

# Allyl Ether-Modified Unsaturated Polyesters for UV/Air Dual-Curable Coatings. II: UV and Air-Curing Behavior

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**ABSTRACT:** The photoinduced and peroxide-induced polymerization behavior of dual-curable allyl ether-modified unsaturated polyester (AUPE) and vinyl ether (VE) used as a reactive diluent for dual-curable coating have been studied by infrared spectroscopy (IR). For UV curing systems in N<sub>2</sub> atmosphere, the maleate's conversion and total conversion decrease with the increasing of allyloxy content. However, the rate and of copolymerization and conversion of VE are independent of allyloxy concentration. The copolymerization of allyl ether (AE) and vinyl ether occurs in the presence of maleate (MA) under UV irradiation. For air curing, the rate of copolymerization increases with allyloxy

content. The ultimate conversion is the same irrespective of the allyloxy concentration. Because the electron-rich double bond of allyloxy would become an electron-deficient one through oxidation, the conversion of maleate decreases with increasing of the allyloxy content due to the enhancement of copolymerization of AE with VE. The ATR-IR showed that different curing mechanisms occur in AUPE/VE system during air-curing process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2771–2776, 2004

**Key words:** coatings; oligomers; NMR; FT-IR

## INTRODUCTION

Radical homopolymerization of allyl monomers proceeds with low rate, giving low molecular-weight products. Because of autoinhibition (the process of hydrogen abstraction from the allylic methylene group, leading to stable radicals), the share of degradative chain transfer to monomers is higher than that of propagation. Despite of this, allyl monomers are often used in the copolymerization with acceptor monomers as well as in the synthesis of unsaturated polyester resins (UPE).

Despite some articles describing allyl ether compounds using as an auto-oxidizable monomer in air-drying resins or as a reagent for eliminating oxygen inhibitor in photoinduced or peroxide-induced curing systems,<sup>1,2</sup> no article was found to deal with the UV/air dual-curing kinetics of allyl ether-modified unsaturated polyester for dual-curable resins and the correlation of characteristic properties to the curing behavior. The objective of the present work is to study the kinetics of the copolymerization of vinyl ether, allyloxy, and maleate-based UPE, and to find the balance between UV and air curing to shed some light on the polymerization mechanism.

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## EXPERIMENTAL

### Materials

The dual curable coating formulation used in this work was mentioned in the previous article.<sup>3</sup> Three samples labeled A1, A2, and A3 were used.

### Irradiation

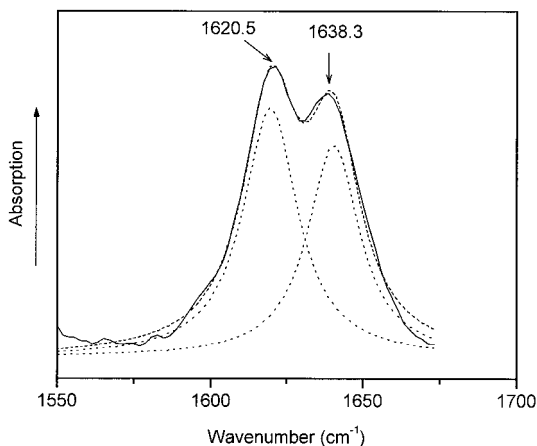
The mixture of dual curable coating was coated on a silicon crystal. The thickness of sample was 20 μm. The mixture was then exposed to the UV radiation from a medium-pressure mercury lamp (250 W). The light intensity was measured to be 3.83 mW/cm<sup>2</sup> (the detector was sensitive in the wavelength range of 320–400 nm) at the sample position. The infrared spectra of samples with different UV curing times were recorded on a Nicolet 210 FTIR at 4 cm<sup>-1</sup> resolutions with 32 scans per spectrum.

### Air curing

The mixture mentioned above was exposed in air instead of irradiated by UV light. The infrared spectra were recorded at different times with the same instrument.

### Analysis

We can easily calculate the final conversion from the area of the double bond absorption when there was

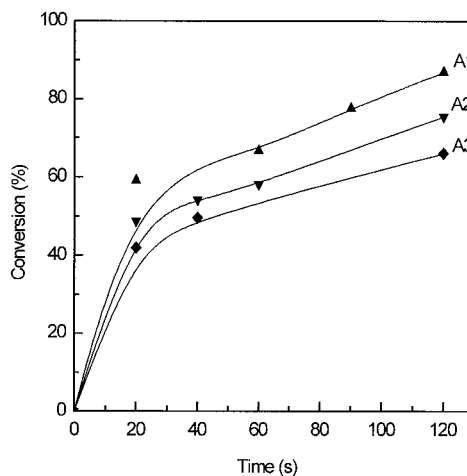


**Figure 1** The deconvolution of the IR spectrum using the Lorentzian function.

no any disturbance. Figure 1 is the IR spectrum of the sample showing the VE C=C stretching band ( $1620.5\text{ cm}^{-1}$ ) and the MA/AE C=C stretching band ( $1638.3\text{ cm}^{-1}$ ). The overlapped spectrum can be deconvoluted by assuming a Lorentzian contour for individual band. A satisfied coincidence is shown in Figure 1, confirming the separation of these two bands.

Conversion was measured using baseline correction of the VE band at  $1620\text{ cm}^{-1}$  and the MA band at  $1296\text{ cm}^{-1}$ . The total conversion of carbon-carbon double bond of the mixture was monitored by the C=C stretching band from  $1566\text{ cm}^{-1}$  to  $1673\text{ cm}^{-1}$ . The band at  $1386\text{ cm}^{-1}$  from the methyl group was used as an internal reference.

The same mixture of dual curable coating as mentioned above was exposed in air for 24 h. The thickness of sample was  $130\text{ }\mu\text{m}$ . Two sides of the film were separately put on the KRS-5  $45^\circ$  single internal reflection (ATR) prisms at ambient temperature. ATR-IR spectra of the surface and the bulk of cured film were obtained using a model 210 (Nicolet USA Corp.) instrument equipped with an ATR unit (KRS 5-crystal;  $45^\circ$ ; 14 reflection) and 64 scans at a nominal resolution of  $4\text{ cm}^{-1}$ . The subtraction spectrum was obtained by subtracting the bulk spectrum from the surface spectrum. The band at  $1386\text{ cm}^{-1}$  from methyl group was used as an internal reference.



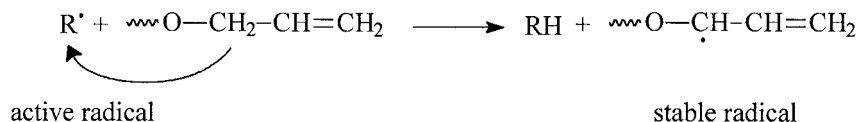
**Figure 2** Effect of allyloxy content on UV curing kinetics of dual-curable systems in  $\text{N}_2$ .

## RESULTS AND DISCUSSION

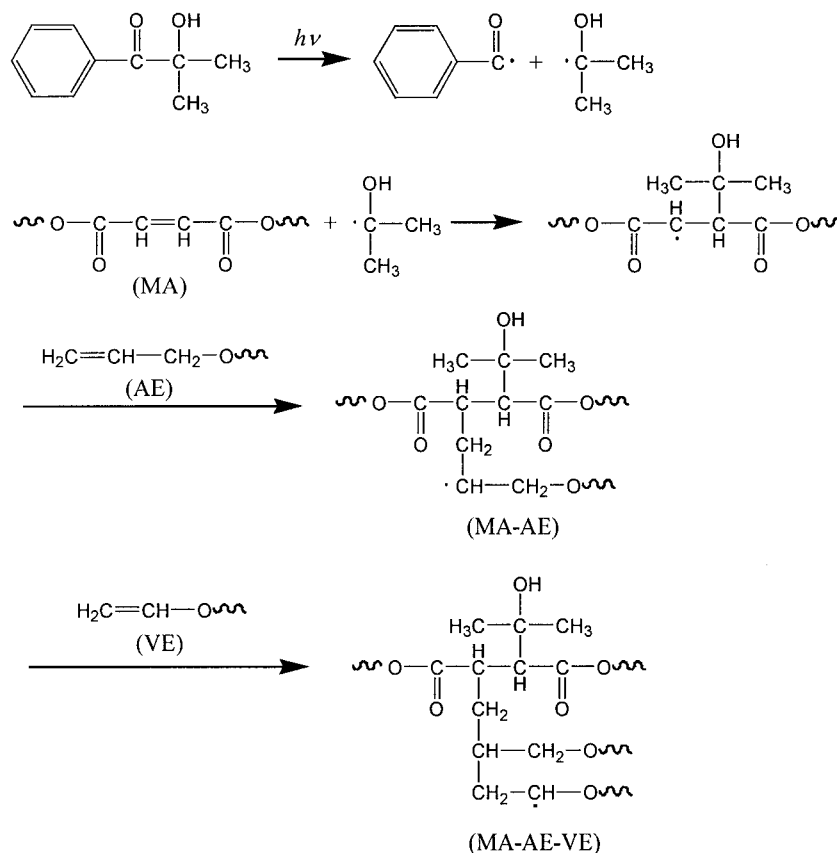
### Kinetics of copolymerization under UV irradiation

Figure 2 shows that with the increasing of allyloxy content in the system the rate of VE, MA, and AE ternary polymerization decreased and the total conversion of dual curable coating systems also reduced. This may due to the self-inhibition of allyl unit in which the  $\alpha$ -hydrogen is readily abstracted by the active radicals to form stable radicals as shown in Scheme 1.

When DVE-3 and UPE was separately exposed to UV radiation in the presence of a radical photoinitiator Darocur 1173 (5 wt %), no homopolymerization occurred to any measurable extent by either differential photocalorimetry (DPC) or FTIR analysis. When DVE-3 and TMPAE were exposed to UV radiation in an inert atmosphere under the same condition, no significant copolymerization could be detected from the DPC trace either.<sup>4</sup> In contrast, a fast copolymerization was found to proceed when the mixture was irradiated under the same condition. Without the presence of AE, VE, and MA can form a charge transfer complex (CTC), which can homopolymerize in the photoinduced condition. However, when the allyloxy was introduced into the systems, VE and MA no longer copolymerize with 1 : 1 ratio. The three kinds of



**Scheme 1** The formation of stable radical.



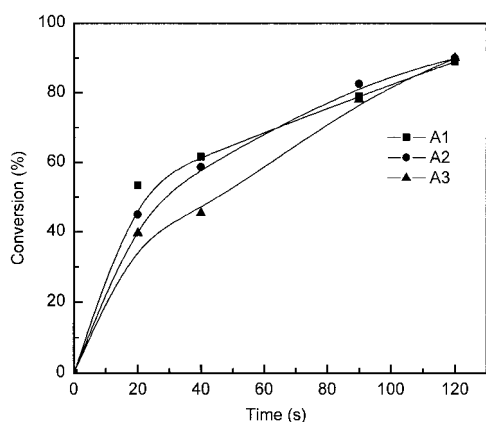
**Scheme 2** The terpolymerization of maleate, vinyl ether, and allyl ether.

C=C bonds in the VE/MA system containing AE may polymerize in the manner as shown in Scheme 2.

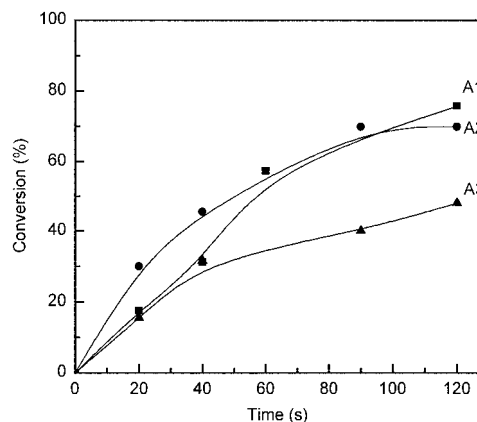
Figure 3 shows that the allyloxy content had little effect on the conversion of VE. However, it can be found from Figure 4 that the conversion of MA decreased with the increasing of allyloxy content. This may be due to the fact that VE can copolymerize with

AE in the existence of MA. When the double bond ratio of VE to MA was 1 : 1, some VE had copolymerized with AE, so that less VE could react with MA; therefore, the conversion of MA decreased.

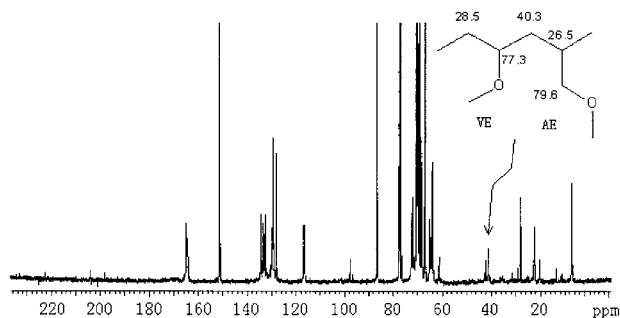
The copolymerization of VE with AE may be confirmed by the results of  $^{13}\text{C}$ -NMR of cured film with low crosslinking density, in which the signal of the



**Figure 3** Vinyl ether conversion curve for the UV curing process in  $\text{N}_2$  of dual curable systems with different allyloxy content.



**Figure 4** Maleate conversion curve for the UV curing process in  $\text{N}_2$  of dual durable systems with different allyloxy content.



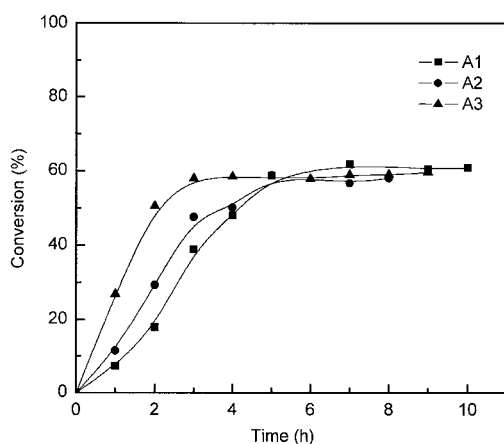
**Figure 5**  $^{13}\text{C}$ -NMR spectrum of dual-curable coating with low crosslinking density after UV irradiation in  $\text{N}_2$ .

characteristic chemical shift of  $-\text{CH}_2-$  in the  $-\text{VE}-\text{AE}-$  unit appeared at around 40 ppm (Fig. 5).

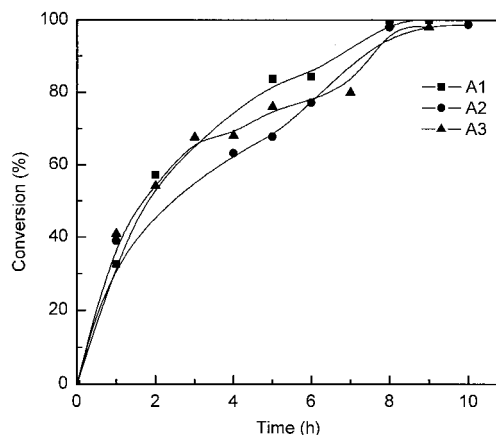
### Kinetics of copolymerization in air

High conversion could be obtained for reactions in the air. However, the conversion of the double bond through a peroxide curing mechanism was almost unaffected by the amount of AE. The concentration of AE plays an important role in the copolymerization kinetics because it controls the rate of initiation. Figure 6 shows the experimentally observed rate with various AE concentrations. With increasing AE, the concentration of the initiating species also increased; therefore, the rate of copolymerization increased with increasing the allyloxy content.

It is found from Figure 7 that the conversion of VE in the air curing process reached a high value, and the AE content had little effect on the polymerization rate and the conversion of VE. However, the reaction rate and conversion of MA decreased with increasing AE content (Fig. 8). These can be explained by the mechanism shown in Scheme 3;<sup>5</sup> with



**Figure 6** Conversion curve for the air-curing process of dual-curable systems with different allyloxy content.

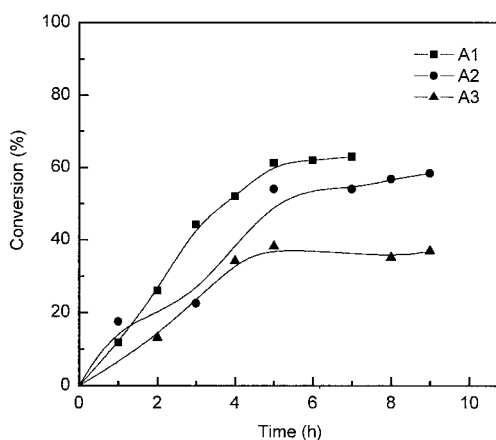


**Figure 7** Vinyl ether conversion curve for the air-curing process of dual-curable systems with different allyloxy content.

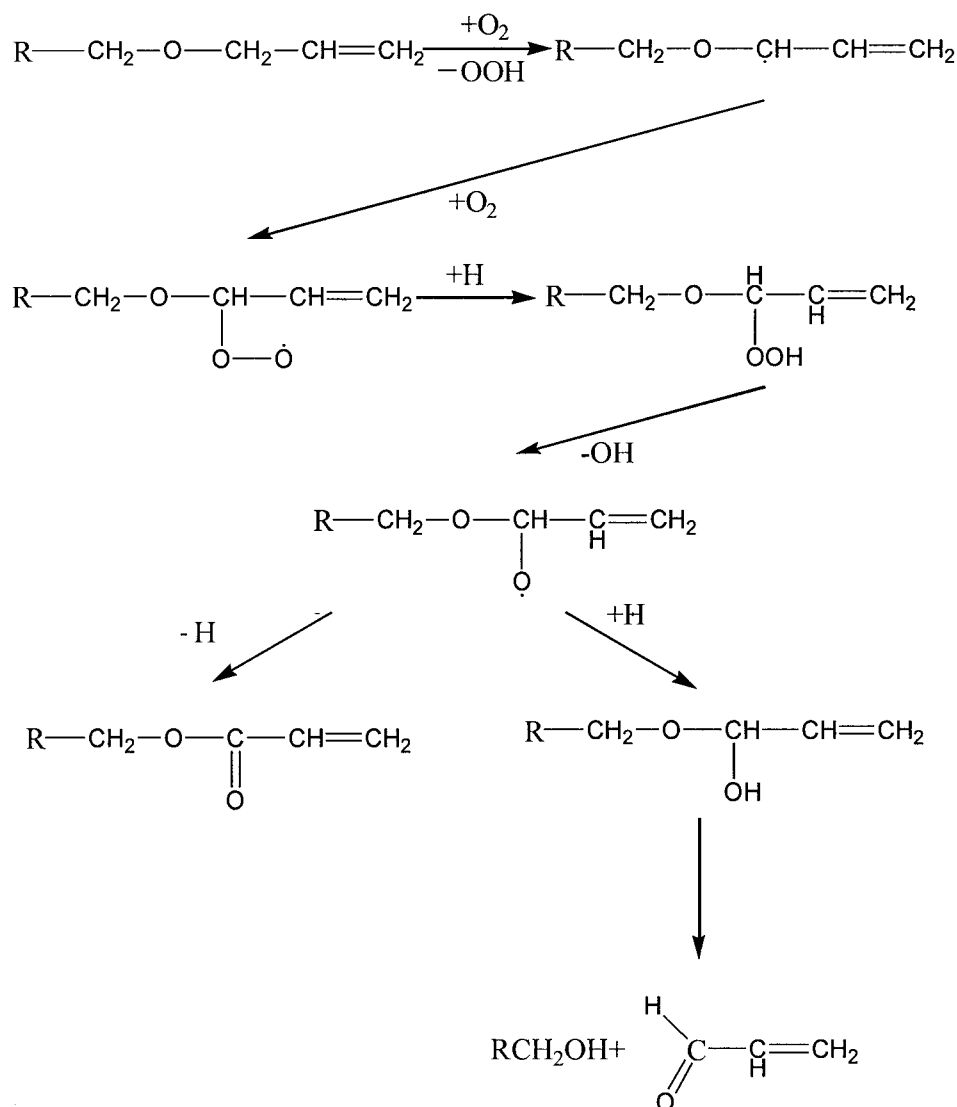
allyloxy changing to acrylate or olefinic aldehyde under the action of  $\text{O}_2$ , the electron-rich double bond becomes an electron-deficient one, which competes with MA in the copolymerization with VE, an electron-rich monomer.

### ATR-IR spectra for air-curing behavior through the peroxide mechanism

The difference of IR absorption of the surface and bulk of cured film had been tested by means of ATR-IR spectra, as shown in Figure 9. The strong absorption peaks at about  $2982$  and  $1702\text{ cm}^{-1}$  reveal the formation of aldehyde with a high level in the surface of cured film, but little or no aldehyde formed in the bulk. The absorption band of the MA  $=\text{C}-\text{H}$  out of plane bending can also be seen at  $1635\text{ cm}^{-1}$ , suggesting that the content of the MA double bond at the surface was higher than that in



**Figure 8** Maleate conversion curve for the air-curing process of dual-curable systems with different allyloxy content.



Scheme 3 The reaction of allyloxy in air.

the bulk of the cured film. On the other hand, the sharp absorption of the C—O—C unit in AE at 1164 and 1092  $\text{cm}^{-1}$  appeared as negative peaks, implying that the C—O—C structure in AE was destroyed at the surface, while still remained in the bulk after air curing. It is obvious that, for dual-curable AUPE/VE systems, two different cure mechanisms exist in the film, that is, with an autoxidative polymerization at the surface and a free radical polymerization occurring in the bulk.<sup>6</sup>

### CONCLUSION

In UV curing systems in  $\text{N}_2$  atmosphere, the rate and conversion of VE are independent of allyloxy concentration. This is due to a crosslinking between VE and allyloxy when MA is present. However,

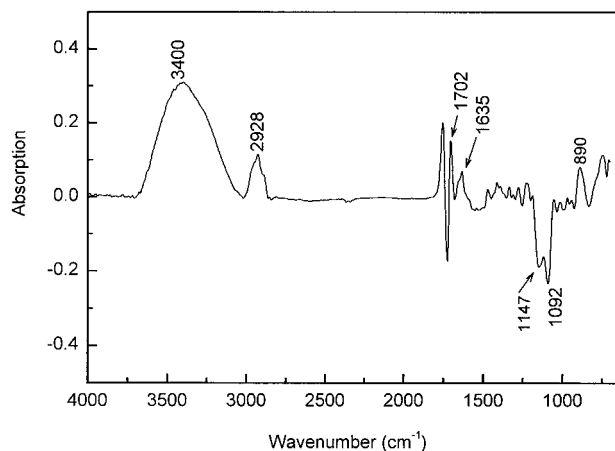


Figure 9 ATR-IR subtraction spectrum of surface-cured film and underneath-cured film through air curing.

with the higher allyloxy content the individual conversion of MA and total conversion decrease. In the air-curing system, with increasing the AE, the concentration of the initiating species also increases. The curing rate increases with the increasing of the allyloxy content. The conversion remains the same irrespective of the allyloxy concentration. The conversion of MA decreases with increasing the allyloxy content due to the enhancement of the copolymerization of AE and VE. In the air-curing process the electron-rich double bond of the allyloxy would become an electron-deficient one through oxidation. The ATR-IR indicates that different curing mechanisms occurred in the AUPE/VE system through the air-curing process.

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