



STUDIES ON CATIONIC UV CURING OF EPOXIDISED PALM OIL (EPO) FOR SURFACE COATINGS

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ABSTRACT

Epoxidised palm oil (EPO) resin can be cured by ultraviolet (UV) radiation either by radical, cationic or hybrid system. Cationic curing system has been chosen in this study due to the fact that epoxy groups present in EPO can be utilised directly to form crosslinking. Curing was done by means of a 20 cm wide UV IST machine with the conditions of 7.5 A current and 4 m/min conveyor speed. Sulphonium and ferrocenium salts were used as cationic photoinitiator. A formulations study was performed on the selected grades of EPO with other materials. These include types and concentration of photoinitiator, monomers, concentration of EPO and post-cure. The properties of the cured film such as pendulum hardness, percentage of gel content and tensile strength were determined. It was found that triarylsulphonium hexafluorophosphate has a very low solubility in EPO. Addition of vinyl ether monomer to the formulation did not enhance pendulum hardness and gel content of the cured films. It is also found that the post cure temperature has no significant effect on the cured film.

ABSTRAK

Resin minyak sawit boleh dimatangkan dengan sinaran ultraviolet (UV) melalui beberapa sistem pematangan iaitu samada radikal, kationik atau hibrid. Walau bagaimanapun sistem kationik telah dipilih kerana wujudnya kumpulan epoksi dalam EPO yang boleh diutilisasikan secara terus untuk membentuk sambung-silang. Pematangan telah dilakukan dengan mesin UV keluaran IST berukuran 20 cm lebar, mempunyai kekuatan arus 7.5A dan konveyor berhalaju 4 m/min. Garam sulfonium dan ferosenium telah digunakan sebagai bahan fotopemula. Kajian formulasi dijalankan keatas gred EPO yang terpilih dengan bahan-bahan lain. Ini termasuklah kesan jenis dan kepekatan fotopemula, monomer, peratusan EPO dan juga kesan pos pematangan. Sifat filem termatang seperti kekerasan pendulum, peratusan kandungan gel dan kekuatan tegangan telah diperiksa. Didapati fotopemula triarilsulfonium heksafluorofosfat mempunyai keterlarutan yang rendah dalam EPO. Penambahan vinil eter monomer dalam formulasi juga didapati tidak dapat meningkatkan kekerasan pendulum dan juga kandungan gel filem termatang. Pos pematangan juga tidak memberi kesan keatas filem termatang.



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INTRODUCTION

In recent years, there are growing trends in using vegetable oil as a raw materials in resin production. It is generally accepted that products derived from natural oils and fats are more readily biodegradable than the corresponding products made from petroleum and hence their impact on the environment is less. Development of new products from palm oil derivatives such as epoxidised palm oil (EPO) is of particular interest to this country (Salmiah et al. 1987). EPO has been shown to have a number of commercially realistic end uses such as additives in the plastic industry, as an effective starting material to make polyol and pre-polymer in surface coating formulation.

Acrylated palm oil has been employed as the prepolymer in the free radical by Mohd. Hilmi et al. 1991 and the results are encouraging. This however requires an additional acrylation step before it can be cured in coating formulations. The current focus of the present work was to evaluate EPO as a partial substitute of cycloaliphatic diepoxide in the cationically curable system. The conversion of double bonds present in EPO to epoxy groups makes them amenable to cationic photopolymerization. Cationic photopolymerization of epoxy system has emerged as an attractive method for many thin films application such as coating, inks and adhesive. Oxygen inhibition, that is prevalent involving from radical photoinitiator, is not a problem in this system. This paper reports the investigation of various effects on UV curable system formulation from cycloaliphatic diepoxide and EPO.

EXPERIMENTAL

Materials

Epoxidised palm oil (EPO) was provided from Malaysian Palm Oil Board (MPOB). Cycloaliphatic diepoxide (ECC) and the cationic photoinitiator ; Triarilsulphonium hexafluorophosphate (UVI 6990) and triarilsulphonium hexafluoroantimonate (UVI 6974) were all supplied by the Union Carbide Company. Surfactant : Polyalkylene oxide modified dimethylpolysiloxane (Silwet L-7604) and ferrocenium salt (Irgacure 261) were obtained from Ciba-Geigy, Switzerland. 1,4 cyclohexane dimethanol divinyl ether (CHVE) and triethylene glycol divinyl ether (DVE-3) from GAF were used as monomers.

Methods

The mixtures were prepared at least one day before curing. They were then applied on to glass plates using a hand bar coater (RDS 30, Japan), and cured using a 20 cm wide IST UV machine under the conditions of 7.5 A current and 4 m/min conveyor speed. After the irradiation, the sample was post-cured in an oven. The number of passes to cure these films were determined by checking the tackiness of the surface of the irradiated films. The hardness of the cured film was measured on a pendulum hardness tester (Labotron, Byk) in accordance with DIN 53157. The measurements of gel percentage were taken by extracting the cured films in a Soxhlet extractor for 16 hours using acetone as the solvent. The extracted samples were then air dried for 30 minutes before drying in a vacuum oven to constant weight. The difference in weights of the cured film before and after the extraction determines the gel content. The physical properties were measured using a Strograph - R1 tester (Toyoseiki).

RESULTS AND DISCUSSION

Effect of photoinitiators

For this study, a number of formulations were prepared using sulphonium salts and a ferrocenium salt. A three percent photoinitiator was used in all formulations. Table 1 shows the range of composition of the cycloaliphatic diepoxide-EPO, in which the photoinitiator is soluble. 3% of triarylsulphonium hexafluorophosphate (UVI 6990) is not soluble in 30% of EPO, while cumene hexafluoroantimonate iron II cyclopentadienyle (Irgacure 261) dissolves easily. This is because the photoinitiator, being ionic in nature, has a very low solubility in the relatively non-polar monomers such as EPO. For this reason, the initial attempts to polymerize epoxidised oils using such photoinitiators resulted in failure.

Table 1 : Effect of the various photoinitiators

Formulations/ chemicals	25/261	26/261	25/6974	26/6974	25/6990	26/6990
EPO	20	30	20	30	20	30
ECC	76.5	66.5	76.5	66.5	76.5	66.5
L-7604	0.5	0.5	0.5	0.5	0.5	0.5
PI : Irga 261	3	3	-	-	-	-
UVI 6974	-	-	3	3	-	-
UVI 6990	-	-	-	-	3	3
Solubility	soluble	soluble	Soluble	soluble	soluble	not soluble
No.of passes to cure (4m/min)	6	10	3	4	3	-
% Pendulum hardness	65	9	61	10	41	-
% Gel fraction	85	72	87	83	88	-

Table 1 also shows the percentages of pendulum hardness and gel fraction of the mixtures after irradiating at different number of passes. Among the photoinitiators used, Cyracure UVI 6974 with SbF_6^- as the counter ion, is the most reactive compared to Cyracure UVI 6990 or Irgacure 261 (both with PF_6^- as the counter ion). The cure speed of epoxidised oils is dependant on the nature of the counter ion present in the photoinitiator. The cure speed is maximum with SbF_6^- as the counter ion. This is due to it nucleophilic being less than the other anions and hence, causes fewer termination reactions during polymerization (Abadie et al. 1995). The no. of passes required for curing is found to be less for mixtures containing the photoinitiator Cyracure UVI 6974 (25/6974 and 26/6974) compared with those containing Cyracure UVI 6990 or Irgacure 261. The gel fraction analysis showed that under the given irradiation condition (no. of passes to cure) the mixture containing 20% EPO was sufficiently crosslinked up to the order of 84 - 88%.

Effects of the photoinitiator concentration and post-curing

Fig. 1 illustrates the hardness values being almost constant as the photoinitiator is increased to 2.0%, after which the hardness began to increase. The optimum UV cure rate of the mixture is obtained at a 2.0 - 2.5% weight percent of photoinitiator for formulations with sulphonium hexafluoroantimonate (UVI 6974), 2.5 - 3.0% with ferrocenium salt (Irgacure 261) and 1.5 - 2.0 w% with sulphonium hexafluoro phosphate (UVI 6990). These results could be attributed to the plasticization - antiplasticization effect of the initiator fragments with the coating. Udagawa et al. 1992 and Udagawa et al. 1991 have reported that dynamic properties and molecular motions of cycloaliphatic epoxy resins cured by UV- induced sulphonium salt initiator depending on the concentration of the initiator. Fig. 2 shows the tensile properties of 30% EPO against the concentration of photoinitiator UVI 6974. The tensile strength and elongation at break values are almost constant as the photoinitiator increases up to 2.0%, when it began to decrease. Decreasing the photoinitiator concentration will reduce the crosslinking density and hence give a more loose structure.

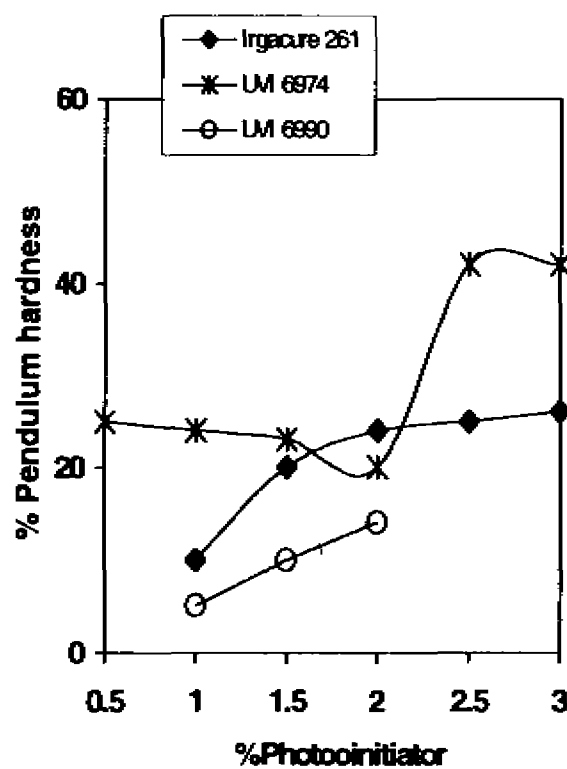


Fig. 1 : Effect of photoinitiator concentration on pendulum hardness, formulation : 30% EPO, 66-69% ECC

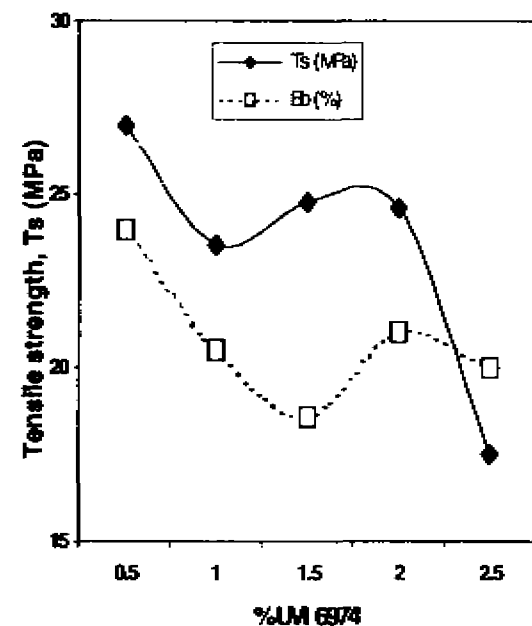


Fig. 2 : Effect of photoinitiator concentration on tensile strength & elongation at break, formulation : 30%EPO, 66-69%ECC, 0.5 - 2.5% UVI 6974

Figures 3 and 4 show that the post-cure temperatures have no significant effect on the hardness and gel fraction. This is an interesting observation and could be due to the complete crosslinking in the former and these films possess good thermal stability.

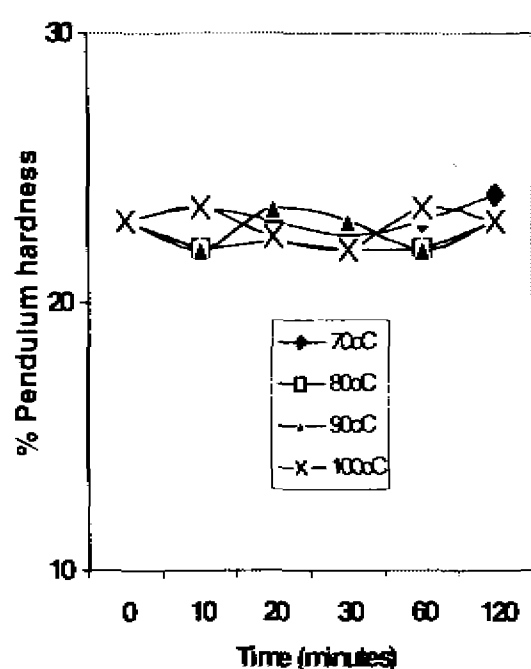


Fig. 3 : Effect of post cure on %pendulum hardness, formulation: 30%EPO, 2%UM 6974

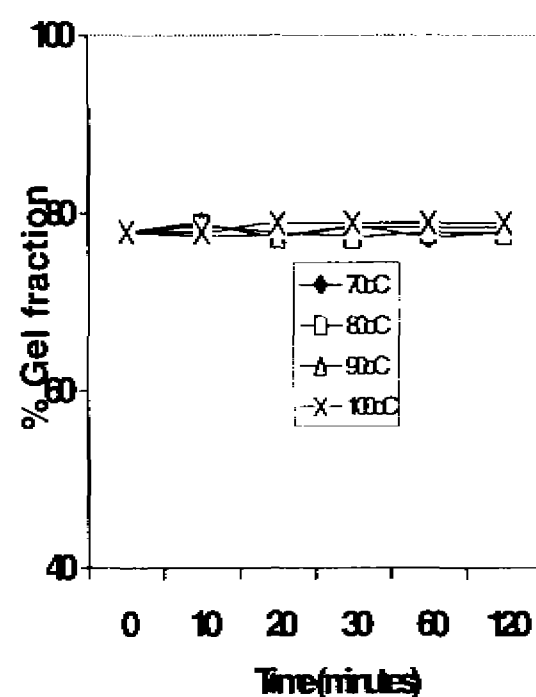


Fig4: Effect of post cure on %gel fraction formulation 30%EPO, 2%UM 6974

The influence of EPO content

The tack-free cure rate and mechanical properties of the cured films are dependent on the epoxy content in the formulation. In general, formulations with a higher epoxy content yield hard, crosslinked polymer films having shorter cure time. This is also indicated by a higher hardness value and gel fraction. Figures 5 shows that the value of hardness and gel fraction decrease as the EPO content increases. Cationic UV polymerization is initiated by photolysis of arylsulfonium salt which produces a strong acid after exposure to UV light. The acid generated polymerizes the oxirane ring of epoxides via ring opening and will also initiate the polymerization of vinyl ethers and the copolymerization of alcohols in combination with epoxides. Low values of oxirane oxygen in the EPO will decrease the hardness and gel fraction of the cured films.

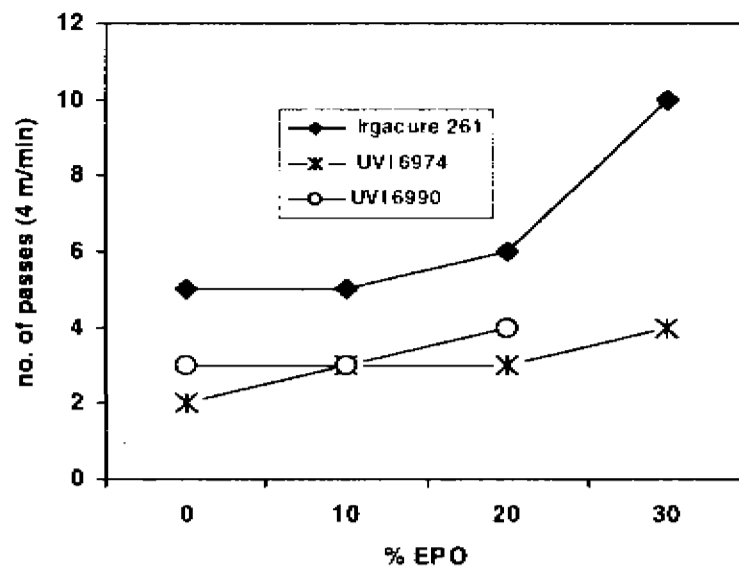


Fig.5 : Effect of EPO content on the curing speed

Effects of the vinyl ether monomers

Figure 6 shows that the hardness values and % gel fraction decrease with the addition of the monomer. The addition of vinyl ether monomers such as CHVE and DVE-3 did not enhance the crosslinking density or curing rate of the films.

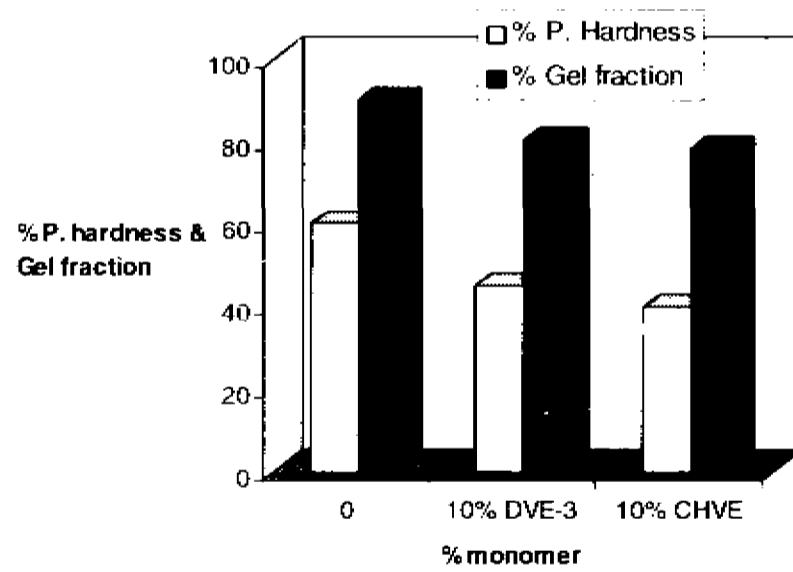


Fig.6 : Effect of monomers content on hardness and gel fraction, formulation: 20% EPO, 2.5% UVI 6974

CONCLUSION

This study showed that a combination of the epoxidised palm oil and cationic photoinitiator, such as sulphonium and ferrocenium salts, can be polymerized using UV light. The photopolymerized films possess good thermal stability and tensile strength.

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