Indian Journal of Natural Rubber Research, 8(2) : 85-90, 1995

CHLORINATION OF LIQUID NATURAL RUBBER

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Veeralakshmanan, B., Nair, N.R., Mathew, N.M. and Sasimohan, A.L. (1995). Chlorination of liquid natural rubber. *Indian Journal of Natural Rubber Research,* 8(2) : 85-90.

Natural rubber (NR) on chlorination turns into a white thermoplastic material which is widely used by the paint and lacquer industries taking advantage of its improved ageing properties, flame retardance, adhesion to various substrates etc. A major impediment in the manufacture of chlorinated natural rubber is the gel content of raw NR which makes preparation of solution difficult. In this study this problem has been solved to a great extent by using depolymerised liquid natural rubber (LNR). Substantially higher amounts (upto 20%) of LNR could be dissolved in carbontetrachloride to obtain a liquid mass that could be stirred and homogenized during the course of chlorination. This has resulted in manifold increase in the output compared to conventional method of chlorination of NR solution. Properties of the product have been found comparable with chlorinated rubber prepared from raw NR.

Key words : Natural rubber, Depolymerisation, Chlorination, Liquid natural rubber.

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INTRODUCTION

The process of chlorination of NR has been a subject of extensive investigation ever since it was first attempted in 1930s. Chlorination of NR in solution form was reported by Bloomfield (1944) and that in latex stage by Van Amerongen (1952). Latex stage chlorination has problems due to various side reactions encountered in the aqueous medium. Starting from dry rubber, preparation of chlorinated rubber by treating NR in solution with gaseous chlorine has been reported by Ramakrishnan *et al.* (1953). The solvent used was carbontetrachloride. Dissolution of NR in the solvent is a major problem because of its limited solubility, more time for dissolution, high viscosity of the resultant solution, gel content etc. Use of low molecular weight guayule rubber (Mn 75,000) as a feed stock for preparation of coatings grade chlorinated rubber has been reported by Thames and Kaleem (1990). This was intended for economic utilization of the low molecular weight fraction of guayule rubber. Use of a 5 per cent solution was reported in this case. Solutions containing even 5 per cent of NR are extremely difficult to stir and so homogeneity is affected when NR solutions of higher concentrations are used for the reaction. Therefore, lower concentrations are being used, resulting in lower output per batch. Premastication is another requirement when NR solutions are to be prepared for which a mixing mill is needed. The possible advantages of using LNR are the ease of preparation of the solution of a higher concentration, more efficient stirring during chlorination and higher output per batch from a given reactor.

MATERIALS AND METHODS

LNR used in this study was a thermally depolymerised sample of molecular weight ($\bar{M}w$) in the range 47000-48000 and Brookfield viscosity 1,62,000 mPas at 38°C (Claramma *et al.,* 1991). Industrial grade chlorine gas was used for chlorinaion. Carbontetrachloride used as the solvent and the catalyst azobisisobutyronitrile were of reagent grade. Nitrogen of industrial purity was used as purge gas.

The apparatus for chlorination consisted of a three-necked round bottomed flask equipped with a magnetic stirrer, reflux condenser, a gas inlet tube and a thermometer. LNR was agitated with carbontetrachloride to form a uniform solution in the reaction vessel. Chlorine gas, dried by passing through concentrated sulphuric acid, was bubbled through the solution at a steady rate. Liberated HCI gas and unreacted chlorine were let out through the other end of the reflux condenser and absorbed in sodium hydroxide solution. Samples were drawn from the reaction mixture at definite intervals and the chlorinated hydrocarbon was separated by flash distillation. The solid mass was collected, powdered and dried to constant weight at 70°C.

The solution viscosities were measured using a Brookfield viscometer. Test samples collected from the reaction vessel at different intervals were cooled to 80°C and their viscosities measured. Chlorine content in the product was estimated by volumetric method after fusion with a mixture of sodium carbonate and potassium carbonate. Thermogravimetric studies were conducted on a TGA apparatus, Du Pont model 1090. DSC measurements were made on a Perkin Elmer Delta series Differential Scanning Calorimeter Model DSC 7. Infrared spectroscopic studies were carried out using a Shimadzu FTIR spectrophotometer model DR-8001.

RESULTS AND DISCUSSION

Solubility of polymer and viscosity of solutions

Natural rubber contains substantial amount of gel which limits the quantity of rubber that can go into solution. It has been observed that LNR readily dissolves in carbontetrachloride and yields solutions which can be stirred or agitated even at concentrations as high as 15 to 20 per cent. Viscosities of solutions of LNR in carbontetrachloride with different concentrations are given in Table 1. The lower viscisoty of LNR solutions has made it possible to maintain homogeneity of the liquid mass during the course of the reaction. Parameters those control the dissolution of polymer are many. Configuration of NR and LNR molecules being similar, the factor contributing most to the increased solubility of LNR is its reduced molecular mass and gel content. Lower molecular mass of LNR renders phase separation less effective and less affected by temperature (Tager, 1978). Gel acts as solid elastic bodies and above the yield stress only they attain irrecoverable flow deformation. NR, even after mastication, contains some quantity of gel which offer resistance to flow of the solution. On the other hand smaller molecules of LNR in the solvent result in a solution of much lower viscosity that can be easily stirred and homogenised. The fact that viscosity increases during chlorination demands a lower concentration of solution to start with. For the present study a 15 per cent solution of LNR in carbontetrachloride was used. Change in viscosity with time of chlorination is given in Figure 1. An in-

Table 1. Viscosity of LNR solutions

Concentration,	Viscosity, mPas
10	32
15	48
20	110

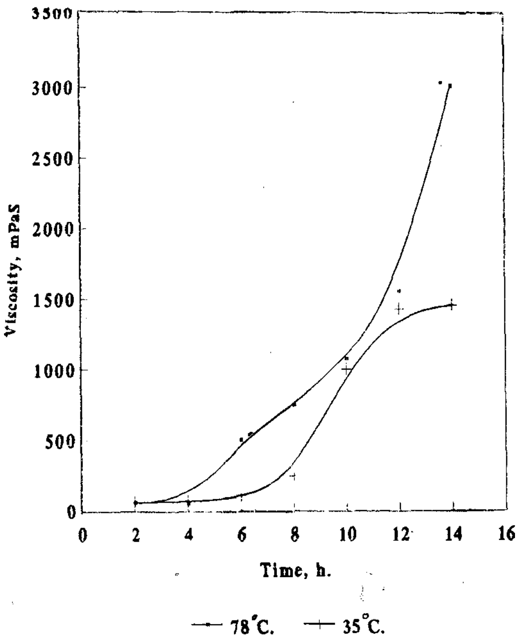

Fig. 1. Influence of chlorination on viscosity

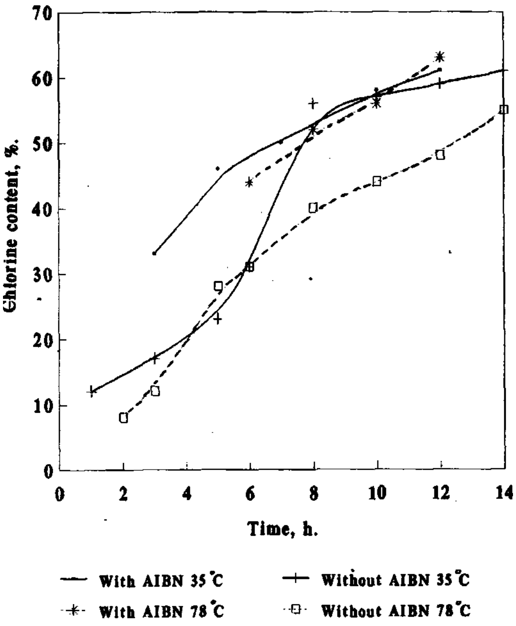

Fig. 2. Effect of AIBN and temperature

crease in viscosity was observed with progress in chlorination. A decrease in viscosity as reported by Troussier (1956) for NR solutions was not observed for LNR in carbontetrachloride. The reduction was attributed to the scission of macromolecules. In the case of LNR, as the macromolecules had already undergone size reduction, the effect was not pronounced. However, the subsequent increase in viscosity, as observed earlier, was seen for LNR also. This could be due to the development of polarity in the polyisoprene chain and the consequent change in interaction between the polymer and the solvent.

Effect of temperature on chlorination

The increase in chlorine content of the product with progress in reaction time at the two temperatures is shown in Figure 2. In general, the chlorine content increases with reaction time. However, the rate of increase is significantly different at the two temperatures studied. Chlorine content of the product is significantly higher when the reaction is carried out at 35°C, except that there is an intermediate stage when the chlorine content is more or less identical at both the temperatures. It is also worth noting that the reaction takes place at different rates, especially at 35°C. At this temperature the chlorine content increases slowly upto a period of around 5 h and then increases suddenly upto around 7 h and thereafter increases only slowly. However, at 78°C the rate of increase is comparatively rapid initially upto around 5 h and further increase is slower. It was reported by Ramakrishnan *et al.* (1953) that chlorination of natural rubber proceeds through different mechanisms. They identified four stages in the reaction, (1) substitution with concomitant cyclisation, (2) substitution, (3) addition (which takes place when the chlorine content of the product is above 30 per cent) followed by (4) substitution. The changes in the rate of increase in chlorine content could be attributed to the changes in the mechanism of the reaction. The initial slow rate of increase in chlorine content at 35°C is due to the predominantly substitutive reaction. However, the significantly higher extent of chlorination at this temperature compared to that at 78°C is attributed to the exothermic nature of the reaction (D' Ianni *et al.*, 1947) The sudden increase in the rate of chlorination after 5 h is evidently owing to addition reaction. It may also be noted that at this stage the chlorine content is above 30 per cent. After this, the reaction again becomes substitution and the rate decreases. The final chlorine content of the product is also significantly higher when the reaction is carried out at 35°C, further indicating the exothermic nature of the predominantly substitutive reaction.

Influence of catalyst AIBN

Effect of addition of 0.5 per cent of catalyst AIBN into the reaction mixture was also studied. Figure 2 also shows the effect of AIBN on the progress of the reaction at 35 and 78°C. AIBN was found to increase the rate of reaction in both the cases, but the effect was more pronounced at the higher temperature. At 78°C chlorine content was 49 per cent in the absence of AIBN after 12 h of reaction. In the presence of the catalyst it has increased to 63 per cent. The initial vigour of the reaction tended to subside with time, but in the presence of the catalyst the reaction rate was consistently high. At 35°C also addition of AIBN increased the reaction rate but only during the initial stages. This effect narrowed down as the reaction progressed beyond 8 h. The consistently higher activity of the catalyst at higher temperature is owing to its homolysis at liquid phase at higher temperature, the activation energy of dissociation being 132 kJ mol/ (Issac, 1974).

Properties of chlorinated rubber

Appearance

The chlorinated rubber obtained from LNR was a light grey powder. Chlorination starting from natural rubber often gives a product white in colour. In this case liquid natural rubber was made by thermal depolymerisation. The process employs high temperatures causing charring of some low molecular weight compounds present in natural rubber. Since chlorine has no action on carbon, the colour of the product appeared grey. This, however, is not a serious disadvantage as bright colours are not an important requirement in most applications of chlorinated rubber like fire retardants, corrosion resistant products, etc.

Chlorine content

Chemically estimated chlorine content of the samples chlorinated for different periods in presence and absence of the catalyst are also given in Figure 2. Steady increase in chlorine content was observed with increasing time of reaction and a level above 60 per cent was attained in 12 h. Figure 3 is the infrared absorption spectrum of chlorinated LNR. A broad peak at 762cm^{-1} was obtained. This corresponds to C-Cl bond. In addition to the above, peaks were observed at 2990 cm^{-1} corresponding to CH_3, 1400 cm^{-1} corresponding to CH_2 and 930 cm^{-1} corresponding to CH of polyisoprene.

Stability

The TGA thermogram of the chlorinated rubber sample containing 62 per cent chlorine is presented in Figure 4. The weight loss occurred distinctly at 3 stages, around 100°C, 250°C and 500°C. The first transition can be attributed to the loss of solvent and other volatiles from the sample. The weight loss at 200°C is attributed to evolution of HCl from the sample and that at 500°C to

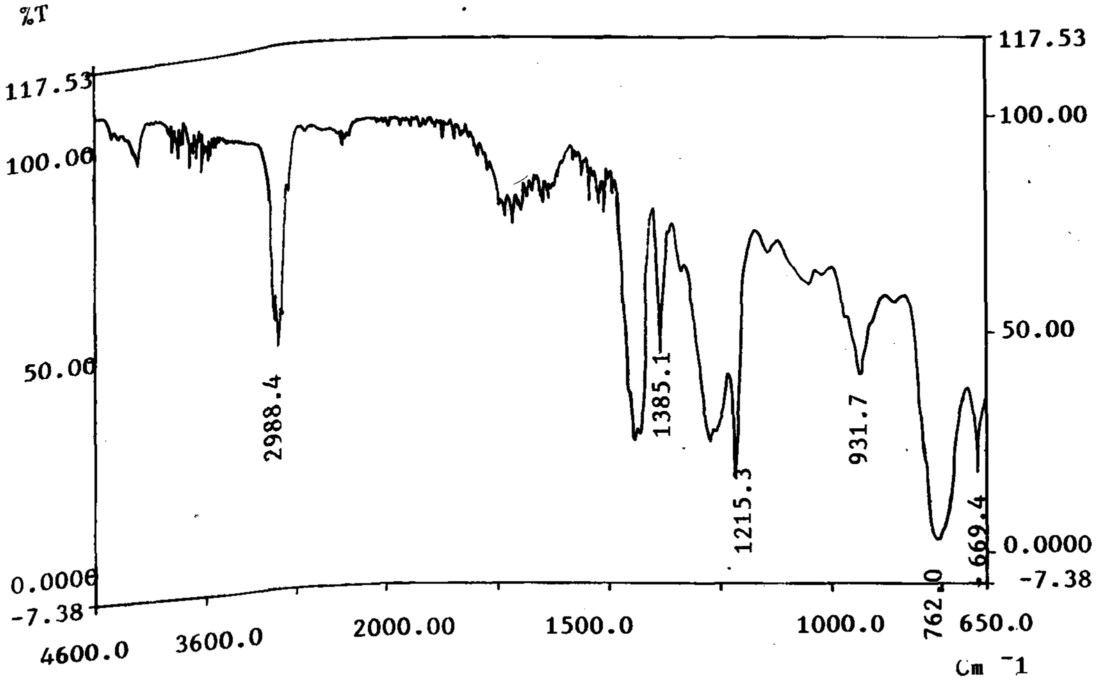

Fig. 3. Spectrum of chlorinated LNR

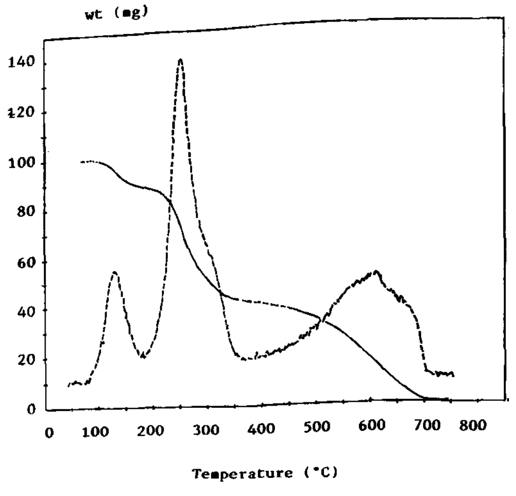

Fig. 4. TGA Thermogram of chlorinated LNR

charring. Thus the sample was found thermally stable upto 250°C. This was further evidenced by the differential scanning calorimetric studies. Figure 5 is the DSC thermogram of the sample containing 62 per cent chlorine.

In general, chlorinated rubber samples with higher chlorine content, were found stable on storage whereas the samples with lower chlorine content turned borwnish and became less soluble in chloroform and other solvents. This change is owing to elimination HCl molecules leading to cyclic and hyperconjugated structures of reduced solubility. This phenomenon is less prominent in highly chlorinated samples for want of enough hydrogen atoms to evolve HCl (Bateman, 1950).

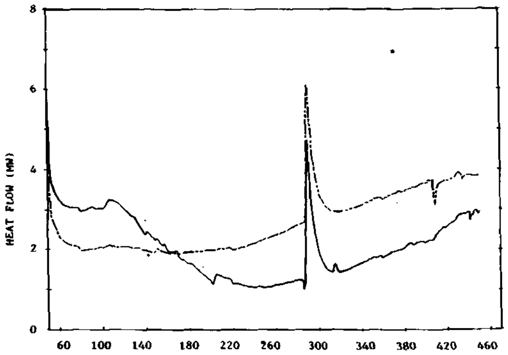

Fig. 5. DSC plot of chlorinated LNR

SUMMARY AND CONCLUSIONS

Liquid natural rubber was found to be a good starting material for the preparation of chlorinated natural rubber taking into account its easy miscibility with the solvent and dissolution to high concentrations. The formation of solutions of much lower viscosities than natural rubber solutions helped to carry out the reaction homogeneously. With the use of LNR, solutions of rubber hydrocarbon concentration as high as 15 per cent (w/w) , suitable for chlorination process, could be made, which in turn, made it possible to increase the output of the reaction 3 to 5 times than that by the conventional method. Optimum temperature of the reaction was found to be 78°C in the presence of the catalyst AIBN. The product obtained was light grey in colour, and stable upto 250°C.

ACKNOWLEDGEMENT

The authors are grateful to Dr. M.R. Sethuraj, Director, Rubber Research Institute of India for providing facilities.

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