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PRODUCTION OF LIQUID NATURAL RUBBER BY THERMAL DEPOLYMERIZATION

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Depolymerization of natural rubber, using a combination of mechanical and thermal energies aided by a peptiser, has been attempted. Peptiser dosage, temperature and heating time for producing liquid natural rubber (LNR) of desired viscosity were optimised. LNR can be produced by thermal depolymerization, with or without the addition of a peptiser. Possibility to produce LNR of desired viscosity by appropriately fixing the peptiser dosage, temperature and duration of heating was revealed. As degradation was found rapid at higher temperatures depolymerization at lower temperature is desirable. Properties of the liquid rubber such as Brookfield viscosity, intrinsic viscosity, iodine value and acetone extract have been determined. IR and NMR studies were also carried out. Vulcanization of LNR with sulphur resulted in very poor strength properties.

Key words:- Liquid natural rubber, Depolymerization, Peptiser, Intrinsic viscosity, Brookfield viscosity.

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INTRODUCTION

Liquid natural rubber (LNR) is a modified form of natural rubber (NR) prepared by size reduction of molecular chains of the naturally occurring polymer. This can be achieved by the application of mechanical energy, chemicals, heat or high energy radiation, alone or in combination. Depolymerization can be carried out in latex stage or in dry rubber stage. Commercial production of LNR in USA was carried out by depolymerizing solid NR (Hardman and Lang, 1950), while a pilot plant for the production of LNR in latex stage, using phenyl hydrazine/air redox system, was reported to be set up in Ivory Coast (Allet-Don and Lemoine, 1986).

Several studies have been reported on the depolymerization of natural rubber. According to Mayo *et al.* (1968a), cobalt compounds are active metal catalysts for oxidation of rubber. Metal stearates are also reported to catalyse thermal oxidation of NR (Phan Van Ninh *et al.*, 1987). The pro-oxidant effects of hydrazines and sulphur compounds have been described by Mayo *et al.* (1968b). Preparation of liquid rubber by depolymerization of NR in solution in the presence of phenylhydrazine–$FeCl_2$–O is reported by Mori and Fujii (1976). Pautrat and Marteau (1975) used 4 methyl benzene sulphinic acid and hydrogen peroxide to prepare oligomers of low molecular weight. The use of solar energy for preparation of LNR has also been reported (Tillekeratne *et al.*, 1977). Photochemical degradation of NR solution in the presence of H_2O_2 resulted in hydroxyl terminated LNR (Ravindran *et al.*, 1988). Depolymerization of NR using a combination of mechanical energy and thermal energy aided by a peptiser has been attempted in the present study. Optimisation of peptiser dosage, temperature and heating time and characterization of the resulting LNR have also been attempted.

EXPERIMENTAL

Materials

The experiments were carried out using ISNR 5, all the samples being from the same block. Activated pentachlorothiophenol, supplied by Bayer India Limited, was the peptiser used. Chemicals used for vulcanization were of commercial grade.

Apparatus

An apparatus, with provisions for stirring and controlling temperature, was fabricated and used for depolymerization. During experiments, temperature could be controlled to an accuracy of ± 2°C. Brookfield viscometer (RVT Model) was used for determining Brookfield viscosity and Ubbelohde viscometer for intrinsic viscosity. Perkin-Elmer IR Spectrophotometer (Model No. 237) was used for infra-red analysis. A Hitachi R-600 FT Spectrometer at 60 MHz using TMS as an internal standard was used for recording the nuclear magnetic resonance (^{1}H NMR) spectrum.

Procedure

Rubber was masticated on a laboratory size two roll mill (15 x 30 cm) at a friction ratio of 1:1.25. Uniform mastication was effected on all samples by choosing the same nip gap and time. For optimising peptiser dosage, appropriate quantities of the peptiser was added during mastication. The sheet finally milled at a nip gap of 3 mm, was cut into pieces and loaded into the depolymerizer and heated to the required temperature. Stirring was started after softening. Heating and stirring continued for the predetermined time and the liquid natural rubber poured out from the vessel. Brookfield viscosity of the samples was measured at 38°C. Vulcanization studies were carried out using LNR sample in the medium viscosity range. The ingredients were prepared as a dispersion in the plasticiser and mixed with LNR thoroughly. Sheets of about 1 mm thickness were cast in glass shells and tensile test specimens punched out from the vulcanized sheets using a standard die.

RESULTS AND DISCUSSION

With the progress in heating time the solid rubber softens and is gradually converted into a free flowing liquid, the viscosity of which undergoes further reduction on continued heating. Depolymerization was attempted at different temperatures in the range of 220–260°C. At 220°C the material obtained, even after 5 h of heating, was a semi-solid of very high viscosity. Temperatures higher than 260°C resulted in faster reduction in viscosity, inadequate heat conduction time, charring of the product and inflammability problems. Detailed studies therefore were conducted only at 230, 240, 250 and 260°C.

Table 1 shows the effect of mastication of ISNR 5 with and without peptiser. Peptiser (activated pentachlorothiophenol) was added during mastication of the rubber. In all cases the time was 20 min for mastication. It is clear that simple mastication of NR for 20 min has reduced the initial Mooney viscosity of 65 to 35. A further reduction by 6 units was possible by the addition of 0.6 phr of the peptiser. The effect of peptiser in enhancing the efficiency of mastication was not pronounced. This is evidently due to the predominantly mechanical mastication occurring on cold mill mastication as reported by Bristow and Watson (1963).

Table 1. **Effect of mastication of natural rubber on Mooney viscosity**

Initial viscosity – 65

Peptiser dosage	Mooney viscosity ML (1+4) at 100°C after mastication for 20'
0	35
0.2	34
0.4	31
0.6	29

Figure 1 shows the effect of heating time and peptiser dosage at 230°C on Brookfield viscosity of the resulting LNR. Heating for 3 h at 230°C resulted in a high viscosity product, of values above 8 x 10^5 cps at 38°C. Increase in heating time from 3 to 5 h resulted in a viscosity of 5 x 10^5 cps for NR alone and 3 x 10^5 cps for NR with 0.6 phr of the peptiser. On 7 h heating the corresponding values were 4 x 10^5 cps and 2 x 10^5 cps respectively. As evident from the slope of the curves, the molecular chain scission was at a faster rate during the early stages of heating. A comparison of samples with and without peptiser revealed that those containing the peptiser were depolymerized to a lower viscosity in the initial stages of heating itself. On increasing the duration of heating, this effect of the peptiser became less significant and the viscosity of the resultant product was closer. In general, it can be concluded that by depolymerization at 230°C, LNR in the high viscosity range i.e. 2 x 10^5 to 5 x 10^5 cps at 38°C only can be produced in a reasonable period of time.

Figure 2 shows the change in Brookfield viscosity of LNR with peptiser dosage and duration of heating at 240°C. This also shows that addition of peptiser and increase

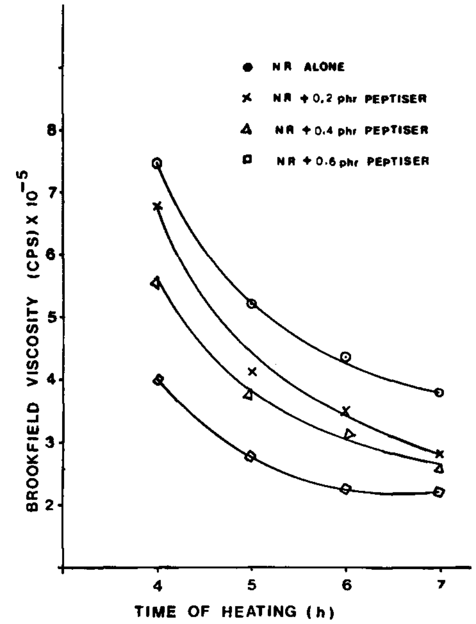

Fig. 1. Effect of peptiser dosage and heating time at 230°C on Brookfield viscosity

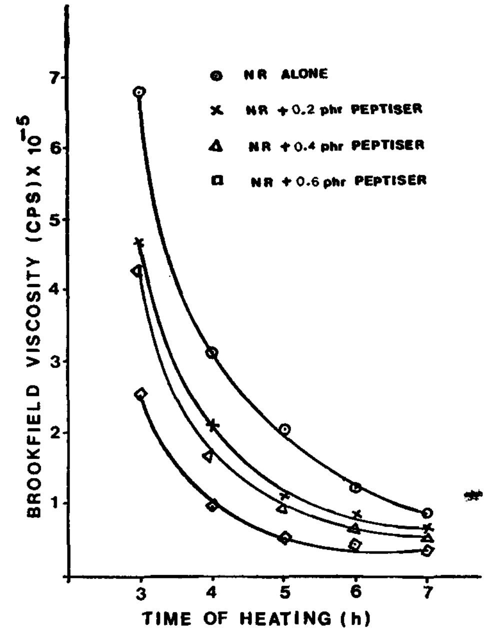

Fig. 2. Effect of peptiser dosage and heating time at 240°C on Brookfield viscosity

in heating time decreased the viscosity of LNR. It is also seen that production of LNR of Brookfield viscosity less than 1 x 10^5 cps without peptiser requires a heating time of 7 h at 240°C. Further reduction in heating time can be achieved by incorporation of peptiser at the time of mastication. An increase of temperature significantly accelerates the depolymerization reaction. The results thus reveal that by selecting parameters such as peptiser dosage, temperature and time of heating, it is possible to produce LNR of desired viscosity.

Figure 3 is a plot of log viscosity versus temperature for different periods of heating of NR without peptiser. The straight lines obtained indicate clearly that. viscosity has a logarithmic dependence on depolymerization temperature. The slope of the lines at different periods of heating is almost the same and is indicative of the same effect at different temperatures.

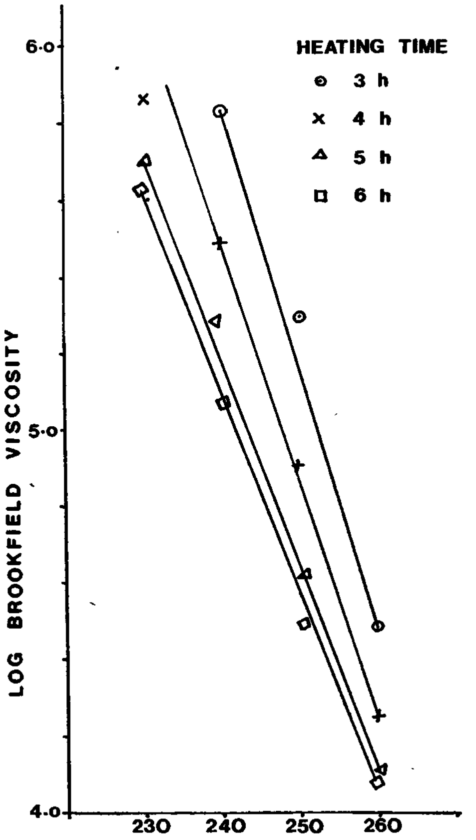

Fig. 3. Effect of temperature and heating time on log Brookfield viscosity

Figure 4 shows the IR spectrum of depolymerized rubber. Absorptions at 830 cm^{-1} is due to C = C cis, at 1380 cm^{-1} due to CH_3 deformation, at 1450 cm^{-1} due to CH_2 bending and at 1660 cm^{-1} due to C = C stretching. Moreover, the weak peak at 1700cm^{-1} indicates the formation of C = O groups during the depolymerization process.

Figure 5 shows the ^1H NMR spectrum of the depolymerized rubber. The resonance at 1.69 ppm corresponds to $(cis - CH_3\overset{|}{C} =)$, 2.05 ppm corresponds to $(- CH_2\overset{|}{C} =)$ and 5.1 ppm corresponds to $(-\overset{|}{C} = CH -)$. The spectrum also contains weak peaks at 0.9, 2.7 and 3.4 ppm indicating the probable presence of side products. However, as these peaks are very weak the polymer backbone is not seriously affected by the depolymerization process.

Table 2 gives the content of acetone extractables in LNR of different viscosities, prepared under different conditions. It is observed that, irrespective of the conditions of preparation, the quantity of acetone extractables has a direct bearing on Brookfield viscosity and thereby on the molecular weight of the samples. The quantity of acetone extractables increases as the viscosity decreases. This may be due to the formation of a higher amount of very low molecular weight fractions.

Brookfield viscosity, intrinsic viscosity and iodine value of a few representative samples of high, medium and low viscosity are given in Table 3. Iodine value is a measure of unsaturation and the results show that depoly-

Fig. 4. IR spectrum of depolymerized rubber

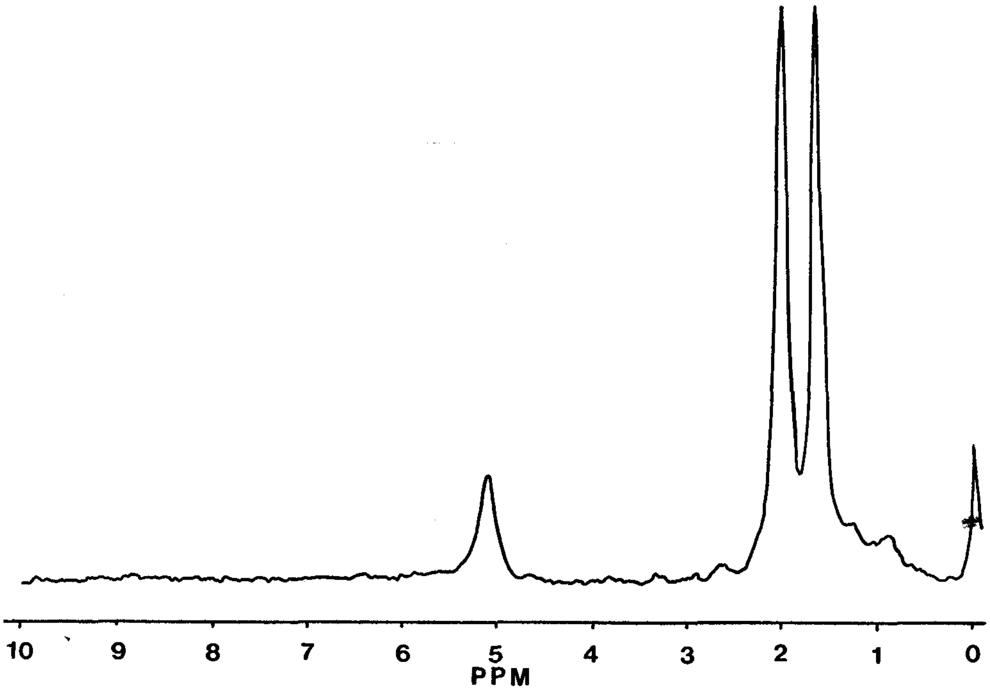

Fig. 5. ^{1}H NMR spectrum of depolymerized rubber

Table 2. **Acetone extractables and viscosity of LNR samples prepared under different conditions**

Temperature of reaction (°C)	Peptiser dosage (phr)	Time of heating (h)	Brookfield viscosity at 38°C (cps)	Acetone extractables (%)
230	0.0	6	4.44×10^{6}	5.26
230	0.6	7	2.20×10^{6}	6.48
240	0.0	5	2.04×10^{6}	6.41
240	0.4	3	4.50×10^{6}	5.55
240	0.6	5	0.48×10^{6}	9.06
240	0.6	6	0.43×10^{6}	9.89

merization has taken place without much loss in unsaturation. However, a gradual reduction in unsaturation is observed which is probably resulting from cyclisation reactions brought about by heat. It is also observed that the reduction in intrinsic viscosity is not proportional to the reduction in Brookfield viscosity. For a ten fold reduction in Brookfield viscosity the reduction in intrinsic viscosity was only two-fold.

Table 3. **Brookfield viscosity/Intrinsic viscosity and Iodine value of LNR samples**

Brookfield viscosity at 38°C (cps)	Intrinsic viscosity at 25°C (dl/g)	Iodine value
312,000	0.296	305
77,000	0.240	295
47,000	0.200	300
34,000	0.158	286
Raw natural rubber	3.176	322

Table 4 gives the formulation used for studying vulcanization of LNR. The ingredients were prepared as dispersion in the plasticiser in order to make their dispersion in LNR easier and more uniform. This necessitated addition of a large proportion of the plasticiser in the case of the filled compound.

Table 4. **Compound formulation**

Ingredients	Parts by weight
Liquid natural rubber	100
Sulphur	5
Zinc stearate	5
Zinc diethyldithiocarbamate	5
Naphthenic oil	10

Vulcanized at 80°C for 4 h.

Vulcanizate properties are given in Table 5. In general, the strength of LNR vulcanizates was much lower than that of raw natural rubber vulcanizates.

Table 5. **Vulcanizate properties**

Properties	
Tensile strength ($kg\ cm^{-2}$)	8.2
Modulus at 100% elongation ($kg\ cm^{-2}$)	4.0
Modulus at 200% elongation ($kg\ cm^{-2}$)	6.1
Elongation at break (%)	268.0
Tear strength ($kg\ cm^{-1}$)	4.7

Table 6. **Formulations of filled LNR compounds**

Ingredients	Parts by weight		
	I	II	III
Liquid natural rubber	100	100	100
Sulphur	5	5	5
Zinc stearate	5	5	5
Zinc diethyldithiocarbamate	5	5	5
Naphthenic oil	40	40	40
Silica	..	10	..
SAF black	..	..	10

Vulcanized at 80°C for 4 h.

Table 7. **Vulcanizate properties**

Properties	I	II	III
Tensile strength MPa (kg cm^{-2})	2.8	3.2	2.3
Modulus at 100% elongation (kg cm^{-2})	2.0	2.7	2.2
Elongation at break(%)	163	141	126
Tear strength kNm^{-1} (kg cm^{-1})	1.7	1.9	1.6

SAF black and silica (Table 6) did not improve the vulcanizate properties of LNR compounds (Table 7). As incorporation of fillers necessitated addition of high proportions of naphthenic oil, improvement in strength properties could not be achieved. In fact all the strength properties were adversely affected by the addition of oil and filler.

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