UV Curing of Surface Coating System Consisting of Cycloaliphatic Diepoxide-ENR-Glycidyl Methacrylate by Cationic Photoinitiators—Characterization of the Cured Film by FTIR Spectroscopy

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ABSTRACT: This paper reports the results of spectroscopic investigations carried out on film cast from a system consisting of cycloaliphatic diepoxide, epoxidized natural rubber (ENR-50), and glycidyl methacrylate (GMA) and cured by the UV radiation. GMA acts as a reactive diluent for the ENR. Triphenyl sulphonium hexafluoro antimonate was used as the cationic photoinitiator. Results reported in a previous paper showed that ENR acts as a toughening agent. Optical microscopic studies were suggestive of the existence of two-phase morphology consisting of an elastomeric domain and the resin matrix domain. For effective toughening, it is essential that good adhesion exists between these two domains. It was of interest, therefore, to know whether favorable interactions occurred between the different components of the coating systems employed in our studies to promote effective adhesion between the elastomeric domain and the resin matrix. Systematic spectral studies were, therefore, conducted with a view to understanding how different components of the hybrid coating system interact. The results showed that the acrylic double bonds, as well as the epoxy groups of GMA, the isoprene double bonds and epoxy groups of ENR, and the epoxy groups of cycloaliphatic epoxide resin all participate in a scheme of photoinitiated polymerization and crosslinking reactions ultimately producing an interpenetrating polymer network, a result conducive to effective toughening of the epoxy resins, which are intrinsically brittle. © 19991999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1569-1577, 1999

Key words: epoxidized natural rubber (ENR-50); glycidyl methacrylate; cycloaliphatic diepoxide resin; cationic photo curing; photoinitiator; Fourier transform infrared spectroscopy (FTIR); hybrid system; interpenetrating polymer network

INTRODUCTION

Cationic photopolymerization of epoxides and vinyl ethers has assumed great importance in the past few years for effecting rapid pollution-free curing of surface coatings. Cationic curing systems are insensitive to oxygen inhibition in contrast to their free radical counterparts. The possibility of "dark reactions" after the UV irradiation source is removed enables the curing reactions to continue long after irradiation has ceased. Photopolymerization of epoxides with triphenyl sulphonium salts as the photoinitiator has been extensively studied by Crivello.^{1–9}

We reported in our earlier paper¹⁰ the results of investigations carried out on the coating sys-

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tem consisting of cycloaliphatic di-epoxide, epoxidized natural rubber (ENR-50) and glycidyl methacrylate cured by UV radiation with the cationic photoinitiator, triphenyl sulphonium hexafluorophosphate. The coating system employed in our studies, in addition to having the advantages of the cationic curing process as outlined above, has one more advantage, because epoxidized natural rubber, one of the components of the coating system, is a derivative of the renewable resource (natural rubber) abundantly available in Malaysia. Therefore, ENR provides a strong economic incentive for use in UV curable formulations. ENR was employed earlier as an acrylated oligomer by Dahlan et al.¹¹ in UV curable formulations employing the free radical photoinitiators. Decker et al.¹²⁻¹⁴ published results on the investigations on acrylated ENR and liquid ENR. In all the above investigations, however, no reactive diluent was employed. In the present investigation, glycidyl methacrylate was employed as the reactive diluent in which solid ENR is soluble. This monomer was chosen, because the molecule is endowed with two reactive functional groups; namely, epoxy group and acrylic group. The advantages of using GMA are: (1) it can dissolve solid ENR-50 and, hence, can function as a reactive diluent; (2) the epoxy rings can be opened by the Bronsted acid generated by the photolysis of cationic photoinitiators; this, in turn, can lead further copolymerization with the to cvcloaliphatic diepoxide; and (3) the acrylic groups of GMA can crosslink with the unsaturated isoprene double bonds of the ENR initiated by free radicals formed during the photolysis of the cationic photoinitiator. In our previous publication,¹⁰ we reported the properties of the UV-cured surface coatings based on cyclo aliphatic epoxide-ENR and glycidyl methacrylate (hybrid system).

It was also reported earlier that an increase in ENR-50 in the formulation composed of ENR-50cycloaliphatic epoxide-GMA causes a corresponding increase in the toughness, as evidenced by the increase in the values of the Gardener Impact strength. Preliminary microscopic investigations¹⁰ indicated the presence of elastomeric domain in the continuous epoxide matrix. Such a morphology is conducive to efficient stress transfer,¹¹ absorption of stresses, and prevention of crack propagation. Efficient toughening requires good adhesion between the elastomeric domain and the resin matrix. Such an adhesion is very likely to exist in the films cured from the present hybrid system employed for the UV irradiation. The functional groups present on the elastomer back bone (epoxy and isoprene unsaturation) could react with the corresponding groups of GMA and the cycloaliphatic epoxy resin to produce interpenetrating polymer network. It would, therefore, be interesting to study and confirm how different components of the hybrid system could interact when exposed to UV radiation in the presence of photoinitiators. The chemical reactions underlying the above phenomenon are rather complex. To understand the curing phenomena occurring in the hybrid system more precisely, instrumental methods such as Fourier transform infrared spectroscopy (FTIR), thermographic analysis (TGA), and microscopy were employed. In this paper, the results of the FTIR are reported.

EXPERIMENTAL

The nature of epoxide ring opening polymerization was followed by systematic spectroscopic studies. Because the hybrid system, per se, is quite complicated for such studies, spectral investigations were carried out on simple systems comprising a single component, two components, and three components, incorporating photoinitiator in each case. The spectra of such systems were recorded both before and after UV irradiation. The disappearance and appearance of appropriate functional groups attributable to UV irradiation would, therefore, be expected to throw light on the mode of participation of these functional groups leading to interpenetrating polymer network.

Materials

First, cycloaliphatic di-epoxide used was, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (Dagacure K 126) from Degussa AG. Second, glycidyl methacrylate was obtained from Fluka Chemie AG. Third, ENR 50 (epoxyprene) was obtained from M/S Guthrie Research Chemara, Malaysia. Fourth, bis[4-(diphenylsulfonio)phenyl] sulfide-bis-hexafluorophosphate (Degacure KI 85) was obtained from Degussa, and the corresponding antimonate was obtained from Union Carbide.

Methods and Measurements

The following systems were taken up for spectroscopic studies. First, ENR was dissolved in tolu-

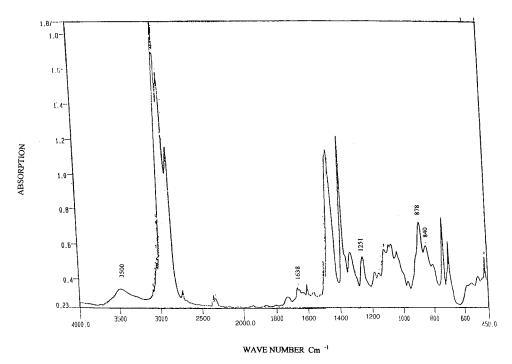


Figure 1 FTIR spectrum of ENR film (from toluene solution) before UV curing.

ene containing photoinitiator KI85. The solution was coated on KBr as a thin film, and the solvent was evaporated. The film so obtained was used both as such and after UV irradiation for the FTIR studies. The UV irradiation was carried out by exposing the film to a 80 W/cm Portacure 1,000 source supplied by American Ultraviolet. Figures 1 and 2 depict the spectra before and after UV

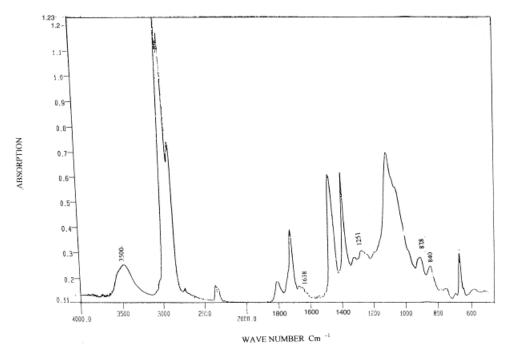


Figure 2 FTIR spectrum of ENR film (from toluene solution) after UV exposure and postcure.

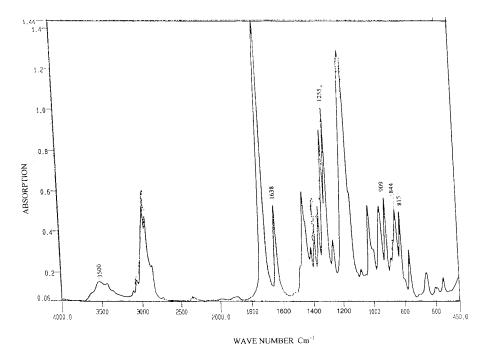


Figure 3 FTIR spectrum of ENR film containing glycidyl methacrylate before UV irradiation.

irradiation and postcuring. Second, ENR-50 was dissolved in GMA containing the photoinitiator KI85. Films were cast as before, and the FTIR spectra of the films were taken for both irradiated and unirradiated samples. Figures 3 and 4 show the spectra of the films before and after UV irradiation and postcuring. Third, films made from the epoxy-ENR-GMA hybrid system containing

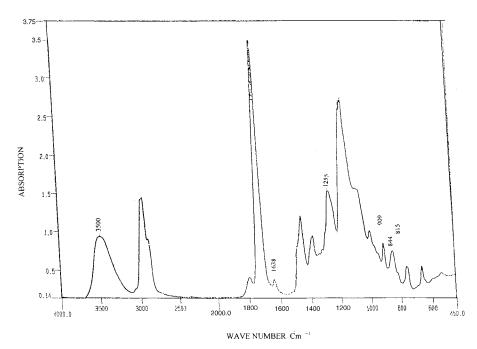


Figure 4 FTIR spectrum of ENR containing glycidyl methacrylate after UV irradiation.

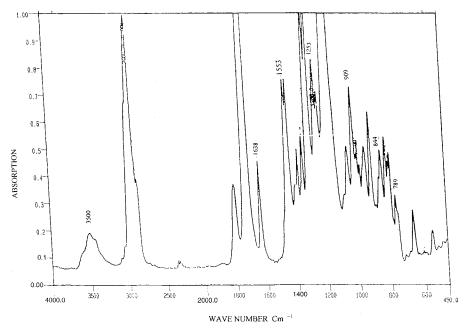


Figure 5 FTIR spectrum of cycloaliphatic epoxide-ENR-GMA hybrid system.

the photoinitiator KI85 were used for the FTIR spectra before and after irradiation and postcure. These spectra are shown in Figures 5–7. The spectral studies described above were made using Perkin–Elmer spectrophotometer 2000 FTIR.

RESULTS AND DISCUSSION

It can be noted from the spectra that the UV irradiation of the coatings results in disappearance of the epoxy groups and isoprene double

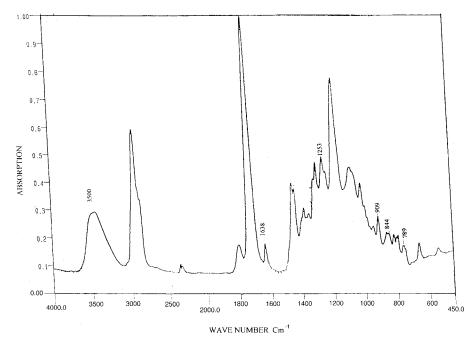


Figure 6 FTIR spectrum of cycloaliphatic epoxide-ENR-GMA hybrid system after UV irradiation.

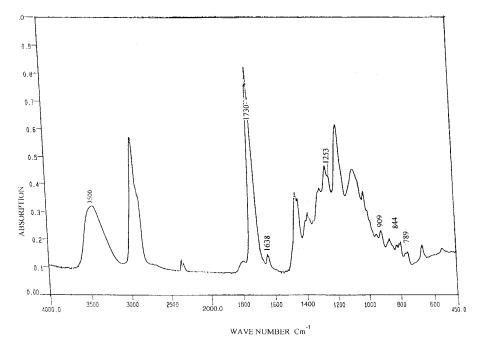


Figure 7 FTIR spectrum of cycloaliphatic epoxide-ENR-GMA hybrid system after UV exposure and postcure.

bands and appearance of hydroxyl groups. Table I shows the most significant infrared (IR) absorption and their respective assignments before and after irradiation of the coating systems.

The cycloaliphatic epoxy–GMA-ENR-based coating system exhibited the following characteristic absorption bands: (1) absorption bands corresponding to epoxy groups: (a) whole epoxy ring stretching^{14,17} at 1255 cm⁻¹; (b) terminal oxiranes of GMA¹⁸ at 909 cm⁻¹; (c) weak symmetric in-plane ring deformation of internal oxirane¹⁸ at 814-815 cm⁻¹; (d) half-ring stretching of cycloepoxy group¹⁴ at 789 cm⁻¹; (2) absorption bands at 1638 cm⁻¹ and 844-858 cm⁻¹ are attributed to the isoprene groups of ENR-50; (3) acrylic double bonds of GMA at 1638 cm⁻¹ and 815 cm⁻¹: The

Wavenumber	UV			
(cm^{-1})	Vibration	Exposure	Postcure	References
3,444-3,516	OH stretching	7	7	14, 17, 11, 19
1,730-1,736	C=O stretching	\checkmark	\checkmark	14, 17, 11, 19
1,638	Isoprene: C=C stretch of cis-1,4	\checkmark	\checkmark	14, 17, 11, 19
1,255	Epoxy: whole ring stretching	\checkmark	\checkmark	14, 17, 11
1,173–1,174	COO ester stretch	\checkmark	\checkmark	11
	C—O—C aliphatic and five membered cyclic ether:			
1,077	asymmetric stretching	7	7	11
909	Terminal oxiranes of GMA	\searrow	\checkmark	18
844-858	Isoprene: CH wagging	\checkmark	\checkmark	17
	Internal oxirane: symmetric in-			
	plane ring deformation. (Bussi et			
814-815	al. 1994)	\checkmark	\checkmark	18
789	Cycloepoxy: half-ring stretching	\checkmark	\checkmark	14

Table IMost Significant IR Absorption Maxima of Epoxy-ENR 50-GMA Hybrid System before UVExposure and after UV Exposure and Postcure

reduction in the absorption peaks of these bands on UV irradiation shows that both epoxy groups as well as the double bonds of isoprene and GMA took an active part in the photopolymerization. Similar results have been reported by Decker¹⁶ and Xuan.¹⁷ Marked increase in the OH stretching at 3,444-3,516 cm⁻¹ on UV exposure with concurrent decrease in the absorption bands corresponding to $1,255 \text{ cm}^{-1}$ (epoxy: whole ring stretching), 909 cm⁻¹ (terminal oxirane of GMA), 814-815 cm⁻¹ (internal oxirane: symmetric in plane deformation), and 789 cm^{-1} (cycloepoxy: half-ring stretching) establishes the successful accomplishment of ring-opening polymerization. The increase of $1,077 \text{ cm}^{-1}$ region can be attributed to the formation of an ether bond that can be a part of aliphatic and/or of cyclic structure.¹⁶

The marked decrease in the absorption bands of isoprene double bond at 1,638 cm⁻¹ (C=C stretch of cis 1,4) and 844–858 cm⁻¹ (isoprene C—H wagging) showed that the free radicals concurrently generated along with the cations during the photolysis of the initiator cause simultaneous radical polymerization involving the isoprene double bonds of the ENR and the acrylic double bonds of GMA.

The absorption band at $908-909 \text{ cm}^{-1}$ corresponding to the terminal oxiranes of GMA is present in the unexposed GMA-ENR solutions. This band disappears on UV irradiation. This suggests that the epoxy ring of GMA opens up during irradiation for participating in the polymerization reactions. The absorption band at 909 cm⁻¹ is attributable to the terminal oxirane of the GMA, and the absorption band at 788–789 cm⁻¹ corresponds to the epoxy group half-ring stretching.

Suggested Mechanism of Curing Process and Possible Structure of Interpenetrating Polymer in Cured Film on the Basis of FTIR Studies on a Single, Two, and Three Components

Spectra of ENR Alone in Presence of Photoinitiator Before and After UV Exposure

Typical FTIR spectra of ENR before and after irradiation, as shown in Figures 1 and 2 show significant reduction in the absorption of epoxy groups and the isoprene double bands at the following frequencies:

 $870-876 \text{ cm}^{-1} = \text{epoxy group}$ 1,251 cm⁻¹ = epoxy group 1,664 cm⁻¹ = isoprene double bonds

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840 cm^{-1} = isoprene double bonds

The disappearance of the absorption in the peaks above accompanied by an increase in the absorption corresponding to $3,463 \text{ cm}^{-1}$ attributable to O—H stretching affirms that epoxy rings of ENR have been opened by the Bronsted acid generated during the photolysis of the cationic photoinitiator. The reduction in the absorption at $1,664 \text{ cm}^{-1}$ and 840 cm^{-1} indicates the disappearance of isoprene double bonds attributable to involvement of these bonds in polymerization and crosslinking reactions. This reaction is promoted by free radicals, which are also produced when cationic photoinitiator undergo photolysis.

Spectra of ENR-GMA Film Before and After UV Exposure and the Role of GMA in the Hybrid System

A 20% solution of ENR-50 in GMA containing the photoinitiator was subjected to UV exposure and postcure. The spectra before and after irradiation and postcure are shown in Figures 3 and 4.

The spectrum in Figure 3 depicts the absorption of GMA-ENR solution before UV irradiation with the typical terminal oxirane absorption at 909 cm^{-1} and the absorption attributable to acrylic double bonds at 1.638 cm^{-1} and 815 cm^{-1} . The spectrum also shows the absorption bands characteristic of epoxy groups of ENR at 1,255 cm^{-1} and 870 cm^{-1} and those characteristic of isoprene double bonds of ENR at 1,639 cm⁻¹ and 844 cm^{-1} . It can be seen that the exposure to UV radiation has caused a decrease in the absorption at 1,637–1,638 cm⁻¹ and 844–849 cm⁻¹ (for isoprene double bond) and at 1,255-1,264 cm⁻¹ and 879 cm^{-1} (for epoxide). The absorption bands at 815 cm⁻¹ present in unirradiated ENR-GMA system disappear on UV exposure. This absorption band is attributable to internal oxirane symmetric in-plane ring deformation.¹⁸

Exposure of the films made from the above solution to the ultraviolet radiation results in a substantial reduction in the absorption at the above frequencies. Furthermore, there is an increase in absorption at $3,483 \text{ cm}^{-1}$ corresponding to O—H stretching.

These changes in the absorption pattern in the FTIR as a result of UV irradiation provide evidence on the possible involvement of the respective functional groups in the formation of interpenetrating polymer network structure.

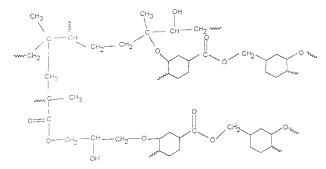


Figure 8 Probable structure of the interpenetrating polymer network derived from the hybrid system after the UV cure.

Spectra of the Films Made from the Coating Systems Consisting of Cycloaliphatic Diepoxide, ENR, and GMA, before and after UV Exposure

The FTIR spectra of the hybrid system (comprising cycloaliphatic epoxide, ENR, and GMA) before, after UV irradiation, and after UV irradiation and postcure are given in Figures 5, 6, and 7. The characteristic absorptions of the unreacted functionalities, namely, epoxy, acrylic, and isoprene groups, as shown in Figure 5 are as follows.

	oxirane ring of GMA half-ring stretching of cycloaliphatic ep-
	oxide
	epoxy groups of ENR
$844 \text{ cm}^{-1} =$	isoprene double bonds
$1,638 \text{ cm}^{-1} =$	isoprene double bonds

Figure 6 shows the IR spectra after UV irradiation. All the prominent absorption characteristics of the functional groups mentioned above are noticeably suppressed after UV exposure and postcure. The appearance of OH absorption is very significant.

The systematic FTIR studies carried out on both individual (isolated) systems, as well as the combined systems before and after UV irradiation, provide adequate evidence to show that the epoxy groups of ENR, cycloaliphatic epoxide, and GMA, the isoprene and acrylic unsaturations participate actively in a complex scheme of polymerization and crosslinking reactions. Both cations and free radicals are generated by the photolysis of the cationic photoinitiator under the influence of the UV radiation. Therefore, it is probable that the final crosslinked films may have the structure given in Figure 8. For an effective toughening of brittle resins, the following requirements must be fulfilled: (1) toughening agent and the resin must be immiscible; (2) interfacial adhesion between the elastomeric domain and the resin phase should be strong; and, (3) microdomain morphology must be preserved by crosslinking.

In the present system, the microdomain morphology has been effected by the UV radiation by compositional and morphological quenching during the curing process. The interphase adhesion has been promoted further by the formation of an interpenetrating polymer network, as shown by the spectroscopic studies.

CONCLUSIONS

The FTIR studies conducted on the films cast from the hybrid system comprising ENR-GMAcycloaliphatic epoxide show that the acrylic double bonds and the epoxy groups of GMA, the isoprene double bonds, epoxy groups of ENR, and the epoxy groups of cycloaliphatic epoxide resin undergo mutual interaction during the cationic UV curing in the presence of triphenyl sulphonium hexafluoro antimonate. These interactions are suggestive of the possibility of formation of an interpenetrating polymer network, a consequence highly favorable to promotion of adhesion between the elastomeric domain and the resin matrix in the cured coating. This, in effect, enhances the toughening of the otherwise brittle epoxy resin.

SUMMARY

The UV radiation curing of coatings made from a hybrid system consisting of ENR, GMA, and cycloaliphatic resin in presence of cationic photoinitiator was carried out. Films were obtained by irradiating the coatings by UV radiation. The FTIR spectra were obtained for these cured films. Because the spectra based on the final composition of the coating formulations would be too complicated to interpret, a single, two, and three component systems were taken up for curing, and the films thus obtained were subjected to spectral studies. Detailed examination of these spectra revealed the disappearance of acrylic double bonds of GMA, isoprene double bonds of ENR as well as disappearance of the epoxy groups of GMA, ENR, and cycloaliphatic epoxide. These results confirm the formation of an interpenetrating polymer network as a result of polymerization and crosslinking reactions taking place between the various

functional groups present in the compounds mentioned above. Formation of such an interpenetrating network tends to promote the adhesion between the elastomeric domain and the epoxy matrix, a condition conducive to the toughening of the epoxy system.

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