Dynamic Mechanical Properties of UV-Curable Polyurethane Acrylate with Various Reactive Diluents

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SYNOPSIS

UV-curable polyurethane acrylate (PUA) based on polycaprolactone and m-tetramethylxylene diisocyanate were considered with different acrylate monomers as reactive diluents: ethylhexylacrylate, hexanediol diacrylate, and isobornyl acrylate. The effect of the chemical structure and functionality of the reactive diluent (33 wt %) on their thermal and mechanical properties were investigated. The synthetized PUA networks are homogeneous from a thermodynamical point of view. The initial glass transition temperature (T_g) and the functionality of the reactive diluent do not affect the onset value of the glass transition temperature of the network. Nevertheless, the main mechanical relaxation, denoted α, associated with the glass transition temperature becomes broader as the T_g of the homopolymer of the considered reactive diluent becomes higher than the T_g of the PU soft segments. The increase of the amount of the diacrylate monomer leads to an increase in the equilibrium and storage moduli in the rubbery state and to a decrease in the amplitude of the α relaxation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

UV-curable polymers are now widely used as coatings because of their low temperature of curing, the absence of solvent, and their high curing rate that leads to high productivity.[1] Thus, UV-cured films having good mechanical performances are used to coated paper, plastics, glass, wood, and metals.[2] Usual radiation-cured coating formulations are based on an oligomer (epoxy, urethane, or polyester–acrylate), reactive diluents, photoinitiators, and various additives such as surfactants, pigments, polymer wax, etc.[2] The reactive diluents are acrylate monomers with double bond functionalities. The photoiniator system is responsible of the free radical formation; and its nature and concentration depend on the composition of the formulation, on the type of the atmosphere (inert or oxidant),[3] and on the thickness of the coating. The photoinitiator system is based on a photoinitiator, a photosensitizer, and a tertiary amine.[4] Acrylate double bonds display a

higher reactivity than methacrylate ones, but the glass transition temperature of the resulting coatings is generally lower.[5] The ratio between the initiation and propagation rates is one of the most important parameters for controlling the polymerization process. Tobita and Hamielec[6] showed a drastic increase of the radical concentration during a free radical polymerization. This effect corresponds to a decrease of the termination rate due to an increase of the growing chain length and the presence of entanglements that prevent the diffusion of the reactive chains. This autoacceleration phenomena, called the Tromsdorff effect, occurs before gelation. It is also well known that during the free radical polymerization, cyclization reactions and formation of microgels occur before macrogelation.[7–11] In the pregelation stage, the reaction kinetics and the viscosity changes are the major parameters used to follow the reaction. In addition, the miscibility between the monomer sol phase and the microgel phase can determine the final morphologies. In fact, during the pregel stage, microgels are formed and some intermolecular reactions controlled by a diffusion process are developed in those microgels before and during macrogelation.[6,8] The changes from the rubber gel

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to the glassy network, depending on the real sample cure temperature, leads to a large decrease of the free radical mobility, thus to an increase of their lifetime. The maximum for the glass transition temperature, T_g, of the resulting networks also depends on the real polymerization temperature, which is not room temperature for the UV reaction. The increase of the temperature in the sample is due to the heat generated by the exothermic reaction and overall by the vicinity of the UV source.

A photoinitiator system produces radicals either by fragmentation from the photoexcited state (photoinitiator denoted RR' in the following structure) or by a two-step process by hydrogen transfer (photosensitizer, coinitiator denoted Z and CH, respectively):

$$RR' \xrightarrow{h\nu} R^{\cdot} + R'^{\cdot}$$

$$Z \rightarrow Z^* \rightarrow ZH^{\cdot} + C^{\cdot}$$
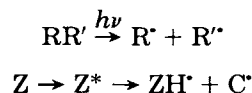
Photosensitizers are often used with a coinitiator, commonly a tertiary amine. The photosensitizer undergoes excitation and transfers the energy to the coinitiator that becomes a radical by H abstraction. Schematically, the photoinitiator is used for polymerization in the bulk and the photosensitizer–coinitiator pair leads to a tack-free surface because of its ability to prevent an oxygen initiation.[12]

Urethane acrylates are often used as oligomers for toughness, abrasion resistance, and flexibility of the resulting coatings. The influences of the composition of the urethane acrylate oligomer and of the reactive diluent on the thermal and mechanical properties were studied by Cooper et al.[13-18] In these studies the N-vinyl pyrrolidone (NVP) and the hydroxyethyl methacrylate (HEMA) and diacrylates with different chain length, such as polyethylene glycol diacrylate, were used as reactive diluents. Urethane acrylates were based either on isocyanate-terminated acrylates, such as isocyanatoethyl methacrylate (IEM) or on hydroxy-terminated acrylates, such as HEMA.
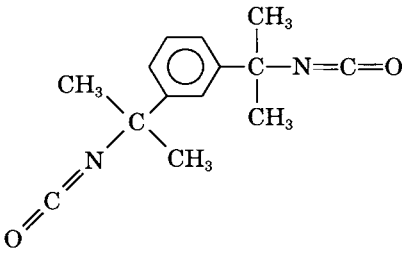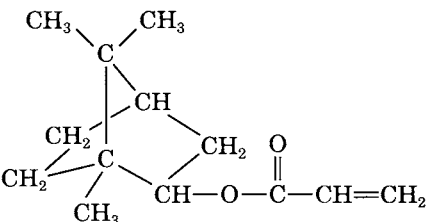
For polyurethane acrylate (PUA) based on HEMA, various combinations of diisocyanates with the macrodiols were reported: toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), or 4,4'-diphenylmethane diisocyanate (MDI)/polytetramethylene oxide (PTMO)[13,15,17]; metatetramethyl xylene diisocyanate (TMXDI) or IPDI/polycaprolactone (PCL)[18]; MDI, TDI, or 1,6-hexane diisocyanate (HDI)/polydimethylsiloxane (PDMS)[19]; 4,4'-dicyclohexylmethane diisocyanate (HMDI)/polypropylene glycol (PPG),[20] HMDI, or MDI/

polybutadiene (PBD).[20,21] In most cases, HEMA-functionalized PUA exhibit a two-phase structure. The introduction of the reactive diluent lowers the prepolymer viscosity[18,20] and emphasizes the phase separation driven by thermodynamics. As a consequence, for the resulting materials the Young's modulus increases and the ultimate elongation is lower. The reactive diluent is incorporated in the hard segment phase. The nature and the molar mass of the soft segment are the most important factors controlling the miscibility and thermomechanical behavior. Decreasing the molar mass of the soft segment leads to a lower strain at break but to a higher tensile strength. Slight differences of the glass transition temperature and mechanical properties are noted by changing the nature of the isocyanate.[13,17] However, Xu et al. demonstrated that TMXDI leads to lower properties in comparison with TDI or IPDI.[18] In the same way, MDI-based PUAs have higher Young's modulus and stress at break than IPDI-based ones,[17] confirming the conclusions of Chiang and Shu[19] who reported the following order according to the mechanical properties: MDI > TDI > HDI.

Different functionalized macrodiols were used to prepare the PUA based on IEM, PTMO–IEM (with number average molar masses, $\bar{M}_n$, between 1,000 and 2,000 g mol^{-1}),[13-15] polycarbonate (PC, $\bar{M}_n$ = 1,020 g mol^{-1}),[14,15] PDMS ($\bar{M}_n$ from 1,000 to 1,800 g mol^{-1}),[19] and PCL ($\bar{M}_n$ from 2,000 to 3,000 g mol^{-1}).[13,14,18] Other polyols were also considered such as castor oil.[22] PUA based on IEM was found to be more homogeneous than those obtained from HEMA. This phenomenon could be explained by considering the way to obtain the oligomer acrylate. In the PUA based on IEM, the oligomer is prepared in a one-step reaction and phase separation is driven by the thermodynamics between the soft segment molecules (containing the macrodiol) and the hard segments corresponding to the growing of the polyacrylate (PA) chains. This process is less likely than in the case of the PUA based on HEMA or hexylethyl acrylate (HEA) for which the oligomer is synthesized in a two-step reaction. In this case, the soft segment molecules may segregate from the PA chains but also from acrylate-functionalized residual DI associated with the hard segments. Moreover, the PUA based on IEM exhibits lower tensile properties.[15,18] The glass transition temperature and the dynamic mechanical properties were found to also strongly be dependent on the molar mass of the soft segment.

Levy and Massey[23] showed that the dilution of the UA with the ethoxy–ethoxy ethyl acrylate (EEEA)

Table I   Monomers Used for Synthesis of PUA Networks

Monomer	Molar Mass (g mol^{-1})	Chemical Formula	Supplier
PCL550	550	$\left[H\left(O(CH_2)_5C\underset{O}{\overset{\|}{}}\right)_n O\right]_2 R$	Interox
TMXDI	244	(aromatic ring with CH_3, $C(CH_3)_2$—N=C=O substituent and $C(CH_3)_2$—N=C=O)	Cyanamid
HEA	130	$HO(CH_2)_2O-\underset{O}{\overset{\|}{C}}-CH=CH_2$	Aldrich
HEMA	144	$HO(CH_2)_2O-\underset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{\|}{C}}=CH_2$	Aldrich
EHA	184	$CH_3-\underset{CH_2-CH_3}{\overset{\|}{CH}}(CH_2)_4O-\underset{O}{\overset{\|}{C}}-CH=CH_2$	Aldrich
HDDA	226	$CH_2=CH-\underset{O}{\overset{\|}{C}}-O(CH_2)_6O-\underset{O}{\overset{\|}{C}}-CH=CH_2$	Aldrich
IA	208	(branched structure with $C(CH_3)_2$, CH, CH_2, C, CH_3 groups, $CH-O-\underset{O}{\overset{\|}{C}}-CH=CH_2$)	Cray Valley
TPGDA	300	$CH_2=CH-\underset{O}{\overset{\|}{C}}-O(CH_2-\underset{CH_3}{\overset{\|}{CH}}-O)_3\underset{O}{\overset{\|}{C}}-CH=CH_2$	Cray Valley

and NVP leads to a decrease of all the mechanical properties (modulus, ultimate stress, and strain). This effect could be attributed to the homopolymerization of the EEEA, which has a high reactivity in comparison to the acrylate double bonds.

Previous studies were devoted to the changes in T_g and mechanical properties with the nature and the molar mass of the macrodiol soft segments on PU and PUA without reactive diluents.[24,25] For these two types of networks, the T_g decreases as the amount of soft segment increases. PUA based on macrodiols with different molar masses exhibits a one-phase structure that turns to a two-phase structure for the highest molar masses and/or for a large excess of DI.[25] As reported, the free radical mechanism that leads to long chains in the beginning of the polymerization process favors the formation of inhomogeneities due to cyclization and excluded volume effects.[12,26] For PUA, this effect could be enhanced by the poor compatibility between the PU and PA chains. In fact, the compatibility is lower when the molar mass of the macrodiol increases and
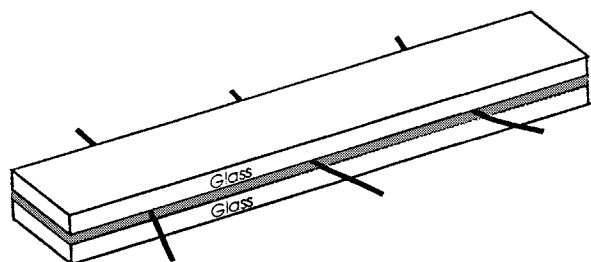
Figure 1 PUA networks tested as a thin interlayer between two glass plates (dynamic mechanical spectroscopy).

with an excess of DI.[25] In such networks, even if no thermodynamical phase separation occurs, the distribution of the crosslinks is not spatially uniform and the concept of clusters could be used to describe the dependence of the relaxed modulus and/or the shear modulus in the rubbery state.[24,25] The clusters are based on structures chemically bonded by rigid units, for example, the short diacrylate chains in the PUA networks. Thus, the networks could be described as rigid clusters connected with elastically active chains.

This article is devoted to the understanding, for a given viscosity of the reactive mixture, of the influence of the reactive diluent composition on the thermal and dynamic mechanical properties of UA networks.

EXPERIMENTAL

Reagents

1,3-Bis-2,2′(2-isocyanatopropyl)benzene or TMXDI (from Cyanamid) were used as received. PCL α,ω-diols (from Solvay) were degassed at 80°C for 2 h under vaccum before use. Different acrylate monomers were used (see Table I).

The photoinitiator system was supplied by Cray Valley and is based on 20% (by wt) of benzophenone as photosensitizer, 20% (by wt) of diethoxyacetophenone as photoinitiator, and a monoacrylate ter-
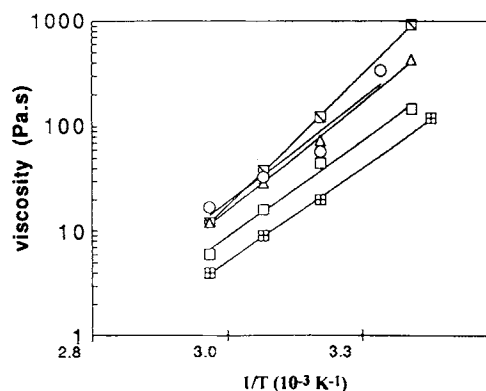

Figure 2 Temperature dependence of the viscosity of the UA oligomers (Arrhenius plot): (-■-) PCL550-TMXDI-HEA 1,2,2; (-□-) PCL550-TMXDI-HEMA 1,2,2; (-⊞-) PCL550-TMXDI-HEMA 1,3,4; (-△-) PCL1000-TMXDI-HEMA 1,2,2; and (-O-) PCL2000-TMXDI-HEMA 1,2,2.

tiary amine (60% by wt). In the following synthesis, the concentration of double bonds of the tertiary amine coinitiator was not taken into account.

Synthesis of UA Prepolymer

PCL-based UA prepolymers were prepared in a two-step synthesis. First, 1 mol of macrodiol was mixed with A mol of DI ($A > 1$; stoichiometric ratio $= 1/A = (OH)_o/(NCO)_o$) under vacuum at 80°C for 4 h for a complete reaction. The second step consisted of adding $2(A - 1)$ mol HEMA (or HEA). With this stoichiometry, all the isocyanate groups reacted with HEMA or HEA as confirmed by the IR measurements.

The different PUA networks are denoted by the oligomer nature and from the amounts of the various reactive diluents. For example, PCL550-TMXDI-HEMA 1,2,2/30 IA/20 TPGDA denotes a PUA based on 1 mol (1) of PCL macrodiol having a molar mass equal to 550 g mol^{-1}, 2 mol (2) of TMXDI and 2 mol (2) of HEMA with a mixture of the diluents

Table II Viscosity (Pa s) of UA and UMMA Oligomers

Temperature (°C)	PCL550-TMXDI-HEA 1,2,2	PCL550-TMXDI-HEMA 1,2,2	PCL550-TMXDI-HEMA 1,3,4	PCL1,000-TMXDI-HEMA 1,2,2	PCL2,000-TMXDI-HEMA 1,2,2
25	930	146	120[a]	430	340[b]
40	122	45	20	74	58
50	38	16	9	29	33
60	12	6	4	12	17

[a] At 22°C.
[b] At 30°C.

Table III   Temperature Dependence of Viscosity (η) of UA and UMMA Oligomers

Oligomer	E_a (kJ mol^{-1})
PCL2,000-TMXDI-HEMA 1,2,2	40.7
PCL1,000-TMXDI-HEMA 1,2,2	42.5
PCL550-TMXDI-HEMA 1,3,4	36.8
PCL550-TMXDI-HEMA 1,2,2	37.9
PCL550-TMXDI-HEA 1,2,2	51.6

$\eta = B \exp(E_a/T)$.

Table IV   Dependence of Viscosity at 25°C of UA PCL550-TMXDI-HEA 1,2,2 as a Function of Amount of Reactive Diluent, HDDA

HDDA (phr)	HDDA (%)	Viscosity (Pa s)
0	0	932
10	9.1	130
20	16.7	29
30	23.1	12
40	28.6	6.5

prepared from 30 phr of isobornyl acrylate (IA) and 20 phr of tripropylene glycol diacrylate (TPGDA).

UV Curing

The UV-cured UA films were prepared by passing the reactive mixture under a medium pressure UV lamp (80 W cm^{-1}) equipped with a parabolic reflector. The distance between the sample and the lamp was equal to 30 mm. These samples (440-μm thick films) studied by dynamic mechanical spectroscopy were polymerized between two polymethylmethacrylate (PMMA) plates and calibrated using a polytetrafluoroethylene (PTFE) sheet. The PUA systems as 7 or 19 μm thick interlayers were also UV polymerized between two glass plates (Fig. 1).

Characterization

Viscosity measurements were performed using a Rheomat 115 viscosimeter (from Contraves) at a constant temperature for different shear rates (from 6 to 200 s^{-1}).

The glass transition temperature, T_g, and the change of heat capacity, ΔC_p, at T_g were recorded using a Mettler TA3000 calorimeter with closed pressure proof crucibles during an heating rate of 7.5 K min^{-1}. T_g and ΔC_p were recorded after the UV polymerization with low pressure crucibles.

FTIR spectra were obtained using a Nicolet MX1 spectrometer in a transmission mode (KBr pellets; 32 scans/min, resolution 4 cm^{-1}). The extent of the alcohol–isocyanate reaction after the first step of the synthesis was checked by looking at the peak located at 2,270 cm^{-1}, which is associated with the NCO vibration group.

A Rheometrics Solid Analyzer (RSA2) was used to obtain the dynamic mechanical spectra (E', E'', and tan δ as a function of temperature) from -150 to 150°C at 10 Hz. The tension mode on 440-μm-thick films was considered for such studies. From

these measurements, the shear modulus in the rubbery state (50 K over the tan δ peak associated with T_g, denoted T_a), G'_{rub}, was calculated assuming the Poisson's ratio equal to 0.5. The shear equilibrium modulus, $G_{equilibrium}$, was determined from a stress relaxation test at the same temperature. The measurements were done in a temperature steps mode (i.e., the properties were measured for a constant temperature after 3 min as soak time). For the PUA systems polymerized between two glass plates, the sandwich systems (glass plate/PUA interlayer/glass plate) were tested in a dual cantilever mode at 1 Hz. From the recorded dynamic mechanical spectra, the storage modulus at room temperature (E' at RT) and the temperatures of the tan δ and E'' (T_{max} tan δ and $T_{max}E''$, respectively) were determined.

RESULTS AND DISCUSSION

Viscosity of UA Oligomers

The influence of the MA or acrylate chain ends and of the excess of DI on the viscosity, η, is reported in Table II. It could be noted that PCL550-TMXDI-
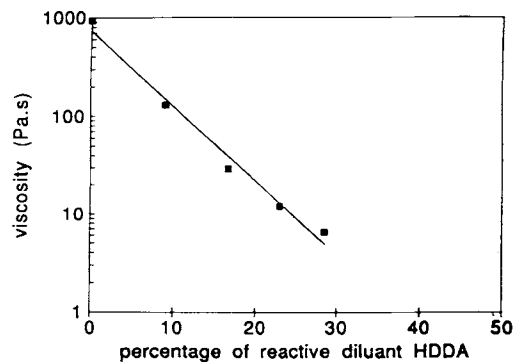
Figure 3 Dependence of the viscosity of the UA oligomer (PCL550-TMXDI-HEA 1,2,2) on the amount of HDDA as reactive diluent.

Table V   Composition of Various PUA Reactive Systems Based on PCL550–TMXDI–HEA 1,2,2

System	HDDA (phr)	EHA (phr)	TPGDA (phr)	IA (phr)	x_{db} Concn of Double Bonds ($\times 10^4$ mol g^{-1})	Photoinitiator (phr)	Viscosity at 25°C (Pa s)
A1	0	50	—	—	28.6	10	1.3
A2	10	40	—	—	30.9	9.2	—
A3	20	30	—	—	33.2	8.6	1.6
A4	30	20	—	—	35.4	8.1	—
A5	40	10	—	—	37.7	7.6	1.9
A6	50	0	—	—	40	7.2	—
B1	—	—	0	50	26.5	10.8	—
B2	—	—	25	25	29.6	9.7	—
B3	—	—	50	0	32.7	8.7	—

HEA 1,2,2, PCL550–TMXDI–HEMA 1,2,2, and PCL550–TMXDI–HEMA 1,3,4 oligomers exhibit a Newtonian behavior in the considered shear rates. As expected, the viscosity largely decreases as the temperature increases. Such dependence could be described by means of an Arrhenius law (Fig. 2) with an activation energy denoted E_a (Table III).
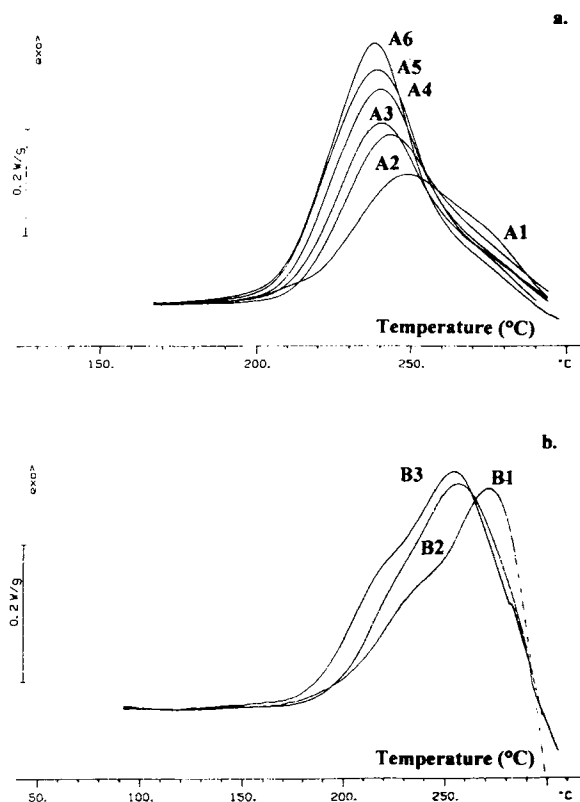

Figure 4 DSC recordings for PCL550–TMXDI–HEA with different reactive diluent mixtures: (a) A series (from A1 to A6) and (b) B series (from B1 to B3) (see Table VI). Heating rate: 7.5 K min^{-1}.

The viscosity of the acrylate oligomers is higher than the MA-based ones; but for these oligomers, η is more temperature sensitive. The isocyanate excess controls the chain extension and the number average molar mass, $\bar{M}_n$, of the prepolymer. As demonstrated in previous studies,[24,25] a two-step polycondensation leads to a double distribution of molecules: those including the soft segment and those corresponding to the residual isocyanate after the first step. For example, the measured $\bar{M}_n$ for PCL550–TMXDI–HEMA 1,2,2 and PCL550–TMXDI–HEMA 1,3,4 are 1,298 and 901 g mol^{-1}, respectively; thus, this last prepolymer displays the lowest viscosity. Nevertheless, the activation energy is the same regardless of what the mole number of DI (2 or 3) is. In addition, the molar mass of the initial macrodiol is also an important parameter because the viscosity decreases as the molar mass of the PCL decreases from 2,000 to 550 g mol.

To study the influence of the amount of reactive diluent on the viscosity of the reactive system, various amounts of diacrylate (HDDA) reactive diluent were added to the PCL550–TMXDI–HEA 1,2,2 oligomer. The viscosity of the oligomer decreased rapidly with the percentage of reactive diluent, in agreement with Cooper et al.[18] (Table IV, Fig. 3).

For a practical point of view, we chose 1 Pa s (100 cP) as the desired viscosity. As a consequence, the mass percentage of reactive diluent necessary is about 40% (i.e., 40% of diluent and 60% of oligomer).

Glass Transition Temperatures and Dynamic Mechanical Properties of PUA Networks

In this work, several reactive systems were considered to understand the effects of the nature and the percentage of reactive diluent on the thermal and dynamic mechanical behavior of the resulting PUA network. The amount of photoinitiator was adjusted according

to the number of double bonds (10 phr of photoinitiator system for 28.6×10^{-4} mol g^{-1} of double bonds) (Table V). In addition, as reported previously, the PUA networks were prepared with 50 phr of reactive diluents (based on monoacrylate, diacrylate, and/or a mixture of mono- and diacrylate diluents).

The thermal polymerization of nine formulations was studied by means of differential scanning calorimetry (DSC) in closed pressure proof pans in order to avoid the evaporation of the monomers. The thermograms clearly show that the thermal polymerization with diacrylate proceeds faster than for the reactive system including the monoacrylate [Fig. 4(a,b)]. As the relative amount of monoacrylate increases, the exotherm peak becomes broader and shifts to a higher temperature (Table VI). The enthalpy of reaction per mole of double bonds is relatively constant and is in agreement with those reported in the literature for MMA polymerization[27] (i.e., 57.8 kJ mol^{-1}). In addition, no exothermal effect was observed during a second scan.

For the UV polymerization, it was necessary to take into account, in addition to the exothermicity of the polymerization reaction, the heat emitted by the UV lamp. Thus, UV coatings are not really polymerized at room temperature. To quantify the real temperature of the reactive mixture during the UV-polymerization process, the temperature was measured just after switching on the lamp. As reported in Figure 5, the temperature increases continuously from RT to 100°C in 40 min. It is well known that the temperature influences the polymerization rate, r_p, and the instantaneous number average chain length, x_n, of the polymer formed.[28]

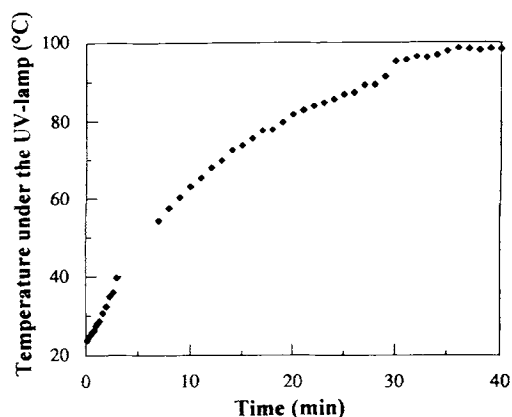$$dr_p/dT = (E_p + E_d/2 - E_t/2)/RT^2$$
$$dx_n/dT = (E_p - E_d/2 - E_t/2)/RT^2$$

Figure 5 Evolution of the temperature with the exposure time under the UV lamp.

where E_d, E_p, and E_t correspond to the activation energies of the initiator decomposition, of the propagation, and of the terminasion rates, respectively. For the UV-curable systems, the effect of a slight change of temperature of the curing sample could be evaluated. In fact $E_d \sim 0$ and $E_p - E_t/2 \sim 20$ kcal mol^{-1}. Thus,

$$\ln(r_p(T_2)/r_p(T_1)) = \ln(x_n(T_2)/x_n(T_1))$$
$$= -20 \times 10^3/R(1/T_2 - 1/T_1)$$

The increase of temperature from 50 to 60°C induces an increase of 25% of the polymerization rate, r_p, and of the instantaneous number average chain length. The curing temperature measured by putting a thermocouple on the reactive system varies with the specific heat of the plates used to calibrate the samples (Fig. 6).

The glass transition temperatures are measured for the cured films prepared for the dynamic me-

Table VI   Enthalpies of Reaction (ΔH) and Temperatures of Exotherm (T_{ex}) Recorded by DSC for Various PUA Series

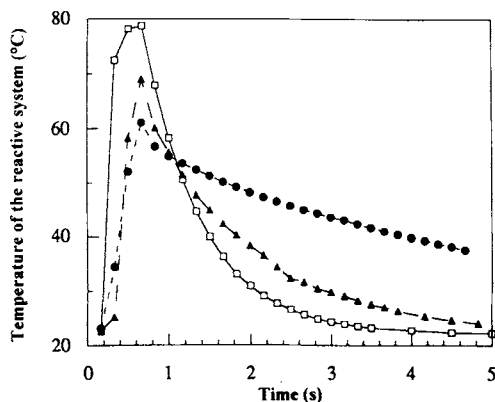| System	HDDA (phr)	EHA (phr)	TPGDA (phr)	IA (phr)	ΔH (J g^{-1})	ΔH (kJ mol^{-1})	T_{ex} (°C)
A1	0	50	—	—	143.8	50.3	249
A2	10	40	—	—	167.5	54.2	243
A3	20	30	—	—	169.8	51.1	240
A4	30	20	—	—	204.1	57.7	239
A5	40	10	—	—	218.4	57.9	239
A6	50	0	—	—	219.9	55	239
B1	—	—	0	50	143.2	54.1	272
B2	—	—	25	25	159.8	54	257
B3	—	—	50	0	184	56.3	255

Heating rate 5 K min^1.

Figure 6 Evolution of the temperature of the UV-curable system during six passes under the UV lamp in different conditions: (-●-) under a PMMA sheet, (-□-) under a glass plate, and (-▲-) without any upper cover plate.

chanical measurements, i.e., the samples polymerized between two PMMA plates. For curing, six runs under the UV lamps were done and the resulting films were all transparent. The glass transition zone, quantified as ΔT, becomes broader as the amount of hexanediol diacrylate (HDDA) in the A series increased (Table VII). However, the T_g onset changed slightly (from -22 to $-16°C$) as the composition of the reactive diluent was modified. Kim et al.[20] obtained similar results on UA networks based on polypropylene oxide, hexamethylene diisocyanate, and HEA with various monoacrylate diluents such as acrylic acid, 2-ethyl hexyl acrylate (EHA), n-butyl ester acrylic acid, lauryl methacrylate, and NVP. This effect is attributed to the nature of the soft segment that governs the T_g, whereas the reactive diluent is preferably associated with the hard segment phase.[18] Such interpretation supposes a two-phase character of the resulting networks even
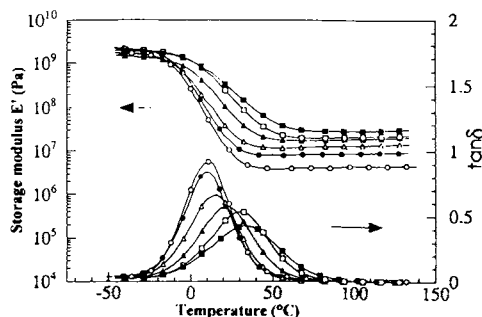

Figure 7 Dynamic mechanical spectra of the A series of the PUA networks at 10 Hz (see Table VIII): (O) A1, (●) A2, (△) A3, (▲) A4, (□) A5, and (■) A6.

though in our case, the materials seem to exhibit a one-phase structure. In fact, the dynamic mechanical spectra of the two series of PUA networks display only one main relaxation associated with the glass transition process (Figs. 7, 8). This phenomenon could be attributed to the low excess of DI and the lower mass of the macrodiol in comparison with the systems considered by Cooper et al.[14-18]

As expected, the increase of crosslink density leads to an increase of the storage modulus measured in the rubbery state (Table VIII). The decrease of the mobility of the macromolecular chains, as the crosslink density increases, leads to a lower amplitude of the α peak (tan δ_α) associated with the T_g. Nevertheless, the motions of the chains having the highest mobility (low temperature part of the α peak) occur in the same temperature range for all of the networks, as expected from the T_g-onset measurements. However, for the A series, the tan δ peaks become broader as the amount of HDDA increases. Thus, the maximum of the tan δ peak is continuously shifted to the highest temperatures (Fig. 7). For the B series, the effect of the structure of the reactive diluent on the

Table VII DSC Measurements on UV-Cured PUA Networks Based on PCL550–TMXDI–HEA 1,2,2

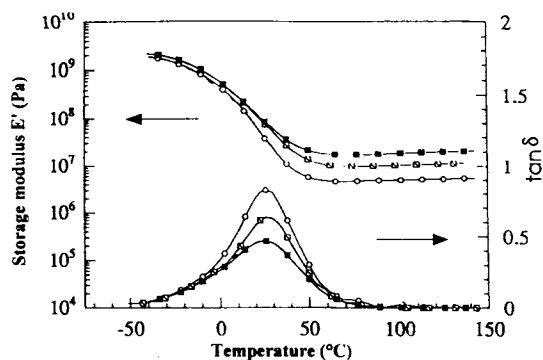| System	HDDA (phr)	EHA (phr)	TPGDA (phr)	IA (phr)	T_g (°C)	ΔT (°C)	ΔC_p (J g^{-1} K^{-1})
A1	0	50	—	—	-22	15	0.30
A2	10	40	—	—	-19	18	0.32
A3	20	30	—	—	-19	21	0.32
A4	30	20	—	—	-19	19	0.34
A5	40	10	—	—	-17	22	0.32
A6	50	0	—	—	-16	23	0.33
B1	—	—	0	50	-16	26	0.45
B2	—	—	25	25	-18	26	26
B3	—	—	50	0	-21	28	0.52

Heating rate 5 K min^{-1}.

Figure 8 Dynamic mechanical spectra of the B series of the PUA networks at 10 Hz (see Table VIII): (O) B1, (▣) B2, and (■) B3.

dynamic mechanical spectrum of the PUA networks can be seen (Fig. 8). The maximum of the loss factor peak is located at a temperature higher for the PUA based on IA and TPGDA than for those based on EHA and HDDA. This effect could be due to the structural features of the diluents: the EHA segment is aliphatic and very flexible and the IA unit is cycloaliphatic and as a consequence, more rigid. In fact, the T_g of the EHA and IA homopolymers are equal to -50 and $70°C$, respectively. In the same way, HDDA homopolymer displays a lower T_g than the TPGDA, which contains ether groups. Thus, the difference in T_g between the resulting homopolymers of the reactive diluents used in the two series could explain the broadness of the α–tan δ peak.

As reported previously on thermally cured PU and PU,[24,25] the equilibrium modulus in the rubbery state (at 50 K over the temperature of the tan δ peak associated with the glass transition, α) is slightly lower than those determined from the dynamic mechanical spectra recorded at a fixed frequency (Table VIII). Although all the double bonds are not reacted, the

equilibrium modulus could be plotted versus the calculated total concentration of double bonds, x_{db}, and of the double bonds contributing to the crosslinks, $x_{db,c}$ (i.e., the double bonds from the diacrylate molecules). The equilibrium modulus is found to be dependent on the molar concentration of diacrylate double bonds (Fig. 9). In fact, the monoacrylate reactive diluents do not influence the concentration of the elastically active network chains, v_e, whereas the diacrylate molecules, having a functionality of 4 and three connections linked to the whole network, contribute to increase of v_e. As all of the PUA networks are on the same curve, it indicates that the chemical structure of the reactive diluent does not influence the equilibrium modulus. The functionality of the diluent molecule seems to be the main parameter.

Characterization of PUA Networks as Thin Interlayers Between Two Glass Plates

A bending test was used to measure the dynamic mechanical properties of the PUA networks as thin interlayers between two glass plates. Other authors used such experiments to characterize the damping behavior of viscoelastic interlayers.[30–32] Obviously, the UV-curing conditions (temperature and UV irradiation) are not the same as for the thicker films prepared between two PMMA sheets studied previously. Nevertheless, the same tendency is observed on the storage modulus E', the loss modulus E'', and the loss factor tan δ for the two types of specimens ("free" films tested in tension and "sandwiches") (Fig. 10, Table IX). It is necessary to remember that it is difficult to directly compare the moduli measured on films and on the sandwiched interlayers because of the different states of stress of the polymer in the two modes.[29] As a consequence, the existing mechanical coupling between the glass plates,

Table VIII Dynamic Mechanical Measurements at 10 Hz Made on UV-Cured PUA Networks

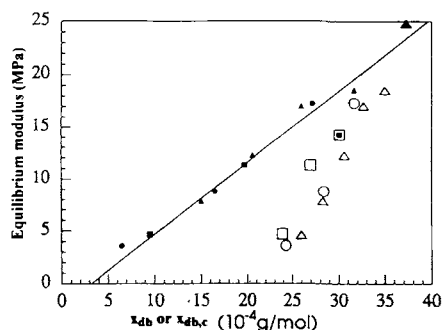| System	EHA (phr)	HDDA (phr)	TPGDA (phr)	IA (phr)	T_α (Amplitude tan δ) (°C)	G' at $T_\alpha + 50$ K (MPa)	$G_{equilibrium}$ at $T_\alpha + 50$ K (MPa)
A1	50	0	—	—	11 (0.97)	4.6	5
A2	40	10	—	—	12 (0.89)	7.8	8
A3	30	20	—	—	16 (0.70)	12.2	13
A4	20	30	—	—	21 (0.60)	17	18
A5	10	40	—	—	33 (0.55)	18.5	20
A6	0	50	—	—	33 (0.44)	24.8	28
B1	—	—	0	50	52 (0.79)	4.7	5
B2	—	—	25	25	45 (0.65)	11.3	12
B3	—	—	50	0	48 (0.55)	14.2	15

Figure 9 Equilibrium moduli (determined at $T_\alpha + 50$ K) of the PUA networks as a function of the total concentration of double bonds, x_{db}: ($\triangle$) A series, ($\square$) B series; and as a function of the concentration of double bonds of the diacrylate molecules, $x_{db,c}$: ($\blacktriangle$) A series and ($\blacksquare$) B series.

Figure 10 Dynamic mechanical spectra of PUA networks cured and tested as 19-μm-thick interlayers between glass plates at 10 Hz: ($\bigcirc$) A1, ($\bullet$) A2, ($\triangle$) A3, ($\blacktriangle$) A4, ($\square$) A5, and ($\blacksquare$) A6.

which only have an elastic behavior, and the viscoelastic PUA interlayer, leads to an apparent modulus E^* and could induce a shift of the mechanical relaxation peaks (E'' or tan δ maxima). Similar results are obtained, however, for the thickness of the PUA interlayer, 7 or 19 μm (Figs. 10, 11). According to the previous remarks on the mechanical effects of testing the PUA as thin interlayers, the increase of the temperature of the E'' maximum and of the width of the relaxation (22, 34, and 40°C for 7, 19, and 440 μm, respectively) as the thickness decreases, cannot be explained directly as a decrease of the mobility of the macromolecular chains. Nevertheless, the relative amplitude of the tan δ peak is very sensitive to the changes of the PUA composition.

CONCLUSION

UV-cured PUAs based on PCL and TMXDI were prepared. The influence of the percentage of the reactive diluent on the viscosity was also studied. A constant amount of the reactive diluent (50 phr) was considered to obtain an initial value of the viscosity that was constant in all cases. The composition of the reactive diluents mixture was varied in order to study its influence on the glass transition temperature and dynamic mechanical properties.

Two series of PUAs were based either on EHA and HDDA (denoted A series) or IA and TPGDA (denoted B series). From the DSC experiments and the dynamic mechanical spectroscopy, both the thermally cured and UV-cured PUA networks exhibited a one-phase structure. In addition, the onset T_g of the UV-cured PUA was not dependent on the reactive diluent composition. As the amount of diacrylate increased, the glass transition zone became
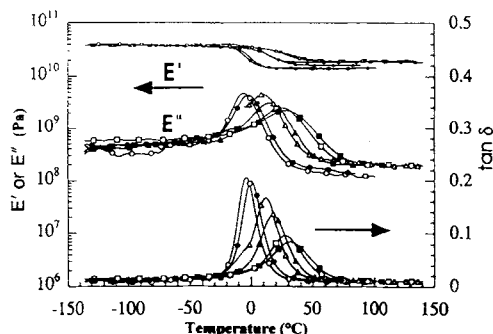
broader for the A series, which was not the case for the B series. This phenomenon could be associated with the T_g of the homopolymers of the reactive diluents: the T_g of the homopolymers from EHA and HDDA was lower than those from IA and TPGDA. For the two series, the polymerization proceeded faster when the amount of diacrylate increased.

The dependence of the T_g on the nature and composition of the reactive diluent mixture was verified by considering the dynamic mechanical properties of the networks. The storage modulus in the rubbery state increased as the amount of diacrylate increased. The same trends were qualitatively reproduced for PUA interlayers tested between two glass plates (7- and 19-μm-thick layers). As the amount of the diacrylate increased, the crosslink density increased inducing a decrease in the mobility of the macromolecular chains. As a consequence, the shape of the tan δ peak was changed (lower amplitude and broader peak due to the larger distribution of the crosslink density). Especially the low temperatures component of the α
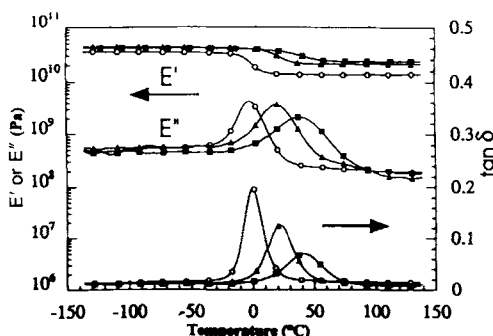

Figure 11 Dynamic mechanical spectra of PUA networks cured and tested as 7-μm-thick interlayers between glass plates at 10 Hz: ($\bigcirc$) A1, ($\blacktriangle$) A4, and ($\blacksquare$) A6.

Table IX   Dynamic Mechanical Properties of UV-Cured PUA Films

	Film Composition		Film Thickness					
			19 μm			7 μm		
System	EHA (phr)	HDDA (phr)	E' at RT (GPa)	T_{max} tan δ (Amplitude) (°C)	T_{max} E'' (°C)	E' at RT (GPa)	T_{max} tan δ (Amplitude) (°C)	T_{max} E'' (°C)
A1	50	0	14.3	−3 (0.23)	−5	13.6	1 (0.23)	−1
A2	40	10	13.6	1 (0.22)	−1	—	—	—
A3	30	20	16.9	14 (0.16)	11	—	—	—
A4	20	30	16.1	18 (0.14)	14	21.3	22 (0.13)	14
A5	10	40	19.3	28 (0.098)	24	—	—	—
A6	0	50	19.5	32 (0.086)	30	23.4	41 (0.072)	30

Films sandwiched between two glass plates (at 1 Hz).

peaks associated with the motions of the soft segments occurred at the same temperature for all the networks.

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