

Allyl Ether-Modified Unsaturated Polyesters for UV/Air Dual-Curable Coatings. I: Synthesis and Characterization of the Oligomers and their Cured Films

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ABSTRACT: Allyl ether (AE)-modified unsaturated polyester oligomers were synthesized from polyethylene glycol (PEG), maleic anhydride (MAH), and trimethylolpropane mono allyl ether (TMPAE), and characterized by Fourier transform infrared (FTIR) spectra. The UV/air dual-curable coatings were prepared from the oligomers using vinyl ether (VE) as a reactive diluent. FTIR spectra showed that C=C bonds in the coating composition had polymerized partially after cured by UV or air. The investigation of rheological behavior of the dual curable composition suggested that all the systems belonged to pseudoplastic fluid, and the increasing allyloxy content in oligomer resulted in a higher viscosity.

Differential scanning calorimetry (DSC) analysis showed that the increasing TMPAE-PEG molar ratio resulted in lower T_g , and all samples had the same glass transition temperature irrespective of the type of curing. The results of TGA for cured films indicated that UV-cured film had better thermal stability than the air-cured one. The air-cured film showed superior pencil hardness, impact strength, and flexibility to the UV-cured counterpart. However, the air-cured film had poor adhesion and electric resistance properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2765–2770, 2004

Key words: coatings; oligomers; FT-IR; DSC

INTRODUCTION

UV-curable coating has received considerable attention in the past decades due to its merits in environmental protection, efficiency, and less energy consumption. As conventional UV coating, however, polymerization of photoinitiated compositions occurs only in those regions that have been subjected to the activating radiation, with secondary cure mechanism being required to effect polymerization in unirradiated "shadow" areas.¹

Allyl ether (AE) is a class of oxygen-sensitive monomers; it can react through two possible reaction pathways. One is the addition to the double bond through radical polymerization. The second one involves abstraction of α -hydrogens to give stabilized radicals in the presence of oxygen. These undergo redox reaction with added cobalt salts to give reactive alkoxy radicals. The second reaction pathway is of great importance for photoinduced system in that peroxides are generated *in situ*, and the peroxides serve to initiate the secondary reaction and reduce or eliminate the inhibiting effect of oxygen in UV curing in air.² Ro-

kicki et al. have studied the effect of different structures of AE on unsaturated polyester.³

For traditional maleate-based unsaturated polyester resins used in thermally curable or radiation-curable systems, styrene is preferred as a reactive diluent because of the lower cost.^{4,5} However, there is growing concern about the health risks of the volatile compounds used in the maleate (MA) or maleate-acrylate-based photopolymer systems, especially for the large amount of styrene added for the primary function of viscosity control. Allylic or vinyl ether (VE) monomers are preferred to replace or reduce the amount of styrene or acrylate monomers. As a new kind of less harmful reactive diluent, VE with its electron-rich double bond, may form a charge transfer complex with highly electron-deficient MA, which gives alternating copolymers.⁶

The aim of this work was to synthesize AE-modified unsaturated polyester oligomer (AUPE), and then to advance a kind of UV/air dual-curable coating from the oligomer obtained using VE as a reactive diluent. Rheological behavior of the AUPE/VE system was investigated. The thermal and physical properties of the cured film through different curing mechanisms were also studied.

EXPERIMENTAL

Materials

The dual-curing formulation mainly used in this work contained four components: (1) divinyl ether of trieth-

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TABLE I
The Formulation of AE-Modified Unsaturated Polyesters (AUPEs)

Sample	a1	a2	a3
polyethylene glycol (PEG) :	1 : 1 : 2	1 : 2 : 3	1 : 3 : 4
trimethylolpropane monoallyl ether (TMPAE) :			
maleic anhydride (MAH) (mol)			

ylene glycol (RapiCure DVE-3 from International Speciality Products, Inc., USA) as a reactive diluent; (2) unsaturated polyester containing MA and AE (AUPE) synthesized by the following process; (3) a hydroxyphenyl ketone photoinitiator (Darocur 1173 from CIBA); and (4) cobalt naphthenate (JINYIN Chemical Products, Inc., China). The formulation of AUPE is given in Table I, in which all chemicals used were analytically pure.

Synthesis of the AUPEs

The component mentioned in Table I, 0.05 g of *p*-toluene sulfonic acid, as a catalyst, and 0.5 g of hydroquinone, used as inhibitor, were put into a 250-mL three-necked flask with mechanical stirrer, rectifying column, and purging system. The mixture was heated to 160°C in an oil bath and refluxed for 3 h with mechanical stirring (stirring speed was approximately 200 rpm). Then the system was subjected to a vacuum of 40 mmHg. The temperature of the bath was raised to 190°C for 2 h. Then the reaction was performed in a vacuum of 40 mmHg and at a temperature of 160°C for an hour to remove water in the system. The reaction was performed under N₂ protection (Scheme 1).

Preparation of UV-cured films

The formulations of dual-curable coatings listed in Table II were applied on various substrates and placed on a UV-curing line equipped with a 2400 W medium-pressure mercury lamp. The light intensity was mea-

TABLE II
The Formulation of Dual Curable Coatings

Sample	A1 (wt %)	A2 (wt %)	A3 (wt %)
AUPE	70 (a1)	70 (a2)	70 (a3)
DVE-3	30	30	30
Cobalt naphthenate	0.2	0.2	0.2
Darocur 1173	5	5	5

sured to be 37.5 mW/cm² (the detector was sensitive in the wavelength range of 320–400 nm) at the sample position. The mixture was polymerized in the presence of air, by a single pass under the lamp at a speed of 50 m/min.

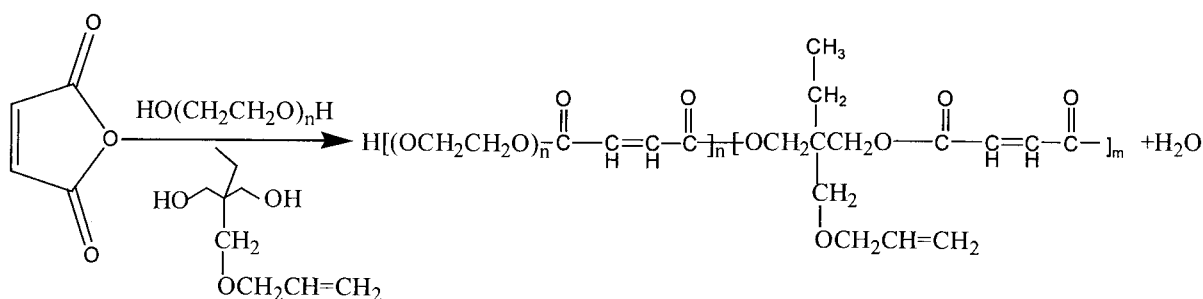
Preparation of air-cured films

The formulations of dual-curable coatings listed in Table II were applied by means of a bar-coater onto glass plates in the air at 25°C and stored at 75% relative humidity for 24 h.

Measurements

The acid value of obtained AUPE was determined by titration with 0.1 mol/L KOH/ethanol solution, which was used to monitor the degree of polycondensation. The conversion used in the present study was over 90% and their molecular weight were 1806, 1562, and 1674, respectively. The molecular weight distributions were 1.55, 1.42, and 1.40, respectively, as determined by GPC.

The infrared spectra were recorded on a Nicolet 210 FTIR at 4 cm⁻¹ resolutions with 32 scans per spectrum. Viscosity and rheology properties were measured by using rotary viscometer (Brookfield viscometer Model DV-II+) with spindle speed varying from 0.1 to 2 rpm at ambient condition. The *T_g* of film samples was measured using a TA 2100 Modulated DSC instrument, with a heating rate of 10°C/min and heated from 0–100°C. The kinetics of degradation of the cured films was measured using a Shimadzu TGA-50 instrument from room temperature to 500°C at a heating



Scheme 1 Synthesis of AE- modified unsaturated polyester (UPE).

TABLE III
Dual-Cured Film Test Procedures

Property	Procedure
Gloss	GB 1743-79
Pencil hardness	GB/T1730-93
Adhesion	GB 1720-79
Impact strength	GB/T1732-93
Flexibility	GB/T1731-93

rate of 20°C/min and a nitrogen or an air purging (50 mL/min). Some physical properties of the AE-UPE were measured according to Chinese National Standard Test procedures listed in Table III.⁷ The resistance of cured films was measured using a ZC36 high-resistance instrument (Shanghai No.6 Ammeter Factory) at 25°C and at a relative humidity of 75%.

RESULTS AND DISCUSSION

FTIR observation for the oligomer

The FTIR spectrum of the oligomer is showed in Figure 1. The emergence of the strong absorption peaks at about 1297 and 1159 cm⁻¹, assigned to C—O stretching of esters, implied the formation of esters. No peaks at 1760 and 1850 cm⁻¹ for the anhydride group could be observed, and the disappearance of the 910 cm⁻¹ peak assigned to C—O stretching of anhydride further confirmed the formation of target substance.

FTIR observation for the coating compositions before and after curing

FTIR spectra of the dual-curable coating and its cured films are showed in Figure 2. To investigate the polymerization of VE, MA, and AE, the VE C=C stretching band (1620 cm⁻¹) and the MA/AE C—C stretching band (1638.3 cm⁻¹) were generally used. In comparison with that of dual-curable coating prior to UV irradiation and air curing, the sharp C=C absorption

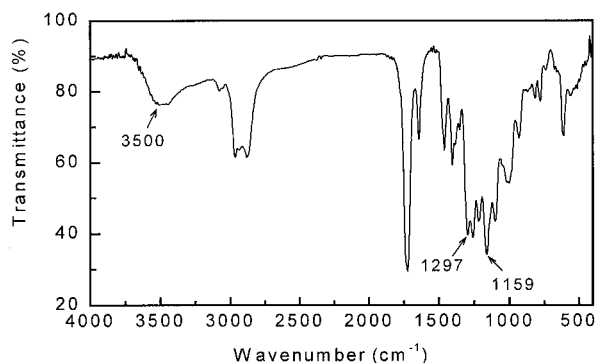


Figure 1 FTIR spectrum of AUPE oligomer.

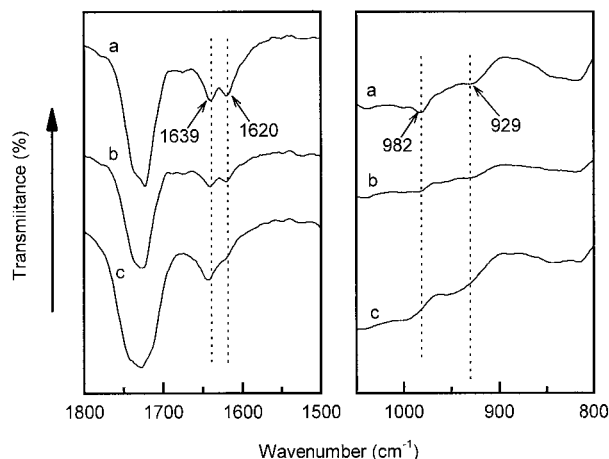


Figure 2 FTIR spectra of dual-curable coatings films (a) before curing, (b) after UV curing, and (c) after air curing.

at 1639 and 1620 cm⁻¹ and the alkene =C—H out of plane bending at 929 and 982 cm⁻¹ depleted after UV irradiation or air curing. The absorption peaks did not disappear completely, suggesting that the C=C bonds had not fully polymerized. It is difficult to observe the reaction behavior of the C=C bond individually for MA and AE by FTIR, for the IR absorptions of these two kinds of C=C bond are closer and cannot be identified separately.

Rheological behavior of dual-curable coatings

It is well known that rheological behavior of a fluid can be described by the following power law equation:

$$\tau = K \times D^n$$

where τ is the shear stress, D is the shear rate, n is the flow index, and K is the viscosity coefficient.

The above equation is transformed into the following logarithmic form:

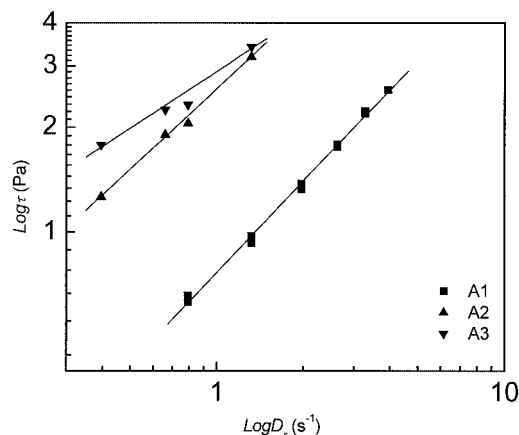


Figure 3 The plots of $\text{Log}D_r - \text{Log}\tau$ of AUPE/VE systems.

TABLE IV
Effects of Different AE Content on the Rheological Parameters of AUPE

Sample	A1	A2	A3
n	0.83	0.77	0.54
K (Pa · s)	0.93	2.58	2.90

$$\text{Log } \tau = \text{Log } K + n \text{Log } D$$

where n and K can be calculated from the slope and the intercept of the plot of $\log \tau$ vs. $\log D$, respectively.

The shear thinning behavior of the dual-curable coating could be observed from shear stress for the systems as a function of shear rate, given in Figure 3.

Table IV showed some rheological parameters of the AUPE/AE systems. All the systems had a flow index of less than 1, implying that the rheological behavior of the systems deviates from Newtonian flow. Increasing the AE content in the unsaturated polyesters, the flow index decreased; however, the viscosity coefficient increased. A high viscosity coefficient suggested that the sample of A2 and A3 display high apparent viscosity.

Thermal properties of the cured films

In a conventional UPE/styrene system, the copolymerization results in the formation of a heterogeneous structure through strong intermolecular reactions and phase separation. It consists of at least two phases: a UPEs crosslinked phase, and a polystyrene-rich phase. However, DSC results show only one glass transition in the AUPE/VE cured films (Fig. 4). They exhibit good miscibility due to the fact that no VE and MA homopolymerization occurred to any measurable extent in UV curing.

Increasing the polyol-to-TMPAE ratio increases the content of C—O—C segment, which enhances the chain flexibility and hence lower T_g . On the other

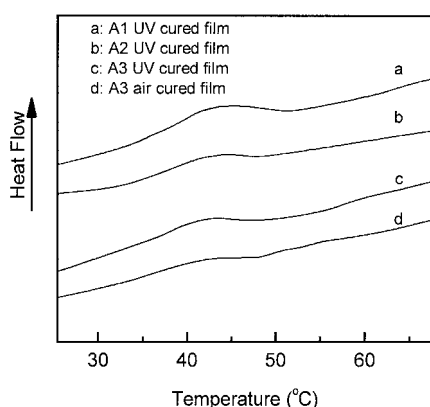


Figure 4 DSC traces for AUPE/VE-cured films.

TABLE V
Glass Transition Temperatures of AUPE/VE-cured Films

Samples	T_g (°C)	T_{gonset} (°C)	T_{gend} (°C)
A1 UV-cured film	38.5	33.1	43.0
A2 UV-cured film	37.5	31.5	42.7
A3 UV-cured film	35.3	28.6	40.1
A3 air-cured film	35.3	28.7	40.1

hand, the greater the TMPAE concentration, the shorter the backbone chain while the side chains are longer, which can reduce the packing density of chains and the T_g shifts to lower temperature. The increase of allyloxy concentration causes a drop of T_g because it tends to form medium-molecular weight products due to autoinhibition (the process of hydrogen abstraction from allyl group, leading to stable radical), the share of degradative chain transfer to monomer is higher than that of propagation.

The results from DSC show that the glass transition temperature of AUPE/VE-cured film was independent of curing type (Table V).

The thermogravimetric curves (Fig. 5) show only a single degradation process under nitrogen atmosphere for all samples. The crosslinked resins, irrespective of the composition of polyester oligomer, undergo spontaneous decomposition near 300°C even in the absence of oxygen. This is characteristic of vinyl copolymers, which are degraded into monomeric units at high temperatures, unlike nonvinyl crosslinked thermosets, such as the phenolic and epoxy resins, which tend to carbonize.

The UV-cured film has better thermal stability than air-cured film in N_2 atmosphere. The ether groups have been oxidized in air curing condition, which has an unfavorable effect on the thermal stability of samples.

It can be seen from DTG curves (Fig. 6) that the thermal degradation pattern of the crosslinked sam-

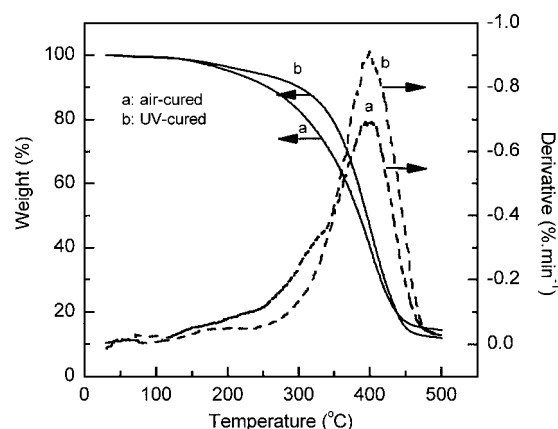


Figure 5 Effect of curing types of the A3 sample on TGA behavior in N_2 .

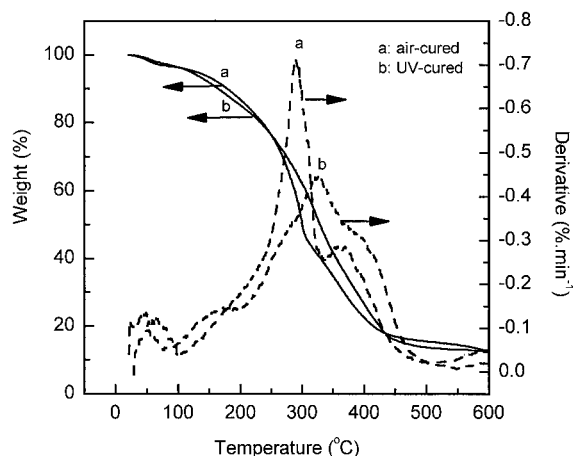


Figure 6 Effect of curing types of the A3 sample on TGA behavior in air.

ples in air exhibits three degradation stages. Parameters evaluated from the TG and DTG thermograms of the crosslinked samples are summarized in Table VI. In the first degradation process, the ether groups of UV-cured sample are oxidized to form ester or aldehyde at about 150°C. The air-cured film is more stable than the UV-cured one in this process. It is well established that the amount of weight loss of the second region is correlated with cleavage of —OCO— bonds and evolution of CO₂, while the last process reflects the decomposition of different kinds of covalent linkages to form a char as an end product.^{8,9}

Physical properties of the cured films

Table VII compares the physical properties of films cured with different curing mechanisms. It is obvious

that all of these films possess excellent gloss. The air-cured films show superior impact strength and flexibility to the UV-cured ones. Peroxide-induced crosslinked film may induce high interchain interaction through hydrogen bonding between allylic reactive α -hydrogen. This will enable the hard segments to dominate the properties of cured films, thus giving a higher hardness and impact strength. The increase of allyloxy concentration causes a rise in crosslinking density, because the size of molecular segments between the crosslinking points is probably less. The flexibility for these samples increases with the increase of PEG-to-TMPAE molar ratio. This is attributed to the decrease of the crosslinking density and the reduced hydrogen bonding either inter- or intramolecularly.

It is well known that the charge concentration, drift mobility, and the carriers may affect electric conductivity. As far as the structures of AUPE-cured films are concerned, when the content of the —C—O—C— segment decreased in the cured films, the crosslinked samples became more rigid, so sample A3 shows the highest electrical resistance. At the same time, VE and MA double bond can form a charge-transfer complex. These may be incorporated into polymeric chains while still retaining to a large extent their conductive properties.

CONCLUSION

The AE-modified MA-based unsaturated polyester/VE system can be used for UV/air dual-curable coating. FTIR spectra identified the dual-curing process. The rheological behavior of AUPE/VE systems suggested that all these systems belong to pseudoplastic fluid, and display the characteristics of common

TABLE VI
TGA Parameters of A-3-Cured Films

Sample	T_{1on} (°C)	T_{1max} (°C)	T_{2on} (°C)	T_{2max} (°C)	T_{3on} (°C)	T_{3max} (°C)
A3 air-cured	89.8	148.9	212.1	323.7	370.4	406.7
A3 UV-cured	101.9	181.9	230.3	289.0	334.3	364.5

TABLE VII
Physical Properties of the AUPE/VE-Cured Films

Samples	Gloss (60°)	Impact strength (kg/cm ²)	Pencil hardness	Adhesion (grade)	Flexibility (mm)	ρ_s^a (Ω)	ρ_v^b ($\Omega \cdot \text{cm}$)
A1 UV-cured	104.3	20	2H	3	2	3.69E + 13	6.22E + 12
A2 UV-cured	104.4	15	3H	1	2	1.6E + 14	2.45E + 13
A3 UV-cured	104.5	15	5H	1	4	2.31E + 14	3.27E + 14
A1 air-cured	106.5	40	3H	4	1	4.41E + 11	9.81E + 10
A2 air-cured	107.4	45	5H	4	2	1.02E + 12	5.03E + 11
A3 air-cured	107.9	50	6H	2	2	3.35E + 12	2.18E + 12

^a Surface resistivity.

^b Volume resistivity.

polymer fluid. DSC analysis showed that all samples have only one glass transition temperature. The increasing of TMPAE-to-PEG molar ratio resulted in a lower T_g and a changing of the miscibility in the cured films. The TGA results indicated that the UV-cured films have better thermal stability than the air-cured counterpart. Measurement of physical properties showed that the dual-cured films exhibited excellent adhesion, gloss, flexibility, and impact strength. The air-cured films had worse electrical properties than the UV-cured ones due to the increasing of ester group in the cured films.

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