IMPROVEMENT OF PLASTICITY RETENTION INDEX OF EPOXIDISED NATURAL RUBBER

Benny George and N.M. Mathew

Rubber Research Institute of India,
Kottayam-686009

ABSTRACT

Latex stage epoxidation of natural rubber (NR) by performic acid, formed *in situ* by the reaction between formic acid and hydrogen peroxide, produces epoxidised natural rubber (ENR) with negligible ring opened products, when performed under controlled conditions. However, the naturally occurring antioxidants are destroyed during the reaction or are physically removed during washing and the subsequent processing of ENR. This leads to very low plasticity retntion index (PRI) values, the improvement of which requires addition of antioxidants. The effect of addition of different phenolic and amine type antioxidants at different concentrations are investigated. The antioxidants used include 2,6-di-t--butyl-p-cresol, styrenated phenol, polymerised 1,2-dihydro-2,2,4-trimethyl-quinoline, N-phenyl-N'-isopropyl-p-phenylenediamine, 2-mercaptobenzimidazole and zinc salt of 2-mercaptobenzimidazole. It was observed that 0.25 phr each of 2,6-di-t-butyl-p-cresol and polymerised 1,2-dihydro 2,2,4-trimethylquinoline and 0.5 phr of styrenated phenol impart PRI values within the accepted range.

Success through technology: Proceedings of the National Rubber Conference, 14-15 November 1994. (Eds. D. Joseph Francis and P.K. Mohamed). Allied Publishers, New Delhi, pp. 313-

INTRODUCTION

Epoxidation of natural rubber and other unsaturated elastomers by peracids has been well studied (Colclough, 1963; Udupi, 1979; Ng and Gaw, 1981; Gelling, 1985). Desired levels of epoxidation could be achieved by epoxidising NR latex by performic acid formed in situ (George et al, 1992). When the reaction is carried out under controlled conditions the primarily formed epoxide ring could be preserved leading to consistency in properties. Epoxidised natural rubber is a new polymer which retains the strain crystallising character of NR and hence good tensile properties and at the same time possesses good oil resistance, low air permeability, high damping and high wet skid resistance along with low rolling resistance. Making use of these special properties, ENR can open up new applications such as oil resistant hoses, oil seals, axle boots tyre inner tubes, antivibration mountings and conveyor belting. The excellent bonding properties of ENR makes it suitable for application in adhesives and sealants.

Epoxidation of NR latex by in situ formed performic acid provides a method by which new properties could be imparted to NR at a reasonable cost. However, during the preparation of ENR from NR latex, the natural antioxidants are destroyed or physically removed. This leads to poor oxidation resistance to the raw rubber which is indicated by the very low plasticity retention index values of ENR. It can even lead to melting of the rubber during drying. So it is essential to improve the PRI values of ENR by the addition of antioxidants to ENR latex before coagulation. In this paper the influence of phenolic and amine type antioxidants and their dose on the PRI values of ENR 50 is studied.

The antioxidants tried were polymerised 2,2,4-trimethyl-1,2-dihydroquinoline, N-isopropyl-N'-phenyl-p-phenylenediamine, 2-mercaptobenzimidazole, zinc salt of 2-mercaptobenzimidazole, styrenated phenol and 2,6-di-tert-butyl-p-cresol.

EXPERIMENTAL

Concentrated latex preserved with the low ammonia/ tetramethylthiuramdisulphide (TMTD) - zinc oxide system (LATZ latex) was used for the study. Formic acid (98%), hydrogen peroxide (30%), formalin (40%) and ammonia (25%) were laboratory reagent grade. The antioxidants were of commercial grade. All the antioxidants except styrenated phenol, were made into 50 per cent dispersion in water. Styrenated phenol was made into an emulsion using oleic acid and ammonia as emulsifying agent. The nonionic stabilizer used was Vulcastab VL, the active ingredient of which is an ethylene oxide condensate.

50 mole per cent epoxidised natural rubber was prepared by carrying out the reaction at 50°C for 17 h according to the reaction recipe given in Table 1. At the end of the reaction the required amount of phenolic antioxidants were added and stirred for 0.5 h. The amine type antioxidants were added after neutralising the latex with ammonia to a pH of 8 - 8.5 and stirred for 0.5 h. In all cases latex was coagulated by adding 40 per cent ammonium sulphate solution and heating the latex to 70°C. The coagulum was processed into crepe, washed and dried at 50°C for 2-3 days.

Table 1. Reaction recipe.

Reagent	Concentration
Rubber hydrocarbon (RH)	2.94 moles of isoprene units/litre.
Formic acid	0.955 moles/litre.
Hydrogen peroxide	3.75 moles/litre.
Nonionic stabilizer	3 phr

The epoxy content was determined using IR spectrophotometry. The plasticity value (P_o) was determined using a Wallace Rapid Plastimeter. For determining PRI, sample pellets were aged at 140°C for 30 min in a PRI ageing oven followed by determining the plasticity value (P_{30}). PRI was expressed as a percentage of the original plasticity retained after ageing.

RESULTS AND DISCUSSION

The extent of improvement in PRI value of ENR 50 by the phenolic and amine type antioxidants at concentration levels of 0.25 phr to 1 phr is given in Table 2.

Table 2. Effect of antioxidants on PRI of ENR.

Antioxidant type	Concentration, phr	P_o	P_{30}	PRI	Staining behaviour
Control, NR	-	54	35	65	
ENR 50	0	44	9	20	
Polymerised 2,2,4-trimethyl, 1,2-dihydroquinoline (Antioxidant HS)	0.25	45	34	76	low
	0.5	46	30	65	high
	1.0	52	48	92	high
N-isopropyl-N'-phenyl-p-phenylenediamine (4010 NA)	0.25	40	30	75	high
	0.5	41	29	71	high
	1.0	40	38	95	high
2-mercaptobenzimidazole (MBI)	0.25	15	melted	-	Nil
	0.5	11	melted	-	Nil
	1.0	10	melted	-	Nil
Zinc salt of 2-mercaptobenzimidazole (ZMBI)	0.25	10	melted	-	Nil
	0.5	10	melted	-	Nil
	1.0	8	melted	-	Nil
Styrenated phenol (Antioxidant SP)	0.25	40	10	25	Nil
	0.5	41	21	50	Nil
	1.0	40	16	40	Nil
2,6-di-tert-butyl-p-cresol	0.25	40	20	50	Nil
	0.5	42	27	64	Nil
	1.0	42	29	69	Nil

The amine type antioxidants were added after neutralising the latex as otherwise the amine would be converted to a quaternary ammonium compound (Perera, 1990). The lower P_o value of all the ENR samples compared to the control NR sample shows that NR undergoes main chain scission during epoxidation and the subsequent processing. The fact that the natural antioxidants in NR latex get destryoed during epoxidation and the subsequent processing is evident from the very low PRI values of ENR having no added antioxidant. However, the reasonably high P_o value of the same sample shows that the extent of main chain scission during the reaction and the subsequent processing is not significantly high. Amine type antioxidants, HS and 4010 NA, gave very high PRI values. However, 4010 NA is highly staining and cannot be recommended for use. Above 0.25 phr HS is also found to be highly staining. At 0.25 phr it gives a reasonably high level of oxidation resistance to ENR with negligible staining.

Both mercaptobenzimidazole and its zinc salt are not only ineffective in protecting rubber from oxidative degradation, but has a peptising action on the raw ENR. These antioxidants, in all the concentrations tried, reduced the P_o value to a very low level. In fact the rubber was flowing down when it was kept for drying at 50°C. These antioxidants may be reacting with the epoxy group leading to ring opening with a further rearrangement reaction, to reduce steric inhibition, leading to chain scission. Further studies are required to confirm the mechanism.

Among the phenolic type antioxidants, 2,6-ditert-butyl-p-cresol provides high PRI values for ENR at all the concentrations tried. Styrenated phenol is found to give only a low level of protection.

CONCLUSION

The poor oxidation resistance of epoxidised natural rubber, measured in terms of plasticity retention index, could be substantially improved by the addition of small quantities of antioxidants to ENR latex before coagulation. Among the various antioxidants tried, polymerised 2,2,4-trimethyl-1,2-dihydroquinoline (Antioxidant HS) was found to be the best and a concentration of 0.25 phr was found to be adequate.

REFERENCES

Colclough, T. (1963). Crosslinking NR. II. Introduction of epoxide groups into NR and their subsequent utilisation in crosslinking. Chemical Abstracts, 59:15457h

Gelling, I.R. (1985). Modification of NR latex with peracetic acid. Rubber Chemistry and Technology, 58 : 86-96.

George, B., Abraham, S. and Mathew, N.M. (1992). In situ epoxidation of NR latex by performic acid and the kineties of the reaction. Indian Journal of Natural Rubber Research, 5 (1&2) : 179-187.

Ng, S.C. and Gaw, L.H. (1981). Reaction of NR latex by performic acid. European Polymer Journal, 17 : 1073 - 1077.

Perera, M.C.S. (1990). Reaction of aromatic amines with ENR latex. Journal of Applied Polymer Science , 39 : 749 - 758.

Udupi, K. (1979). Epoxides of styrene-butadiene block polymers. I. Journal of Applied Polymer Science, 23 : 3301 - 3309.