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Properties of ultra-violet curable polyurethane acrylates

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The relationship between the chemical structure and physical properties of ultra-violet cured isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI) based urethane acrylates were studied. The two systems were prepared with varying soft-segment molecular weight and cross-linker content. Dynamic mechanical test results show one-phase or two-phase materials may be obtained depending on the soft-segment molecular weight. With increasing soft-segment molecular weight, the polyol glass transition shifts to lower temperatures. Increasing the cross-linker content using either N-vinylpyrrolidone (NVP) or polyethyleneglycol diacrylate (PEGDA) causes an increase in Young's modulus and ultimate tensile strength. Cross-linking with NVP causes an increase in toughness in the two-phase materials and shifts the high-temperature glass transition peak to higher temperatures. In contrast, an increase in PEGDA content does not improve the toughness of the two-phase materials or affect the position of the high-temperature glass transition peak. Comparison of the tensile properties of the TDI- and IPDI-based systems shows no significant differences.

1. Introduction

High-intensity radiation from electron beams or ultra-violet (u.v.) sources has been shown to be an effective means to initiate polymerization in reactive urethane oligomer systems. The advantages of this technology include higher throughput, savings in energy and reduced or eliminated solvent emissions compared to the solvent based systems, since most formulations are 100% reactive oligomeric liquids. In general, the system employs a reactive mixture of urethane oligomers tipped with acrylic functionality, combined with vinyl monomers which are added to make harder products and/or to reduce the viscosity of the precursor liquid to obtain better processability.

The most important of these components in determining the ultimate physical properties of a flexible, radiation-curable coating system is the reactive urethane oligomer. Commercially-available urethane photopolymers [1–3] employ aromatic diisocyanates such as toluene diisocyanate (TDI) and xylidine diisocyanate (XDI). Isophorone diisocyanate (IPDI) is also a good candidate for the urethane component due to its inherent stability against u.v. degradation [4].

The starting material for the urethane oligomer is a low glass transition temperature, T_g, polyether or polyester macroglycol or triol "soft-segment". Polyester segments impart toughness, abrasion resistance, tear strength and polarity to the resin system. The polyethers impart improved low-temperature properties and hydrolytic stability. Typically, polyether or polyester macroglycols are sequentially tipped by TDI and 2-hydroxyethylacrylate (HEA). With and without combination of acrylate monomers, this system is highly responsive to radiation, producing strong cross-linked films [5, 6].

U.v. irradiation-induced polymerization is accomplished by the incorporation of suitable ketone-type initiators, usually in a combination of accelerators or proton donors [7–10], which produce free radicals upon exposure to light of the appropriate wavelength. This technology is

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now extensively used in the printing industry, where photoreproduction is possible, and in coating applications. Only recently, however, have any publications appeared describing the physical properties of urethane acrylates in any detail [4, 11–17].

Oraby and Walsh [11, 12] studied the mechanical properties of electron-beam cured polyester urethane acrylates based on TDI, as a function of oligomer structure and monomer diluent. Stress–strain and thermal property measurements showed that increasing the molecular weight of urethane acrylates from 1000 to 4600 resulted in decreases in the ultimate tensile strength, Young's modulus and glass transition temperature, while the ultimate elongation increased. They suggested [13] that the cured materials had multi-rayed star-shaped cross-link structures. Wadhwa and Walsh [13] studied the relations between morphology and mechanical properties using dynamic mechanical measurements and microscopy on the same TDI-based urethane acrylates. The observation of a single T_g suggested that the material had a one-phase morphology, in which hard segments and soft segments were homogeneously mixed.

From another point of view, radiation-cured urethane acrylates are in a similar category to cross-linked polyurethanes. Ophir and Wilkes [18] studied peroxide cross-linked MDI-based polyester polyurethanes. They showed that higher cross-linking interfered with phase separation and resulted in lower modulus.

The present study focuses on the structure–mechanical property relationships of u.v.-curable urethane acrylate systems. The materials considered in this study are TDI- and IPDI-based urethane acrylates with polyester and polyether soft segments. The effects of oligomer molecular weight, and cross-link type and amount on mechanical properties were investigated.

2. Experimental procedure

2.1. Materials

U.v.-curable urethane acrylates were synthesized using a two-step reaction procedure. The reaction components consisted of a difunctional polyol soft segment, a diisocyanate hard segment tipped with vinyl acrylate, and a low molecular weight cross-linker containing vinyl functionality. The urethane acrylates were based either on isophorone diiso-

TABLE I Sample characterization

Sample	System type	Cross-linker content	Hard-segment content* (wt%)	Soft-segment molecular weight
I–ET650-0	HEA/IPDI/PTMO	None	51.6	650
I–ET650-10N	HEA/IPDI/PTMO	10 wt% NVP	46.4	650
I–ET650-25N	HEA/IPDI/PTMO	25 wt% NVP	38.7	650
I–ET1000-10N	HEA/IPDI/PTMO	10 wt% NVP	40.9	1000
I–ET2000-0	HEA/IPDI/PTMO	None	25.7	2000
I–ET2000-10N	HEA/IPDI/PTMO	10 wt% NVP	23.1	2000
I–ET2000-25N	HEA/IPDI/PTMO	25 wt% NVP	19.3	2000
I–ES530-10N	HEA/IPDI/PCL	10 wt% NVP	50.6	530
I–ES830-10N	HEA/IPDI/PCL	10 wt% NVP	40.9	830
I–ES1250-10N	HEA/IPDI/PCL	10 wt% NVP	36.8	1250
I–ES2000-10N	HEA/IPDI/PCL	10 wt% NVP	23.1	2000
T–ET1000-0	HEA/TDI/PTMO	None	33.8	1000
T–ET1000-10N	HEA/TDI/PTMO	10 wt% NVP	30.4	1000
T–ET1000-25N	HEA/TDI/PTMO	25 wt% NVP	25.3	1000
T–ET1000-10D	HEA/TDI/PTMO	10 wt% PEGDA	30.4	1000
T–ET1000-25D	HEA/TDI/PTMO	25 wt% PEGDA	25.3	1000
T–ET2000-0	HEA/TDI/PTMO	None	23.0	2000
T–ET2000-10N	HEA/TDI/PTMO	10 wt% NVP	20.7	2000
T–ET2000-25N	HEA/TDI/PTMO	25 wt% NVP	17.3	2000
T–ET2000-10D	HEA/TDI/PTMO	10 wt% PEGDA	20.7	2000
T–ET2000-25D	HEA/TDI/PTMO	25 wt% PEGDA	17.3	2000

*HEA and diisocyanate segment.

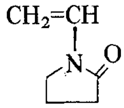
cyanate (IPDI) or toluene diisocyanate (TDI) in combination with polycaprolactone diol (PCL) and polytetramethylene oxide diol (PTMO).

For the IPDI-based system, one mole of IPDI and hydroxyethylacrylate (HEA), and one-half mole of the PCL or PTMO of various molecular weights were reacted [19]. The molecular weight of the PCL used ranged from 530 to 2000 while that of the PTMO was varied from 650 to 2000. The IPDI-based materials were synthesized and supplied by Freeman Chemical Corporation of Port Washington, Wisconsin.

The TDI-based urethane acrylates were synthesized in our laboratory. TDI (BASF Wyandotte) and PTMO (Polyscience Chemical Co.) were dehydrated under vacuum at room temperature for 48 h. 2-hydroxyethylacrylate (HEA) (Polyscience Chemical Co.) and stannous octate (M and T Chemicals) were used as-received.

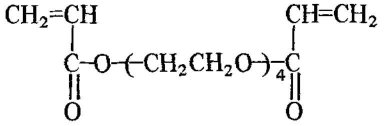
An equimolar amount of HEA was added dropwize to TDI under a nitrogen atmosphere. The temperature was kept below 45° C to avoid thermal polymerization of the HEA. After the temperature of the mixture started to drop, a stoichiometric quantity of PTMO was added with catalyst (stannous octate) and the mixture heated to 70° C. This mixture was agitated for 2 h. Schematic structures of urethane acrylates synthesized are shown below:

The photo-initiator used was a 1 : 1 mixture of 2,2′-diethoxyacetophenone (Polyscience Chemical Co.) and N-methyldiethanolamine (Aldrich Chemical Co.). 0.67 wt% of the initiator mixture was added to the urethane acrylates. The cross-linkers used were N-vinylpyrrolidone (NVP) (Aldrich Chemical Co.) and polyethylene glycol 200 diacrylate (PEGDA) (Sartomer Chemical Co.):



NVP

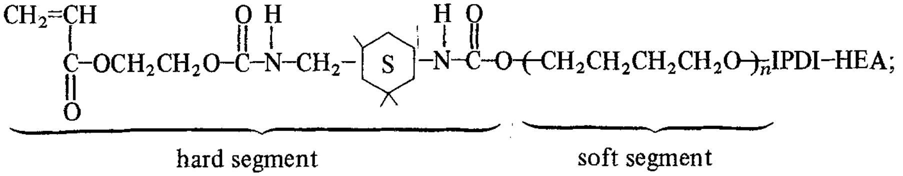
and



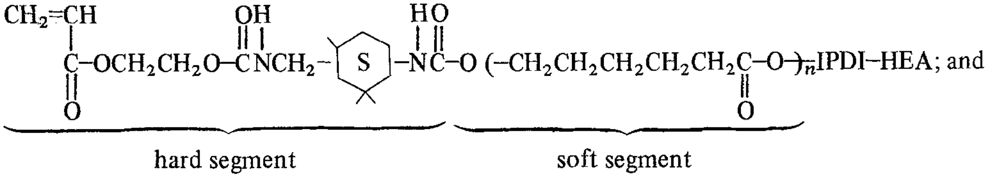
$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}(CH_2CH_2O)_4{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2$$

PEGDA

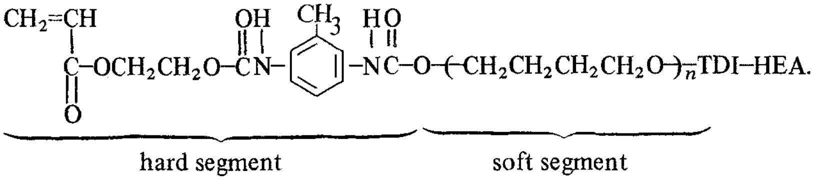
The composition of the u.v. curable urethane acrylate systems was varied in two ways. First, the molecular weight of soft-segment polyols was varied while the cross-linker content was kept constant. In a second series of experiments, the content of the cross-linkers was varied. In total, three systems comprising 21 samples were studied. A description of each of the materials studied is given in Table I. Designation codes for each



HEA/IPDI/PTMO (I–ET series)



HEA/IPDI/PCL (I–ES series)



HEA/TDI/PTMO (T–ET series)

material were: I–ET for HEA/IPDI/PTMO, I–ES for HEA/IPDI/PCL and T–ET for HEA/TDI/PTMO. Although all the materials are characterized with respect to system type, cross-linker content, and soft-segment molecular weight in Table I, it is helpful to further explain the codes used in the designation of the materials. For ET (polyether) and ES (polyester) materials, the number immediately following the system name refers to the soft-segment molecular weight, while 0, 10, or 25 following the dash refers to the cross-linker content (wt%). The last letter, N or D, refers to NVP or PEGDA, respectively.

2.2. Sample preparation

The mixture of urethane acrylate pre-polymer, photo-initiator, and cross-linker was heated at 90° C for 20 min to reduce the viscosity and to eliminate bubbles from the resin mixture. This extent of heating was shown to produce negligible thermally-induced polymerization by infra-red spectroscopy. The liquid resin was poured onto a glass plate. The thickness of the sample films was varied from 50 to 250 μm depending on the requirements for a particular physical test. The samples were irradiated from one side under a nitrogen atmosphere. The irradiation source was a bank of 20 W mercury lamps (Westinghouse, F20T12/BLB). The extent of the reaction was uniform in the direction of film thickness and was independent of the 50 to 250 μm film thickness because of the low concentration and small extinction coefficient of the initiator [20]. An irradiation time of 10 min was used. After the irradiation, samples were stored in a desiccator containing silica gel to minimize water absorption.

2.3. Characterization methods

2.3.1. Soxhlet extraction

The gel fraction of the cured samples was evaluated by Soxhlet extraction using a toluene–methanol (4:1 v/v) mixture for 24 h. The insoluble gel fraction was dried under reduced pressure for 48 h at 60° C and weighed to evaluate the gel fraction.

2.3.2. Infra-red spectra measurements

Infra-red spectra of I–ET2000-10N were taken before and after u.v. irradiation using a Perkin–Elmer Model 180 double-beam infra-red spectrophotometer. The resolution was 2.0 $\mathrm{cm^{-1}}$. Changes in the absorption peaks at 1635 and 1615 $\mathrm{cm^{-1}}$, assigned to the C=C stretching of NVP and the HEA terminated oligomer, were used to follow the conversion of the vinyl groups with irradiation time.

2.3.3. Stress–strain measurements

Stress–strain measurements were carried out using a table model Instron tensile testing machine at a cross-head speed of 2.54 $\mathrm{cm\,min^{-1}}$. The u.v. cured samples with thickness 150 ± 30 μm were stamped out using an ASTM D412 die. The dumb-bell samples were strained to failure at room temperature.

2.3.4. Dynamic mechanical measurements

Dynamic mechanical data were obtained using a Rheovibron dynamic viscoelastometer Model DDV-II (Toyo Measuring Instruments Co. Ltd) at 110 Hz. The temperature range covered was − 150 to 200° C. Irradiated sample strips were quenched to − 150° C and heated up to 200° C at 2° C $\mathrm{min^{-1}}$, while readings were taken every 2 to 3° C. The sample chamber was kept dry by a stream of moisture-free nitrogen.

2.3.5. Differential scanning calorimetry (DSC)

The samples for DSC study included both the photopolymerized oligomer–cross-linker mixtures as well as photopolymerized NVP and PEGDA, prepared using the same conditions and apparatus. Each sample (20 ± 1 mg) was cooled to − 123° C at 40° C $\mathrm{min^{-1}}$, and its DSC thermogram obtained over the temperature range − 123° C to 117° C (or 217° C). The thermograms were recorded using a Perkin–Elmer Model DSC-II differential scanning calorimeter at a heating rate of 20° C $\mathrm{min^{-1}}$ and a sensitivity of 5 $\mathrm{mcal\,sec^{-1}}$ under a He purge. After the first run, the sample was quenched to − 123° C, and its thermogram again recorded in the same manner.

3. Results and discussion

3.1. The extent of photochemical reaction

Fig. 1 shows the infra-red spectrum of I–ET2000-10N before and after 20 min of u.v. irradiation. Pronounced decreases in absorptions at 1635 and 1615 $\mathrm{cm^{-1}}$, assigned to the C=C stretching, are observed. The absorption decreases at 1720, 1190, and 805 $\mathrm{cm^{-1}}$ are typical changes for acrylate-based photopolymers. These changes suggest the possibility of side reactions, associated with the acrylate carbonyl, which have not been well-identified.

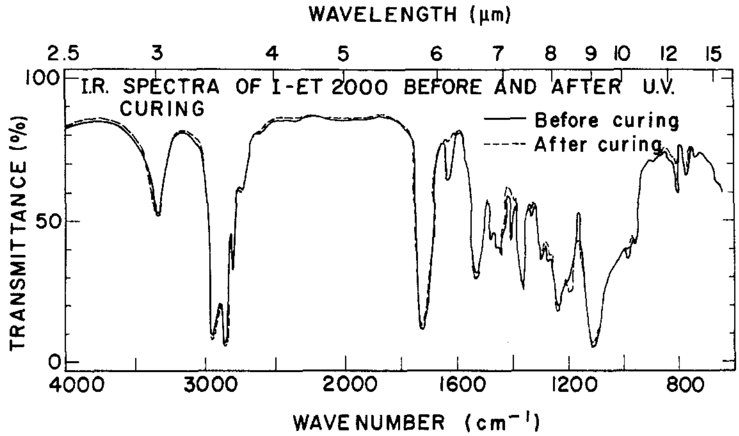


Figure 1 Infra-red spectra of I–ET2000-10N before and after u.v. curing.

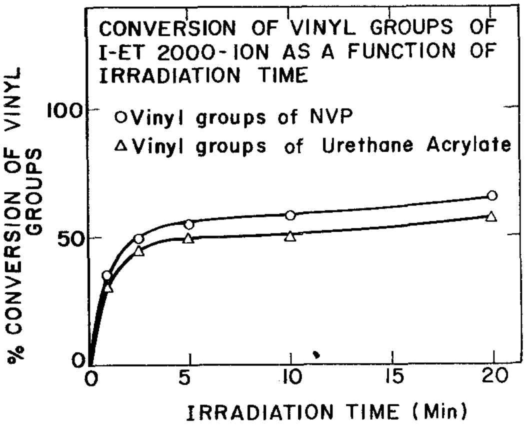


Figure 2 Conversion of vinyl groups of I–ET2000-10N as a function of irradiation time.

Beachell *et al.* [21, 22] reported on the gradual u.v.-decomposition of urethane compounds. In the present case, minimal changes in the spectral regions where urethane decomposition products absorb indicate urethane stability during the photopolymerization. Thus, the primary photochemical reaction is polymerization of the vinyl groups.

Fig. 2 shows the conversion of vinyl groups as a function of irradiation time. Table II shows the gel fraction of I–ET2000 and I–ET650 series samples irradiated for 10 min evaluated by Soxhlet extraction. Although about half of the vinyl groups initially present remain unreacted, the gel fraction is almost 100%. In addition, the ultimate tensile strength of the cured samples levels off after 5 min of u.v. irradiation, and the dynamic mechanical data in the temperature range – 150 to 200° C, of samples irradiated at 5, 10 and 20 min showed little change. It is apparent that an approach to the properties of a fully-cured sample is obtained at 50% conversion of vinyl groups. Incomplete reaction is probably due to a drastic increase in viscosity, accompanied by a transformation of the liquid resin to a glassy solid with u.v. irradiation.

3.2. Mechanical properties

3.2.1. I–ET system

The Young's modulus, ultimate tensile strength and ultimate elongation of the I–ET series of materials are listed in Table III. Fig. 3 shows the stress–strain curves of samples, I–ET650 and I–ET2000 with 0, 10, and 25 wt% NVP crosslinker.

Increasing the NVP content leads to an increase in Young's modulus and ultimate tensile strength. However, the ultimate elongation of I–ET650 decreases with NVP content while that of I–ET2000 increases. An increase in molecular weight of PTMO causes a decrease in Young's modulus and ultimate tensile strength. Oraby and Walsh [11] reported that increases in polyol molecular weight caused an increase in ultimate elongation. However, the results in Table III suggest that ultimate elongation is not a simple function of polyol molecular weight.

TABLE II Gel fractions of u.v.-cured urethane acrylates

Sample	Gel fraction (%)
I–ET650-0	98.4
I–ET650-10N	98.0
I–ET650-25N	98.0
I–ET2000-0	97.9
I–ET2000-10N	98.1
I–ET2000-25N	97.8
I–ES530-10N	99.0
I–ES830-10N	98.0
I–ES1250-10N	98.1
I–ES2000-10N	97.8

TABLE III Tensile properties of urethane acrylates

Sample	Young's modulus ($N\,m^{-2}$)	Ultimate tensile strength ($N\,m^{-2}$)	Ultimate elongation (%)	Yield strength ($N\,m^{-2}$)
I–ET650-0	2.65×10^7	1.07×10^7	77.1	–
I–ET650-10N	4.36×10^8	2.07×10^7	48.3	–
I–ET650-25N	1.46×10^9	4.48×10^7	4.6	–
I–ET1000-10N	4.34×10^7	1.29×10^7	100.0	–
I–ET2000-0	3.98×10^6	2.14×10^6	80.6	–
I–ET2000-10N	1.29×10^7	6.52×10^6	96.7	–
I–ET2000-25N	1.38×10^8	1.83×10^7	162.5	–
I–ES530-10N	5.22×10^8	2.11×10^7	44.2	1.73×10^7
I–ES830-10N	7.99×10^7	1.71×10^7	100.2	–
I–ES1250-10N	1.54×10^7	1.37×10^7	126.0	–
I–ES2000-10N	7.81×10^6	7.21×10^6	127.0	–
T–ET1000-0	4.16×10^7	1.86×10^7	62.2	–
T–ET1000-10N	1.29×10^8	3.18×10^7	76.6	–
T–ET1000-25N	9.04×10^8	8.95×10^7	78.7	–
T–ET1000-10D	5.76×10^7	2.22×10^7	56.3	–
T–ET1000-25D	9.01×10^7	2.42×10^7	40.7	–
T–ET2000-0	5.83×10^6	3.84×10^6	91.8	–
T–ET2000-10N	1.92×10^7	7.99×10^6	112.0	–
T–ET2000-25N	1.27×10^8	2.08×10^7	140.0	–
T–ET2000-10D	1.03×10^7	5.48×10^6	86.3	–
T–ET2000-25D	2.33×10^7	7.58×10^6	58.5	–

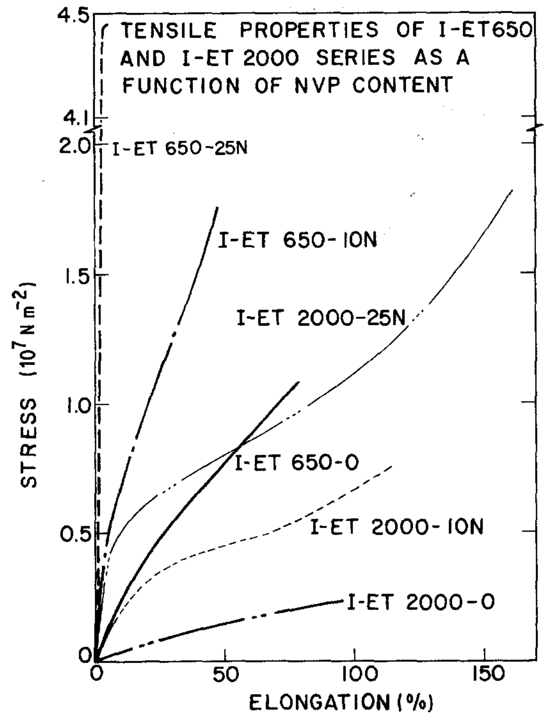


Figure 3 Effect of NVP content on the tensile properties of the I–ET650 and I–ET2000 series.

Fig. 4 shows the dynamic mechanical properties of I–ET650 with 0, 10, and 25 wt% NVP. A low-temperature transition located at about − 120° C is attributed to localized motion in polytetramethylene oxide sequences [23]. A small peak at − 60° C is attributed to the local motion of absorbed water [24]. Besides the peaks at − 120° C and − 60° C, a major glass transition peak that possesses a slight shoulder is observed between 0 and 25° C. The presence of a single glass transition peak implies that for the most part the I–ET650 series of polymers have a one-phase morphology where hard and soft segments and polymerized NVP are mixed homogeneously. However, the low-temperature shoulder in the T_g-peak suggests a slight incompatibility of the soft-segment phase. Increases in NVP content cause the glass transition to shift to higher temperatures. This increase in T_g accounts for the substantial increase in Young's modulus as the T_g shifts through the testing temperature.

The shift of the glass transition to higher temperatures may be accounted for by one of the well-known equations for the prediction of the

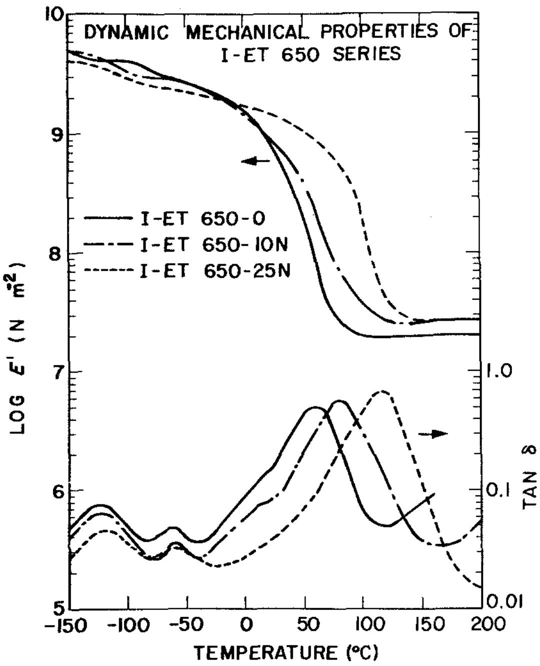


Figure 4 Effect of NVP content on the storage modulus and loss tangent of the I–ET650 series.

glass transition of random co-polymers [25]:

$$\frac{1}{T_g} = \sum_i \frac{W_i}{T_{gi}}, \qquad (1)$$

where W_i and T_{gi} are the weight fraction and glass transition temperature of component i. In the case of a homogeneous three-component u.v. curable elastomer

$$\frac{1}{T_g} = \frac{W_s}{T_{gs}} + \frac{W_h}{T_{gh}} + \frac{W_c}{T_{gc}}, \qquad (2)$$

where s, h, and c designate the soft-segment, hard-segment and cross-linker, respectively. Poly-N-vinylpyrrolidone has a glass transition over 100° C at 110 Hz according to the estimation proposed by Nielsen [26]. This assumes an activation energy of 75 kcal mol^{-1} for the 73° C glass transition temperature of NVP, determined by DSC. Thus, an increase in the relative amount of NVP causes a shift of the glass transition to higher temperatures. The effect of cross-linking on glass transition [27] increases T_g slightly at moderate levels of cross-linking. The cross-linking effect is clearly seen by the slight increase in modulus in the rubbery region and a decrease in the tan δ minimum above the glass transition temperature [28]. The increase in cross-link density and glass transition temperature accounts for the tendency of these one-phase materials to become brittle at higher levels of NVP incorporation.

Fig. 5 shows the dynamic mechanical properties of the I–ET2000 series of materials. These polymers contain two glass transition temperatures which are indicative of phase-separated polymer systems [23]. With increasing NVP content, the soft-segment glass transition peak decreases in magnitude without changing its position at − 50° C. This is the typical transition temperature of PTMO-containing segmented co-polymers [29]. Thus, good phase separation is obtained, despite the fact that the system is cross-linked. The higher-temperature glass transition peak, associated with the hard-segment domains, increases in its magnitude and shifts to higher temperatures with increasing amounts of NVP. It can be deduced that the hard-segment domains consist mainly of urethane linkages and polymerized vinyl components including NVP. The shift of the hard domain transition peak with NVP content is explained by the relatively high T_g of the NVP component. An increased NVP content also raises the volume-fraction of hard domain and results in an increase in toughness of these two-phase materials, as shown in Table III and Fig. 3.

Fig. 6 shows the dynamic mechanical properties of the I–ET system of materials as a function

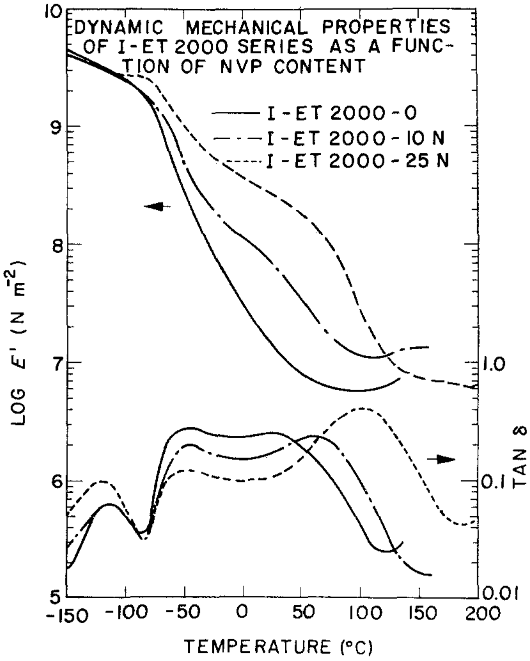


Figure 5 Effect of NVP content on the storage modulus and loss tangent of the I–ET2000 series.

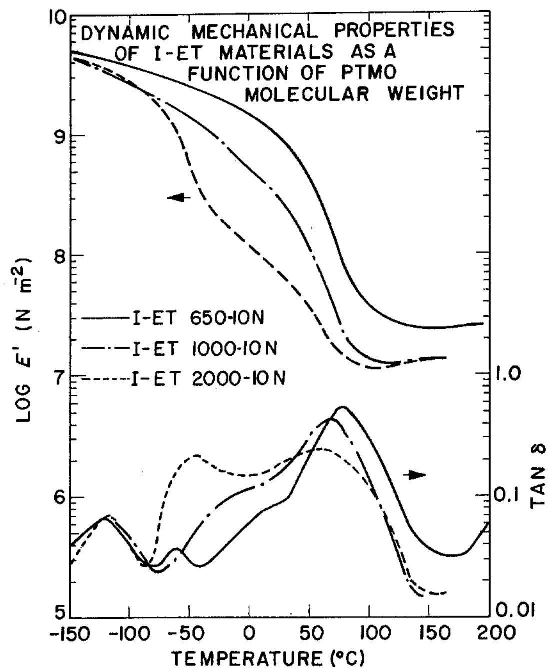


Figure 6 Effect of PTMO molecular weight on the storage modulus and loss tangent of the I–ET system with 10 wt% NVP cross-linker.

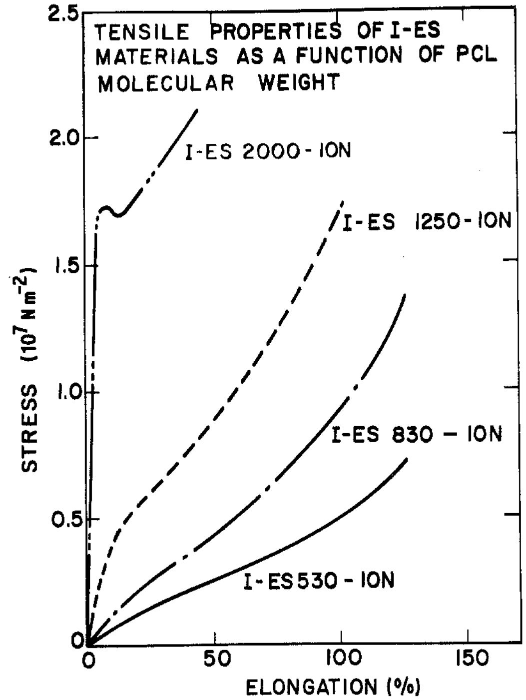


Figure 7 Effect of PCL molecular weight on the tensile properties of the I–ES systems.

of soft-segment molecular weight. An increase in the molecular weight of PTMO causes an increase in magnitude and a shift to lower temperature of the soft-segment glass transition peak. The greater degree of phase separation allowed by the longer segment lengths results in greater phase purity and a lower T_g of the soft-segment phase [30]. In contrast, the hard-segment domain glass transition peak shifts slightly to lower temperatures and decreases in amplitude with increasing PTMO molecular weight. This slight shift to lower temperatures may be accounted for by a small increase in the PTMO dissolved in the hard-segment phase.

3.2.2. *I–ES system*

The tensile properties of the I–ES system are summarized in Table III and Fig. 7. Fig. 8 shows the dynamic mechanical properties of the I–ES series of materials which contain different PCL molecular weights. The trends of Young's modulus and ultimate tensile strength with increasing soft-segment molecular weight are the same as those found in the I–ET system. With increasing PCL molecular weight the soft-segment glass transition peak is enhanced and is shifted to lower temperatures while the hard-segment domain glass transition peak decreases in magnitude and shifts slightly to lower temperatures. However, unlike Sample I–ET2000-10N, Sample I–ES2000-10N does not clearly possess two glass transition peaks. This may be due to the higher polarity of PCL compared to

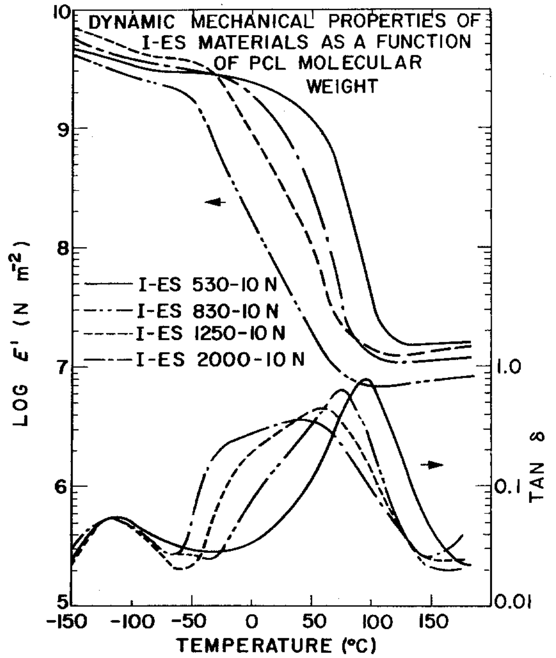


Figure 8 Effect of PCL molecular weight on the storage modulus and loss tangent of the I–ES systems.

PTMO which results in a lower degree of phase separation [31].

3.2.3. *T–ET system*

The tensile properties of the T–ET2000 series of materials are shown in Table III and Fig. 9. The dynamic mechanical properties of the series are shown in Fig. 10. It is apparent that the trends in physical property changes with increasing NVP content are similar to those observed in the I–ET and I–ES systems.

In contrast, the series of materials containing the PEGDA cross-linker shows different behaviour. The dynamic mechanical measurements in Fig. 10 indicate the presence of two phases. With increasing PEGDA content, the hard-segment glass transition peak increases in magnitude without changing its position. Stress–strain measurements in Fig. 9 show that PEGDA does not improve the toughness of the two-phase materials, where toughness is defined as the area under the stress–strain curve. These tendencies are attributed to the lower glass transition temperature of PEGDA as compared to NVP. The glass transition temperatures of photopolymerized pure NVP and PEGDA, obtained by DSC measurements, were 73 and 21° C, respectively. By applying Nielsen's criteria [26], PEGDA should have a glass transition peak of about 50° C at 110 Hz, which is close to the high-temperature glass transition of T–ET2000-0.

The dynamic mechanical properties of the T–ET1000 series of materials are shown in Fig. 11 and their tensile properties are summarized in Table III. Although the dynamic mechanical measurements indicate T–ET1000-0 is in the intermediate region between a one-phase and two-phase material, the general tendencies with changes in cross-linker content are the same as those for the two-phase materials.

Comparison of the tensile properties of the T–ET2000 series and I–ET2000 series of materials shows the TDI-based urethane acrylates exhibit slightly higher Young's modulus, ultimate tensile strength, and ultimate elongation. This might imply subtle differences in domain morphology or that the cohesive strength of the TDI-based hard-segment domain is higher. In any event, both series of materials have similar properties so that conclusions on the effect of hard-segment type in these systems must remain speculative.

3.3. Thermal analysis

Differential scanning calorimetry (DSC) thermograms of the I–ET2000 series of materials are

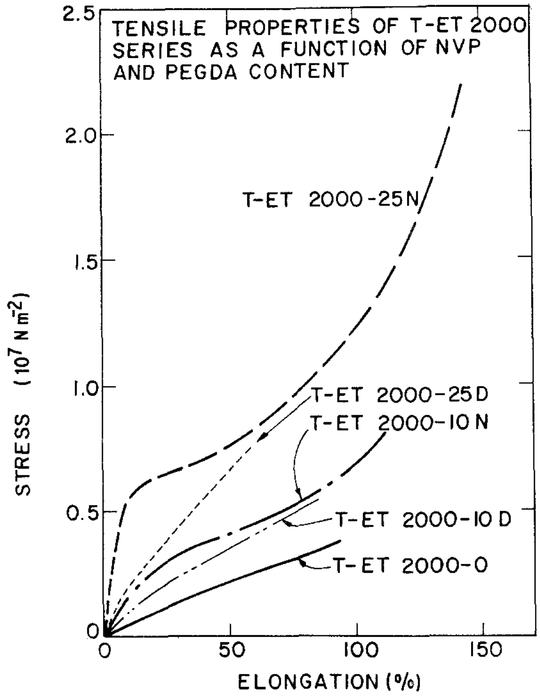


Figure 9 Effect of NVP and PEGDA content on the tensile properties of the T–ET2000 series.

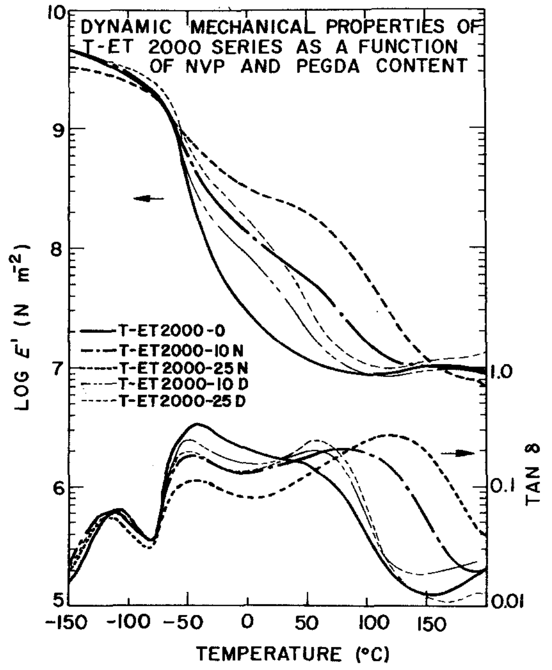


Figure 10 Effect of cross-linker content on the storage modulus and loss tangent of the T–ET2000 series (NVP and PEGDA cross-linkers).

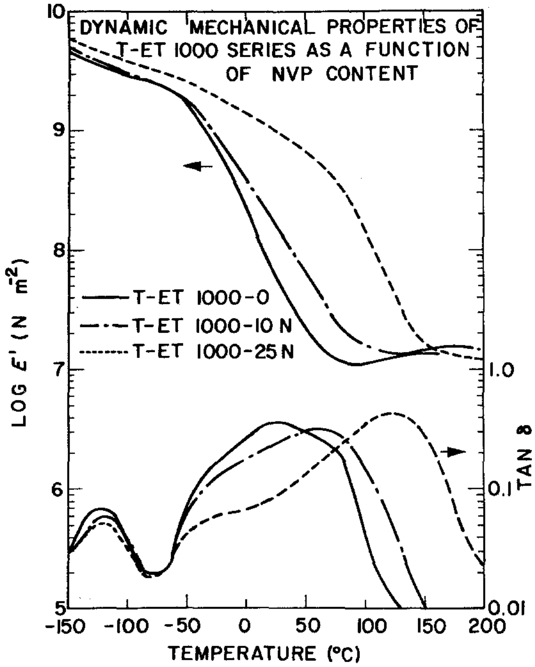


Figure 11 Effect of NVP content on the storage modulus and loss tangent of the T–ET1000 series.

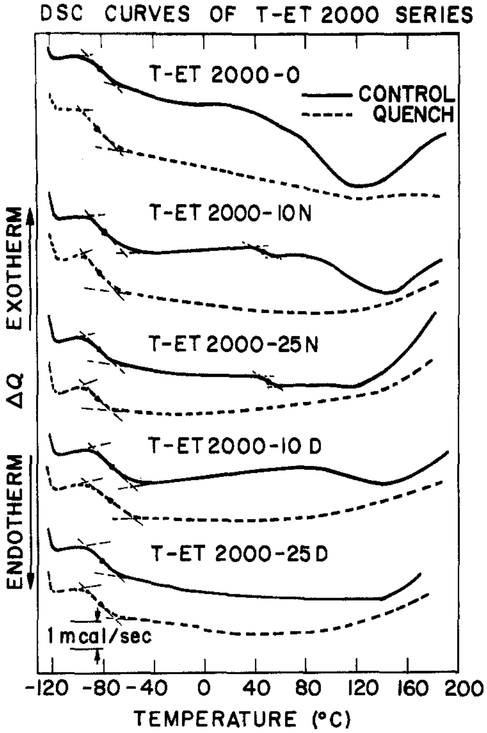


Figure 12 DSC curves of T–ET2000 series.

shown in Fig. 12. The glass transition and endotherm temperatures for each sample are listed in Table IV. The glass transition temperatures of one-phase materials and the hard-segment phase glass transitions of some of two-phase materials were not observable.

Comparison of the low-temperature DSC glass transitions, T_{g1} with the positions of the low-temperature glass transitions of the dynamic mechanical measurements shows good correspondence. The DSC high-temperature glass transition observed in the T–ET system shifts slightly to higher temperatures and the specific heat change, ΔC_p, between the glassy and rubbery states at T_{g2} increases with an increase in NVP content. These tendencies correspond to the shift of the higher-temperature glass transition peak and its increase in magnitude observed in the dynamic mechanical measurements. The small, broad, high-temperature endothermic peak located above 125° C decreases with addition of cross-linkers and disappears after quenching. This suggests that the endotherm is due to a short-range ordering associated with urethane linkages in the hard-segment domains [32–34]. The DSC traces observed in Samples I–ET650-0 and I–ES530-10N were consistent with their one-phase morphology.

4. Conclusions

A systematic study of the structure–property relationships in a variety of u.v. curable acrylates has been accomplished using stress–strain, dynamic mechanical measurements and differential scanning calorimetry.

Increasing molecular weight of the polyols allows greater phase separation, resulting in higher phase purity and lower T_g of the soft-segment phase. The glass transition of the hard-segment phase, which consists of urethane components, cross-linker and dissolved polyol, shifts slightly to lower temperatures at higher soft-segment molecular weight. This is attributed to a decrease in the relative amount of hard-segment.

An increase in cross-linker content caused an increase in Young's modulus and ultimate tensile strength of the materials. Significant differences in the effect of cross-linker content and structure on physical properties were observed. An increase in NVP caused the single glass transition observed for one-phase materials to shift to higher temperatures. This accounts for the substantial increase in Young's modulus as T_g shifts through the testing temperature range. It appears, in addition, that NVP makes the one-phase materials brittle due to the formation of a tightly cross-linked network. For the

TABLE IV Thermal properties of urethane acrylates, NVP and PEGDA

Sample	Glass transition temperature (° C)				Endotherm temperature (° C)	
	T_{g_1}		T_{g_2}		Control	Quench
	Control	Quench	Control	Quench		
I–ET650-0	–	–	–	–	52.6, 163.0	–
I–ET1000-10N	–47.6	–43.0	38.8	–	141.0	–
I–ET2000-0	–73.5	–71.0	–	–	156.0	–
I–ET2000-10N	–73.0	–71.0	–	–	166.0	–
I–ET2000-25N	–73.0	–72.0	–	–	–	–
I–ES530-10N	–	–	–	–	59.0, 147.0	–
I–ES830-10N	–	–	–	–	159.0	–
I–ES1250-10N	–46.0	–45.0	–	–	144.6	–
I–ES2000-10N	–62.0	–55.0	–	–	–	–
T–ET1000-0	–58.0	–58.0	–	–	128.4	–
T–ET1000-10N	–60.0	–60.0	39.0	–	132.6	–
T–ET1000-25N	–58.0	–58.0	40.0	–	134.5	–
T–ET1000-10D	–56.0	–56.0	–	–	133.8	–
T–ET1000-25D	–58.0	–62.0	–	–	142.0	–
T–ET2000-0	–78.0	–84.0	–	–	124.4	–
T–ET2000-10N	–80.0	–84.0	40.0	–	140.4	–
T–ET2000-25N	–80.0	–84.0	42.0	–	133.0	–
T–ET2000-10D	–77.0	–79.0	–	–	138.5	–
T–ET2000-25D	–80.0	–80.0	–	–	146.0	–
Cured NVP	–	–	73.2	73.2	–	–
Cured PEGDA	–	–	21.0	21.0	–	–

two-phase materials, the soft-segment transition peak decreases in magnitude without changing its position and the hard-segment domain transition increases with increasing NVP and PEGDA content.

The comparison of mechanical properties of TDI-based and IPDI-based urethane acrylates shows little difference in Young's modulus, ultimate tensile strength, and ultimate elongation.

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