

Electron Beam Curing of Aliphatic Unsaturated Polyesters. I. Mechanistic Study on Converting to Pressure-Sensitive Adhesives

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ABSTRACT: Aliphatic unsaturated polyesters (UPEs) mixed with *N,N*-diethylaminoethyl methacrylate (DEAEMA) were convertible by electron beam irradiation to soft solids of high peeling strength. Double bond conversions, gel contents, molecular weight distributions, and crosslinking densities of the irradiated mixtures were studied in comparison with those of UPE–vinyl acetate mixtures, which gave very low peel strength on irradiation. The latter system started gel formation even at earlier stages of irradiation and had higher cross-linking densities as a result of copolymerization between polyester and monomer double bonds. In contrast, the UPE–DEAEMA system exhibited

slow gel formation with predominant conversion of monomer double bonds, indicating formation of graft copolymers. This system also had lower crosslinking densities than the other system. Therefore, it was concluded that the pressure-sensitive adhesive nature of the electron-beam-cured UPE–DEAEMA mixtures could be attributed to the formation of flexible graft polymers entangled in a loosely crosslinked network. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1854–1857, 2003

Key words: electron beam curing; adhesives; polyesters; graft copolymers

INTRODUCTION

Unsaturated polyester resins, a typical example of which is a poly(propylene maleate phthalate)–styrene mixture, have been mainly used for coatings and fiber-reinforced plastic composites because of the rigid properties of their cured products. A specific feature of this resin system is that it is a 100% solid system, whereas other resin systems for coatings are mostly solvent-based. These resins were among the earliest investigated in the radiation-curing field^{1,2} because their mechanism of curing or crosslinking is radical copolymerization between fumarate and styrene. In the course of developing electron beam (EB) curing processes, which are essentially beneficial nonsolvent systems, we found that aliphatic unsaturated polyesters (UPEs) were potential candidates for producing pressure-sensitive adhesives (PSA).³ Our previous report³ contains a wide range of survey of polyester structures and monomers appropriate for PSA. In this work, the mechanism to achieve adhesive properties was investigated.

EXPERIMENTAL

Materials

Raw materials for synthesizing UPEs, monomers, and solvents were of reagent grade and used as received. UPEs were prepared with a common polycondensation reaction⁴ by heating reaction mixtures to ~200°C in nitrogen atmosphere but in the absence of any solvent. The reactions were stopped when the acid value reached <40. The compositions of UPEs used in this work are shown in Table I. The UPEs thus obtained were cooled to room temperature and mixed with a monomer at a 0.5 molar ratio of monomer to polyester double bond.

Irradiation

Irradiation of samples was performed with electron beams generated from a cascade type (3 MeV Dynamitron) accelerator at an accelerating voltage of 1.0 MV and a beam current of 2.0 mA using a conveyor system. Two types of samples were used. For investigation of hardening behavior, ~5 g of a polyester mixture was poured into an aluminum cup of 5-cm diameter, and a 50- μ m thick poly(ethylene terephthalate) (PET) film was covered on the surface. For measurements of adhesive properties, a resin formulation was coated on the backing substrate (50 μ m Toray PET film) to a thickness of ~30 μ m with a Baker-type

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TABLE I
Formulation of Unsaturated Polyesters^a

Chemical	UPE-A	UPE-B
Maleic anhydride	4	6
Tetrahydrophthalic anhydride	4	—
Sebacic acid	2	—
Adipic acid	—	4
2-Ethyl-1,3-hexanediol	10	10

^a Charged amounts are shown by molar ratio.

applicator and then covered with silicone-release PET film. The dosages shown in this article are nominal and were not corrected for sample thickness.

In reference experiments, ultraviolet (UV) irradiation was performed with an 80 W/cm high-pressure mercury lamp, and 3 phr of 2,2-dimethoxy-2-phenyl acetophenone was added to a UPE/monomer mixture.

Testing and measurement

Adhesive strength was evaluated in terms of the 180° peel test according to JIS-Z 1529, where a 10-cm strip of 1-in. width was allowed to adhere onto a stainless steel panel (SUS 304) and pressed twice back and forth with a 7-kg roller. The measurement was performed at 20°C and a crosshead speed of 300 mm/min immediately after (initial) or 24 h (permanent) after pressing. Evaluation of cohesion was done with a 1-kg dead load test up to 5×10^4 s on a 1-in. wide tape applied at 40°C as already described. Surface tack was evaluated with either a ball tack test, at a 30° slope with a 10-cm strip, or a probe tack test, by contacting the specimen with a 5-mm diameter probe for 1 s and then pulling off the probe at a speed of 10 mm/s.

Gel content was determined by extracting irradiated samples with acetone, initially for 3 h at room temperature followed by 16 h at the boiling temperature. Dried gel was further immersed in ethanol for 24 h at room temperature, and then swelled gel was wiped with filter paper to measure its weight-swelling ratio.

The monomer conversion was determined from the weight loss measured by the following procedure. An irradiated sample was weighed into another aluminum cup and then kept soaking in acetone for 6 h in a desiccator. The sample thus swollen was first air-dried at room temperature, then dried at 40°C for 72 h under vacuum, and then weighed.

The conversion of polyester unsaturation was calculated from the ratio of absorbance at 980 cm^{-1} (*trans*-vinylene, δCH) to that at 2980 cm^{-1} (methyl, $\nu_{\text{as}}\text{CH}$) in the infrared (IR) spectrum taken on a NaCl prism with a JASCO A-302 IR spectrometer.

Molecular weights were estimated from gel permeation chromatograms measured in tetrahydrofuran (THF) at a flow rate of 1 mL/min and 40°C with a

Waters HPLC-6000 equipped with a UV detector (Schoeffel Instruments SF770) and calibrated with polystyrene standard samples.

RESULTS AND DISCUSSION

Effect of cure degree on adhesive properties

The type A polyester (UPE-A), which contained both an alicyclic moiety and side chains, was synthesized according to the results in the previous report.³ A mixture of *N,N*-diethylaminoethyl methacrylate (DEAEMA) and UPE-A (double bond ratio: 0.5/1) was irradiated with various doses of an EB. The peel and cohesive strengths of the irradiated samples are plotted against the gel content in Figure 1. The peel strength has a maximum value at a rather low gel fraction, followed by gradual decrease with increasing gel fraction. On the other hand, the cohesive strength (holding time) is quite low at the maximum point of the peel strength and then increases steeply with lowering peel strength and increasing gel fraction. Considering the failure modes in the peeling test, as shown in the figure, it seems that favorable adhesive properties could be obtained at ~40% gel. Although monomer conversion was not measured in this series of experiments, the irradiated samples of >30% gels were odorless and it was considered that they did not contain any residual monomer.

The finding that the UPE-DEAEMA mixture is convertible with EB to an excellent PSA at such an unexpectedly low gel content and without the aid of any tackifier was thought very unique. Therefore, further studies were performed to characterize irradiated samples with the polyester B (UPE-B) synthesized with a simpler composition than UPE-A.

Comparison of adhesive properties between two formulations

The results in Table II show the adhesion properties when UPE-B was mixed with DEAEMA or vinyl ace-

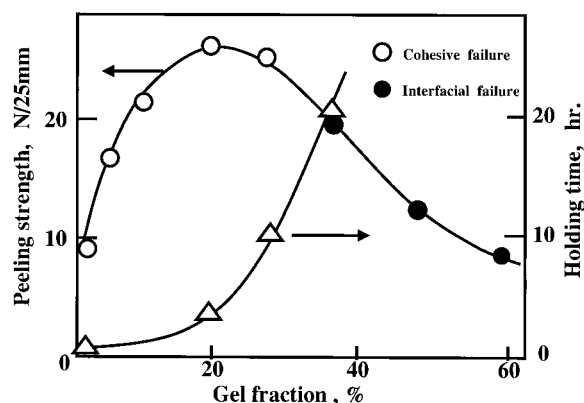


Figure 1 Effect of gel fraction on adhesive properties.

TABLE II
Adhesive Properties of Irradiated UPE-DEAMA and UPE-VAc Mixtures^a

Monomer	DEAMA	VAc
Dose, kGy	60	20
Peel strength, N/25mm		
Initial	13.7	0.11
Permanent	15.2	0.48
Ball tack	4	4
Probe tack, g	500	71
Cohesion, 10 ⁴ s	>5	>5

^a Double bond molar ratio: UPE/monomer = 1.0/0.5

tate (VAc), which is often used in the conventional UPE resins as well as various formulations for adhesive applications. The UPE-B-DEAEMA mixture exhibits good adhesive properties, and UPE-B-VAc gives poor peel strength in spite of satisfactory cohesion. It was also noted that the peel strength increased in the UPE-B-DEAEMA system but was unchanged in the other system when the monomer content was increased.

It is anticipated, therefore, that comparative study on curing mechanisms and resulting chemical structures of these two formulations may clarify the reason for the excellent pressure-sensitive adhesive properties of the UPE-DEAEMA mixed system.

Double bond conversion

The conversions of double bonds and gel contents in UPE-B-DEAEMA and UPE-B-VAc mixtures are shown in Figures 2 and 3, respectively. It is clearly demonstrated in Figure 2 that the double bonds of DEAEMA are mostly converted at 60 kGy where gel formation starts, whereas double bonds in PE-B are converted very slowly. These results indicate that the monomer homopolymerizes, or grafts onto the UPE-B backbones, which occupy ~82% by weight in the mixture and therefore yield most of radicals.

For reference, additional experiments were carried out. First, the PE-B-DEAEMA mixture was irradiated

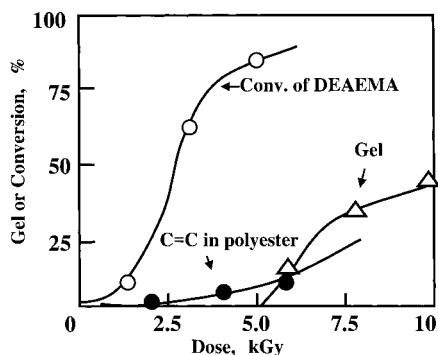


Figure 2 Effect of dose on double bond conversion and gel formation in the UPE-DEAEMA mixture.

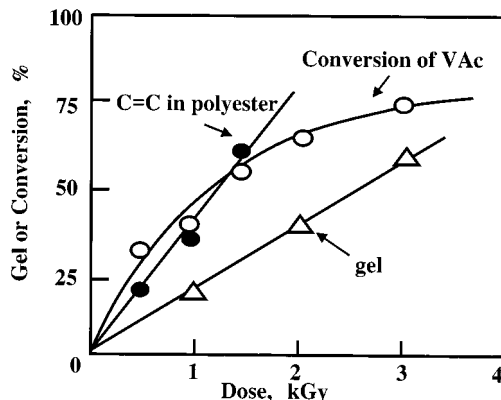


Figure 3 Effect of dose on double bond conversion and gel formation in the UPE-VAc mixture.

with UV light in the presence of a photoinitiator, which resulted in a little increase of viscosity and cohesive strength. This fact indicates that those radicals formed from the photoinitiator predominantly contribute to polymerization of the monomer rather than to transfer to the polyester backbones. Secondly, a mixture of the polyester and poly(DEAEMA), prepared by EB-induced polymerization of the monomer, was irradiated to 200 kGy with an EB but remained a merely viscous state as in the unirradiated mixture. These observations suggest that the presence of graft copolymer in the EB-irradiated PE-B-DEAEMA mixtures plays an important role for pressure-sensitive properties.

Unlike the case for VAc, the copolymerization reactivity ratios of DEAEMA and maleate or fumarate are not available in the literature.⁵ However, in survey experiments on radiation-induced copolymerization of methacrylates and diethyl fumarate, it was observed that homopolymerization of methacrylates takes place.⁶ This observation also supports the production of graft copolymers in EB-irradiated PE-B-DEAEMA mixtures.

On the contrary, the results in Figure 3 clearly show that double bonds in VAc and UPE-B are consumed rapidly at lower dose levels and that gel formation is rapid. It is known that the copolymerization reactivity ratios of either VAc (M_1) and diethyl maleate or diethyl fumarate (M_2) are much <1.0 ($r_1 = 0.171$ and $r_2 = 0.040$; $r_1 = 0.090$ and $r_2 = 0.33$, respectively).⁵ Therefore the aforementioned results indicate that VAc and UPE-B are most likely to copolymerize alternatively to form three-dimensional networks.

Reaction products at lower doses

For further characterization of these irradiated polyester-monomer mixtures, their molecular distributions were studied by gel permeation chromatography (GPC). The chromatograms of UPE-B-DEAEMA and

UPE-B-VAc mixtures irradiated to such doses as to start gel formation are shown in Figures 4a and 4b, respectively.

In the former mixture (Figure 4a), the original sample irradiated to 30 kGy has a bimodal elution curve with two peaks around molecular weight of 4000 and 26,000, the lower one being that of UPE-B as shown with the dotted line. The UPE-B component was separated by repeating dissolution in acetone and precipitation in petroleum ether 10 times, resulting in the chromatogram indicated with the broken line. Therefore, the higher peak can be attributed to UPE-B-g-DEAEMA and DEAEMA homopolymers.

The latter mixture irradiated only to 2.4 kGy still contained microgels that were insoluble in THF. Accordingly, GPC measurement was performed after filtering the sample solution through a Millipore filter. The obtained chromatogram (solid line) completely corresponds to that of PE-B (dotted line), as can be seen in Figure 4b. These facts strongly indicate that VAc copolymerizes with polyester double bonds even in the initial stage of irradiations to form networks.

Swelling ratios

The weight swelling ratios in ethyl alcohol of various degrees of gels obtained from UPE-B-DEAEMA and UPE-B-VAc mixtures are shown in Figure 5. The swelling ratios of the PE-B-DEAEMA gel are much higher than those of the other gel. This fact indicates

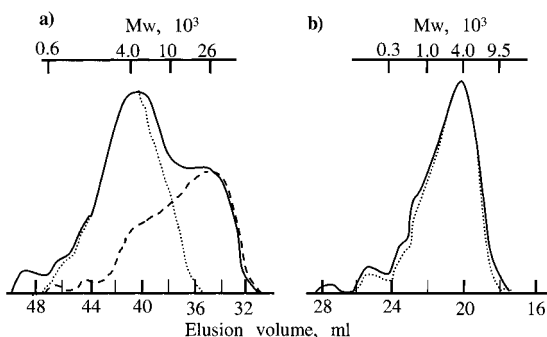


Figure 4 Gel permeation chromatograms of (a) UPE-DEAEMA (30 kGy dose) and (b) UPE-VAc (2.4 kGy dose) mixtures.

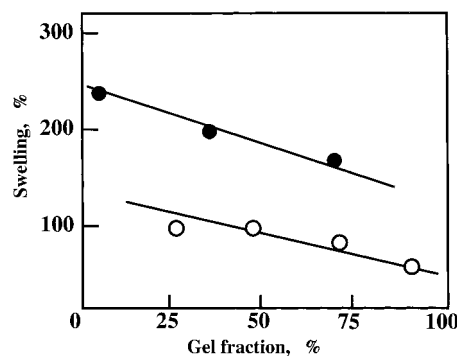


Figure 5 Relationship between percent weight swelling and gel fraction. Key: (○) UPE-DEAEMA mixture; (●) UPE-VAc mixture.

that the former has a looser network structure and higher flexibility than the latter.

CONCLUSIONS

Through the comparative studies just described, it is ascertained that the UPE-DEAEMA mixed system yields a flexible graft copolymer (polyester-g-DEAEMA) via EB irradiation and that the network formed is loose and flexible. It can be concluded that such structures as the graft copolymer are entangled in a loose network and result in excellent pressure-sensitive adhesive products.

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