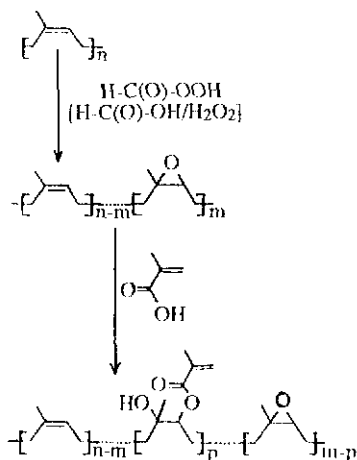


## Fixation of Methacrylic Acid onto Epoxidised Liquid Natural Rubber

D. DEROUET\*, J.C. BROSSE\* AND L.M.K. TILLEKERATNE\*\*

*Epoxidised liquid natural rubber (ELNR) is a derivative of natural rubber obtained by depolymerisation of natural rubber macromolecules in the latex phase using the phenylhydrazine/oxygen system followed by peracid treatment. It is a basic compound which can be subjected to chemical modifications leading to new products with various useful applications. Methacrylic acid grafted ELNR is one such product where the polymerisable unsaturated groups present on the methacrylic acid enable them to be crosslinked by UV radiation, making them useful in the enamel paint industry. This paper reports on the effects of some parameters such as the catalyst, temperature and time, on the fixation reaction between ELNR via the epoxide functions, and methacrylic acid. Addition of the acid on the epoxide functions of ELNR in the presence of *p*-methoxyphenol to avoid homopolymerisation of the acid can be achieved in chloroform, only in the presence of pyridine as the catalyst. Soluble photo-sensitive polymers in organic solvents are obtained.*

Epoxidised liquid natural rubber (ELNR) is a derivative of natural rubber obtained by depolymerisation in the latex phase by a chemical method using the phenylhydrazine/oxygen system followed by peracid treatment<sup>1,2</sup>. It is a basic compound which can be subjected to subsequent chemical modifications leading to new products with various useful applications. One such chemically modified form of ELNR is the methacrylic acid grafted ELNR:



It is well known that carboxylic acids can react on epoxide functions to form  $\beta$ -hydroxy esters. This reaction has been previously used to vulcanise epoxidised natural rubber (ENR) with organic acids<sup>3</sup>. The polymerisable unsaturated groups present on the methacrylic acid grafted ELNR enable them to be crosslinked by means of UV radiation, making them useful in the paint and varnish industry. UV spectroscopy has been used extensively in photo-sensitive polymers, notably by Azuma *et al.*<sup>4,5,6</sup> who have studied the photo-crosslinking of rubbers containing pendant cinnamate groups.

This paper reports on the effects of some parameters such as the catalyst, temperature and time on the fixation reaction between ELNR via epoxide functions, and methacrylic acid.

### EXPERIMENTAL

#### Methods

<sup>1</sup>H NMR spectra were recorded on a Varian EM 90 (90 M Hz) spectrometer. Tetramethylsilane (TMS) was used as a reference and

\* Laboratoire de Chimie et Physicochimie Macromoléculaire, Unité de Recherche Associée au C.N.R.S. No 509, Université du Maine, Route de Laval, BP 535, 72017 Le Mans, France

\*\* Rubber Research Institute of Sri Lanka, Telewala Road, Ratmalana, Sri Lanka

chemical shifts are given in parts per million. IR spectra were recorded on a Fourier transform Perkin-Elmer 1750 spectrometer. Titrations were achieved on a Mettler potentiometer (Impulsomat 614; Dosigraph 625; pH meter 632 and Dosimat 655).

## Materials

Solvents were purified by the usual methods. The 30% ELNR sample, supplied by the Institute of Applied Research on Polymers of Le Mans (IRAP), was purified by dissolving in *toluene* followed by filtration through a No. 3 sintered glass crucible under suction and precipitation in methanol. The purified sample was dried up in vacuum at 60°C, until constant weight was obtained. Analysis of the level of epoxidation of the ELNR sample was cross checked by <sup>1</sup>H NMR spectrometry.

Methacrylic acid (Janssen product; 98.5% of purity) was purified by distillation under reduced pressure, a few hours before use. The collected fractions from the distillation were analysed by <sup>1</sup>H NMR, to verify that they are free from polymerised contaminants, and stored under refrigeration until they are used.

p-Methoxyphenol used as the crosslinking inhibitor is a Aldrich product (purity = 99%). Tetramethylammonium methacrylate was prepared by neutralising a known weight of the distilled methacrylic acid with 0.45 N solution of tetramethylammonium hydroxide in methanol (Aldrich product). The end-point was detected by potentiometric titration. The salt thus obtained at pH 11.4–11.7 was isolated after removal of the solvent and dried in vacuum at 50°C. Its purity was determined by <sup>1</sup>H NMR spectroscopy.

Pyridine, potassium hydroxide and triphenylphosphine were pure commercial products.

## Preparation of Stock Solutions

A 3 M solution of methacrylic acid containing the catalyst (tetramethylammonium methacrylate, potassium hydroxide, triphenylphosphine or pyridine) in the molar ratio

[catalyst]/[methacrylic acid] = 0.1 was prepared in chloroform for the coupling reactions. Where tetramethylammonium methacrylate was used as the catalyst, the solution was prepared as follows: 6.46 g of methacrylic acid ( $7.5 \times 10^{-2}$  mol) freshly distilled was mixed with 20 ml of methanol and then treated with 0.45 M tetramethylammonium hydroxide solution to the neutral point. To the dry salt obtained after evaporation of the solvent, 64.6 g of methacrylic acid was added and the solution was made up to 250 ml with chloroform.

A second 3 M solution of oxirane functions was prepared by dissolving 72.8 g of 30% epoxidised ELNR in chloroform and the solution was made up to 100 ml.

## Procedure

5 ml of the ELNR solution and 5 ml of the acid stock solution containing one of the three catalysts in the molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1 mixed with  $1.5 \times 10^{-2}$  mol of the inhibitor (p-methoxyphenol) were heated to 100°C in a thermo-statically controlled oil bath and 2 ml samples of the mixture were pipetted out at different intervals of time ranging from 5 h to 10 h. Those samples were tested for residual acid content by means of potentiometric titration with 0.45 N solution of tetramethylammonium hydroxide in methanol.

When the residual acid concentration reached a steady value, the solution mixtures in the tubes were taken out, coagulated with excess of methanol and dried in vacuum at room temperature until constant weight was reached for NMR analysis.

## RESULTS AND DISCUSSION

Four types of bases were used as the catalyst to couple the oxirane of ELNR with methacrylic acid:

- Tetramethylammonium methacrylate, according to Soutif Procedure<sup>7</sup>
- Potassium hydroxide
- Pyridine
- Triphenylphosphine.

Most of the coupling reactions carried out in this study were done with the tetramethylammonium salt of the acid as the catalyst for the reaction according to earlier workers<sup>7</sup> who have shown that the best results of fixation of a carboxylic acid on an epoxide were obtained in the presence of this catalyst. According to them, all the experiments were carried out in chloroform, with the molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1.

To avoid homopolymerisation of the acid in these experiments, p-methoxyphenol was used as the inhibitor in the mixture. It was shown that the concentration of the inhibitor in the medium played a prominent part in the reaction: in all cases where p-methoxyphenol was used in concentrations less than  $1.5 \times 10^{-2}$  mol under the conditions used for the reaction and in the cases where it was not used, there was a thick precipitate formation. This precipitate which, after washing and drying, was insoluble in any solvent, was identified as the polymerised or crosslinked acid. However, the crosslinking reaction was completely suppressed when  $1.5 \times 10^{-2}$  mol or more of the p-methoxyphenol was introduced. It was also noticed that in the presence of the tetramethylammonium salt of methacrylic acid, the tendency of the acid to homopolymerisation was much higher than with the other catalysts.

When ELNR modification was carried out with tetramethylammonium methacrylate, it was observed that there was no change in the initial acid content in the mixture even after 72 h heating at 100°C. However, when there was no inhibitor in the system, a white precipitate of homopolymerised acid formed rapidly, lowering the residual acid content. Further, the <sup>1</sup>H NMR spectrum of the rubbery product recovered by methanol coagulation did not show any sign of acid fixation on the ELNR or even a drop in the epoxide content in the original ELNR used. Similar results were obtained in the presence of KOH as the catalyst because it had no catalytic effect.

When triphenylphosphine was used as the catalyst in the same molar ratio as above and in the presence of the inhibitor, it was

observed that the residual acid content decreased gradually and reached a steady level at 0.083 mol in about 73 h. The level of fixation calculated on the basis of the change in acid concentration at this point is 10.8% (Figure 1). However, in the <sup>1</sup>H NMR spectrum of the polymer recovered by methanol coagulation, there was no sign of methacrylic acid fixation on ELNR. But the signal due to the resonance of the hydrogen atom attached to the epoxide group disappeared after heating for 62 h.

In a pyridine-catalysed system in the presence of p-methoxyphenol, it was observed that the residual acid content decreased to 0.065 mol in about 75 h and according to that, the level of fixation at this point was 13.3% (Figure 2). Further, there was clear evidence on the <sup>1</sup>H NMR spectrum of ELNR recovered by methanol coagulation that there was methacrylic acid fixation on the ELNR. At  $\delta = 5.75$  and 6.3, there were resonance signals due to the two protons attached to the double bond. The resonance bond at  $\delta = 2.7$  in the <sup>1</sup>H NMR spectrum of pure ELNR due to the hydrogen on the epoxide ring disappeared after the reaction. At temperatures below 100°C, there was no evidence of any grafting taking place with any of the above catalysts. Even at temperatures above 100°C, such as 110°C and 120°C, there was no improvement in the grafting efficiency while there were problems to retain the solvent chloroform in the reaction mixture which is extremely volatile at such high temperatures. Hence, all the results reported in this paper were obtained at 100°C, which was found to be the most suitable temperature for this reaction.

## CONCLUSION

Synthesis of photo-sensitive polymers by grafting methacrylic acid onto ELNR can be achieved only in the presence of pyridine as the catalyst. Interesting yields of addition of the acid on the epoxide functions in chloroform medium were obtained at 100°C with the initial molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1 after 72 h of reaction. Though the percentage of grafting achieved by this method was low, the presence of a few unsaturated

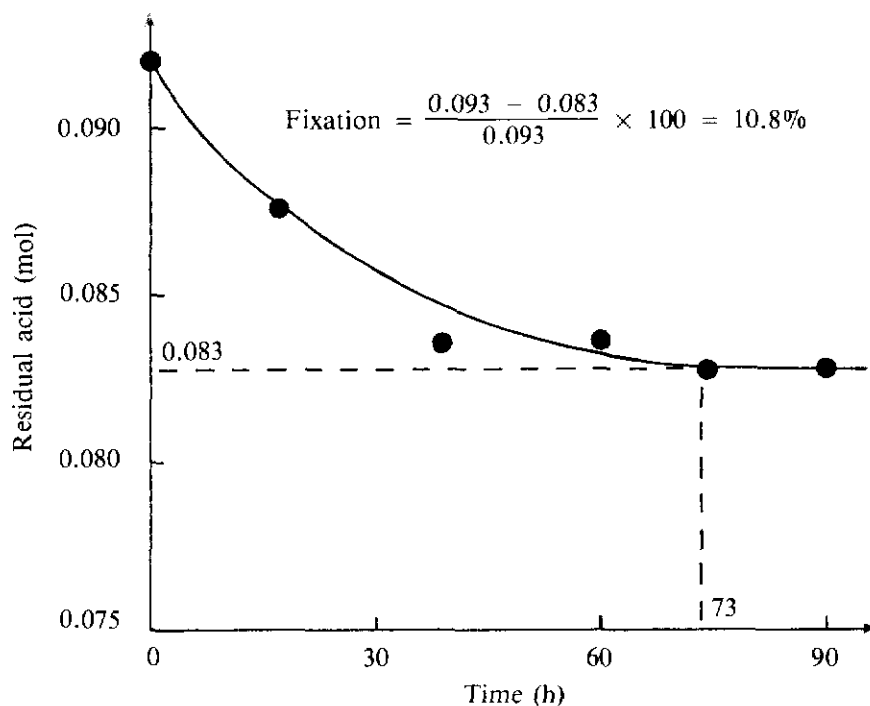


Figure 1. Change in acid molarity during the ELNR/methacrylic acid reaction catalysed by triphenylphosphine at 100°C.

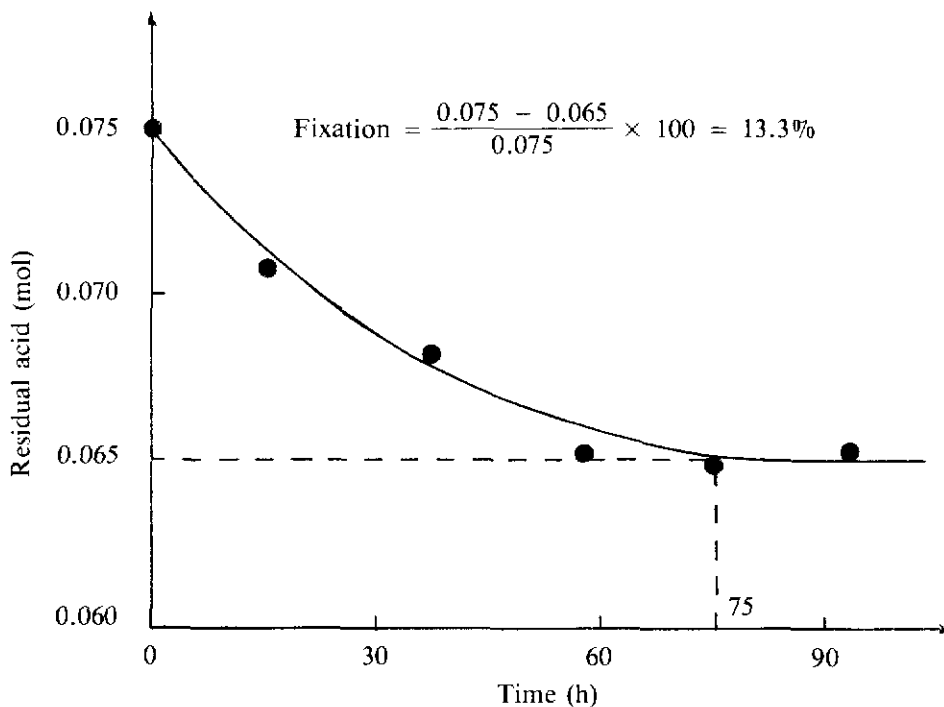


Figure 2. Change in acid molarity during the ELNR/methacrylic acid reaction catalysed by pyridine at 100°C.

groups on the grafted monomer was sufficient to enable them to be photo-crosslinkable by means of UV radiation. Hence, the product obtained is expected to be a useful industrial material in the future.

#### ACKNOWLEDGEMENT

The authors thank the United Nations for Industrial Development Organisation (UNIDO) for financial support. They wish to express their gratitude to Mr De Livonnière of the Rubber Research Institute of Paris (IRCA) for the co-ordination of the work and Mr Boccaccio of the Institute of Applied Research on Polymers of Le Mans for providing the ELNR sample for the present investigation.

*Date of receipt: January 1990*

*Date of acceptance: June 1990*

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