THE USE OF EPOXIDIZED PALM OIL PRODUCTS FOR THE SYNTHESIS OF RADIATION CURABLE RESINS: SEVERAL FACTORS AFFECTING THE SYNTHESIS OF EPOXIDIZED RBD PALM OLEIN ACRYLATE (EPOLA)

Keywords: Synthesis; Epoxidized RBD Palm Olein Acrylate (EPOLA); Epoxidized RBD Palm Olein (EPOL); Acrylic Acid; Gelation; Inhibitor

HUSSIN MOHD NOR *; MOHD HILMI MAHMOOD **; HAMIRIN KIFLI * and MASNI ABDUL RAHMAN *****

* Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia

** Nuclear Energy Unit, Kompleks PUSPATI, Bangi

*** Palm Oil Research Institute of Malaysia

Original manuscript received on August 1991

Several factors such as inhibitor, cooking temperature and catalyst, which affect the preparation of epoxidized RBD palm olein acrylate (EPOLA) have been investigated. Inhibitor and high cooking temperature were respectively found to prevent gelation and shorten the cooking time, while the presence of catalyst was found to accelerate the acrylation reaction.

INTRODUCTION

Radiation curable acrylates can be derived from epoxidized oils by reacting them with acrylic acid (Pappas and Gruber, 1980; Ackerman, 1972; Hashimoto and Saraiya, 1981; Hussin Mohd Nor *et al.*, 1990). Recently we have shown that the molecules of epoxidized palm olein acrylate (EPOLA) contain unsaturated vinyl groups which readily undergo polymerization in the presence of photoinitiator upon exposure to ultraviolet radiation (Hussin Mohd Nor *et al.*, 1990). The main problem encountered in the preparation of EPOLA is gelation, so it is very important to take the necessary steps to prevent this. This article reports a study of the preparation of EPOLA in which the effects of a gelation inhibitor (4-methoxy-phenol), of cooking temperature, and of a catalyst (triethylamine) were investigated.

EXPERIMENTAL PROCEDURES

Materials and Apparatus

Epoxidized RBD palm olein (EPOL) with about 3% per mole oxirane oxygen was prepared (Salmiah *et al.*, 1987). All chemicals employed in this work were of analytical grade.

A reactor consisting of a five-necked flask fitted with stirrer, thermometer, reflux condenser and dropping funnel was used.

It was essential for the apparatus to be very clean, dry, and free of residue peroxide (Holmann and Curing, 1984).

Methods of Synthesis

The basic method of synthesis was described in Hussin Mohd Nor *et al.* (1990). The synthesis in a nitrogen atmosphere was carried out at 115° C using 0.146 mole EPOL and 0.234 mole acrylic acid in the presence of 0.25% triethylamine (TEA) and four different percentages of 4-methoxyphenol, *i.e.* 0.13%, 0.25%, 0.53% and 1.47 per cent. The addition of acrylic acid can be done either at room temperature (28° C) or higher temperature (130° C). The synthesis in air was carried out at three different temperatures, *i.e.* 80° C, 115° C, 130° C in the presence of 0.25% 4-methoxyphenol and 0.0% to 1.0% TEA.

Analysis of Samples

Oxirane oxygen content was determined using the AOCS tentative method Cd 9-57, 1963. The measurement of iodine value was carried out using the AOCS official method Cd 1-25. Acid value was determined as described in Hussin Mohd Nor *et al.* (1990).

Viscosity Measurement

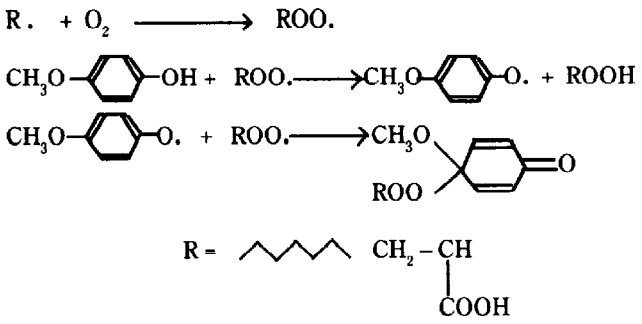
A Wells-Brookfield Cone/Plate Viscometer, model LVTCP was used to measure viscosity at 25° C.

RESULTS AND DISCUSSION

Effect of Inhibitor

Inhibitors play an important role in preventing gelation throughout the synthesis of EPOLA. Gelation is a common phenomenon during the synthesis as a result of self-polymerization of reactant(s) containing more than two functional groups per molecule (Billmeyer, 1984; Rodriguez, 1982). Normally, the amount of inhibitor(s) used in an acrylation reaction is in the range of 100 ppm to 1.0% (Holmann and Curing, 1984). In this synthesis, the products contain a mixture of EPOLA molecules which may have one to three unsaturated vinyl groups per molecule (Hussin Mohd Nor *et al.*, 1990). These groups easily undergo radical addition polymerization (Holmann and Curing, 1984) to yield a gel or network during synthesis. Another hindering factor in the synthesis of EPOLA is the formation of polyacrylic acid: acrylic acid is a very reactive monomer and readily undergoes self-polymerization even at room temperature. However, failure in this synthesis is usually due to gelation rather than to polymerization of acrylic acid. To prevent the occurrence of such polymerizations, a sufficient amount of inhibitor(s) must be added to the reactants; 4-methoxyphenol is one of the inhibitors normally used.

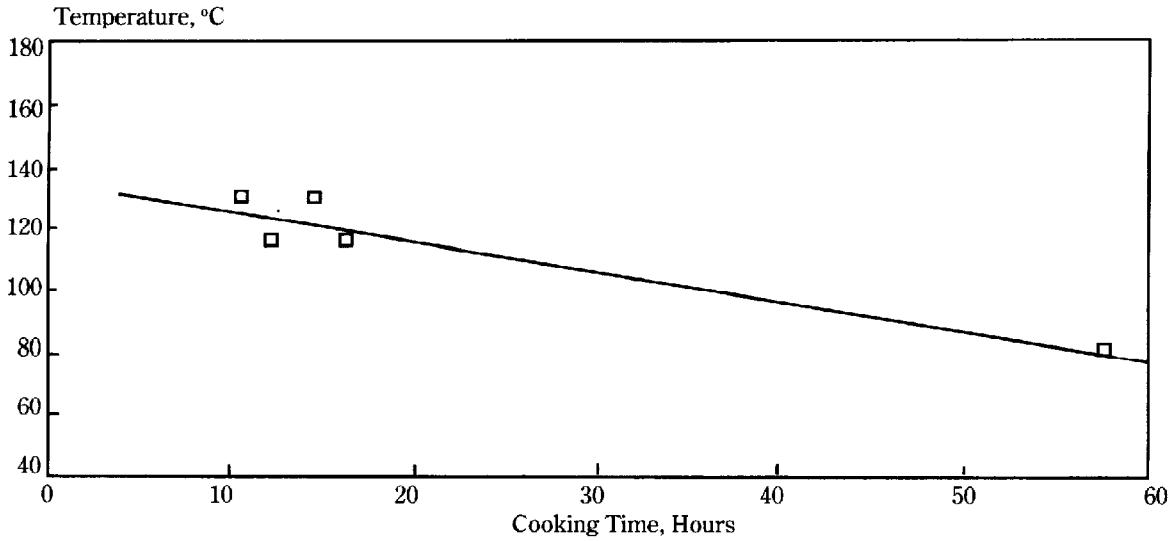
When the synthesis of EPOLA in a nitrogen environment was done using four different percentages of 4-methoxyphenol (0.13%, 0.25%, 0.53% and 1.47%), it was found that gelation occurred easily in all cases except with 1.47% 4-methoxyphenol, whereas the synthesis of EPOLA in air using 0.25% 4-methoxyphenol gave no gelation problem. The apparent differences in inhibiting power of 4-methoxyphenol in the two different conditions are actually due to oxygen inhibition when the synthesis is done in air. Oxygen and 4-methoxyphenol together give a synergistic inhibition of polymerizations of EPOLA molecules and acrylic acid. The following mechanism is proposed:



When synthesizing in nitrogen, oxygen was flashed off the system, and in its absence a larger amount of 4-methoxy-phenol was needed (*i.e.* 1.47%) to prevent gelation and polymerization of acrylic acid.

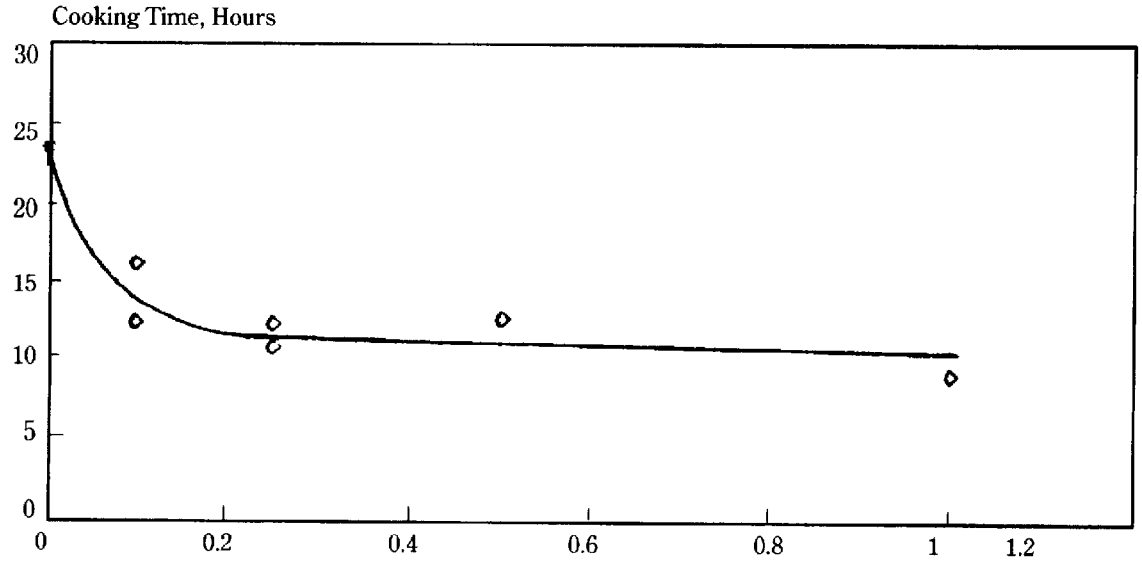
Effect of Cooking Temperature

Temperature is also an important factor in the synthesis. The trend of the relationship between cooking temperature and cooking time in the preparation of EPOLA is shown in *Figure 1*. According to



(TEA= 0.1%, in air)

Figure 1. Effect of Temperature on Cooking Time.



(T= 115 °C, in air)

Figure 2. Effect of TEA on Cooking Time.

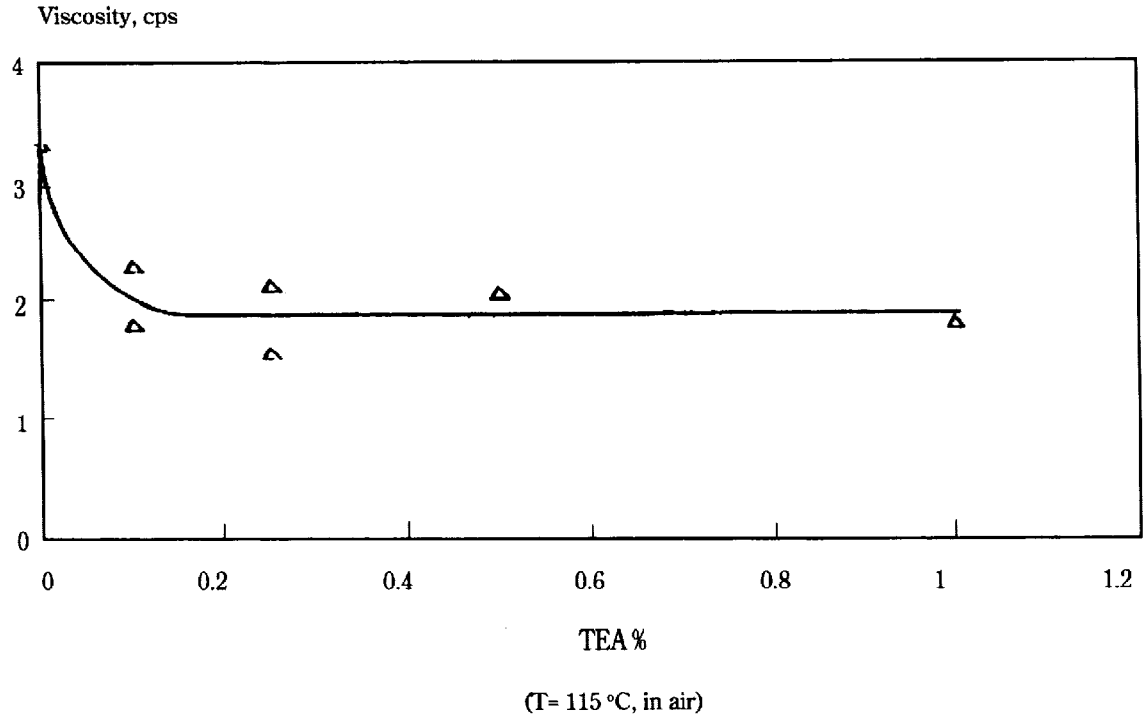


Figure 3. Effect of TEA on Viscosity.

the trend, the cooking time can be shortened by increasing the cooking temperature. However, synthesis at high temperature may result in the formation of gel and/or polyacrylic acid. It is recommended that the cooking temperature for the synthesis of EPOLA should not exceed 130° C; higher temperatures may cause the synthesis to fail. It should be noted here that the reaction of EPOL and acrylic acid is exothermic, and may cause a sudden increase in the cooking temperature of up to about ten degrees Celcius. The cooking temperature must not exceed 139° C, the boiling point of acrylic acid, at which formation of polyacrylic acid can easily occur. On the other hand, a cooking temperature below 100° C will result in an unnecessarily long cooking time, which may also contribute to gelation of EPOLA and/or polymerization of acrylic acid.

Effect of Catalyst

The catalyst is another factor affecting the synthesis of EPOLA. *Figures 2* and *3* exhibit the effects of TEA on the cooking time and EPOLA viscosity respectively. It can be seen from these *Figures* that as the amount of TEA increases up to 0.2%, both the cooking time and the viscosity of EPOLA are markedly reduced. Raising the concentration of TEA from 0.2% to 1.0%, does not have much further effect. According to the results, the use of 0.25% TEA is sufficient to obtain minimum cooking time and less viscous EPOLA (≈ 1700 cps). The use of TEA concentrations lower than 0.1% will extend the cooking time. One can use a higher percentage of TEA (>0.25%) in order to shorten the cooking time, but it will produce a darker yellow EPOLA. The results also suggest that a longer cooking time will yield more viscous EPOLA.

CONCLUSION

It is vitally important for the successful synthesis of EPOLA to use a sufficient amount of gelation inhibitor(s), *e.g.* 4-methoxy-phenol. Either catalyst concentration or cooking temperature can be varied to shorten or prolong the cooking time, with the formation of EPOLA having viscosities ranging from 1500cps to 3500cps. It has been found that, the

desirable working range of temperature is from 115°C to 130°C, and the concentration of TEA is from 0.1% to 0.5 per cent. The EPOLA obtained in this study had the properties listed below:

Properties	EPOLA	EPOL
Iodine value,	20.0 ± 3.0	<1.0
Oxirane oxygen content, % mole	<0.5	≈3.0
Acid value, mg KOH/g Resin	12.0 ± 3.0	<3.0
Viscosity, cps	1500 - 3500	240

ACKNOWLEDGEMENTS

The authors would like to thank the radiation curing group of the Nuclear Energy Unit of PUSPATI for their co-operation. They also wish to thank the Director-General of the Nuclear Energy Unit and the Director-General of PORIM for all their support and great interest in this project. In addition, the authors would like to thank Mr Azman Rafie for preparing epoxidized RBD palm oil samples.

REFERENCES

ACKERMAN, J F; WEINSFEID, J; SAVAGEAU, R G and BERLI, G (1972). U.S. Patent 3, 673,140.

BILLMEYER, F W Jr (1984). *Textbook of Polymer Science,* Third Edition, Interscience Publishers, New York, N.Y., pp. 40-41.

HASHIMOTO, K and SARAIYA, S (1981). *J. Radiat. Curing, pp. 4,6,8-11,15.*

HOLMANN, R; YU, V and CURING, E B (1984). *Formulation for Printing Inks, Coatings and Paint, SITA-Technology, London,* pp. 21-28.

HUSSIN MOHD NOR; MOHD HILMI MAHMOOD; HAMIRIN KIFLI; MASNI ABDUL RAHMAN and RAFIE (1990). *Nuclear Science Journal of Malaysia, 8,* 149-155.

PAPPAS, S P and GRUBER, G W (1980). *UV Curing: Science and Technology, Vol. 1, Technology Marketing Corporation U S A,* pp. 165-167.

RODRIGUEZ, R (1982). *Principles of Polymer Systems,* Second Edition, Hemisphere Publishing Corporation, New York, N.Y., p. 81.

SALMIAH AHMAD; AZMAN RAFIE and ZAHARIAH ISMAIL (1987). *PORIM Report PO (125a).*