

UV 경화가 비닐에스터와 불포화폴리에스터 블랜드 시스템의 물성 특성에 미치는 영향

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Effect of Radiation Intensity on Mechanical Properties of UV-cured Vinylester / Unsaturated Polyester Blend System

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Key Words: Photopolymerization, UV-Curing, Vinylester, Unsaturated polyester, Mechanical properties

ABSTRACT

UV curing technology becomes important in various sectors of applications due to the high efficiency, environmental protection, and saving of energy. The effect of different proportion of vinylester (VE) and unsaturated polyester (UP) for VE/UP blend system was investigated in context of mechanical properties. The compositions of VE/UP blend were varied within 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0 by weight percent. 1 wt% 1-hydroxy-cyclohexyl-phenyl-ketone was used as photoinitiator. The used intensity of UV light was in the range of 40~70 mW/cm². The flexural strength of vinylester was not sensitive to the intensity of UV light. But the unsaturated polyester was very sensitive to the intensity of UV light. The flexural strength of vinylester was always superior to that of unsaturated polyester. The addition of the vinylester increased the flexural strength of blend system.

1. INTRODUCTION

Photopolymerizations are generally chain polymerizations in which the propagating active center (usually radicals or cations) are produced by a photochemical event. A wide variety of chemical compounds (photoinitiators) are available that produce free radicals upon absorption of photons of the appropriate energy (typically in the UV or visible region of the spectrum). The photochemical mechanism of active-center generation has been well characterized, and generally proceeds by α -cleavage, β -cleavage or hydrogen abstraction.^{1,2} Photopolymerization offers

many advantages that can be exploited for high speed, low cost composites processing. Most notably, the spatial and temporal control of initiation afforded by the use of light rather than heat to initiate the reaction provides cure-on-demand, which can be used to achieve short cycle times while circumventing many problems and limitations of current production methods. Photo-reactions use energy from natural resources (sun radiation) or energy produced by controlled electric energy conversion into emission of UV, VIS and IR wavelengths.³⁻⁵

UV curing process has been recognized as a useful technology to transform instantly liquid photo-reactive materials consisting of monomers and/or prepolymers into cured resins in the presence of photoinitiators.⁶ In the field of surface coating, inks and adhesives, the

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technique is also important for the environmental preservation because of its high energy efficiencies and reduced emission of volatile organic compounds. Moreover, since this procedure generally offers rapid curing with relatively low heat generation, the UV curing resins provide a wide variety of applications such as coatings for optical fibers, substrates for electronics and medical materials.⁷ Most often, a UV curable resin consists of oligomers and multifunctional monomers that polymerize to form a highly crosslinked polymer network, additives of various types, and a photoinitiator that yields reactive initiation species upon UV exposure.

Unsaturated polyesters are the most widely used, fiber-reinforced thermosetting matrix resin for sheet molding, injection molding, resin transfer molding, and pultrusion applications.⁸ Traditionally these composites are thermally cured at elevated temperature (above 100 °C), using initiators, such as t-butyl perbenzoate or methyl ethyl peroxide and 30 to 50% styrene monomer added to the polyester.⁷ A few photopolymerizable unsaturated polyester resins, with a styrene monomer, have been developed.⁹ They show high efficiency and savings of investment and energy. Recently the UV curing of vinyl ester and unsaturated polyester is emphasized because of their environmental concerns. The UV curing suppresses styrene emission by the surface curing of the materials. In these days it has its application in surfboard and some marine structures such as the hull of boat.

In this work, vinyl ester (VE)/unsaturated polyester (UP) blend system was prepared. Then, functional group change and mechanical properties of UV cured system were analyzed with FT-IR and flexural strength measurement.

2. EXPERIMENTAL

2.1 Materials

Vinyl ester (VE) and unsaturated polyester (UP) obtained from Sewon chemical Co. of Korea were used as the resin. A 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184 from Ciba specialty chemicals) was used to generate the free radicals that were to initiate the polymerization of the acrylate monomer. The photocheavage of this molecule produced a benzoyl radical and an α -hydroxyketone radical, both of which were capable to react with the acrylate double bond.¹⁰

2.2 Sample preparation

VE and UP resin were irradiated between 40 and 70

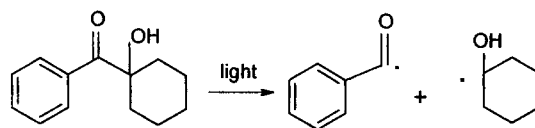


Fig. 1. Chemical structures and photocheavage of the Irgacure 184.

mW/cm² by light curing system (Model 5000 flood, Dymax). The contents of VE/UP blend system was varied within 0/100 ~ 100/0 wt%. One wt% Irgacure 184 was used as a photofragmenting initiator for resins. The mixture of resin and catalyst was thoroughly mixed by using magnetic stirrer. The mixture (VE, UP, VE/UP + Irgacure 184) was then poured into a mold and irradiated from one side using an 60 mW/cm² UV chamber during 3 and 5 min.

2.3 Analysis

Infrared spectra of the cured VE/UP blend system were measured by FT-IR spectroscopy (Hartmann & Brawn Model Bomen MB 102) and the scans were from 400 to 4000 cm⁻¹.

Bending tests were performed following the ASTM D 790M-93 using an UTM (Universal Testing Machine #1125, Lloyd LR 5K). The dimension of the specimen was 50×25×2 mm³. The specimen was loaded in a three-point holder with a 32 mm span and strained at a rate of crosshead speed of 0.85 mm/min.

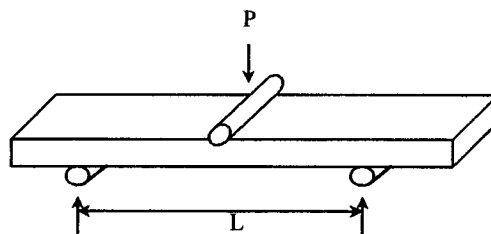


Fig. 2. Scheme of three-points bending test.

3. RESULTS AND DISCUSSION

3.1 FT-IR analysis

Fig. 3 shows FT-IR spectrum of VE/UP blend system after UV irradiation for 3 and 5 min. It is clear from the figure that all the resin systems are fully cured. The band of epoxide group at 860-910 cm⁻¹ is replaced by a band about 1700 cm⁻¹ in the spectra which is due to carbonyl group of ester formed during the acrylation of the

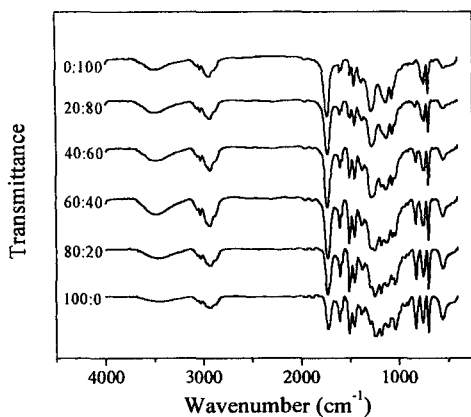


Fig. 3. FT-IR spectra of VE/UP blend system after UV curing.

epoxy.¹¹ A bond corresponding to acryloyl double bond (-C=C-) appeared at 1600 cm^{-1} . A broad band near 3400 , 2900 , and 3050 cm^{-1} shows the presence of -OH group, methyl group and methylene linkages in all the samples.¹²

3.2 Mechanical properties

The mechanical properties of this VE/UP blend system are determined in terms of flexural strength, σ_f for the cured specimens determined from three-point bending tests are calculated using the following equation:

$$\sigma_f = \frac{3PL}{2bd^2} \quad (1)$$

where P is load (N), L is span length (m), b is width of specimen (m), d is thickness of specimen (m).

Fig. 4 shows the flexural strength of VE and UP as a function of intensity of UV light. The flexural strength of vinyl ester is not sensitive to the intensity of UV light. But the unsaturated polyester is very sensitive to the intensity of UV light. In case of VE and UP, 60 mW/cm^{-1} intensity of UV light provides maximum flexural strength. Anyhow the flexural strength of vinyl ester is always superior to that of unsaturated polyester. Their difference is accentuated in low intensity of UV light.

Fig. 5 shows the effect of curing time (3 and 5 min) on flexural strength of VE/UP blend system. For the curing time of 3 min the addition of unsaturated polyester has increased the flexural strength of blend system in the range of 50%. But for the curing time of 5 min the addition of unsaturated polyester has increased the

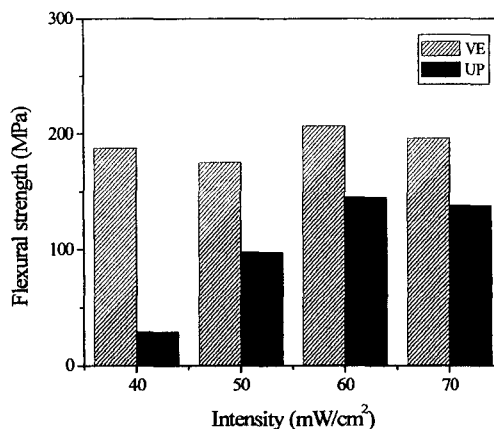


Fig. 4. Flexural strength of VE and UP with the various intensities of UV light.

flexural strength of blend system in the range of 100%. For the curing time of 3 min the 80:20 of VE/UP blend system shows the maximum the flexural strength. For low concentration of unsaturated polyester the 3 min cure shows higher flexural strength than 5 min cure, for medium concentration they showed nearly values. For higher concentration of unsaturated polyester 5 min cure shows much higher flexural strength than 3 min cure.

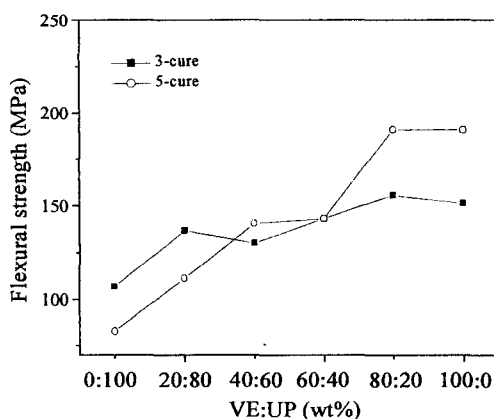


Fig. 5. Flexural strength of VE/UP blend system.

4. CONCLUSION

Mechanical properties of VE/UP blend mixed in varying proportion with 1 wt% 1-hydroxy- cyclohexyl-phenyl-ketone as photoinitiator were studied.

The flexural strength of vinyl ester was not sensitive to

the intensity of UV light. But the unsaturated polyester was very sensitive to the intensity of UV light. The flexural strength of vinyl ester was always superior to that of unsaturated polyester. For the curing time of 3 min the addition of unsaturated polyester has increased the flexural strength of blend system in the range of 50%. But for the curing time of 5 min the addition of unsaturated polyester has increased the flexural strength of blend system in the range of 100%.

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