

Morphology and Mechanical Properties of Radiation-Polymerized Urethane-Acrylates. I. Pure Oligomers

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Synopsis

The morphology of electron beam cured polyacrylo-urethane films based on polyethylene adipate and toluene diisocyanate was characterized to explain their mechanical properties. The polyacrylo-urethane films have a one-phase morphology in which the hard urethane segments and the soft polyester segments are homogeneously mixed. The films obtained from 1000-molecular-weight oligomer are hard and somewhat brittle due to their one-phase morphology in which hard glassy segments play a dominant role. The films obtained from 4600- and 6000-molecular-weight oligomers are soft and tough, once again due to their one-phase morphology in which soft rubbery segments are more effective. The original crystalline structure of 6000-molecular-weight oligomer is retained in the precrystallized γ -irradiated film, but electron-beam-irradiated films showed partial melting of the crystallites due to the heat of polymerization. The solid state polymerized films have a lower elongation, a higher modulus, and a higher breaking strength due to their crystallinity.

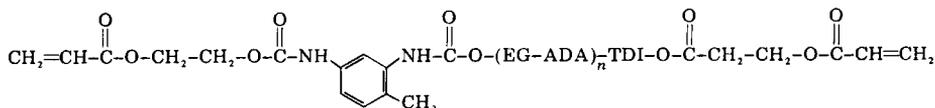
INTRODUCTION

Urethane coatings are commercially applied from a solvent, which causes tremendous pollution problems. Recently, application of high-energy radiation in the coating industry has shown rapid growth and wide acceptance. Radiation-curable coatings are completely reactive and contain no solvent. They are fixed on the base material by the radiation at room temperature. Radiation curable resin often consists of acrylo-urethane oligomers and their mixture with reactive monomers. The electron-beam curing of the resin forms a polymer network through a free radical polymerization mechanism resulting in a multirayed star-shaped structure as discussed by Oraby and Walsh.¹ It cures the pollution problems and saves large amounts of energy due to the elimination of a drying step. Oraby and Walsh^{1,2} studied the mechanical properties of electron-beam-cured films as a function of polyester acrylo-urethane oligomer structure based on toluene-diisocyanate (TDI) and monomer diluent. Joseph et al.³ reported the morphology of electron-beam-cured prepolymer, based on poly(caprolactone) diol, isophorone-diisocyanate and 2-hydroxyethyl-acrylate, and its effect on mechanical properties. The objective of this investigation was to synthesize polyacrylo-urethane films using radiation-curing techniques and characterize the morphology of the films and their mechanical properties. Solid state polymerization was used to modify the morphology of the films and study its effect on the mechanical properties.

EXPERIMENTAL

Materials

A series of reactive radiation-curable acrylo-urethane oligomers of molecular weights 1000, 4600, and 6000 was supplied by Thiokol/Chemical Division. Their molecular formula is given as the following:



where EG is ethylene glycol, ADA is adipic acid, and TDI is toluene-diisocyanate. The molecular weight of the oligomers varied between 1000 and 6000 by increasing the molecular chain length between the two end acrylate groups.

Processing

The electron beam source used was manufactured by the High Voltage Engineering Corp. and has a maximum beam current of 20 mA. It was operated at 500,000 V for all experiments. Each irradiation was given in two passes, one on each side at a dose rate of about one Mrad/s. The γ -radiation was produced by a fixed cobalt 60 source in the form of a "squirrel cage" at 0.3 Mrad/h. The molten oligomers or oligomer-monomer mixtures were cast on Mylar film using wire-wound rods. The film was then irradiated by an electron beam in a sealed polyethylene bag filled with nitrogen. Irradiations were performed at 10 Mrad. Oraby and Walsh¹ determined the percent gel of the cured film by exhaustively extracting the uncrosslinked materials with trichloroethylene at room temperature. The percent conversion of pure oligomers by electron beam radiation are extremely high and "leveled off" after 1 Mrad.

Tensile Testing

Dynamic mechanical properties of the films were measured with Rheovibron Model DDV II in dry nitrogen at 100 cycles/s at a heating rate of 1°C/min over a temperature range of -50°C-200°C. The samples were preheated to 110°C for 15 min in the nitrogen atmosphere, and then cooled to room temperature prior to the testing. The tensile properties were determined by Instron, Model TT-B at both 65% and 0% relative humidity (dry nitrogen); with a gauge length of 1 in. (25.4 mm) and an extension rate of 1 in. (25.4 mm)/min to failure.

RESULTS AND DISCUSSION

Dynamic mechanical analysis characterizes the morphology of the electron beam cured polyurethane acrylate films. The most pronounced dispersion is seen in the glass transition region. The storage modulus E' falls from the glassy state modulus of 10^9 - 10^{10} dyne/cm² to the soft rubbery state of 10^7 - 10^8 dyne/cm², and here a sharp, large absorption appears. This absorption is usually attributed to the initiation of the micro-Brownian motion of the molecular chains from the

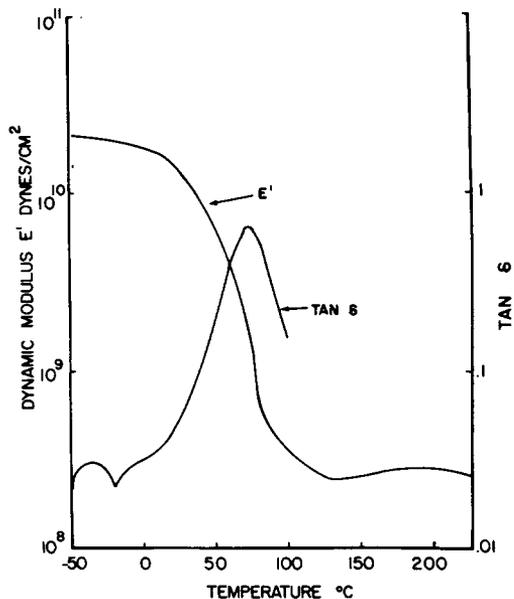


Fig. 1. Dynamic mechanical spectrum of the films obtained from the acrylo-urethane oligomer of 1000 molecular weight.

frozen state. The glass transition temperatures (T_g) of the films obtained from acrylo-urethane oligomers of 1000, 4600, and 6000 molecular weight occurred at 72°C, -18°C, and -6°C, respectively (Figs. 1-3). This trend of glass transition temperatures was expected on the basis of the oligomer structures and the relative mobility of the macromolecules. The observation of a single sharp glass transition temperature suggests that the block copolymer has a one-phase mor-

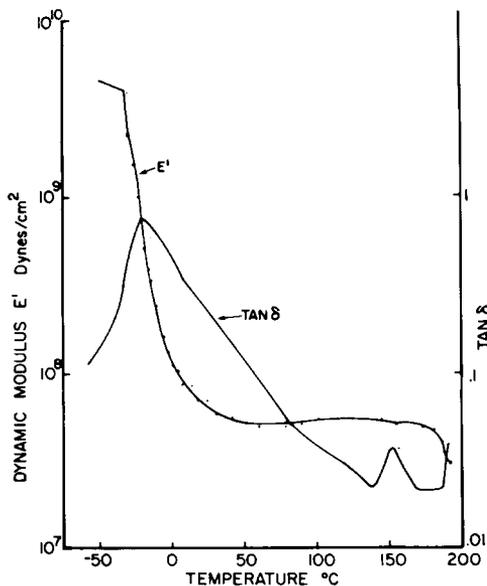


Fig. 2. Dynamic mechanical spectrum of the films obtained from the acrylo-urethane oligomer of 4600 molecular weight.

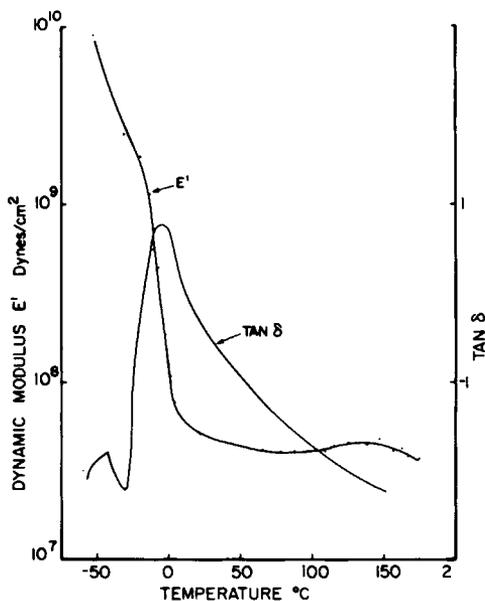


Fig. 3. Dynamic mechanical spectrum of the films obtained from the acrylo-urethane oligomer of 6000 molecular weight.

phology in which the hard urethane segments and the soft polyester segments are homogeneously mixed. The secondary relaxation or so-called β -dispersion around -40°C is probably due to the rotational motion of substituent groups

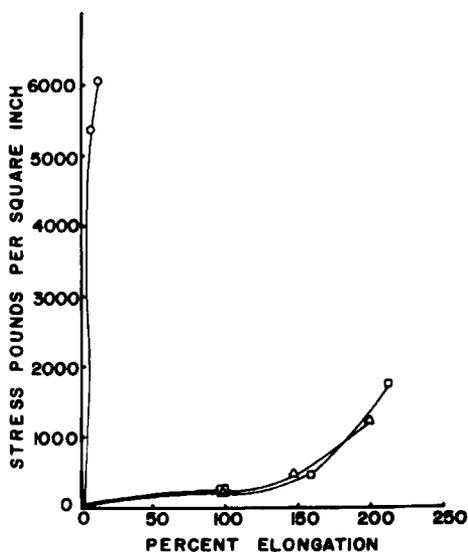


Fig. 4. Stress-strain diagram of the films obtained from the acrylo-urethane oligomers of varying molecular weights at 20°C and 0% relative humidity. (○) 1000 MW oligomer film, (Δ) 4600 MW oligomer film, (□) 6000 MW oligomer film.

TABLE I
Mechanical Properties of Radiation Curable Polymers Obtained from Acrylo-Urethane Oligomers

Molecular wt of oligomer	Weight fraction		Moles of double bonds of oligomer (per 100 g)	Glass transition temperature (°C)	Mechanical properties at 20°C and 65% RH			Mechanical properties at 20°C and 0% RH		
	Hard segments	Soft segments			% elongation	Breaking strength (psi)	100% modulus (psi)	% elongation	Breaking strength (psi)	100% modulus (psi)
1000	0.614	0.386	0.200	72	14	4727	—	11	6059	—
460	0.133	0.867	0.043	-18	197	1106	260	200	1218	246
6000	0.154	0.846	0.033	-6	253	1277	241	226	1768	237
6000 precrystallized	0.154	0.846	0.033	-7	170	939	342	—	—	—
6000 eb cured	0.154	0.846	0.033	—	—	—	—	—	—	—
6000 liquid cast, radiated	0.154	0.846	0.033	—	71	1782	1701 ^a	—	—	—
6000 precrystallized, irradiated	0.154	0.846	0.033	—	—	—	—	—	—	—

^a Indicate 50% modulus.

in the local environment. The electron beam radiation rapidly cures the liquid acrylo-urethane, possibly fixing preformed aggregates of some hard segments, as indicated by a small transition around 152°C in Figure 2. The increase in loss tangent and drop in the dynamic modulus around 190°C (Fig. 3) indicate deblocking of the polyacrylo-urethane and partial melting, which was confirmed by hot stage light microscopical studies. The modulus-temperature profile is similar for all the films over the entire temperature range, but the absolute values of the modulus of the films obtained from 1000-molecular-weight oligomer are higher, probably due to the greater weight fraction of glassy hard segments.

Stress-strain diagrams of the films in Figure 4 show that the films obtained from 1000 molecular weight oligomer are hard and somewhat brittle due to its glassy nature. The films obtained from 4600- and 6000-molecular-weight oligomer are in a rubbery state and contain relatively long flexible polyester chains resulting in a soft and tough polymer. The percent elongation increases and breaking strength decreases with the molecular weight of the oligomer (Table I). The film obtained from 1000-molecular-weight oligomer contains more urethane groups; the latter have cohesive energy density of 8.74 kcal/mol,⁴ and contribute very strong intermolecular forces. The films obtained from 4600- and 6000-molecular-weight oligomers have a higher fraction of the soft polyester segments; the latter have cohesive energy density of 2.90 kcal/mol,⁴ and do not contribute strong intermolecular forces as compared to the urethane groups. The soft segments have a dominant effect in a one-phase morphology of these films accounting for the lower T_g , higher percent elongation and the lower breaking strength. The mechanical properties of the films do not vary significantly with relative humidity except that the breaking strength of the films obtained from acrylo-urethane oligomers of 1000 and 6000 molecular weight is lowered slightly due to the plasticization effect of moisture present in the hard urethane segments.

Solid State Polymerization

The melted 6000 molecular weight acrylo-urethane oligomer was cast on Mylar film and recrystallized by storing at room temperature. The samples were then irradiated by either γ -radiation or electron-beam radiation. The crystalline nature of the pure acrylo-urethane oligomer is seen in the micrograph (Fig. 5).

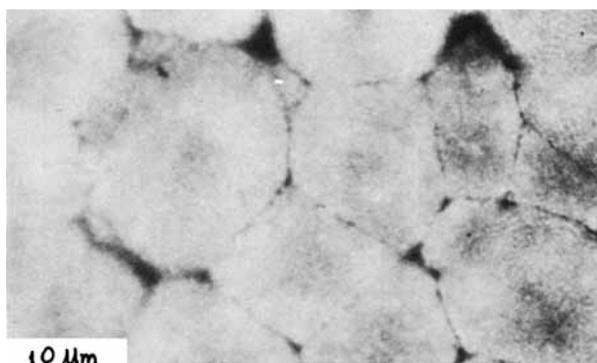


Fig. 5. Micrograph of pure acrylo-urethane oligomer (MW = 6000): magnification 235 \times .

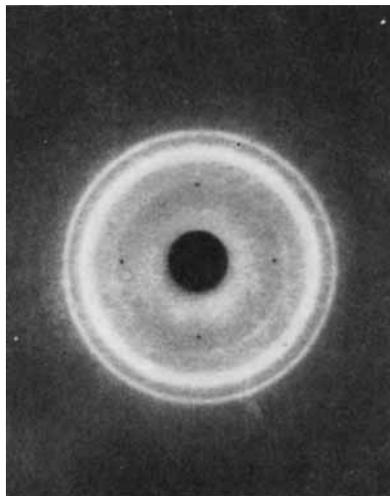


Fig. 6. Wide angle X-ray diffractogram of 6000-molecular-weight acrylo-urethane oligomer.

It produced a clear wide angle X-ray diffraction pattern (Fig. 6). Hot stage microscopical studies showed that these crystals form well-defined spherulites at 40°C, and then melt at 41.6°C. The micrograph of the EB-cured film (Fig. 7) shows that partial melting of the crystallites occurred during curing, due to the exothermic heat of polymerization and the fast kinetics of the electron beam curing. The original crystalline structure of the oligomer is retained in the γ -irradiated film, shown in Figure 8. This is due to the much lower dose rate of γ -irradiation, allowing the heat of polymerization to be dissipated without melting the crystallites. These results are supported by the scanning electron

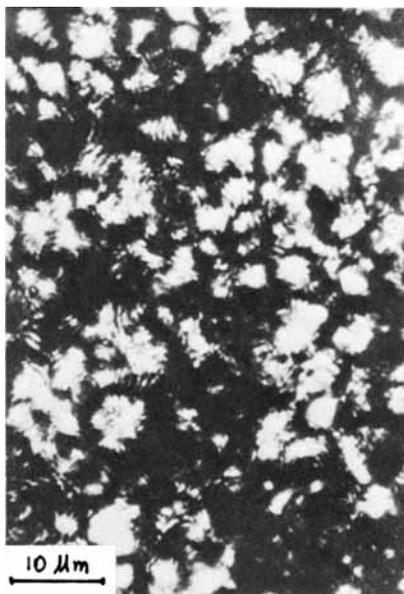


Fig. 7. Micrograph of precrystallized electron-beam-irradiated film obtained from 6000-molecular-weight acrylo-urethane oligomer in the cross-polarized light.

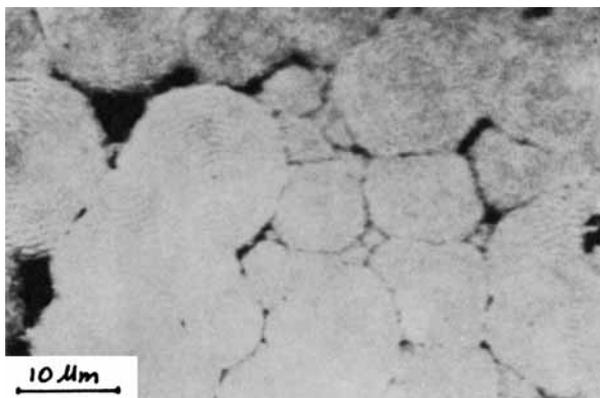


Fig. 8. Micrograph of precrystallized γ -irradiated film obtained from 6000-molecular-weight acrylo-urethane oligomer.

micrographs (Fig. 9) and a wide angle X-ray diffraction pattern identical to that from the precrystallized oligomer (Fig. 6). The wide-angle X-ray diffraction pattern of the precrystallized EB-cured films does not indicate the presence of crystalline structure, possibly due to the very small size of the crystallites. Partial melting of the crystallites in the γ -irradiated film is seen around 44.5°C, and the micrograph shows a similar pattern as that observed in the EB-cured film, indicating the magnitude of the temperature involved during EB radiation. Both the γ -irradiated and EB-cured films exhibit significant birefringence up to 210°C, indicating participation of the hard segments during crystallization in formation of persistent ordered structures.

The glass transition temperatures of the solid-state and the liquid-state EB-cured films are the same (Figs. 3 and 10), probably due to the partial melting of the crystallites on EB radiation, reducing the crystallinity to a point where it has an insignificant effect on the soft segment mobility and hence T_g . The higher dynamic elastic modulus in the rubbery state in the solid-state polymerized film may be due to presence of some ordered structure or a higher degree of cross-linking. The solid-state polymerized γ -irradiated films have a lower elongation,

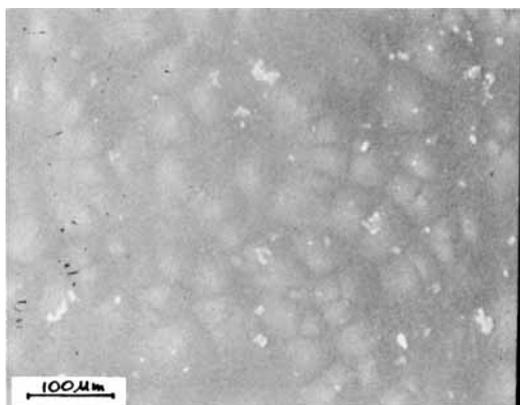


Fig. 9. SEM of the precrystallized γ -irradiated film obtained from acrylo-urethane oligomer of 6000 molecular weight.

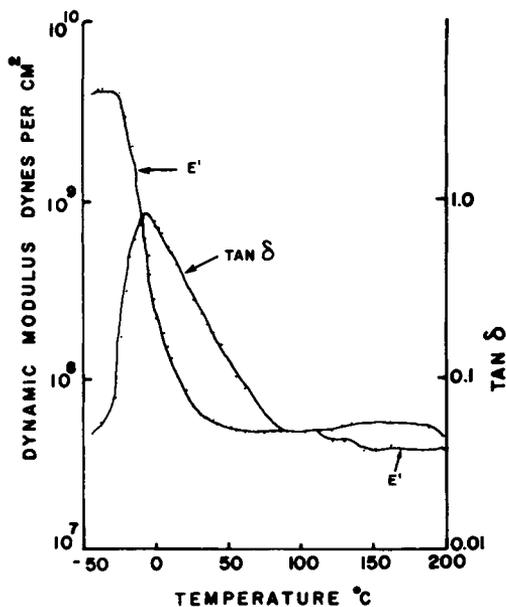


Fig. 10. Dynamic mechanical spectrum of the precrystallized electron-beam-cured films obtained from the acrylo-urethane oligomer of 6000 molecular weight.

a higher modulus, and a higher breaking strength (compare Fig. 11 with Fig. 4). The morphology of the solid-state EB-cured film shows the presence of a small amount of crystallinity which should act as a crosslink and restrict the macromolecular mobility resulting in a lower elongation and higher modulus than films

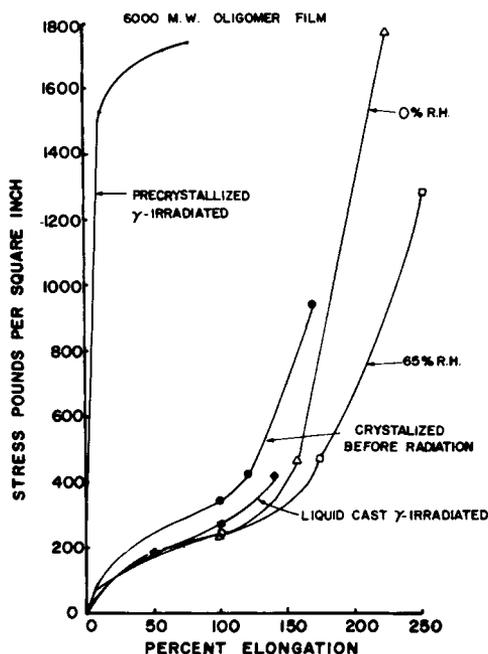


Fig. 11. Stress-strain diagram of the acrylo-urethane oligomer films irradiated either in a liquid state or solid state. Films were EB cured in the crystallized form unless noted otherwise.

EB cured entirely in the liquid state. The precrystallized γ -irradiated film is hard and tough relative to the liquid state γ -irradiated film due to its much higher crystallinity and ability to share load and resist crack propagation. The network in the liquid state γ -irradiated films is probably highly crosslinked, leading to increased ease of crack propagation.

CONCLUSIONS

Electron-beam-cured polyurethane acrylate films have a one-phase morphology in which hard segments and soft segments are homogeneously mixed. The films obtained from 1000 molecular weight oligomer are hard and somewhat brittle due to its glassy nature compared to the films obtained from 4600- and 6000-molecular-weight oligomer. The original crystalline structure of pure 6000-molecular-weight oligomer is retained in the precrystallized γ -irradiated film, but the electron beam irradiated films show partial melting of the crystallites due to the heat of polymerization. The solid state polymerized γ -irradiated films have a lower elongation, a higher modulus, and a higher breaking strength due to their much higher crystallinity.

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