

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



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ABSTRACT

Vision 2020 calls for more efforts towards industrialisation of research findings in Malaysia. One of the strategies is to explore more downstream activities from many natural resources through research and development. In recent years, there are growing trends in using vegetable oil as raw materials in resin production. Development of new products from palm oil derivatives such as epoxidised palm oil (EPO) is of particular interest to this country. The compatibility of EPO with cycloaliphatic diepoxide allows the development of a wide range of radiation curable formulations by cationic photoinitiators. Curing was done by means of a 20 cm wide IST UV machine with the conditions of 7.5A current and 4 m/min conveyor speed. Sulphonium and ferrocenium salts were used as the cationic photoinitiators. A study was formulated to compromise the investigation of various effects on the cured film properties. These effects include ; types and concentration of photoinitiators, formulating ratios, reactive diluents, photosensitizers and postcuring conditions. The effects on the gel fraction, pendulum hardness, tensile strength and elongation at break were investigated. The results showed that 30% of EPO was the maximum value that can be used in the formulation. It was also found that triarylsulphonium hexafluorophosphate has a very low solubility in EPO.

INTRODUCTION

In recent years, it has become increasingly important to use materials and processes that are environmentally compatible. The materials should ideally originate from renewable sources, are inexpensive and less accumulation problems in the environment. Currently, the synthetic material industry relies mainly on petrochemicals as the energy source has decreased remarkably due to limited petroleum reserves. In view of high value-added properties, the petrochemical industry will still remain the major supply as compared to natural sources such

as vegetable oils. However, because of huge potential demand for synthetic materials, the search for new sources as replacement for petroleum is inevitable.

Currently, the trend in using vegetable oils as raw materials in resin production is growing. One of the viable sources is oils and fats. Basic oleochemicals are produced by hydrolysis or methylation of triglycerides in tallow and vegetable oils. Oleochemicals are chemicals derived from natural raw materials in contrast to petrochemicals which are chemicals derived from petroleum. The important basic oleochemicals are fatty acids, fatty esters, fatty alcohols and fatty amines with glycerol being an important by-product. The use of these oleochemicals and their derivatives are consumer-oriented, the important ones being in natural fat-based surfactant, cosmetic and toiletries products, pharmaceuticals and other industrial applications.

In contrast to the large spread of oil crops in other producing regions, sources of oils and fats in the ASEAN region are exclusively confined to just two bearing crops - the oil palm (*elaeis guineensis*) and coconut (*cocos nucifera*). Oil palm produces two types of oil ; palm oil and palm kernel oil. Coconut produces coconut oil which has similar characteristics to palm kernel oil. Palm oil is not a fully saturated oil ; it contains equal amounts of saturated fatty acids and unsaturated fatty acids and should be best described as being partially saturated. The more unsaturated the oil, the faster it will react with oxygen and polymerise.

Table 1 : Types of Oils and Fats of Oil Palm and Coconut

Oil Palm		Coconut
Palm oil	Palm kernel oil	Coconut oil
<u>Main FAs :</u> C16 : 0 = 44%	<u>Main FAs :</u> C12 : 0 = 48%	<u>Main FAs :</u> C10 : 0 = 7%
C18 : 1 = 39%	C14 : 0 = 16%	C12 : 0 = 48%
C18 : 2 = 10%	C18 : 1 = 15%	C14 : 1 = 18%

Palm oil and palm kernel oil are ideal raw materials for the production of a wide range of C12 - C18 fatty acid oleochemical products. As result, the region has witnessed the phenomenal growth of oleochemical production as well. Malaysia is the world's leading exporter of palm oil and palm kernel oil, exporting 7.72 and 0.46 million tonnes respectively in 1997 (Yusof et al. 1998). The production of palm oil in Malaysia is expected to increase continuously and the main outlet is for food application.

Epoxidation of palm oil products has been reported to yield materials namely epoxidised palm oil products, EPOP, suitable as a plasticizer and a stabiliser for plastic (Salmiah et al.1987). Another application of EPOP such as polyols are one of the main raw materials used in the manufacture of polyurethane and are mainly derived from petrochemicals. The development

of new radiation curable materials for the application in radiation curing technology is an important research area. Acrylated palm oil has been employed as the oligomer in the free radical system 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 epoxidised RBD palm oil (EPO) as a partial substitute of cycloaliphatic diepoxide in the cationically curable system. The degree of unsaturation in EPO is half or less than that contain in epoxidised soybean oil (ESBO). The conversion of double bonds present in EPO to epoxy groups makes them amenable to cationic photopolymerization.

Cationic photopolymerization of epoxy systems has emerged as an attractive method for many thin film applications such as coatings, inks and adhesives. Oxygen inhibition, that is prevalent in processes involving free radical photoinitiators, is not a problem in these systems. The cured films display good adhesion to a number of substrates. However, the system performance and cost have severely limited the widespread acceptance of this technology. This paper reports the investigation of various effect on UV curable system formulated from cycloaliphatic diepoxide and EPO.

EXPERIMENTAL

1. Materials : Epoxidised RBD palm olein (EPO) was provided free from the Palm Oil Research Institute of Malaysia, PORIM. Cycloaliphatic diepoxide (ECC) and the cationic photoinitiators : Triarylsulphonium hexafluorophosphate (UVI 6990) and triarylsulphonium 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. Vinyl ethers : DVE-3 and CHVE from GAF were used as monomers.

2. 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

1. 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 2 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 2 : 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 2 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%.

2. Effects of the photoinitiator concentration and post-curing

Figures 1 and 2 illustrate 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), 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. 3 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.

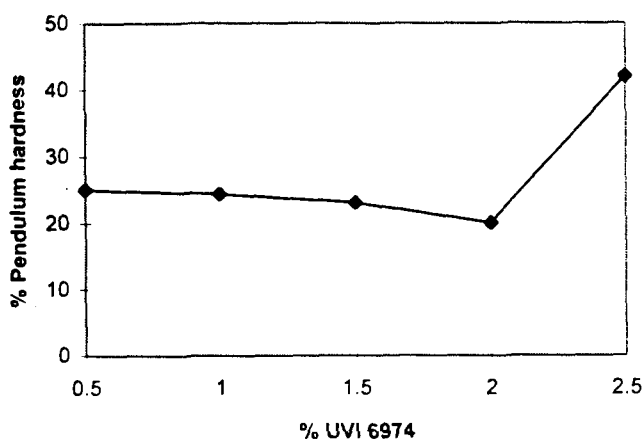


Fig. 1 : Effect of photoinitiator concentration (UVI 6974) on pendulum hardness, formulation: 30% EPO, 66-69% ECC, 0.5-2.5% UVI 6974

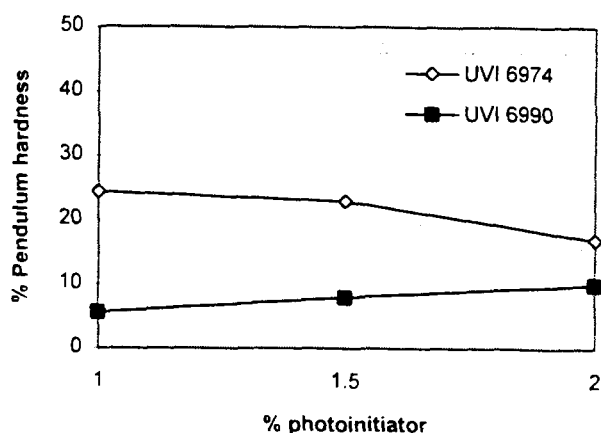


Fig. 2: Effect of photoinitiator concentration on pendulum hardness, formulation: 30% EPO, 66-69% ECC, 1-2% UVI 6974/6990

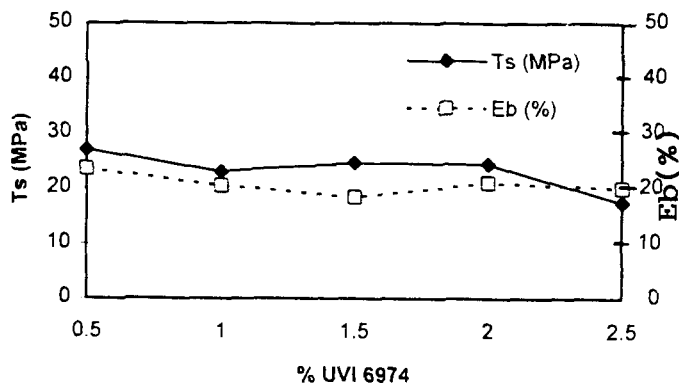


Fig. 3 : Effect of photoinitiator concentration (UVI 6974) on tensile strength & elongation at break, formulation: 30% EPO, 66-69% ECC, 0.5-2.5% UVI 6974

Figures 4 and 5 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.

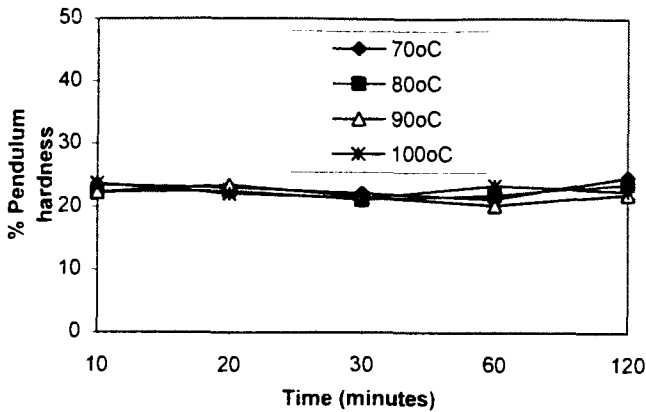


Fig. 4 : Effect of post cure on % pendulum hardness, formulation: 30% EPO, 67.5% ECC, 1.5% UVI 6974

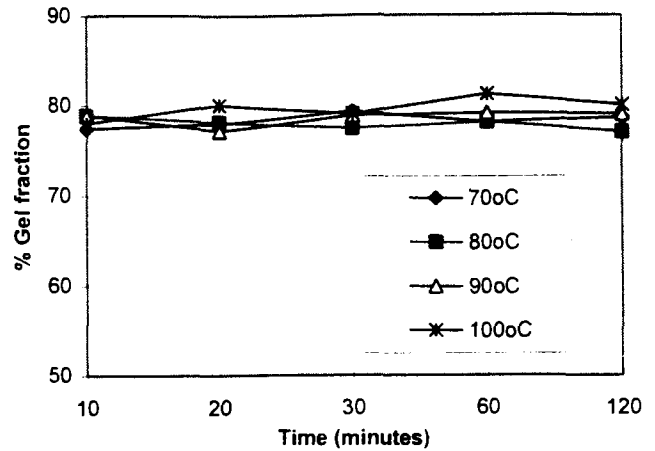


Fig. 5: Effect of post cure on % gel fraction, formulation: 30% EPO, 67.5% ECC, 1.5% UVI 6974

3. 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 6 and 7 show 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.

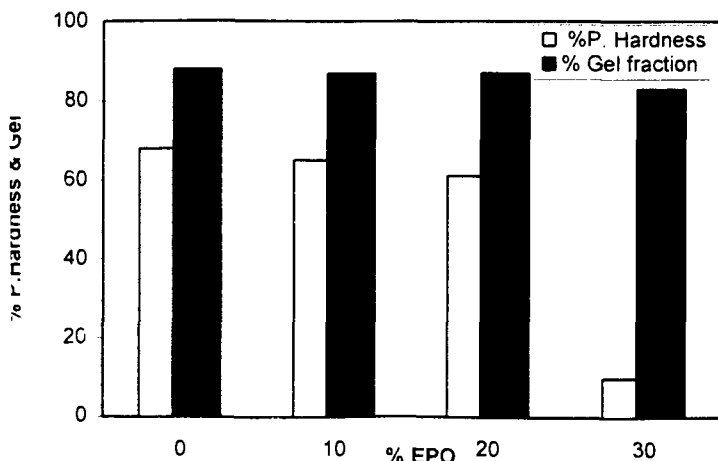


Fig. 6: Effect of EPO content on % pendulum hardness and % gel fraction, formulation: 0-30% EPO, 66-97% ECC, 3% UVI 6974

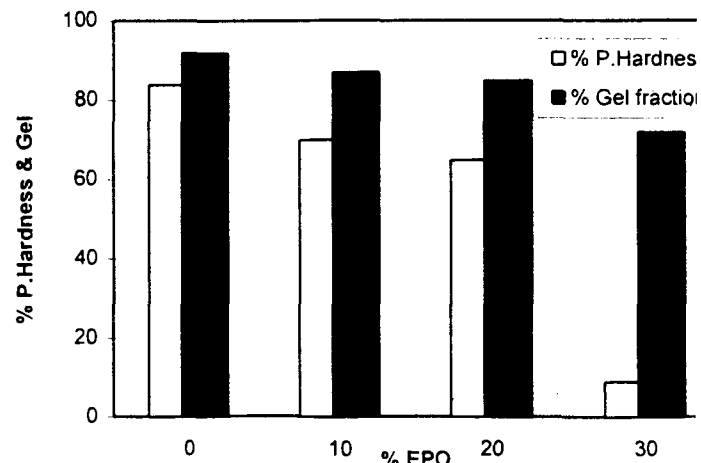


Fig. 7: Effect of EPO content on % pendulum hardness and % gel fraction, formulation: 0-30% EPO, 66-97% ECC, 3% Irgacure 261

4. Effects of the vinyl ether monomers

Figure 8 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.

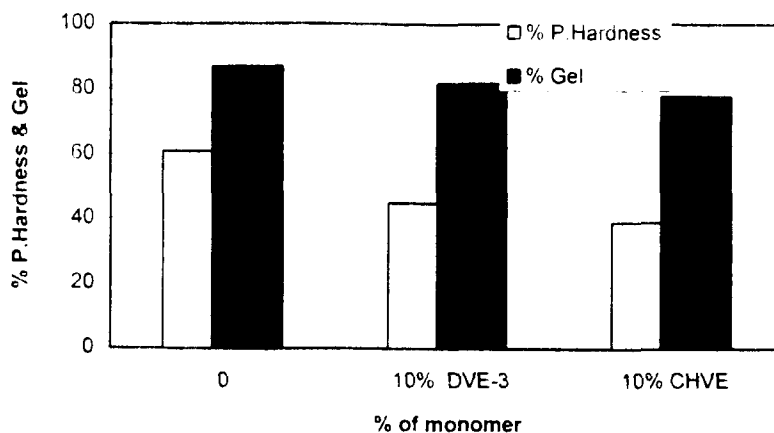


Fig. 8: Effect of monomers content on hardness and gel fraction, formulation: 20% EPO, 66-76% ECC, 3% UVI 6974

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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