

INFLUENCE OF THE CONTENT OF COBALT NAPHTHENATE ACCELATOR ON THE CROSSLINKING OF THE CURABLE SYSTEM ON THE BASE OF A VINYLESTER OF EPOXY-DIANE RESIN AND STYRENE

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ABSTRACT

The influence of the content of cobalt naphthenate accelerator on the crosslinking process of the curable system on the base of vinyl ester of epoxy-diane resin and styrene system has been studied. It was determined by IR – spectroscopic study that acrylate and styrene double bonds sharply decreased during the curing process. The participation of the double bonds to the crosslinking polymerization led to the gelation and change of physico – mechanical properties of the vinyl ester – styrene system. The change of mass ratio of the accelerator / resin system from 0.025 to 0.1 % resulted in decrease of the gelation time, swelling degree and increase of the gel fraction, hardness of the cured coatings.

Keywords: cobalt naphthenate accelerator, crosslinking, vinyl ester, styrene, IR, gel fraction, swelling degree, hardness.

1. INTRODUCTION

As one of the types of unsaturated polyester resins, vinyl ester resins (VE) are often produced by the reaction of epoxy resins such as diglycidyl ether of bisphenol-A: N,N,O-triglycidyl amino-phenol with acrylic or methacrylic acid, and combines the excellent mechanical, thermal properties of epoxy resins with easy processing, fast curing of VE resins. That's why the products of crosslinking polymerization are widely used in many fields [1].

The properties of the cured products on the base of VE resins depend on various factors such as the chemical nature, content of the VE resin and the curable system constituents (diluent, initiators, accelerator, etc) [1 - 8]. Therefore, it is necessary to determine the optimal conditions for crosslinking polymerization of the VE resins based system to obtain cured products with desired properties.

At present there has been only a few research results concerning of VE resins, in general, and curing of the coatings on the base of the resins, in particular, in Vietnam [9-12].

This work presents the influence of cobalt naphthenate accelerator on the crosslinking polymerization of the curable system on the base of a VE of epoxy-diane resin and styrene.

2. EXPERIMENTAL

2.1. Materials

Vinyl ester resin on the base of diglycidyl ether of bisphenol A deluted by styrene (St) with the weight ratio VE/St = 60/40 was obtained from Polymer Technologies PTE Ltd (Singapore). Methyl ethyl ketone peroxide initiator (B) was purchased from Singapore. Cobalt naphthenate accelerator on the base of cobalt naphthenate salt (C) was prepared at the Institute for Tropical Technology (ITT). Chloroform of PA grade from China.

2.2. Analysis

2.2.1 Determination of the thickening point

Thickening point of a curable system was determined by the duration of the time needed for the change of the investigated system from flowable liquid to unpourable state at the ambient temperature [13].

2.2.2. IR analysis

The Infrared spectra of the sample, before and after curing, were recorded by means of an FTIR spectrophotometer (NEXUS 670 from Niolet) at the Institute for Tropical Technology (ITT), Vietnam Academy of Science and Technology (VAST). The changes of the reactive functional groups during the curing were monitored quantitatively by following the variation of their characteristic IR absorption bands using the absorption band at 700 cm⁻¹ characteristic for the C-H bond of benzene ring, which should be unchanged during the curing, as the reference.

2.2.3 Determination of the gel fraction and the swelling degree

The gel fraction was determined by soaking the UV cured sample in chloroform for 24 h at room temperature. The insoluble part of the coating was recovered by filtration and dried at 40 °C to a constant weight. The gel fraction was evaluated from the weight ratio of the insoluble part to the initial sample. The swelling degree was calculated from the weight ratio of the swollen polymer to the dry polymer.

2.2.4. Determination of the relative hardness

Persoz hardness of the cured polymer, coated on a glass plate, was measured by means of a pendulum damping tester (model 300) according to the standard Persoz (NF T 30-016) at the ITT, VAST. The relative hardness of a coating was evaluated by making the ratio of its Persoz hardness to the Persoz hardness of a standard glass plate which was measured to be 425 s.

3. RESULT AND DISCUSSION

3.1. Study of the crosslinking reaction of the VE- styrene system by FTIR spectrometry

3.1.1. IR spectra of the materials and VE-styrene system before and after curing

The IR spectra of the coatings on the base of VE, styrene, B, C compounds before and after 24 h - curing at ambient temperature are presented in Fig. 1. In can be seen in the spectra the absorption bands at 1630, 1411, 992 cm^{-1} characteristic for acrylate double bonds of VE resin, absorption bands at 1630, 1411, 922 and 910 cm^{-1} characteristic for styrene double bonds and absorption band at 700 cm^{-1} characteristic for C-H bond of benzene ring. Absorption band at 910 cm^{-1} almost disappeared, absorption band at 700 cm^{-1} was unchanged after 24 h of the reaction.

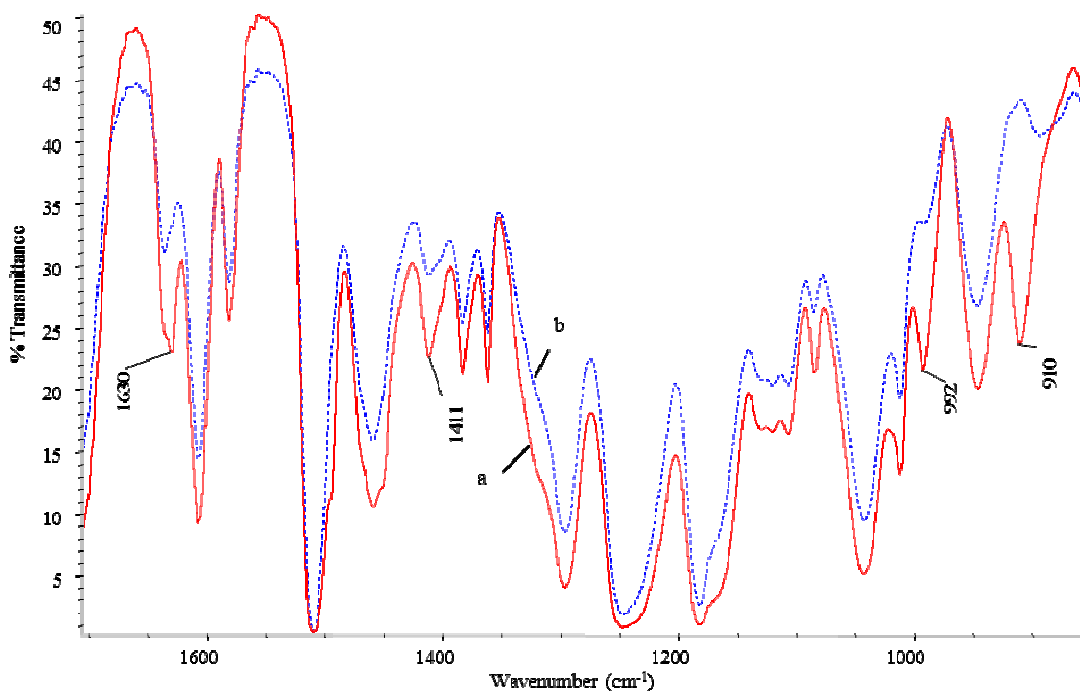


Figure 1. IR spectra of VE – styrene coatings before (a) and after 24 h of curing (b).
B content: 0.75 %, C content: 0.1 %.

So, absorption band at 910 cm^{-1} was chosen for study of the variation of the styrene double bonds during the curing and absorption band at 700 cm^{-1} was used as the reference.

3.1.2. Change of styrene double bonds during the crosslinking

The variation of the styrene double bonds in the VE-styrene system containing 0.75 % B and 0.1 % C is presented in Fig. 2. It is shown from the figure that the styrene double bonds have markedly reduced in the beginning stage of the curing process. There have been only 40.4 % styrene double bonds remained after 120 min of the reaction. After 1440 min the double bonds were almost converted with the residual content of 7 %.

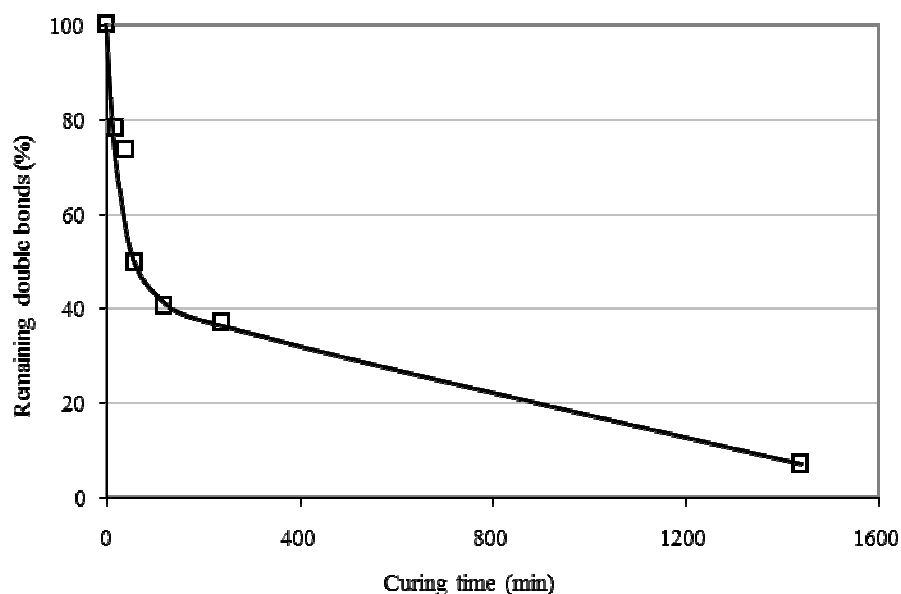


Figure 2. Variation of the styrene double bonds in the VE-styrene system containing 0.75 % B and 0.1 % C.

3.2. Influence of the ratio accelerator / (VE-styrene system) on the crosslinking process

Influence of accelerator content on the crosslinking process have been investigated with the ratio of B/(VE-styrene system) = 0.75 %.

3.2.1. Influence of the ratio promoter/(VE-styrene system) on the gelation point

The thickening time is a parameter needed for processing. So, the influence of the ratio accelerator / (VE-styrene system) has been investigated with the values accelerator / (VE-styrene system) of 0.025, 0.05, 0.075, 0.1, 0.2, 0.3 % at 25 °C in this work. The dependence of the thickening time on the ratio accelerator / (VE-styrene system) is shown in Fig. 3.

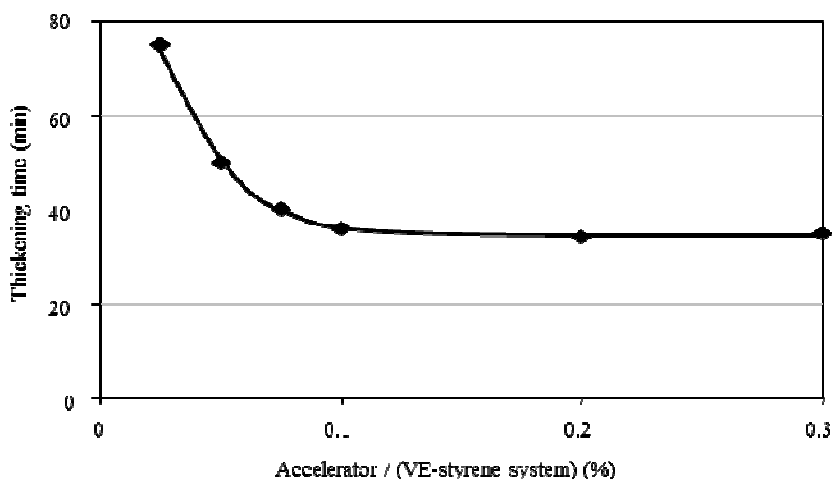


Figure 3. Influence of the ratio accelerator / (VE-styrene system) on the thickening time.

It is indicated from the figure, that increase of the accelerator / (VE-styrene system) ratio from 0.025 to 0.1 % speeds up the curing process and shortens the thickening time from 75 min to 36 min. However, the thickening time is almost unchanged at higher accelerator / (VE-styrene system) value. This can be explained by the fact, that the increase of the promoter/(VE-styrene system) value favors the formation of free radicals leading to increase of the crosslinking rate. However, the initiator amount in the investigated system is limited. When it has been totally converted to free radicals, the further increase of the accelerator can not affect on the change of free radicals in the system and as the consequence, the reaction rate as well as the thickening time. So, the accelerator / (VE-styrene system) ratio chosen for further study was not higher than 0.1 %.

3.2.2. Influence of the ratio accelerator / (VE-styrene system) on the variation of the gel fraction, swelling degree and relative hardness

The influence of the ratio accelerator / (VE-styrene system) on the variation of the gel fraction, swelling degree and relative hardness have been investigated with the values of the accelerator / (VE-styrene system) of 0.025, 0.05, 0.075, 0.1 %.

- Influence of the accelerator / (VE-styrene system) ratio on the variation of the gel fraction.

Figure 4 shows the influence of the accelerator / (VE-styrene system) ratio on the variation of the gel fraction. It can be seen from the figure, that the higher accelerator / (VE-styrene system) ratio, the faster the gel formation in the investigated systems. However, the final gel fractions were 99 %, i.e. the same for all studied samples.

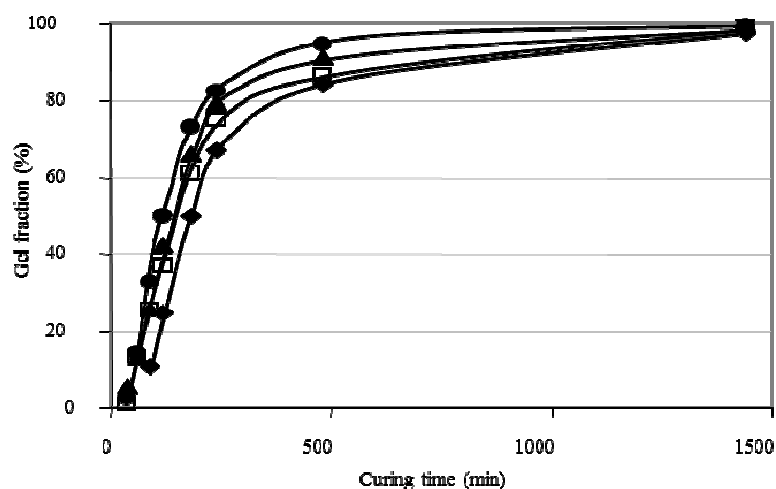


Figure 4. Influence of the accelerator / (VE-styrene system) ratio on the variation of the gel fraction
Accelerator / (VE-styrene system): ◆ 0.025 %, □ 0.05 %, ▲ 0.075 %, ● 0.1 %.

- Influence of the accelerator / (VE-styrene system) ratio on the variation of the swelling degree.

The influence of the accelerator / (VE-styrene system) ratio on the variation of the swelling degree is presented in Fig. 5. As is shown from the figure, the swelling degrees of the investigated samples are reduced during the curing up to the curing time of 480 min, reaching

the values of 400, 340, 290, and 290 % for the samples with the accelerator / (VE-styrene system) ratio of 0.025, 0.05, 0.075, 0.1%), respectively. Then, the swelling degree of samples insignificantly change, reaching the final values of 244 – 220 % after 1440 min. So, in the experimental conditions conducted, the accelerator / (VE-styrene system) ratios have almost no affect on the final swelling degree of the studied samples.

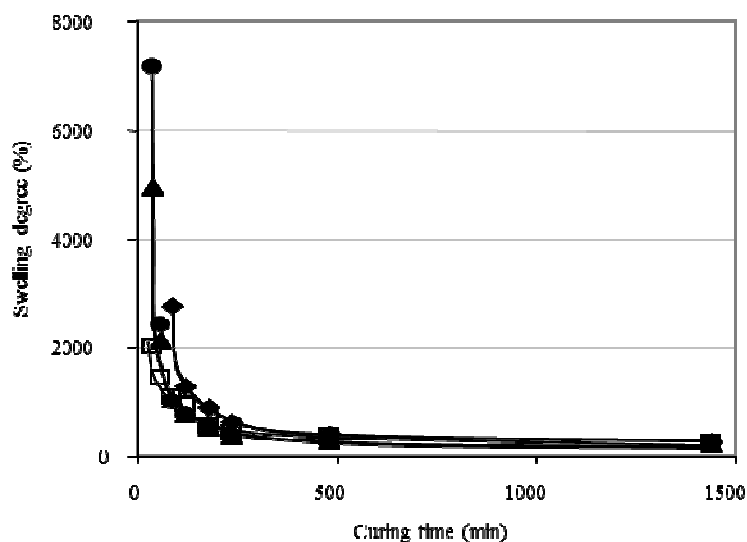


Figure 5. Influence of the accelerator / (VE-styrene system) ratio on the variation of the swelling degree
Accelerator / (VE-styrene system): ◆ 0.025 %, □ 0.05 %, ▲ 0.075%, ● 0.1 %.

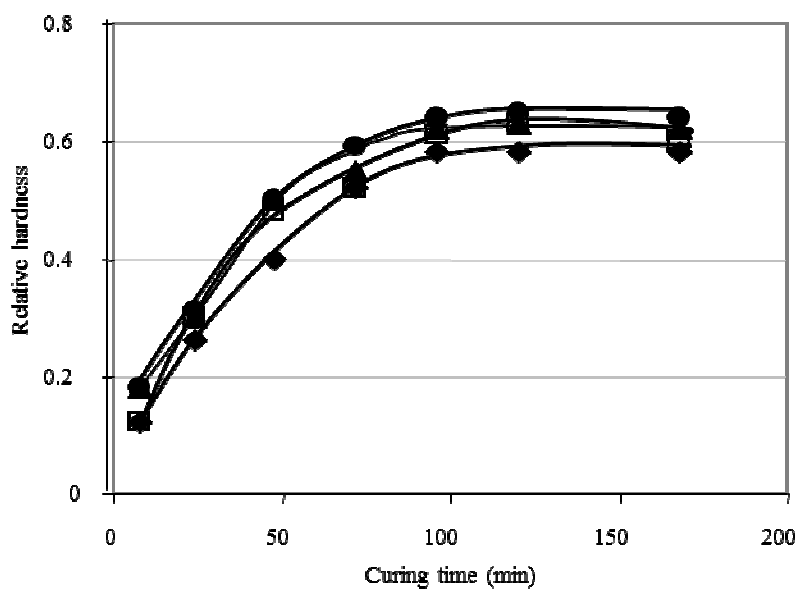


Figure 6. Influence of the accelerator / (VE-styrene system) ratio on the relative hardness
Accelerator / (VE-styrene system): ◆ 0.025 %, □ 0.05 %, ▲ 0.075 %, ● 0.1 %.

- Influence of the accelerator / (VE-styrene system) ratio on the relative hardness.

The influence of the accelerator / (VE-styrene system) ratio on the relative hardness is shown in Fig. 6. It can be seen from the figure that the relative hardness of the investigated samples increased during the curing and reached the highest value after 96 h. The difference in the relative hardness of the samples with various accelerator / (VE-styrene system) was insignificant. After 96 h curing, the relative hardness of the samples having the accelerator content of 0.025, 0.05, 0.075 and 0.1 % were 0.58, 0.61, 0.62 and 0.64, respectively.

4. CONCLUSION

Based on the FTIR research results, the absorption band at 910 cm^{-1} was chosen for quantitative determination of the variation of styrene double bond during the crosslinking of the VE-styrene system containing initiator methyl ethyl ketone peroxide. The absorption band at 700 cm^{-1} characteristic for C-H bond of benzene ring, unchanged during the curing, was used as the reference.

Under conducted experimental conditions, the styrene and acrylic double bonds were involved in the crosslinking copolymerization leading to the significant changes of the physical, mechanical properties of the investigated system.

It was shown that the increase of the accelerator / (VE-styrene system) ratio from 0.025 to 0.1 % speeded up the copolymerization, the thickening, gel formation, the increase of the relative hardness and raised the final relative hardness from 0.58 to 0.64. The optimal value of the accelerator / (VE-styrene system) ratio was determined to be 0.1 %. At the conditions, the investigated coating reached the gel fraction of 99 %, swelling degree of 220 %, relative hardness of 0.64 after 96 h curing.

REFERENCES

1. Kelly A., Zweben C., Talreja R., Aders J., Manson E. - Comprehensive composite materials. Vol. 2, Polymer Matrix composites. Elsevier science Ltd, Oxford, UK, 2000, pp. 18-35.
2. Strarr B., Burts E., Upson J. R. and Riffle J. S. - Polyester dimethacrylate oligomers and networks, *Polymer* **42** (21) (2001) 8727-8736.
3. Le Xuan H. and Decker C. - Photocrosslinking of acrylated natural rubber, *Journal Polymer Science, Polymer Chemistry* **31** (12) (1993) 769-780.
4. Decker C., Viet T. Ng. T. et Le Xuan H. - Photoréticulation de caoutchoucs fonctionnalisés. IV. Synthèse de caoutchoucs à groupements acrylate, *European Polymer Journal* **32** (5) (1996) 549-557.
5. Dahlan Hj Mohd, Abdul Ghani Harun - The use of natural rubber - based material for the preparation of radiation – curable resin, *Journal Sains Nuklear Malaysia* **11** (1) (1993) 11-26.
6. Deruot D., Brosse J. C., Tillekeratne L. M. K. - Fixation of methacrylic acid onto epoxidized liquid natural rubber, *Journal of natural Rubber Resarch* **5** (4) (1990) 296-300.
7. Phinyocheep pranee, Duanf thong Sayan - Ultraviolet – curable liquid natural rubber, *Applied Polymer Science* **78** (8) (2000) 478-1485.

8. Amanda Jacob - Vinyl ester lead the corrosion challenge, Reinforced plastics **47** (6) (2003) 32-45.
9. Tran Vinh Dieu, Tran Kim Dung, Nguyen Thi Thuy, Nguyen Đang Luong - Study of the preparation of the vinyl ester matrix on the base of saturated cyclic epoxy resin, methacrylic acid and application in polymer composite materials, Vietnam Journal of Chemistry **40** (3A) (2002) 34-40.
10. Nguyen Hieu Nieu, Nguyen Đac Thanh, La Thai Ha - Synthesis and study on properties of vinylester resin based on epoxidized soybean oil (ESO) and methacrylic acid, Vietnam Journal of Chemistry **41** (1) (2003) 48-53.
11. Le Xuan Hien, Nguyen Thi Luan, Nguyen Thi Viet Trieu - Study of the influence of some factors on the crosslinking reaction of the crosslikable systems on the base of bisphenol-A diglyxydyl ether diacrylate resin, Journal of Science and Technology **48** (3A) (2010) 129-136.
12. Le Xuan Hien, Nguyen Thien Vuong, Le Mai Thuy, Nguyen Thi Viet Trieu - Study of photocrosslinking reaction of the resin system on the base of copolymer of tung and soyabean oils, methyl methacrylate, styrene, Journal of Science and Technology **48** (3A) (2010) 150-157.
13. Juan De Vicente - Rheology, In Tech Europe, Croatia, 2012.

TÓM TẮT

ẢNH HƯỞNG CỦA HÀM LƯỢNG CHẤT XÚC TIẾN NAPHTENAT COBAN ĐẾN QUÁ TRÌNH KHÂU MẠCH CỦA HỆ ĐÓNG RẮN TRÊN CƠ SỞ VINYLESTE CỦA NHỰA EPOXY DIAN VÀ STYREN

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Nghiên cứu ảnh hưởng của chất xúc tiến cobalt naphlenate đến quá trình khâu mạch của hệ đóng rắn trên cơ sở vinyleste của nhựa epoxy dian và nhựa styren dựa trên phương pháp phổ IR. Trong quá trình nghiên cứu, liên kết đôi của acrylat và styren giảm dần. Sự tham gia của liên kết đôi đến quá trình trùng hợp khâu mạch làm ảnh hưởng tới sự đóng rắn và thay đổi tính chất cơ lí của hệ thống vinyleste – styren. Khi thay đổi tỉ lệ khối lượng của chất xúc tiến / nhựa từ 0,025 – 0,1 % dẫn tới làm giảm thời gian đóng rắn, độ churong, tăng phần gel, độ cứng của lớp ngoài.

Từ khóa: chất xúc tiến coban naphtalen, quá trình khâu mạch, vinyl este, styren, IR, phần gel, độ trương, độ cứng.