

STUDY ON UV-CROSSLINKING PROCESS OF DIANE-EPOXY RESIN/POLY(TETRAHYDROFURANE) DIVINYL ETHER SYSTEM

II. INFLUENCE OF EPOXY RESIN AND POLY-(TETRAHYDROFURANE) DIVINYL ETHER CONTENT ON PHOTOCROSSLINKING OF THE DIANE EPOXY/POLY-(TETRAHYDROFURANE) DIVINYL ETHER SYSTEM

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ABSTRACT

The effect of diane-epoxy resin (DE) and poly(tetrahydrofuran) divinyl ether (DVE) content on photocrosslinking reaction of DE/DVE system with triarylsulfonium salt (TAS) as photo-initiator were investigated by IR spectra, change of relative hardness and gel fraction. The results showed that increasing DVE content improved some of physico-mechanical properties of photocrosslinked coatings although relative hardness and speed of photocrosslinking reaction reduced. The changes of functional groups (IR spectra), relative hardness and gel fraction as well as the physico-mechanical properties of UV-cured coatings based on DE/DVE/TAS system illustrated that suitable mass ratio of constituents was 80/20/5. The UV-cured coating based on the system DE/DVE/TAS = 80/20/5 crosslinked completely after 3.6 seconds UV-exposure and having good physico-mechanical properties: impact resistance reached 180 kg.cm; the flexibility obtained 1mm; the adhesion and relative hardness were point 1 and 0.7, respectively.

Keywords: diane-epoxy resin, poly(tetrahydrofuran) divinyl ether, photocrosslinking.

1. INTRODUCTION

Diane-epoxy resin (DE) has been studied and used widely in the industry such as paint, varnish, composite... [1 - 3, 6]. However, due to their structure, cured diane-epoxy resin was usually brittle, easy peeling and poor impact resistance and thus reducing the value and scope application of diane-epoxy resin. There are many approaches to improve adhesion, impact resistance of cured diane-epoxy resin like either epoxy resin modified by vegetable oils, or adding the plasticizers, or curing with others as plasticizer [1 - 3, 5 - 7].

Outstanding advantages of photocrosslinking method are rapid crosslinking, saving the energy, releasing no organic chemical pollutant and crosslinked product having good physico-mechanical properties. Therefore, the photocrosslinking has attracted scientists studying [4, 5, 6,

8]. Vinyl ether was harmless, active and low viscosity. Consequently, vinyl ether usually used as thinner lead to increasing mobility and crosslink density of UV-curing system and their curing proceeded by a cationic mechanism [11 - 14]. C. Decker used the tri(ethylene glycol) divinyl ether (TEDVE) as the thinner in UV-curable epoxy silicone system with a purpose to improve reaction ability of epoxy resin. Due to presence of TEDVE, the viscosity of system reduced and created polymer had good plastic properties [11]. Other results of UV-curable rubber bearing both epoxy and acrylate groups in its main chain and divinyl ether showed that the photocrosslinking rapidly occurred when the system was irradiated by UV light (50 mW.cm^{-2}) with the presence of 2% triarylsulfonium (TAS), i.e. the double bond $\text{C}=\text{C}$ of vinyl ether groups in the system completely converted after 2s of exposure UV [12]. In other study, photocrosslinking of epoxidized natural rubber (ENR) and di(ethylene glycol) divinyl ether (DEDVE) system was investigated. The obtained results indicated that the reaction occurred fast. The product of UV-cured ENR/DEDVE experienced lower hardness and higher flexibility in comparison with ENR cured. In addition, the ENR/DEDVE cured had good adhesion to metal and plastic surface [13].

The photocrosslinking process of DE/DVE has been studied with a desire using the DVE as a thinner and improving physico-mechanical properties namely improving the flexibility, toughness of cured diene-epoxy resin meeting demand used as decorative protective coating materials, adhesives materials,... The previous research indicated that the suitable content of photo-initiator was 5 % wt. [9]. This work presents continuously the effect of DE and DVE content on the photocrosslinking process of the DE/DVE/TAS system.

2. MATERIALS AND METHODS

2.1. Materials

Diane-epoxy resin (DE) used was of type NEPL-128S that made in Taiwan. Poly (tetrahydrofuran) divinyl ether (DVE) was supplied by BASF Company (Germany). Triarylsulfonium salt type UVI – 6990 (TAS) were purchased from Ciba Specialty Chemicals. Chloroform used was of P grade from China.

2.2. Sample preparation

The photocrosslinking systems were prepared by mixing constituents: DE and DVE with various mass ratio $\text{DE/DVE} = 75/25; 80/20; 85/15; 90/10$ and $95/5$ while content of TAS was constant, at 5 % wt. The various mass ratios of constituents in this study were shown on the Table 1.

Table 1. The mass ratio of constituents in the photocrosslinking system.

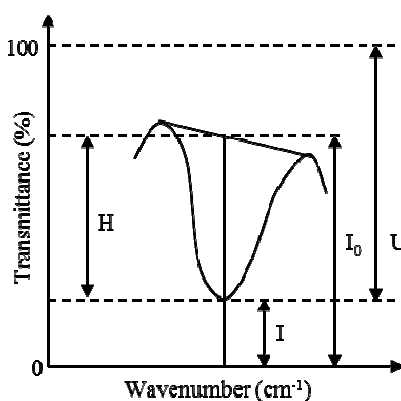
| No | Constituents | | |
|----|--------------|------------|------------|
| | DE (% wt) | DVE (% wt) | TAS (% wt) |
| 1 | 75 | 25 | 5 |
| 2 | 80 | 20 | 5 |
| 3 | 85 | 15 | 5 |
| 4 | 90 | 10 | 5 |
| 5 | 95 | 5 | 5 |

The 30 μm thickness film were cast either on a KBr crystal for infrared spectroscopy (IR) analysis, on the glass plates for relative hardness and gel fraction measurement, or on the copper plate for flexibility determination, or on the steel plate for other physico-mechanical properties determination. After that, the samples were exposed to the UV radiation of a medium pressure mercury lamp from FUSION UV (model F 300S) in the presence of air at ambient temperature. They were passed repeatedly under the lamp at a web speed between 5 and 40 m/s. Each pass at a speed of 5 m/s corresponds to an exposure time of 1.2 s. The intensity of the UV light reaching the sample was measured by radiometry to be 250 mW/cm².

2.3. Analysis

- *IR analysis*: The infrared spectra of the sample, before and after UV irradiation were recorded by means of an FT-IR spectrophotometer (NEXUS 670 from Nicolet). The changes of the reactive functional groups upon UV exposure were monitored quantitatively by following the variation of their characteristic IR absorption bands. According previous studies showed that the absorption bands at 1803 cm⁻¹ (TAS), 914 cm⁻¹ (epoxy group) and 971 cm⁻¹ (divinyl group) were markedly reduced. As expected, the absorption band at 1510 cm⁻¹ (aromatic double bonds) remained essentially unchanged upon UV irradiation. Hence, the absorption bands at 1803, 914 and 971 cm⁻¹ were used for the quantitative evaluation of the changes in the functional groups of the coatings during UV exposure. The absorption band at 1510 cm⁻¹ was used as a reference for our quantitative evaluation of the reaction kinetics [9]. From the decrease of the structural bands, the relative amount of remaining functional groups was determined by making the ratio of the IR absorbance at the corresponding wavenumber after a given exposure time (D_t) to the absorbance of the unexposed sample (D_0) [10]. Remaining group (%) = $D_t/D_0 \times 100$.

Note: $D = \epsilon \cdot l \cdot C = \log(I_0/I) = \log[1+H/(100-U)]$; (H and U value were given by IR application as simulation was presented on scheme 1).



Scheme 1. Simulation of IR spectra calculation [15].

- *Determination of physic-mechanical properties*: The relative hardness of the UV-cured coating was measured by means of a Pendulum Damping Tester (model 299/300), according to the ISO 1522. The impact resistance of the coatings was determined by means of an Impact Tester (model 304) according to the ISO 6272. The adhesion of the coatings on steel was evaluated by using the Elcometer Cross Hach Cutter according to ISO 2409. The flexibility was determined by using IIIГ-1 equipment according to the ГOCT 6806-53.

- *Determination of the gel fraction:* The gel fraction of the photocrosslinked polymers was performed in a Soxhlet equipment according ASTM D 2765. Samples were held by a piece of 120-mesh stainless steel cloth, were weighed, and then immersed in the chloroform solvent at the ambient temperature in 24 hours. After extraction, the specimens were removed, dried, and reweighed as directed. The gel fraction was evaluated from the weight ratio of the insoluble part to the initial sample.

3. RESULTS AND DISCUSSION

3.1. Effect of DE and DVE content on functional group changes in the process of photocrosslinking DE/DVE/TAS system

The changes of epoxy and vinyl ether groups' contents in the process of photocrosslinking were presented on the Fig. 1 and Fig. 2, respectively.

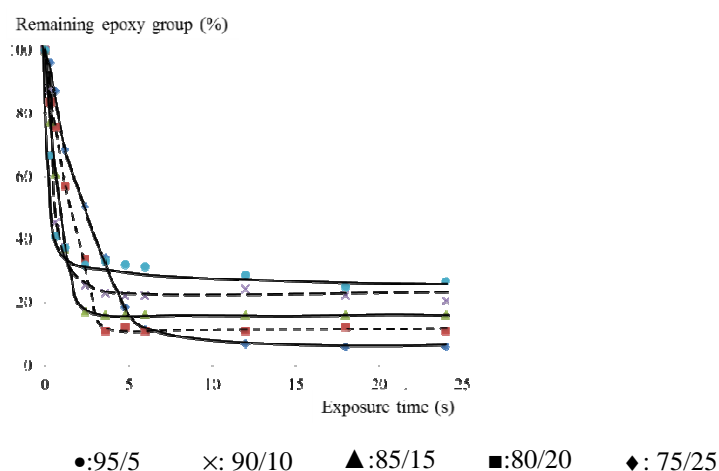


Figure 1. Effect of DE and DVE content on the change of epoxy group content in the photocrosslinking process of DE/DVE/TAS system.

In general, the epoxy groups were reacting rapidly during in the first of 4.8 seconds UV-exposure, after which reaction gradually slowed down. After the first of 3.6 second UV-exposure, the remaining epoxy group contents in the photocrosslinking systems at 80/20; 85/15; 90/10 and 95/5 of DE/DVE mass ratio were 11; 16; 23 and 32 %, respectively, and then the epoxy group converted insignificantly. In comparison with other systems, the speed conversion of epoxy groups of system at mass ratio DE/DVE = 75/25 saw the slowest but conversion epoxy group content experienced lowest content, at 7%. It means that when the content of DVE in system increased, the content of epoxy group and epoxy group concentration reduced and thus falling the speed of conversion of epoxy group. However, the content of DVE increased leading to the flexibility of system also grew. The UV light could irradiate deeper inside coating and thus the photocrosslinking being thorough.

As can be seen from Fig. 2, the UV exposure time for vinyl groups converted totally were longer when increasing the DVE content. It took 6 seconds UV-exposure for system having DE/DVE = 75/25 and 2.4 second for system having DE/DVE = 95/5 to convert completely vinyl groups. It means that the DVE content was, more or less, proportional to conversion vinyl groups' time. Up to a point, the content of DVE had insignificantly effect on the speed of vinyl group converting.

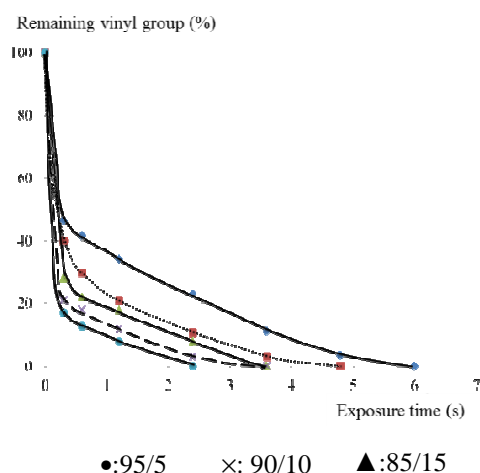


Figure 2. Effect of DE and DVE content on the change of vinyl group content in the photocrosslinking process DE/DVE/TAS system.

The changes of TAS content in photocrosslinking reaction were showed on the Fig. 3. Overall, the speed of conversion TAS was sharp during the first of UV-exposure process, after which the conversion of TAS gradually slowed down. When increasing the DVE content, the speed of TAS conversion reduced but the total of TAS conversion grew. It could explain that increasing the DVE content as the DE content reduced, the compatibility of TAS with DE/DVE system, to some extent, reduced because DE and TAS had similar structure containing benzene rings. After 24 seconds UV-exposure, the remaining TAS group in the photocrosslinking systems at 75/25; 80/20; 85/15; 90/10 and 95/5 of mass ratio DE/DVE were 44; 34; 26; 23 and 19 %, respectively.

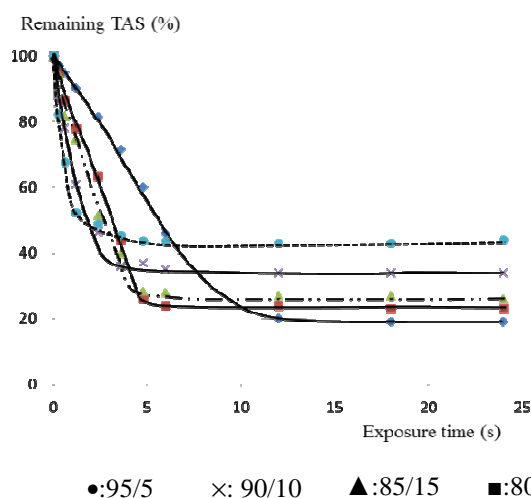


Figure 3. Effect of DE and DVE content on the change of TAS content in the photocrosslinking process DE/DVE/TAS system.

3.2. Effect of DE and DVE content on the changes of gel fraction, relative hardness in the photocrosslinking reaction

The changes of relative hardness value of UV-cured coatings with different DE/DVE mass ratios were displayed in the Fig. 4.

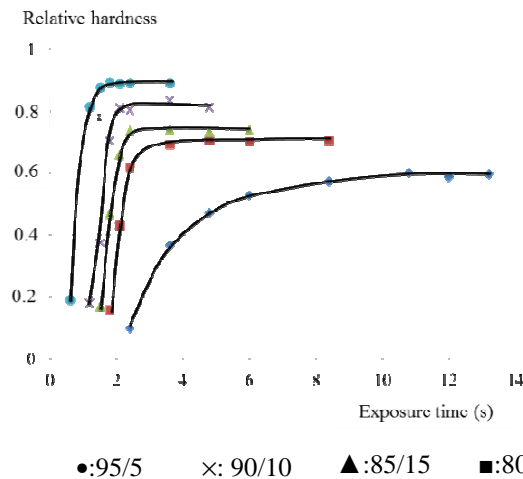


Figure 4. Effect of DE and DVE content on the change of relative hardness in the photocrosslinking process of DE/DVE/TAS system.

From the Fig. 4, the times of appearing and max value of the relative hardness were, to some extent, inversely proportional to DVE content. For the system having DE/DVE ratio being 75/25, the relative hardness appeared after 2.4 second UV-exposure and the max value reached 0.6 after 10.8 second UV-exposure. By contrast, for the system having DE/DVE ratio being 95/5, there was first relative hardness, at 0.2, after 0.6 seconds UV-exposure and then the value of relative hardness increased dramatically, levelling off at 0.9 after 1.8 seconds UV-exposure. This rule also presented through the changes of gel fraction in the photocrosslinking process.

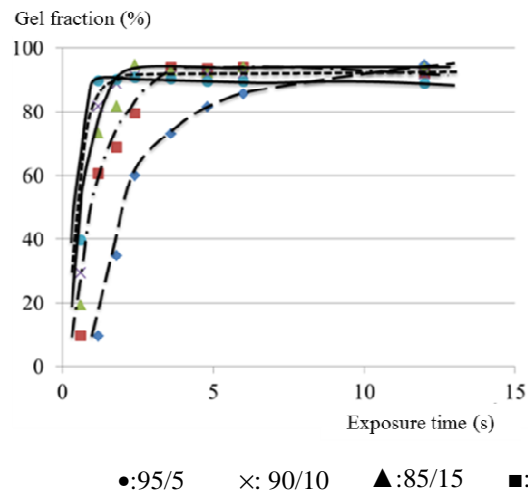


Figure 5. Effect of DVE and DE content on the gel fraction in the photocrosslinking process of DE/DVE/TAS system.

The changes of gel fraction of photocrosslinking systems were presented on the Fig. 5. Overall, the gel fraction grew dramatically in the first stage of UV-exposure process. All of samples reached over 90 % of gel fraction. For the systems at 80/20; 85/15; 90/10 and 95/5 of DE/DVE mass ratio, the value of gel fraction increased rapidly during 3.6 seconds UV-exposure, after which the gel fraction became slow down and remained unchanged after 4.8 seconds UV-exposure. Especially, for photocrosslinking system having DE/DVE mass ratio being 75/25, the gel fraction

experienced the slowest increase but the gel fraction had continuously upward trend to higher point. The DVE content increased (it means the epoxy resin content reduced) leading to flexibility increasing. As a result, the photocrosslinking probably occurred deeper.

3.3. Physico-mechanical properties of cured coating based on DE/DVE/TAS system

From obtained results, the suitable UV-exposure time had been selected for each photocrosslinking system. The physico-mechanical properties were displayed on the Table 2.

Table 2. Physico-mechanical properties of UV cured coating based on DE/DVE/TAS system.

| No | ED/DVE/TAS | UV exposure time (second) | Impact resistance (kg.cm) | Flexibility (mm) | Adhesion (point) | Relative hardness |
|----------|----------------|---------------------------|---------------------------|------------------|------------------|-------------------|
| 1 | 75/25/5 | 12 | >200 | 1 | 0 | 0.6 |
| 2 | 80/20/5 | 3.6 | 180 | 1 | 1 | 0.7 |
| 3 | 85/15/5 | 3.6 | 140 | 3 | 2 | 0.75 |
| 4 | 90/10/5 | 2.4 | 90 | 5 | 3 | 0.8 |
| 5 | 95/5/5 | 2.4 | 20 | >5 | 5 | 0.9 |

From the Fig. 1 – 5 and the Table 2 showed that when DVE increased, the physico-mechanical properties of UV-cured coatings also improved but the speed of photocrosslinking was slow down. The cured coating based on system DE/DVE/TAS = 75/25/5 experienced the best physico-mechanical properties but the slowest speed of photocrosslinking as to complete UV-cured this coating needed 12 seconds UV-exposure. The photocrosslinking system DE/DVE/TAS = 80/20/5 having the conversion functional group quickly, after 3.6 seconds UV-exposure, cured coating having high gel fraction and good physico-mechanical. Therefore, the suitable mass ratio of photocrosslinking based on DE/DVE/TAS was 80/20/5.

4. CONCLUSION

The DVE content was proportional to physico-mechanical properties of UV-cured coating based on photocrosslinking DE/DVE/TAS system and was conversely proportional to speed of photocrosslinking reaction.

The suitable mass ratio DE/DVE/TAS was 80/20/5. The system completely cross-linked after 3.6 second UV-exposure. The UV-cured coating having good physico-mechanical: impact resistance reached 180 kg.cm; flexibility obtained 1mm; adhesion and relative hardness were point 1 and 0.7, respectively.

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TÓM TẮT

NGHIÊN CỨU QUÁ TRÌNH KHÂU MẠCH QUANG CỦA HỆ NHỰA EPOXY DIAN/POLY(TETRAHYDROFURAN) DIVINYL ETE

II. ẢNH HƯỞNG CỦA HÀM LƯỢNG NHỰA EPOXY VÀ POLY- -(TETRAHYDROFURAN) DIVINYL ETE TỚI QUÁ TRÌNH KHÂU MẠCH QUANG CỦA HỆ NHỰA EPOXY DIAN/POLY(TETRAHYDROFURAN) DIVINYL ETE

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Ảnh hưởng của hàm lượng nhựa epoxy dian (DE) và poly(tetrahydrofuran) divinyl ete (DVE) tới phản ứng khâu mạch quang của hệ DE/DVE với chất khơi mào quang muối triarylsulfonium (TAS) đã được nghiên cứu thông qua phổ IR, sự biến đổi độ cứng tương đối và hàm gel. Kết quả cho thấy khi tăng hàm lượng DVE thì màng khâu mạch có độ cứng tương đối thấp, tốc độ khâu mạch chậm nhưng lại nâng cao một số tính chất cơ lí. Sự biến đổi các nhóm định chức, độ cứng tương đối, hàm gel cũng như các tính chất cơ lí của màng khâu mạch quang trên cơ sở DE/DVE/TAS cho thấy tỉ lệ khối lượng thích hợp cho quá trình khâu mạch là 80/20/5. Màng khâu mạch quang trên cơ sở hệ nhựa DE/DVE/TAS với tỉ lệ khối lượng 80/20/5 khâu mạch hoàn toàn sau 3,6 giây chiếu tia tử ngoại và có tính chất cơ lí tốt: độ bền va đập đạt 180 kg.com; độ bền uốn đạt 1mm; độ bám dính và độ cứng tương đối tương ứng là điểm 1 và 0,7.

Từ khóa: nhựa epoxy dian, poly(tetrahydrofuran) divinyl ete, khâu mạch quang.