High-Performance UV-Curable Urethane Acrylates via Deblocking Chemistry

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SYNOPSIS

Research in urethane-acrylate UV-curables has shown that these materials have mechanical properties inferior to those of thermoplastic polyurethanes with very similar composition owing to the high cross-link density in UV-curables; in particular, their ultimate extension is low (less than 100%). Past attempts at increasing the ultimate extension involved compromising the advantages of the UV-curing process. In this work, thermally labile bonds were made and then broken after curing, so as to incorporate thermoplastic polyurethane in the UV-cured polymer. This method achieved the desired improvement in ultimate properties without compromising the advantages of the UV-curing process. Two different reactive diluents and three different chain extenders were utilized, keeping the soft segment type (PPO), hard segment type (IPDI), and their weight fractions constant. The resulting polymers were similar to interpenetrating networks of linear or cross-linked polyurethanes and linear or cross-linked polyacrylates with properties entirely different from their UV-cured precursors, as well as the corresponding polyurethanes. All the materials involved were characterized by tensile testing and dynamic mechanical analysis. The ultimate extensions as well as the ultimate strength of the final polymers were found to be significantly greater than those of the corresponding UV-curable precursors, while the degree of phase separation was found to have changed. The differences in mechanical properties of the UV curables and the polyurethanes cannot be explained in terms of differences in cross-link density or composition and are probably due to differences in their morphology. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A UV-curable polymer may be defined as one made by polymerization of a mixture of a vinyl monomer and a photoinitiator using ultraviolet (UV) radiation. The principal applications of UV-curables include thin film coatings, printing inks, printing plates, and adhesives. Continuing interest in UV-curables is evidenced by several recent publications.[1-4] The subject has also been reviewed in great detail in recent books.[5-7]

The most important UV-curables are based on urethane-acrylate (UA) oligomers. Typical prepolymers of this family are made by reacting a low mo-lecular weight (1000–5000) polyester or polyether diol with an excess of diisocyanate. The remaining diisocyanate functionalities are then tipped with small acrylate-containing species to give long molecules tipped with acrylic functionality at each end. Reactive diluents (small molecules containing one or more vinyl groups) are often employed to reduce the viscosity of the prepolymer. This prepolymer is then cross-linked in a free radical type polymerization by exposure to UV radiation in the presence of a photoinitiator. A recent publication reviews UA UV-curables in considerable detail.[8] Most applications of UV-curables involve coating a substrate with polymer, and, hence, the substrate is first coated with the liquid prepolymer and then exposed to UV-radiation to cause polymerization *in situ* on the substrate. The UV curing process offers several advantages over conventional processes in the coatings

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industry. These benefits include high speed of processing, eliminated solvent emissions (since the prepolymer is a completely reactive liquid), and high energy efficiency (since the polymerization is carried out at room temperature).

From systematic study of urethane-acrylate UV-curables carried out in this laboratory,[9-13] certain conclusions of broad applicability may be drawn.

1. Effect of soft segment molecular weight. The polyester or polyol in the UAs mentioned above is called the soft segment because of its low glass transition temperature and hence its high degree of flexibility. An increase in the soft segment molecular weight (thereby also increasing the weight fraction of the soft segment) causes the prepolymer to have higher viscosity. The cured polymer has better phase separation of the hard and soft segments, lower initial modulus, lower ultimate strength, and higher ultimate elongation.

2. Effect of diluent concentration. An increase in amount of the diluent leads to a large reduction in the prepolymer viscosity. The resulting increase in the total amount of acrylic phase in the polymer gives it higher initial modulus and strength. The effect on the ultimate elongation depends on the functionality of the diluent. For difunctional diluents (i.e., diluents with a single vinyl group), the diluent causes lower cross-link density in the polymer and hence gives greater elongation. Multifunctional diluents (diluents with two or more vinyl groups), on the other hand, cause a higher cross-link density and hence lower ultimate elongation.

3. Hard segment and soft segment type. The hard segment (the isocyanate part of the polymer, which has very little flexibility) and the soft segment affect the properties of the UV-curable to a large extent. These effects are difficult to quantify; however, in general, a well-phase-separated system has better mechanical properties than a poorly phase-separated material.

Literature also reveals that the mechanical properties of these UV-curables are inferior to those of thermoplastic polyurethanes (TPUs) made from the same soft and hard segments. In particular, the ultimate elongation of UV-curables is quite low (usually less than 100%) as compared to several hundred percent for TPUs. This may be attributed to the high cross-link density of UV-curables, which in-hibits good phase separation; it is well known that the superior elastomeric properties of TPUs are derived from hard segment phase separation.

To improve the elongation of UV-curables, an attempt was made[14] to synthesize them using comb-like TPU precursors with pendant acrylic groups. The cured polymers were found to have properties similar to those of TPUs at room temperature and excellent elastomeric properties at high temperatures. However, the synthetic procedure for these polymers was very involved: the TPUs were prepared by a two-step solution polymerization followed by addition of the acrylic groups to the polymer chains followed by UV-curing to get the final product. Moreover, the precursors were solid, high molecular weight polymers, which were unsuitable for solventless coating applications. One may attempt to reduce the viscosity of these precursors by solubilizing them in large amounts of diluent; however, large amounts of difunctional diluent (single vinyl group per diluent molecule) would reduce the rate of UV-curing, while a multifunctional diluent would increase the cross-link density. Thus, improving mechanical properties of UV-curables by using TPU precursors defeats the principal advantages of the UV curing process; the prepolymer is not a liquid, and the synthetic procedure is very complicated.

This article describes an attempt to improve the elongation of UV-curables by reducing their cross-link density and simultaneously incorporating a TPU in the network in a post-curing process. Scheme 1 describes the proposed reaction path. It is described in detail in the synthesis section. Steps 1, 2, and 3 are typical of a conventional UV-curable synthesis. The acrylic tipping agent used in Step 2 is chosen such that the steric hindrance of the large tertiary butyl group makes the urea linkage between the tipping agent and the IPDI thermally labile. Cleavage of this bond may be expected upon annealing, allowing the free isocyanate to react with the chain extender, which is present as a part of the diluent. This causes a reduction in the cross-link density of the acrylic polymer and at the same time allows a TPU to be formed inside the network.

The proposed chemistry may be used to synthesize blends of linear or cross-linked acrylates (using difunctional or multifunctional vinyl diluents, respectively) and cross-linked or linear polyurethanes (using polyols or chain extenders with functionality greater than two or equal to two, respectively). The presence of a PU in the network combined with the lower cross-link density may be expected to give the annealed polymer high elongation and good elastomeric properties. It should be noted that the UV-

curable precursor is a liquid (even with low concentration of diluent), that the UV-curing kinetics are not affected, and that an additional annealing step has been added to the synthetic process.

In this study, the above methodology was tested for a particular urethane-acrylate system using three different chain extenders and two reactive diluents. The UV-curables after annealing were compared with the corresponding polyurethanes with respect to their tensile and dynamic mechanical properties. It may be argued at this stage that a comparison of the annealed UV-curables (comprising of acrylate and polyurethane in certain proportions), with a TPU containing no acrylate at all, is inappropriate. While it would be better to compare the UV-curables with an acrylate-polyurethane blend of the same composition as the UV-curable, blend properties depend greatly on the synthetic procedure employed in blending the polymers. So, rather than introduce additional unknowns, a comparison with pure polyurethanes was made.

EXPERIMENTAL

Materials

Table I lists all the chemicals used along with their chemical structures and commonly used abbreviations. All chemicals were obtained from Aldrich Chemical Co.

Synthesis

UV-curable Polymers

The chemicals used in the UV-curables were poly(propylene oxide) (PPO), isophorone diisocyanate (IPDI), and t-butyl aminoethyl methacrylate (t-BAEMA) in a 1 : 2 : 2 molar ratio, diluents ethylene glycol dimethacrylate (EGDMA) or methyl methacrylate (MMA), DBT catalyst (0.1% of the polyol weight), and photoinitiator (0.1% of the polyol weight). The diluent was 20% of the polyol weight, which corresponds to approximately 10% of the total prepolymer weight. The photoinitiator used was a 1 : 1 (by weight) mixture of DEAP and TEA. Chain extenders (H12MDA, BD, or TEA), were added so as to maintain a 2 : 1 ratio of the isocyanate to the chain extender functionality.

The prepolymer was made in a dry, 60 mL bottle with an airtight cap. The polyol and the IPDI were first charged to the bottle along with the DBT catalyst. The contents were vigorously mixed for about 20 min and then the bottle was left at 50°C for 2 h. On cooling, t-BAEMA and the diluent were added
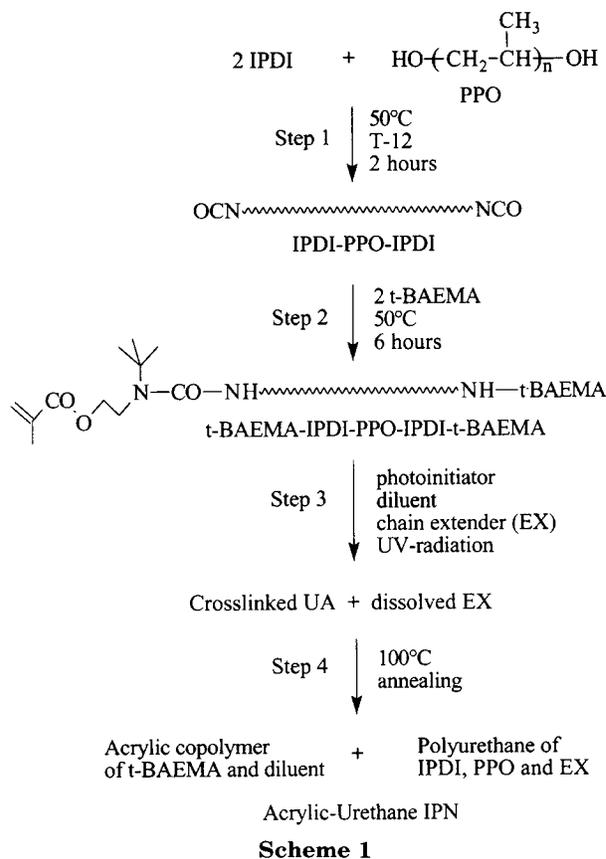
to the bottle, and the contents were stirred for about 10 min. The mixture was then allowed to react at 50°C for at least 6 h. Finally, the photoinitiator and chain extender (if any) were added to the mixture after cooling. All prepolymers were stored in the dark at 5°C and cured within one week of synthesis.

Curing of the prepolymer was done by casting a film of the prepolymer between two Mylar® transparencies separated by a 1 mm thick spacer. The film was then exposed (at room temperature) to an ultraviolet lamp for 16 min. The samples were turned over after 8 min to ensure uniform exposure to the radiation. The temperature changes during curing were monitored with a thermocouple when curing some films. A sudden increase in temperature sometime after the start of the reaction was observed, which is indicative of auto-acceleration. The maximum increase was about 9°C; it should be noted, however, that no attempt was made to insulate the curing films, and the observed temperature changes are approximate.

Linear Polyurethanes

The chemicals required for polyurethane synthesis are PPO, IPDI, and chain extender (H12MDA or

$$2 \text{ IPDI} \quad + \quad \text{HO--}(\text{CH}_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH})_{\overline{n}}\text{--OH}$$

PPO

Step 1 | 50°C, T-12, 2 hours

OCN⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇NCO

IPDI-PPO-IPDI

Step 2 | 2 t-BAEMA, 50°C, 6 hours

⌇⌇⌇CO⌇⌇N—CO—NH⌇⌇⌇⌇⌇⌇⌇⌇NH—tBAEMA

t-BAEMA-IPDI-PPO-IPDI-t-BAEMA

Step 3 | photoinitiator, diluent, chain extender (EX), UV-radiation

Crosslinked UA + dissolved EX

Step 4 | 100°C, annealing

Acrylic copolymer of t-BAEMA and diluent   +   Polyurethane of IPDI, PPO and EX

Acrylic-Urethane IPN

Scheme 1

Table I   Chemicals and Structures

Name, Abbreviation	Structure
Poly(propylene glycol) mol wt 1000 (PPG)	$HO-(CH_2CH-O)_n-H$ with CH_3 on the CH
Isophorone Diisocyanate (IPDI)	Cyclohexane ring with H_3C, H_3C, H_3C substituents, NCO and CH_2NCO
4,4' Methylene (biscyclohexylamine) (H12MDA)	H_2N- (cyclohexyl) $-CH_2-$ (cyclohexyl) $-NH_2$
1,4 Butanediol (BD)	$HO-[CH_2]_4-OH$
Triethanolamine (TEA)	$N[CH_2CH_2OH]_3$
tert-butyl aminoethyl methacrylate (t-BAEMA)	$HN-CH_2CH_2O-CO-C=CH_2$ with $C(CH_3)_3$ on N and CH_3 on C
Ethylenegylcol dimethacrylate (EGDMA)	$(CH_2O-CO-C=CH_2)_2$ with CH_3 on C
Methyl methacrylate (MMA)	$CH_3O-CO-C=CH_2$ with CH_3 on C
2,2 diethoxyacetophenone (DEAP)	(phenyl) $-COCH(OCH_2CH_3)_2$
Dibutyl tindilaureate (DBT)	$[C_{11}H_{23}COO]_2Sn[Bu]_2$
N,N ' Dimethylacetamide (DMAC)	$CH_3CON(CH_3)_2$

BD) in a 1 : 2 : 1 molar ratio. 0.1% by weight of DBT was used as a catalyst, and DMAC (about six times the weight of the total weight) was used as a solvent.

The PPO was dissolved in about half the total DMAC and charged to a three necked flask along with the DBT catalyst, toluene (about 5% of the DMAC weight), and a Teflon coated magnetic stir bar. The three necks of the flask were fitted with a thermometer, a reflux condenser, and a rubber septum, respectively; and the flask was mounted on a heating mantle supported on a magnetic stirrer. An argon purge needle was inserted through the septum, and continuous purge was maintained throughout the synthesis. The flask was first kept at 85°C for 30 min when any moisture in the flask was distilled off since water forms a low boiling azeotrope with toluene at this temperature. Then IPDI dissolved in about half of the remaining DMAC was injected through the septum with a syringe. The reaction

was carried out for 2 h at 70°C. Finally, the chain extender dissolved in the remaining DMAC was injected with a syringe, and the reaction was completed at 85°C over 8 h. The contents were allowed to cool, and the polymer was precipitated in water. It was then washed, redissolved in DMAC or acetone, and cast into films.

Cross-linked Polyurethane

Since cross-linked polymers are set irreversibly into their final shapes, large quantities of solvent cannot be used in their synthesis. The chemicals used here were PPO, IPDI, and TEA in 1 : 2 : 0.67 molar ratios. PPO and IPDI were allowed to react in a dry bottle, along with DBT catalyst, as described in the synthesis of UV-curable prepolymers. Then the mixture was cooled to 5°C (to reduce the rate of the cross-linking reaction), and TEA dissolved in five times its weight of acetone at 5°C was added to it. The

mixture was stirred rapidly and poured into a film. The film was quickly exposed to a vacuum to evaporate the acetone, and the resulting prepolymer film then kept at 80°C on a horizontal surface (to ensure a uniformly thick film) for about 12 h to complete the cross-linking reaction.

Polymer Nomenclature

All polymers made by the UV-curing procedure described above are designated by a prefix "UV." The chain extender and the diluent used are the second and third identifiers, respectively. The identifier "NOEX" is used if no chain extender has been used. Polyurethanes made by the two methods described above are designated by a "PU" followed by the chain extender used in that polymer. The suffix "AN," wherever used, suggests that the polymer was annealed in a post-polymerization process. Annealing was carried out at 100°C for 2 h for most polymers. Only the diol and triol chain-extended UV-curables were annealed for 3 h, since those reactions were found to be slower than the corresponding amine-isocyanate reactions. No significant changes were observed in the extraction results (described later) upon annealing for longer times.

Characterization

Viscosity

Viscosity measurements were made using a Brookfield RVT viscometer with a #21 sample adapter. A recirculating water bath was employed to control the adapter temperature. Viscosity was measured at several different shear rates, at temperatures 50, 60, and 70°C.

Molecular Weight

Molecular weights of linear polymers were found by gel permeation chromatography using DMAC with 2 g/L lithium nitrate as the solvent. Calibration was done using isotactic polystyrene standards of very low polydispersity. Polymer concentrations of about 0.25% by weight were used. The gel columns were maintained at 50°C, and the eluted solution was analyzed using a refractive index detector.

Tensile Properties

Uniaxial tensile stress-strain measurements were made on a table model Instron series 9 tensile testing machine. Samples were cut from cured or cast polymer films using an ASTM D1708 die. All tests were

performed at room temperature at a constant strain rate of 0.5 in/min. At least three runs were performed for each polymer. Tensile stress calculation was based on the initial cross sectional area of the sample. The slope of the stress-strain curve at zero strain was found to exhibit considerable variability due to slight differences in clamping the sample in the instrument jaws. Hence, the slope of a least squares fit to the stress-strain curve between 0.5 and 2.5% strain, which was highly reproducible, was used as a measure of the initial modulus.

Dynamic Mechanical Properties

Temperature sweep dynamic mechanical analysis was performed using a Rheometrics RSA II analyzer. Samples were cut from cured or cast polymer films using an ASTM D1043 die. The autotension mode was used with 3°C temperature steps and a 0.1 min soak time. All tests were conducted at 100 Hz. Tests were started at −150°C and continued until sample failure was detected by the instrument.

RESULTS AND DISCUSSION

Viscosity

Table II shows the viscosity of all the prepolymers used to prepare the UV-curables. All viscosities have been reported at a shear rate of 1 s^{-1}. This shear rate was often inaccessible due to the limited range of the viscometer used; hence, viscosity was measured at several different shear rates, and a least squares fit to the power law model was employed to extrapolate the viscosity to 1 s^{-1}. The power law model used had the form

$$\eta = m\gamma^{n-1}$$

where η is the viscosity, γ the shear rate, and m and n are the power law parameters obtained by a least squares fit. $n = 1$ represents a Newtonian fluid while $n > 1$ and $n < 1$ represent shear thinning and a shear thickening fluids, respectively.

All the prepolymers studied had n between 0.93 and 0.98, suggesting that the fluids are nearly Newtonian between 50 and 70°C. It was also observed that the value of n for all prepolymers decreased slightly with an increase in temperature, indicating that the fluids are somewhat more shear thinning at higher temperatures. A comparison of samples 1 and 2 in Table II shows a five-fold decrease in viscosity by addition of 10% by weight of diluent EGDMA. Also, a comparison of samples 2 and 3

Table II   Viscosity of Prepolymers at 1 s^{-1}

	Viscosity (cp) at		
Sample	50°C	60°C	70°C
1. UV-NOEX without diluent	7700	3500	1600
2. UV-NOEX-EGDMA	1700	900	500
3. UV-NOEX-EGDMA after 1 month at room temperature	1800	900	500
4. UV-BD-EGDMA	1500	800	500
5. UV-TEA-EGDMA	1600	800	400
6. UV-H12MDA-EGDMA	2100	1100	700
7. UV-NOEX-MMA	800	400	300
8. UV-H12MDA-MMA	1600	1100	900

shows a slight change in viscosity over a period of one month, which may be attributed to spontaneous polymerization of the methacrylates.

Extraction

As outlined in the end of the introduction, we expect that annealing will break the bonds between the tipping agent and the isocyanate and allow the isocyanate to react with the chain extender to form linear polyurethane molecules. To test this hypothesis, approximately 0.5 g samples of the UV-cured polymers before and after annealing were immersed in approximately 10 g of DMAC solvent for one day. The solvent from each sample was then withdrawn with a syringe and collected in aluminum pans of known weight. The solvent was allowed to evaporate, and the weight of the extracted residue (all the molecules dissolved in the cross-linked polymer matrix but not bonded to it) was found by reweighing the pans. Table III shows the percent by weight of the original polymer sample extracted by the solvent. The theoretical values of the extracted weight have

been calculated assuming that the chain extender is the only species that can be extracted before annealing and that maximum possible reaction between chain extender and isocyanate has occurred during annealing; i.e., there are no covalent bonds between the acrylic and the urethane polymers after annealing.

As expected of cross-linked polymers, all samples exposed to solvent showed significant swelling at short times. At longer times, UV-BD-EGDMA-AN and UV-H12MDA-EGDMA-AN were observed to fall apart into large fragments. A large portion of these samples (about 50% from Table III) was found to have converted into a linear polymer upon annealing. Removal of this linear polymer causes the rest of the cross-linked network to lose integrity and fragment. All other samples maintained their shape and strength after removal of the solvent, indicating that the cross-linked network was substantially intact in these samples. The residue obtained from UV-BD-EGDMA-AN was a transparent and highly viscous fluid whose molecular weight was determined to be 12,000. The residue obtained from UV-

Table III   Extraction Results

	Wt % Extracted Before Annealing		Wt % Extracted After Annealing	
Sample	Exp.	Theor.	Exp.	Theor.
1. UV-NOEX-EGDMA	3.6	0.0	5.3	0.0
2. UV-BD-EGDMA	3.2	4.3	54.6	72.9
3. UV-TEA-EGDMA	3.4	4.7	7.3	0
4. UV-H12MDA-EGDMA	12.7	9.3	59.4	74.3
5. UV-NOEX-MMA	0.3	0.0	0.4	0.0
6. UV-H12MDA-MMA	9.1	9.3	unavailable	100

Table IV   Mechanical Properties and Glass Transition Temperatures

Polymer	Ultimate Stress (MPa)	Ultimate Strain (%)	Modulus (MPa)	T_g* (°C)
1. UV-NOEX-EGDMA	7.97	40	65.9	−23.7
2. UV-NOEX-EGDMA-AN	7.74	52	40.6	−22.3
3. UV-BD-EGDMA	6.32	30	40.4	−30.0
4. UV-BD-EGDMA-AN	5.01	67	5.3	−19.1
5. UV-TEA-EGDMA	5.51	31	35.2	−23.7
6. UV-TEA-EGDMA-AN	9.35	97	4.9	−20.5
7. UV-H12MDA-EGDMA	2.77	49	6.8	−21.8
8. UV-H12MDA-EGDMA-AN	11.56	116	38.1	−23.2
9. UV-NOEX-MMA	8.20	104	37.4	−23.1
10. UV-NOEX-MMA-AN	7.13	96	35.5	−20.0
11. UV-H12MDA-MMA	4.08	99	7.8	−14.7
12. UV-H12MDA-MMA-AN	19.20	376	97.2	−23.2
13. PU-BD		Too soft to be tested.		
14. PU-BD-AN		Too soft to be tested.		
15. PU-TEA	1.97	349	1.3	−23.7
16. PU-TEA-AN	2.05	222	2.1	−23.2
17. PU-H12MDA	3.15	604	4.6	−29.8
18. PU-H12MDA-AN	8.19	788	8.2	−32.3
19. Extract from UV-H12MDA-EGDMA-AN	1.5	757	4.4	−26.5

* As located by the peak in the E'' curve in the dynamic mechanical data.

H12MDA-EGDMA-AN was a yellow polymer of molecular weight 23,700. It was strong to enough yield a film; hence, the extraction was repeated with larger quantities of the annealed UV-curable, and the film of the extracted polymer characterized by DMA and tensile testing. All the other residues were very small quantities of high viscosity liquids. Extraction was also attempted for UV-H12MDA-MMA. However, no results could be obtained because, after annealing, the sample was found to lose shape completely and form a loose, mobile gel from which the solvent could not be extracted with a syringe. This suggests that substitution of the tetrafunctional, cross-linking diluent EGDMA for a difunctional diluent MMA causes UV-H12MDA-MMA-AN to be very lightly cross-linked. Complete reaction between the deblocked isocyanate and the linear chain extender would cause a total absence of cross-links; hence, we conclude that the low cross-link density in UV-H12MDA-MMA-AN is due to an incomplete deblocking reaction. It should be noted that the experimental values of Table III are somewhat underestimated because the extraction is done somewhat crudely, and a small amount of solvent (and, hence, some residue) is retained in the network even after most of the solvent is withdrawn with a syringe.

Thus, the hypothesis that the isocyanate deblocking reaction can produce a polyurethane within a cross-linked UV-curable is borne out by the experimental results.

Mechanical Properties

The important parameters obtained from tensile tests and dynamic mechanical analysis have been listed in Table IV.

Analysis of Mechanical Properties Before Annealing

Figure 1 compares the stress-strain curves of all the UV-curable polymers before annealing.

Most of the UV-curables are found to have fairly low ultimate strains and moderate breaking stresses, as mentioned in the introduction. A comparison of all the UV-curables containing EGDMA shows that the modulus is significantly reduced by the unreacted chain extender dissolved in the cross-linked polymer matrix. Clearly, the UV-curables are plasticized by the small chain extender molecules. This is evident from a comparison of UV-NOEX-MMA and UV-H12MDA-MMA as well. The chain extender also reduces the ultimate strength, though it does not seriously affect the ultimate strain. The modulii of the polymers containing MMA are lower than those of the corresponding polymers containing EGDMA, while their ultimate strains are higher. This is be-

cause the polymers containing MMA have a lower cross-link density and hence can be deformed more easily than the polymers containing EGDMA.

Figure 2(a)–(b) compare the DMA spectra of all the polymers of Figure 1. The spectra are substantially similar for the samples containing EGDMA over most of the temperature range. Of the two samples containing MMA, UV-NOEX-MMA seems to have better phase separation; otherwise, the spectra are similar. The shoulder in the tan δ curve at −20°C for all the samples represents the soft segment (polyol) glass transition. The peak in the tan δ curve at 50°C represents the glass transition of the hard segment (isocyanate) and methacrylate. Figure 2(a) shows that the modulus of UV-NOEX-EGDMA between 0 and 50°C is substantially higher than that of the other polymers, thereby supporting the conclusion that the unreacted chain extender acts as a plasticizer. The abrupt rise in the damping ratio tan δ, of UV-H12MDA-EGDMA and UV-H12MDA-MMA above 100°C results from deblocking of the isocyanate and its subsequent reaction with the amine chain extender to form urea linkages. (The annealed polymer formed has higher damping ratio at the same temperature, as will be seen from its DMA spectra; hence, the tan δ curve rises as the reaction proceeds.) This is observed only for the amine chain extender because the hydroxyl-isocyanate reactions are slower than the amine-isocyanate ones and, hence, cannot occur within the time scale of the dynamic mechanical test.

Analysis of Mechanical Properties After Annealing

Figure 3 shows the effect of annealing on the mechanical properties of the control samples, UV-NOEX-EGDMA and UV-NOEX-MMA. Figure 3(a) shows that annealing does not have a major effect on ultimate properties; however, it reduces the modulus slightly as is noted in Table IV. This may be because the deblocking is not completely reversible; i.e., all the isocyanate may not react back with the tipping agent. Figure 3(b) corroborates these changes in modulii at room temperature and also shows a somewhat wider tan δ peak for UV-NOEX-EGDMA-AN; however, it does not show any other changes in the polymers caused by annealing. It seems safe to conclude that the control samples do not undergo major changes in mechanical properties upon annealing.

A comparison of the tensile testing data for UV-BD-EGDMA and UV-BD-EGDMA-AN [Fig. 4(a)] shows that the annealed sample has a much lower
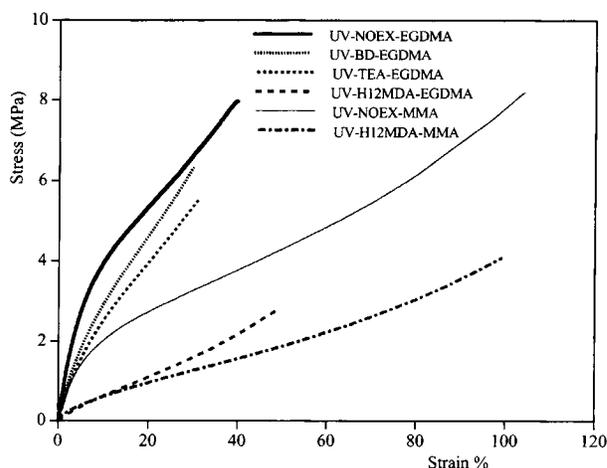
Figure 1 Tensile properties of UV-curables before annealing.

modulus than the unannealed one and can undergo more than twice as much extension before failure. Also, UV-BD-EGDMA-AN shows slight strain hardening, which is not seen in the unannealed polymer. The E' curve of UV-BD-EGDMA-AN [Fig. 4(b)] also shows a significant rubbery plateau above 75°C that has a much lower modulus than the corresponding plateau in the unannealed sample. This decrease in modulus may be indicative of the fact that the cross-link density is lowered upon annealing. However, results for the other systems discussed below suggest that this explanation alone may not be sufficient; significant morphological changes also occur upon annealing. Figure 4(b) also shows that the shoulder at −30°C in the tan δ curve of UV-BD-EGDMA almost disappears after annealing, indicating that there is much less phase separation after annealing. A comparison with the polyurethane PU-BD could not be made because it was too soft to be tested. The number average molecular weight of the PU-BD sample made was more than 30,000, and its lack of rigidity cannot be ascribed to low molecular weight. In general, polyurethanes made from IPDI and PPO give soft polymers, more so if the hard segment fraction is low (about 30% in this case).

A similar comparison for the TEA-containing polymers is shown in Figures 5(a)–(c). The effect of annealing on UV-TEA-EGDMA is similar to that on UV-BD-EGDMA in that annealed samples of both materials show lower modulus, an increase in ultimate elongation, and strain hardening. The annealed sample of UV-TEA-EGDMA, however, shows appreciable increase in ultimate stress as well. Both PU-TEA and PU-TEA-AN were found to be soft and rubbery and exhibited elastic recovery of
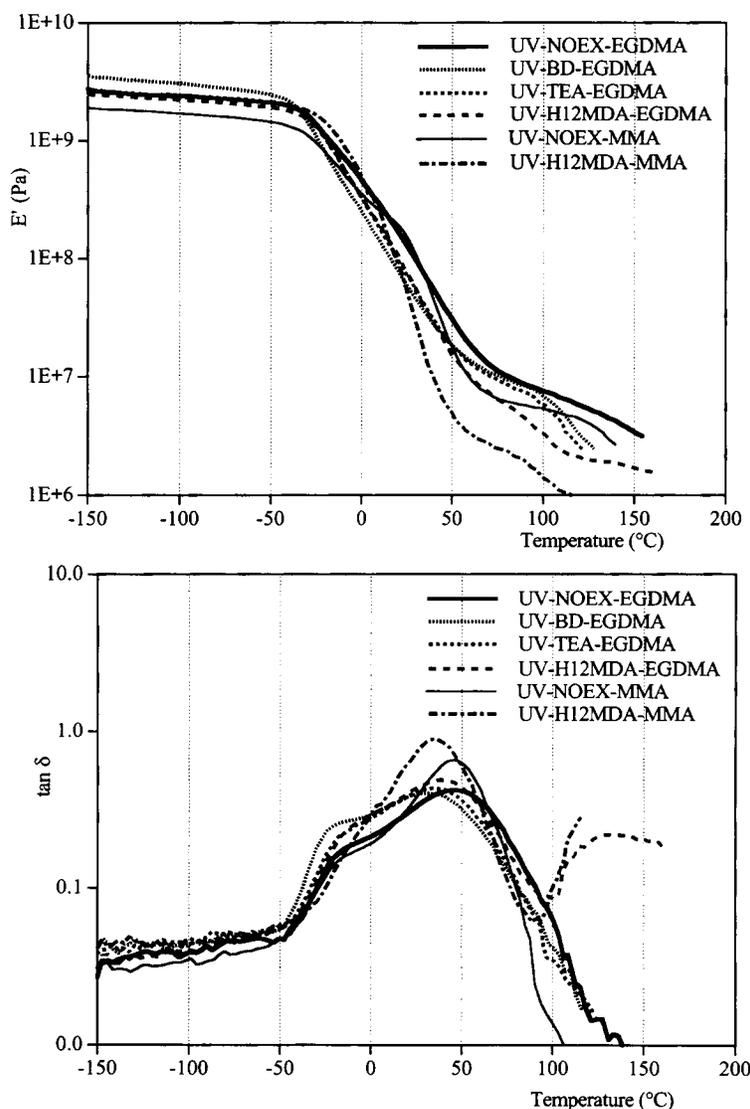
Figure 2 Dynamic mechanical properties of UV-curables before annealing.

deformation subsequent to tensile failure. It should be noted that the UV-cured polymers of Figure 5(a) have much higher moduli and tensile strength than their polyurethane counterparts. This is believed to be due to changes in morphology of the sample and will be discussed in detail later in this article. In Figure 5(b), the E' modulus of UV-TEA-EGDMA-AN increases slightly above 75°C, which is indicative of a true rubbery behavior, which is almost missing in the curve for UV-TEA-EGDMA. The well-developed plateau in E' for UV-TEA-EGDMA-AN suggests that the polyurethane formed as a result of the deblocking reaction is an excellent elastomer at high temperature. In Figure 5(c), the tan δ curve for UV-TEA-EGDMA-AN has almost no shoulder at −20°C, i.e., there is considerable phase miscibility

in the polymer, as indicated by the single broad tan δ peak. Finally, both Figures 5(b) and (c) show almost no change in PU-TEA upon annealing, which is not surprising since cross-linked samples cannot undergo major changes in structure after being synthesized.

Figure 6(a) shows that the tensile properties of UV-H12MDA-EGDMA-AN are far superior to those of UV-H12MDA-EGDMA. This improvement, which may be attributed to the TPU being formed inside the network, was the primary motivation for this work. The corresponding polyurethane PU-H12MDA shows some increase in strength and modulus upon annealing. Such behavior in polyurethanes is usually attributed to better phase separation upon annealing. The polyurethane
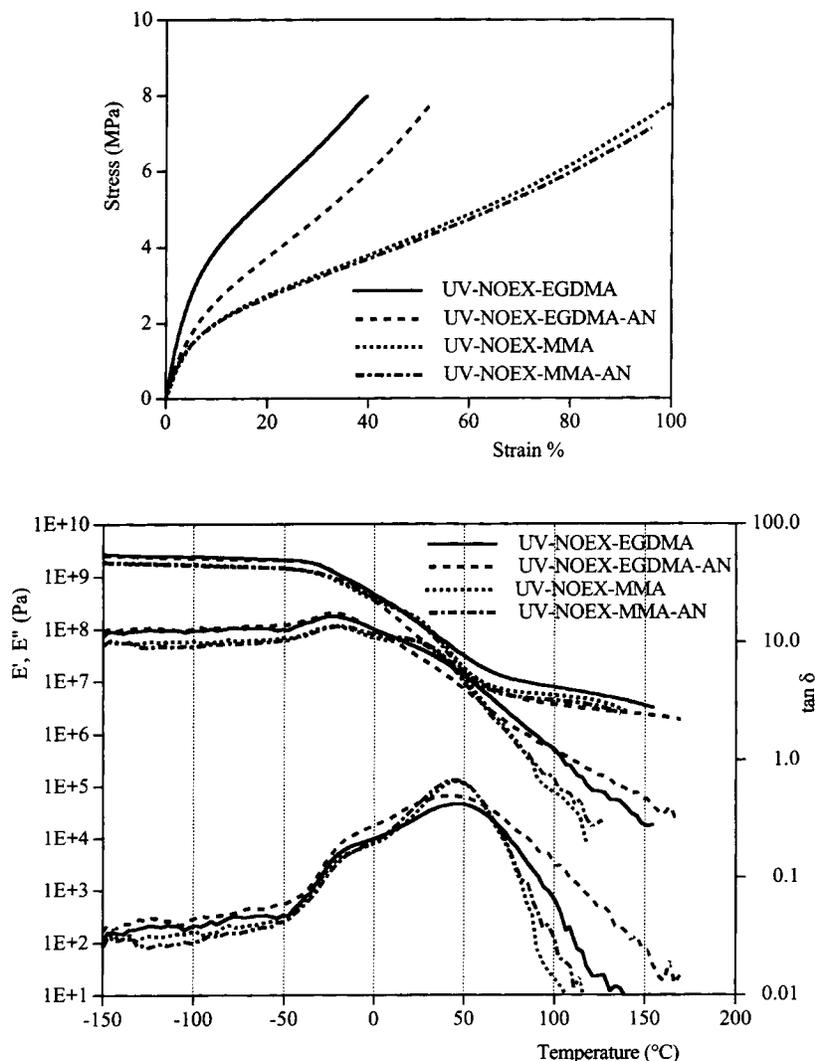
Figure 3 Effect of annealing on control UV-curables.

extracted from the UV-H12MDA-EGDMA-AN shows much lower strength and modulus than PU-H12MDA, to which it is chemically similar. This difference is probably due to the differences in their molecular weights; the extract has a number average molecular weight of 23,700 compared to 41,000 for PU-H12MDA.

Figures 6(b)–(c) show the DMA spectra for the samples in Figure 6(a). The annealed UV-curable shows a broad rubbery plateau at high temperature, which may be attributed to the fact that the polymer has a significant level of cross-linking even after annealing due to the tetrafunctional diluent. (For the same reason, the modulus of UV-NOEX-EGDMA also reaches nearly constant modulus at high temperature, as may be seen in Figure 2(b). The plateau modulus in that case is

higher because UV-NOEX-EGDMA has a much higher cross-link density). As mentioned earlier, the abrupt rise in the E'' and tan δ curves of UV-H12MDA-EGDMA above 100°C demonstrate the reaction of the chain extender very clearly. All three linear polyurethanes in Figure 6(c) show two distinct phases (like typical TPUs) with tan δ peaks at about 20 and 80°C.

Figures 7(a)–(c) show the effect of annealing on UV-H12MDA-MMA and compare it with the same polyurethane as in the earlier section. Almost all the features of the UV-curables noted in Figures 6(a)–(c) are found in Figures 7(a)–(c), and the corresponding conclusions drawn are equally valid. Some differences are that the low-temperature phase in UV-H12MDA-MMA is very poorly developed as compared to UV-H12MDA-EGDMA and also that
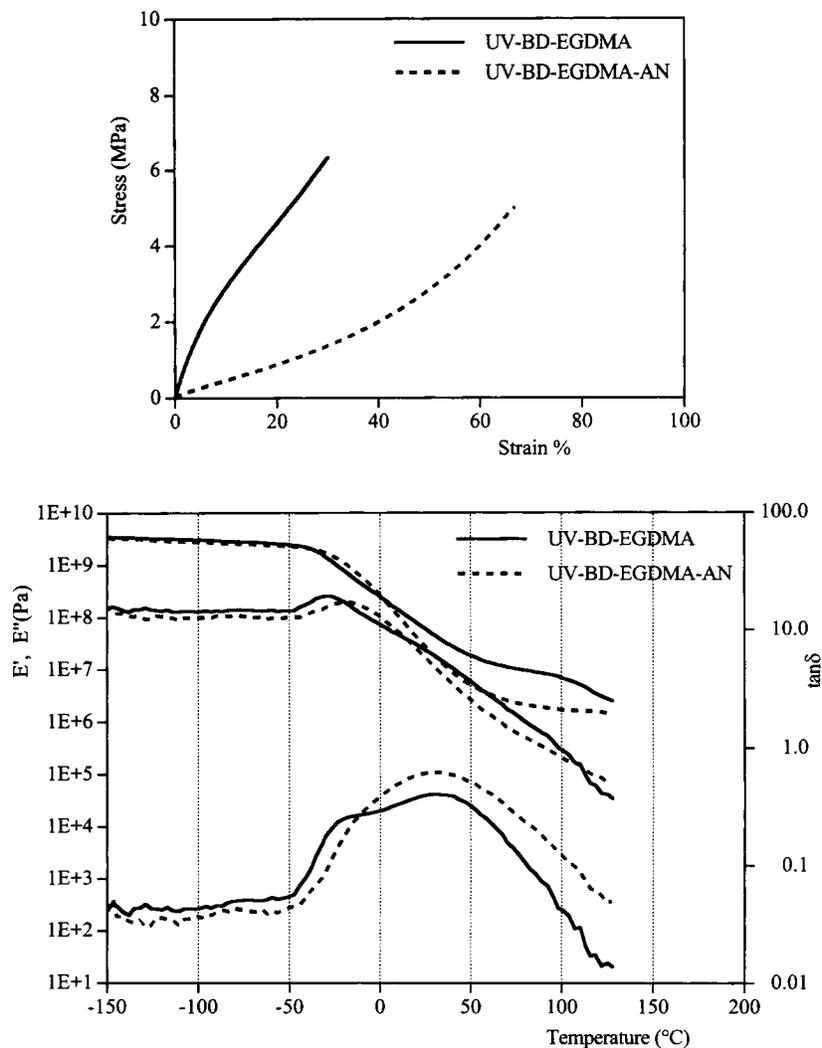
Figure 4   Effect of annealing on UV-BD-EGDMA.

UV-H12MDA-MMA-AN does not show an upturn in modulus before failure at 170°C because it has almost no cross-links (Fig. 8). Hence, the increase in tan δ above 150°C for UV-H12MDA-MMA-AN should be attributed to this decrease in E' and not to a separate phase with a high-temperature transition.

We may speculate on why UV-H12MDA-EGDMA-AN, UV-H12MDA-MMA-AN, and UV-TEA-EGDMA-AN have strengths and moduli higher than those of the corresponding polyurethanes. The presence of the high modulus acrylate as a filler in the annealed UV curables is the most obvious explanation to be considered. Such increases in modulus often correlate well with the Guth-Smallwood equation[15]

$$E_f = E_0(1 + 1.5V_f + 14.1V_f^2)$$

where E_f and E_0 are the modulii with and without filler, respectively, and V_f is the volume fraction of the filler.

All the UV-curables have approximately 25% (by weight) of the acrylic phase (t-BAEMA + diluent), which predicts an increase in modulus by a factor of about 2.5 over the polyurethanes. This is in reasonable agreement with the observed difference in modulus of UV-TEA-EGDMA and PU-TEA, but the increase in moduli of UV-H12MDA-EGDMA-AN and UV-H12MDA-MMA-AN over PU-H12MDA (see Table IV) is well in excess of this prediction. Thus, the presence of acrylate filler alone is not sufficient to explain the modulus differences.

The Guth-Smallwood equation, however, accounts for the presence of the acrylate filler only, whereas the annealed UV curables have an additional difference with the polyurethanes; the UV
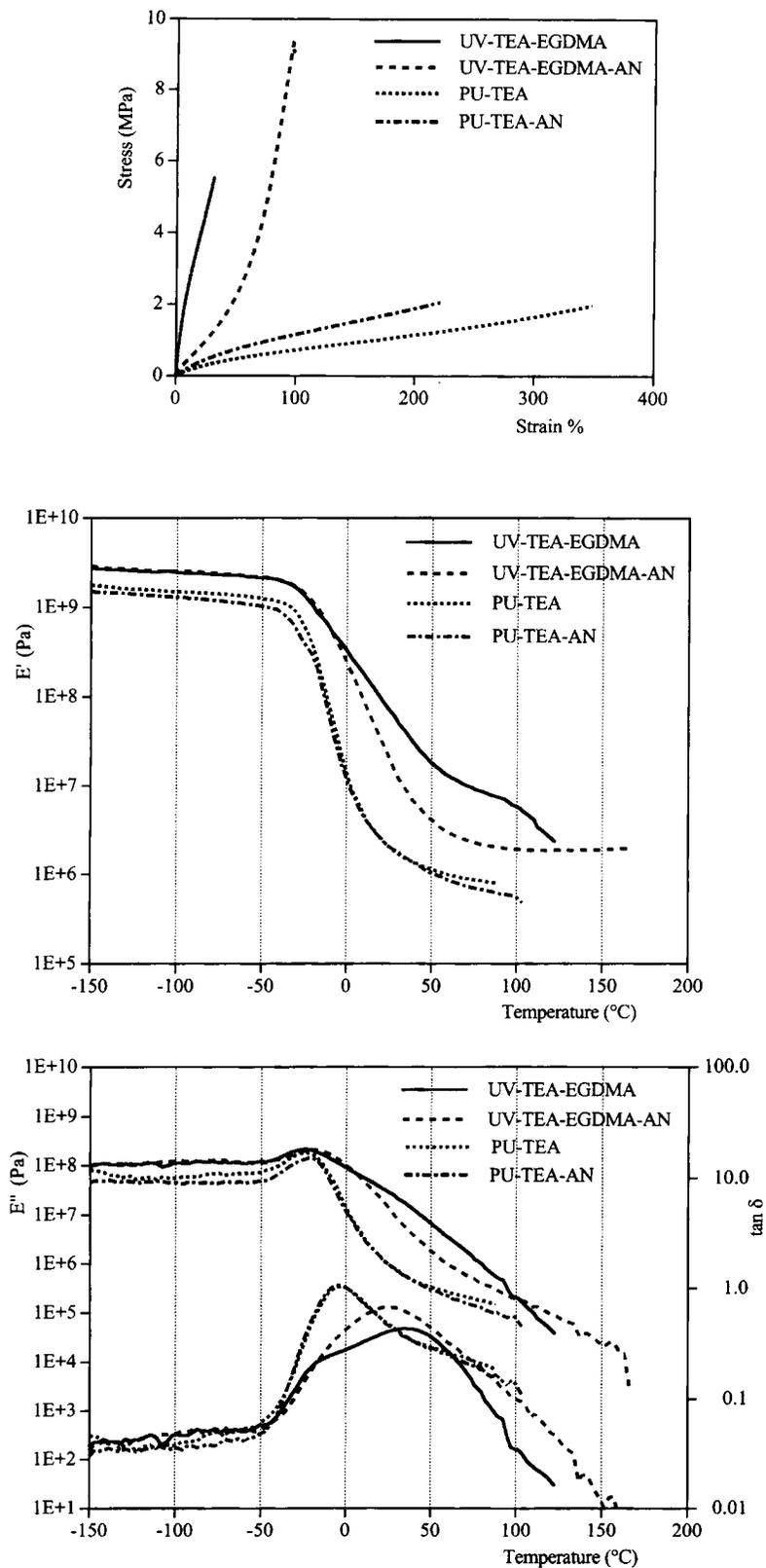
Figure 5 Effect of annealing on UV-TEA-EGDMA: Comparison with PU-TEA.
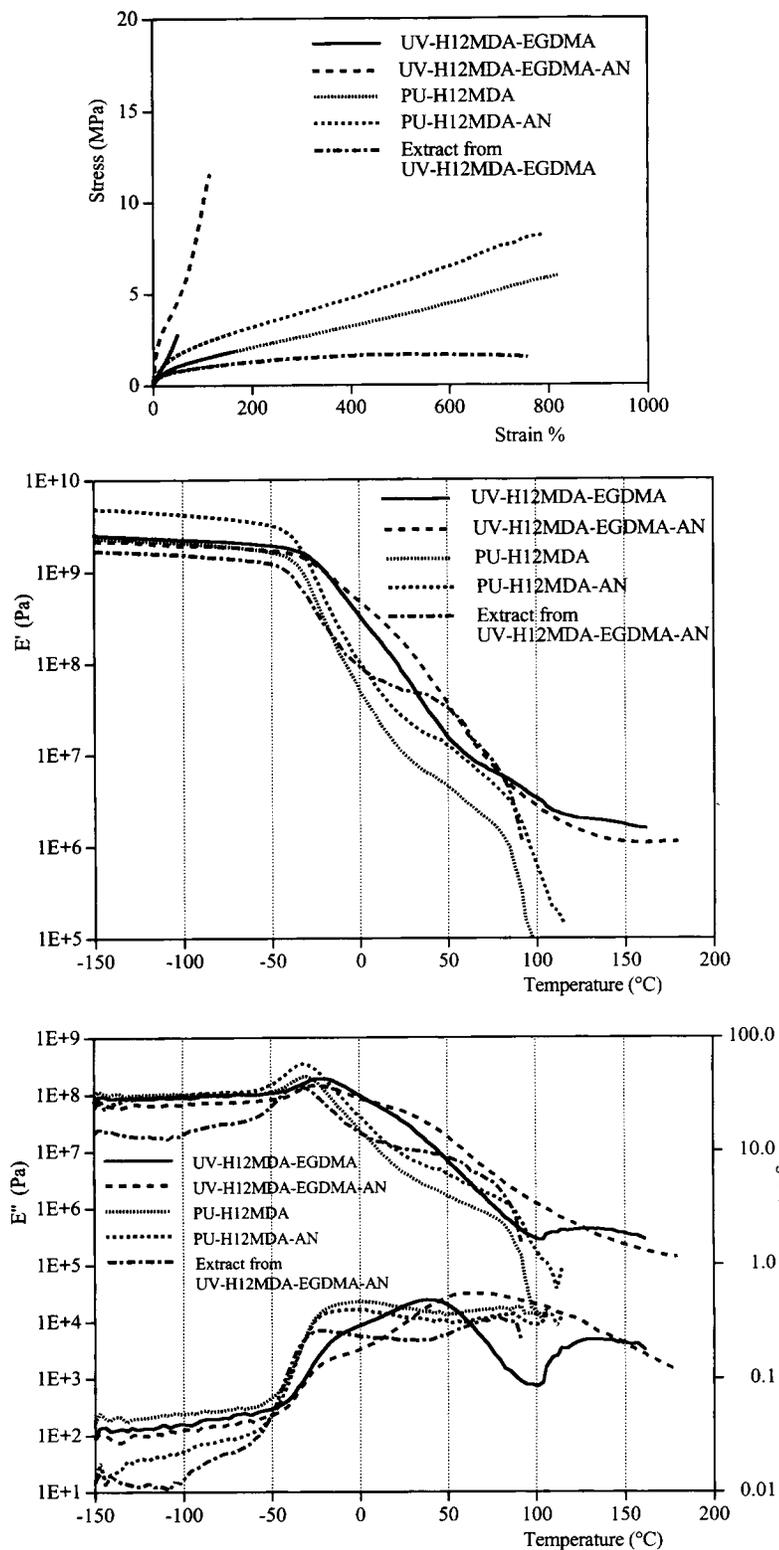
Figure 6 Effect of annealing on UV-H12MDA-EGDMA: Comparison with PU-H12MDA.
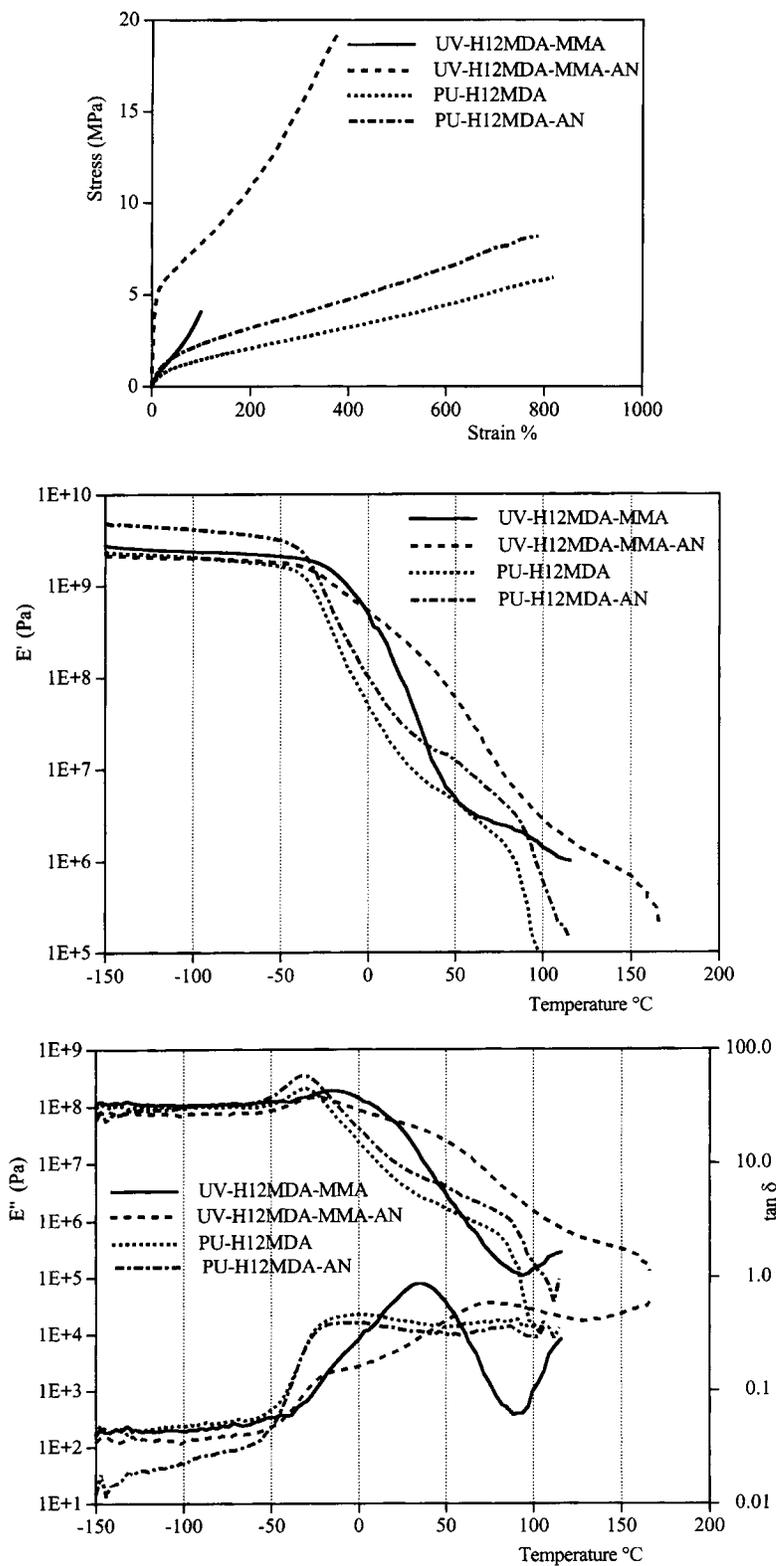
Figure 7 Effect of annealing on UV-H12MDA-MMA: Comparison with PU-H12MDA.
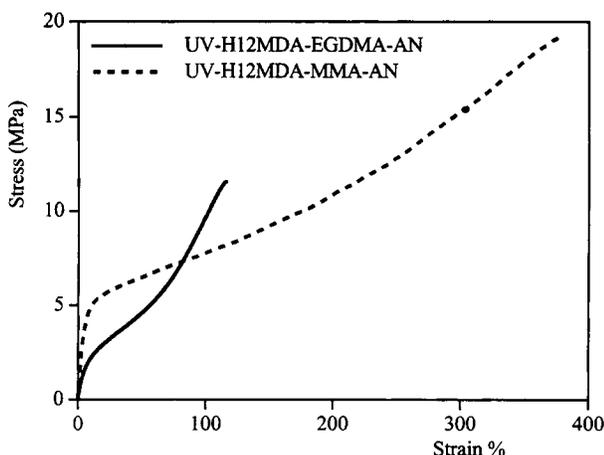
Figure 8 Effect of diluent functionality on H12MDA extended UV-curables.

curables are also cross-linked. Modulus usually increases with cross-link density (and is proportional to the cross-link density for amorphous, rubbery polymers above their glass transition). However, comparing UV-H12MDA-EGDMA-AN with UV-H12MDA-MMA-AN (which have equal acrylate contents), we find that UV-H12MDA-EGDMA-AN has a lower modulus than UV-H12MDA-MMA-AN despite having higher cross-link density. Clearly, while cross-link density might influence the moduli, it does not do so in an expected way.

We must therefore attribute differences in the moduli of the UV curables and their polyurethane counterparts to differences in their morphology. DMA has already shown that the extent of phase separation in these polymers is different; it cannot, however, give information about the nature of these differences. Specifically, it cannot yield information about the size scale of phase separation or the nature of the phase boundaries. Moreover, the chain extended UV curables contain three components: polyol soft segment (about 45%), hard segment (about 30%), and acrylate (25%). All of these are in sufficient quantities to be able to form continuous phases. The mechanical properties may be expected to depend strongly on which of these components are continuous and the extent of interpenetration the phases. Transmission electron microscopy investigations into the morphology of these materials are in progress.

SUMMARY AND CONCLUSIONS

Deblocking of thermally labile urethane-urea linkages can be exploited in UV-cured UAs to achieve

a lower crosslink density. An added chain extender can react with the deblocked isocyanates to form a linear or crosslinked TPU within the network. Blends of linear or cross-linked polyurethanes with linear or cross-linked polyacrylates can be obtained in this fashion.

The present work involved UAs with urethane segments of PPO-1000 and IPDI tipped with t-BAEMA with 10% by weight of methacrylic diluent and different chain extenders at constant urethane : acrylate ratio. All the prepolymers were in the liquid state without added solvent, thus preserving an important advantage of the UV curing process. Polyurethanes similar to those formed within the annealed UV curables were also synthesized for the purposes of comparison.

The success of the deblocking reaction was demonstrated by extraction experiments on samples with linear chain extender and cross-linked acrylate. The amount of soluble phase (i.e., the TPU formed) upon annealing was found to be comparable to the expected value. The deblocking reaction was also observed during dynamic mechanical tests of some polymers.

In all annealed samples containing chain extender, significant changes in tensile properties were observed upon annealing that were not seen in the control samples containing no chain extender. These changes included strain hardening and large changes in modulus, strength, and elongation. Dynamic mechanical analysis showed that the annealed UV curables had excellent elastomeric properties at high temperatures. Changes in the extent of phase separation were also observed. The annealed UV curables also had mechanical properties superior to those of their polyurethane counterparts. These differences in properties cannot be explained in terms of composition differences or in terms of cross-link density. They are probably due to differences in the morphology of the samples and the nature and continuity of the phases within the samples.

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