18-20].

The reactive diluents are acrylic monomers which are added to modify the properties of PU acrylates and to reduce the viscosity of the precursor liquids. The acrylated urethanes ideally combine the high abrasion resistance, toughness, tear strength and good low temperature properties of PU with the superior optical properties and weatherability of polyacrylates[18,21,22]. Generally monofunctional acrylates lead to decreased modulus and increased ductility, whereas multifunctional acrylates such as tripropyleneglycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA), and monofunctional *N*-vinylpyrrolidone (NVP) lead to the opposite[18]. In addition, multifunctional diluents show higher response to radiation.

The reactive diluent phase is more compatible with the hard segments of PU rather than the soft segments, due mainly to the similar polarity and hydrogen-bond formation between urethane NH and acrylate carbonyls. Following Koshiba *et al.*[19], increasing the reactive diluent content permits the development of a second, high glass transition temperature (T_g) phase, thereby leading to the increased modulus and strength. The effect

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of acrylate incorporation on phase behaviour should depend on the phase morphology of PU prior to acrylate incorporation, and the type of acrylate, i.e. the functionality and properties of the acrylate homopolymer. U.v. curing is induced by the incorporation of a suitable ketone-type initiator, in combination with proton donors, which produce free radicals upon exposure to u.v.[23]. Recently a series of u.v.-autocurable multiacrylate resins has also been investigated[24].

Earlier works and applications of this technique have been well documented in books[25,26], patents[27,28] and reviews[18–20]. A number of factors influence the physical properties of PU acrylates. Among others, reactive diluents have most often been encountered[18,19,29,30]. Soft segment type and length have also been extensively investigated[19,20,31]. Rather less work has been devoted to the hard segment type[19,31].

We consider the synthesis and properties of PU anionomer acrylates. PU anionomers were prepared from poly(propylene glycol) (PPG) ($M_n = 2000$), isophorone diisocyanate (IPDI), and dimethylolpropionic acid (DMPA), following a prepolymer mixing process[5–8]. PU acrylates were obtained by tipping the NCO-terminated prepolymers with HEA, followed by u.v. radiation (without diluent). Reactive diluents were subsequently added and cured.

The effects of ionic content, neutralization and type of neutralizing agent, concentration and average functionality of the reactive diluent have been studied in terms of water swell, mechanical, and dynamic mechanical properties.

EXPERIMENTAL

PPG was dried and degassed at 80°C, 1–2 mmHg until no bubbling was observed. Extra pure grade of IPDI (Scholven), dibutyltin dilaurate (DBT), benzophenone and *N*-methyldiethanolamine (MDEA) were used without further purification.

A 500 ml round-bottomed, four-necked separable flask with a mechanical stirrer, thermometer, condenser with drying tube, and a pippette outlet was used as reactor[5]. The reaction was carried out in a constant temperature oil bath. PPG, DBT (0.03 wt%) and DMPA were charged into the dried flask. While stirring, the mixture was heated to 90°C for about 30 min, followed by adding IPDI to the homogenized mixtures. The mixture was heated to 90°C for about 2 h to obtain NCO-terminated prepolymers. The change of NCO value during the reaction was determined using a standard di-*n*-butylamine back-titration[32]. Upon obtaining the theoretical value, the prepolymers were cooled to 60°C, and the neutralizing solution, i.e. triethylamine (TEA) or MDEA, was added and stirred for 1 h while maintaining the temperature at 60°C. The reaction mixture was cooled down to 40°C and HEA was added dropwise. Tipping of NCO-terminated prepolymer with HEA was done for 3 h below 45°C, and 30 min at 60°C. The progress of the reaction was also detected by measuring the NCO value.

The mixture of urethane acrylates, 3 wt% benzophenone (initiator) and reactive diluents were heated slightly above ambient temperature to ensure homogeneous mixing, followed by casting on a glass plate.

Films were about 1 mm in thickness for tensile specimens, and 0.3–0.4 mm for dynamic mechanical test specimens. The samples were irradiated from one side using an 80 W u.v. (365 nm) lamp for 30 s.

To measure the swell, films were immersed in water for 24 h at room temperature, and the percentage swell was determined by measuring the weight increase:

$$\%\ \text{swell} = \frac{w - w_0}{w_0} \times 100$$

where w_0 is the weight of dried film, and w is the weight of swelled film.

Tensile tests were performed following ASTM D-1822 using a tensile tester (Tinius Olsen 1000) at a crosshead speed of 5 mm min^{-1}, and an average of at least five measurements were taken to report. Dynamic mechanical tests were performed using a Rheovibron (Toyo Baldwin DDV-II) at 11 Hz.

RESULT AND DISCUSSION

Effect of DMPA content

Figure 1 shows water swell of the films having different PPG/DMPA compositions. At the earlier stage of swelling, swell generally increases as the DMPA content of PU decreases. However, at equilibrium, films containing a greater amount of DMPA show greater swellability. The film with the greatest PPG content (PPG/DMPA 9/1) shows a maximum swell in about 200 min. Since the PU oligomers were tipped with HEA and subsequently cured by u.v. irradiation, the molecular weight of the oligomer practically corresponds to the molecular weight between crosslinks (M_c). Therefore, as small molecular weight diol (DMPA) replaces high molecular weight polyol (PPG), M_c of PU acrylates decreases, which retards the swell of water into the film at an earlier stage of swelling. At a later stage, the equilibrium swell seems to be governed mainly by a thermodynamic parameter, i.e. the hydrophilicity of the film. The hydrophilicity of the film increases with the increase of DMPA content since DMPA has been

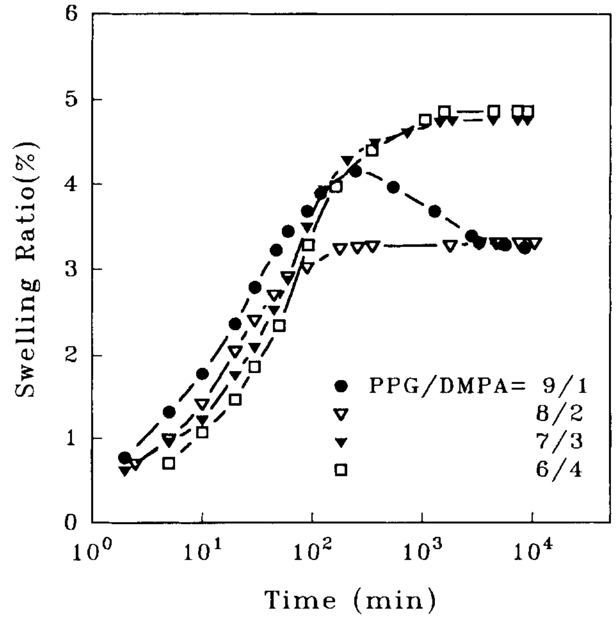

Figure 1 Time-dependent swell of PU anionomer acrylate films having different PPG/DMPA molar ratios

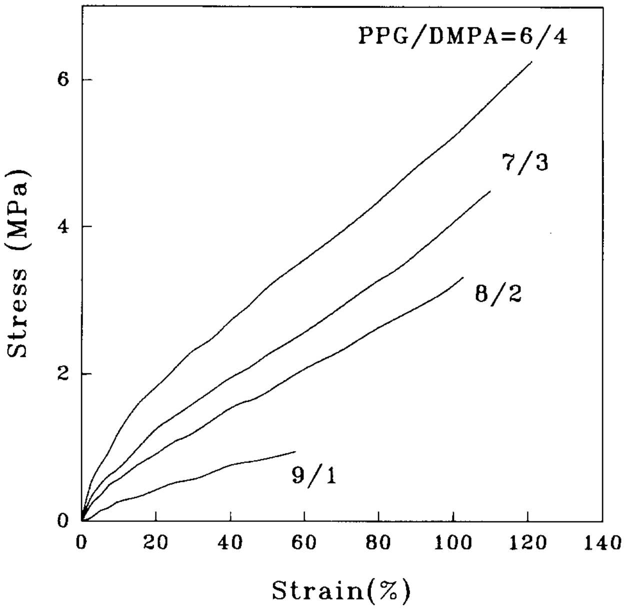

Figure 2 Stress–strain behaviour PU anionomer acrylate films having different PPG/DMPA molar ratios

neutralized with TEA to give an anionic species, which is hydrophilic in nature. A peak in the swell obtained with PPG/DMPA (9/1) film may imply that certain linear polymers or only slightly crosslinked ones are dissolved out of the film at high water content of the film. This seems possible only with hydrophilic polyols such as polyethylene glycol and PPG. The existence of such polymers is most probable with the greatest content of PPG since M_c is greatest in this material (see *Figure 3a*).

Figure 2 shows the stress–strain curve of these materials. As the DMPA content increases, modulus, strength and elongation at break generally increase. The increased hard fraction (IPDI + DMPA) of PU accounts for the augmented modulus and strength, whereas the increased elongation at break is due mainly to the increased soft segment–hard segment phase separation, to follow in dynamic mechanical measurements.

Figure 3 shows the dynamic mechanical properties of these materials. Generally, storage modulus increases and the rubbery plateau region emerges at higher temperature as the DMPA content increases (*Figure 3a*). The increase in rubbery modulus with increasing DMPA content is an indication of smaller M_c (ref. 33), resulting in the physical retardation of water swell in the earlier stage.

The tan δ peaks of these materials are shown in *Figure 3b*. In PPG/DMPA (9/1) material, the glass transition of the soft segment (T_{gs}) is well defined at about −37°C, whereas the hard segment glass transition (T_{gs}) is well defined at about −37°C, whereas the hard segment glass transition (T_{gh}) is a mere shoulder. As the DMPA content increases, two peaks are well defined, implying augmented soft segment and hard segment phase separations. The T_{gs} peak decreases in magnitude without changing its position, whereas the T_{gh} peak becomes well defined and increases in magnitude and shifts to the higher temperature. It seems that increasing the DMPA content permits the development of a high glass transition phase, thereby leading to the high strength (*Figure 2*) and modulus above T_{gs}, whereas increased phase separation leads to the increased elongation at break (*Figure 2*). Below T_{gs}, high T_{gh} and phase separation embrittle the materials and cause a decrease in storage modulus (*Figure 3a*)[18].

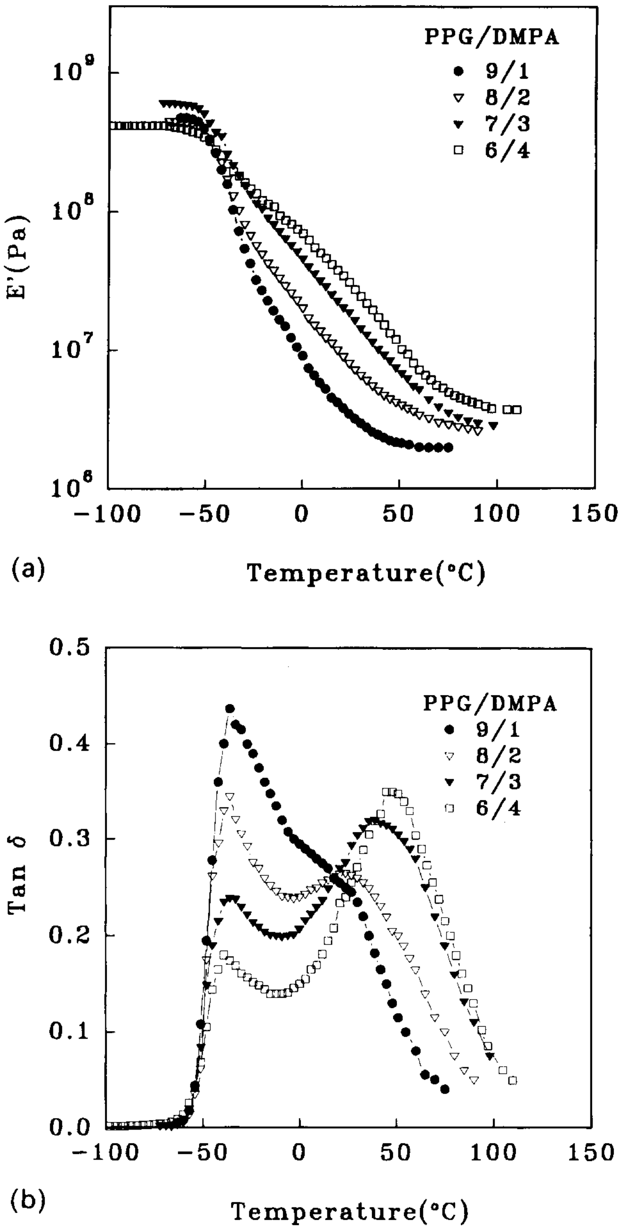

Figure 3 Dynamic mechanical properties of PU anionomer acrylate films having different PPG/DMPA molar ratios: (a) storage modulus; (b) tan δ

Effect of neutralization and neutralization agent

This series of materials was prepared with PPG, IPDI and DMPA. In one case DMPA was not neutralized (non-ionomer), and in the other cases it was neutralized with TEA or MDEA (ionomer). *Figure 4* shows that TEA-neutralized material gives a somewhat higher water swell at the earlier stage as compared with the other two materials. At equilibrium, ionomers, especially MDEA-neutralized ones, are subject to more swelling with water. The higher equilibrium swell by ionomers is due to the hydrophilicity of ionic groups. The greater swell of the MDEA-neutralized ionomer over the TEA-neutralized one is probably the counter-ion effect. The solubility parameter of MDEA (25.09 $J^{1/2}\,cm^{-3/2}$) is closer to that of water (48 $J^{1/2}\,cm^{-3/2}$) than is the value for TEA (15.40 $J^{1/2}\,cm^{-3/2}$)[34].

Figure 5 shows the stress–strain behaviour of these materials. No significant difference is found in tensile properties. However, the TEA-neutralized material has slightly higher strength and elongation at break, and the MDEA-based one has slightly lower values compared to the non-ionomer. The subtle difference is probably due to the ionic interactions (TEA-based material), and u.v. instability and great moisture gain (MDEA-based material).

Dynamic mechanical properties of these materials are shown in *Figure 6*. Regardless of neutralization, these materials are all phase-separated since they show two tan δ peaks (*Figure 6b*). Upon neutralization, the two glass transition peaks migrate inwards, indicating that phase mixing is enhanced in ionomers, especially in the MDEA-neutralized one. Below and above *c.* 0°C, the non-ionomer has slightly lower and higher storage modulus, respectively, than the ionomer due to its lower T_{gs} and higher T_{gh}, which is driven by the greater extent of phase separation of the non-ionomer.

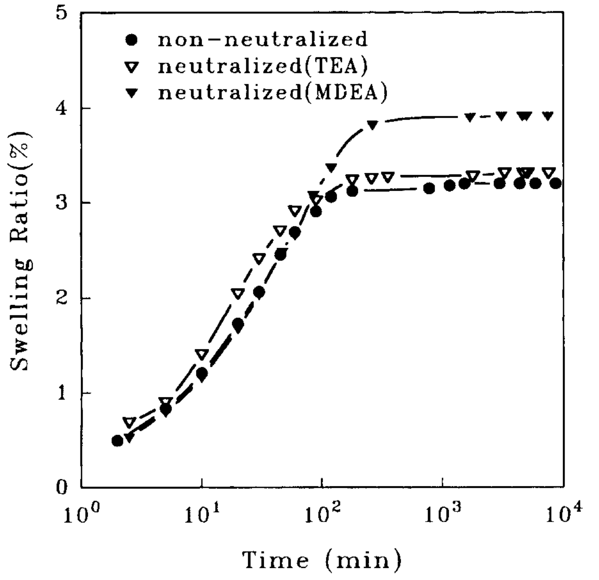

Figure 4 Effect of neutralization and neutralizing agent type on the time-dependent swell of PU acrylate films (PPG/DMPA molar ratio = 8/2)

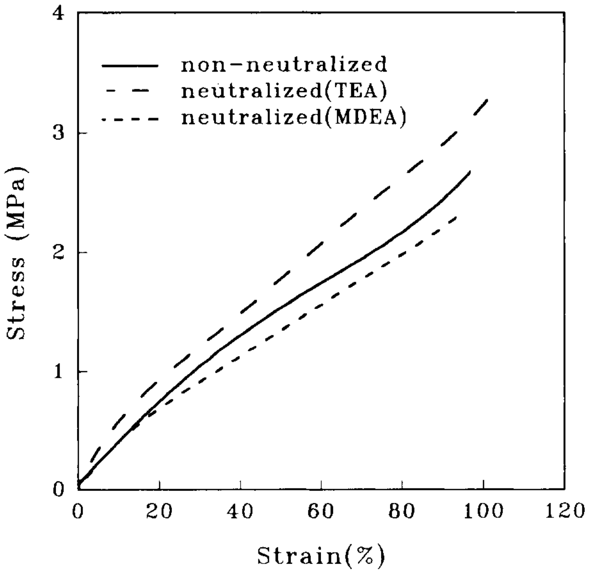

Figure 5 Effect of neutralization and neutralizing agent type on stress–strain behaviour PU acrylates (PPG/DMPA molar ratio = 8/2)

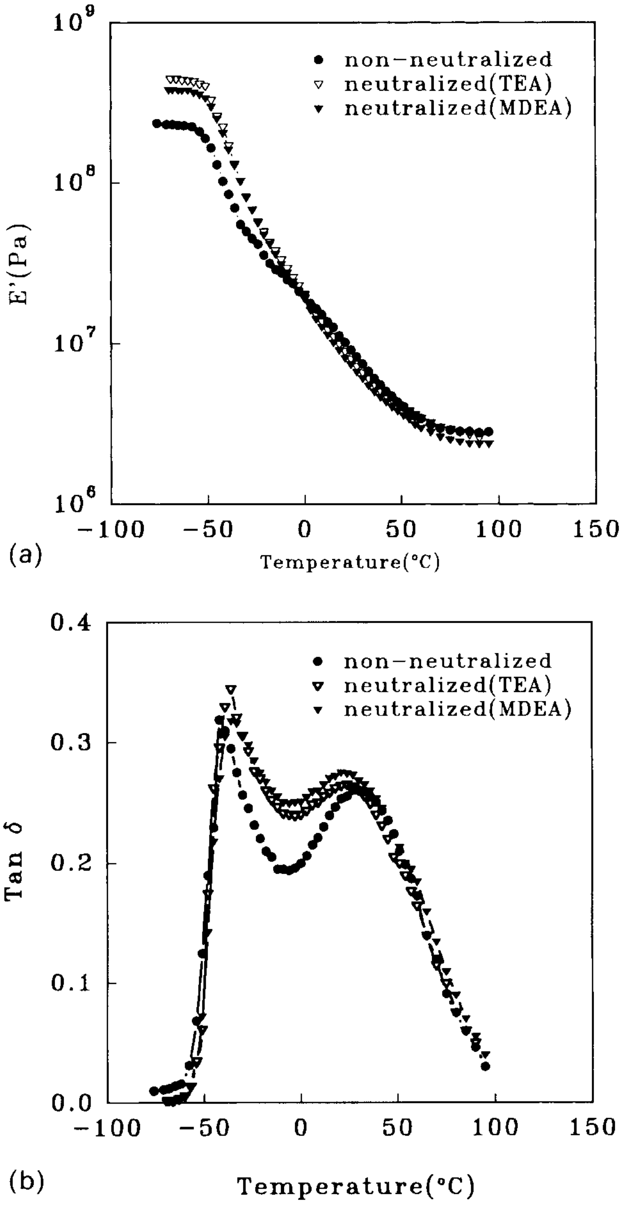

Figure 6 Effect of neutralization and neutralizing agent type on dynamic mechanical properties of PU acrylates: (a) storage modulus; (b) tan δ

Effect of diluent type

The effect of diluent type on swellability has been examined for PPG/DMPA (8/2) film (*Figure 7*). NVP incorporation is most vulnerable to water swell, and TMPTA has the greatest resistance. The former case is mainly due to the more hydrophilic nature of NVP, and the fact that it has the lowest crosslink density. Accordingly, the swell resistance of film with TMPTA

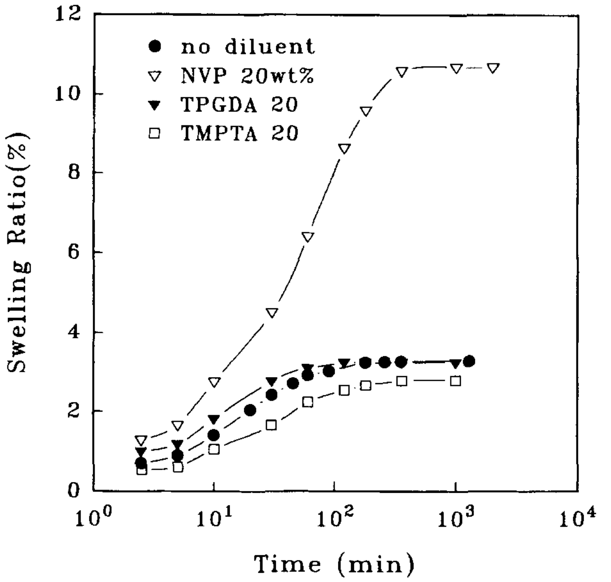

Figure 7 Effect of diluent type on the time-dependent swell of PU anionomer acrylate films (PPG/DMPA molar ratio = 8/2)

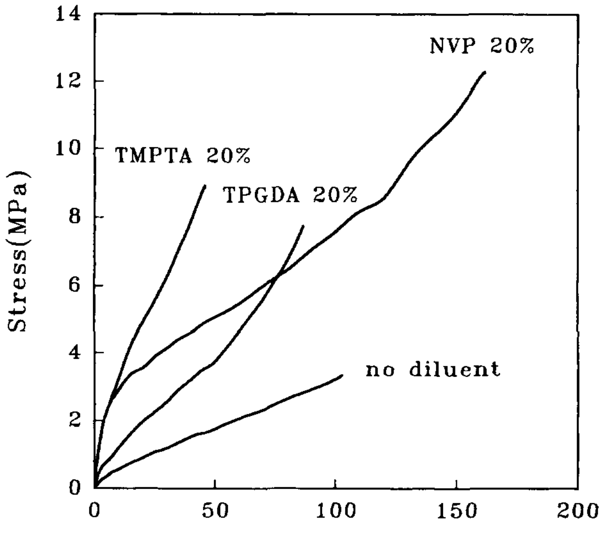

Figure 8 Effect of diluent type on stress–strain behaviour of PU anionomer acrylate films (PPG/DMPA molar ratio = 8/2)

incorporated is due to this material having the highest crosslink density. The relative crosslink density of these materials is visualized in the dynamic mechanical measurements to follow. It is surprising that TPGDA incorporation provides the film with slightly higher swell as compared to the film having no diluent. It seems that the hydrophilicity of reactive diluent is more important than the crosslinking with regard to swell.

The effect of different types of diluent on stress–strain behaviour is shown in *Figure 8*. Regardless of diluent type, modulus and toughness (area under the curve) increase with the addition of diluent. Among multifunctional diluents, TMPTA gives higher modulus and smaller elongation at break, due to the greater crosslinking density of this material. Notably, NVP gives the greatest strength and elongation at break, thus giving the greatest toughness, keeping the modulus similar to TMPTA. The augmented modulus and strength by NVP incorporation is attributed to the superior properties of NVP homopolymer[19]. On the other hand, the surprisingly great elongation at break mainly is due to the linear nature of NVP polymer.

Dynamic mechanical properties of these materials are shown in *Figure 9*. PU acrylate without diluent shows two glass transition peaks at about −40°C and 30°C, each corresponding to T_{gs} and T_{gh} (*Figure 8b*). With the incorporation of reactive diluent (20%), two peaks are again well defined, implying that a good phase separation is obtained despite the fact that the materials are crosslinked. The T_{gs} peak decreases in magnitude without changing its position at *c.* −40°C, corresponding to the typical transition temperature of PPG-containing soft segment, whereas the T_{gh} peak shifts to the higher temperature in the increasing order of no diluent < TPGDA < TMPTA < NVP. The increase in T_{gh} with

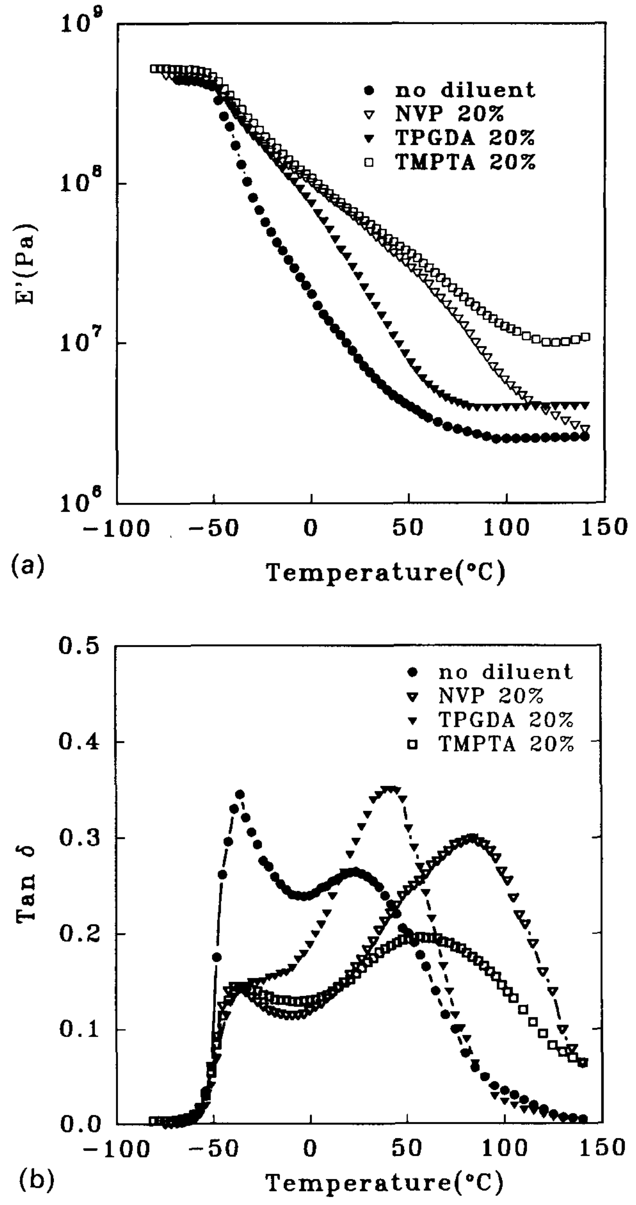

Figure 9 Effect of diluent type on dynamic mechanical properties of PU acrylates: (a) storage modulus; (b) tan δ

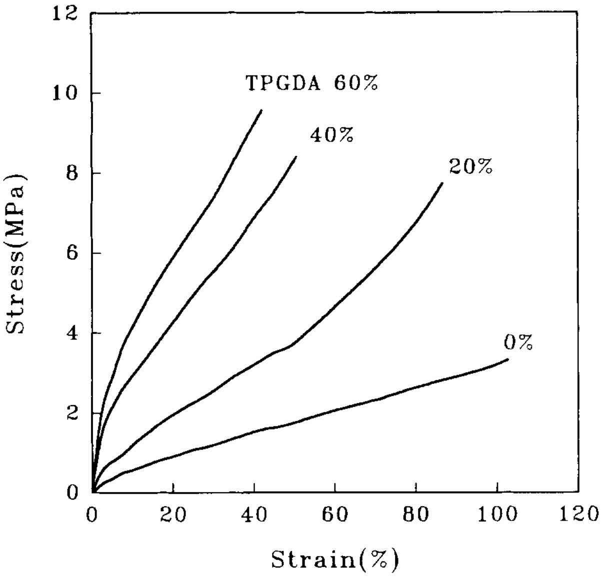

Figure 10 Effect of diluent level on stress–strain behaviour of PU anionomer acrylate films (PPG/DMPA molar ratio = 8/2)

TPGDA and TMPTA is mainly caused by the increased crosslinking density, as evidenced from the increased rubbery plateau modulus (*Figure 9a*). On the other hand, the increase in T_{gh} with NVP is due to the higher glass transition temperature of NVP homopolymer which is about 100°C[18,19]. The greatest increase in T_{gh} with NVP accounts for the increased tensile modulus (*Figure 8*) and storage modulus around room temperature. It should be noted that NVP incorporation does not define the rubbery plateau, and the modulus in the plateau region falls below the TPGDA and TMPTA incorporation. This is due to the linear nature of NVP polymer, resulting in the greater M_c of PU acrylate.

Effect of diluent level

The effects of diluent level on mechanical and dynamic mechanical properties were studied with TPGDA. *Figure 10* shows that tensile modulus and break strength increase, and elongation at break decreases with increasing TPGDA level. With the increase of TPGDA level, the storage modulus (*Figure 11a*) increases, the rubbery plateau region emerges at higher temperature and the T_{gh} peak shifts to the higher temperature, while the T_{gs} peak becomes a shoulder with decreasing magnitude. These mechanical and dynamic mechanical property variations with TPGDA are caused mainly by the increased crosslinking density, as noted from the increase of rubbery modulus. The shift of T_{gh} towards the higher temperature, keeping T_{gs} constant, broadens the temperature difference between T_{gh} and T_{gs}, and this would not mean greater phase separation. Once soft segment–hard segment phase separation increases, the outward migration of both glass transition peaks is expected. Therefore, the shift of T_{gh} to the higher temperature is due mainly to the increased hard segments and crosslinking within the hard segment domains. A linear increase in T_g with increasing crosslinking density is typical of rubber elastomers[33], and it is generally seen (*Figure 11a*).

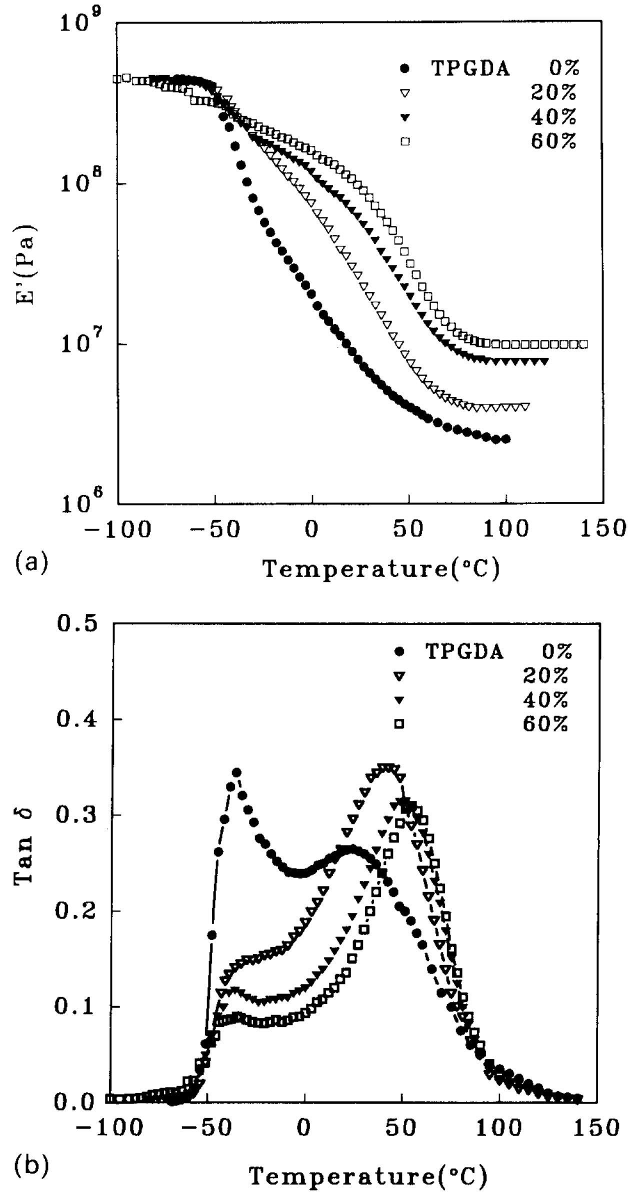

Figure 11 Effect of diluent level on dynamic mechanical properties of PU acrylates: (a) storage modulus; (b) tan δ

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