Flow Properties of Thermally Depolymerized Liquid Natural Rubber

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SYNOPSIS

The flow behavior of liquid natural rubber (LNR) with reference to the effect of molecular weight, shear rate, and temperature has been studied. LNR samples were prepared by thermal depolymerization of rubber (NR) through the combined effect of mechanical, chemical, and thermal energies. High molecular weight samples, especially at lower temperatures, showed pseudoplastic behavior, whereas the low molecular weight samples were Newtonian at all temperatures. The viscosity of LNR considerably decreases with increase in temperature. The activation energy of flow was also calculated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Fundamentally liquid natural rubber (LNR) differs from other liquid elastomers in the method of preparation. It is produced by thermal depolymerization of the naturally occurring high molecular weight polymer. In the case of synthetic rubber oligomers, molecular weight and other parameters can be controlled by regulating the conditions of the polymerization process. For the preparation of LNR, two routes are normally adopted, one starting from dry rubber and the other from latex. Latex-stage depolymerization of natural rubber (NR) using a phenylhydrazine/air redox system to LNR has been reported by Boccassio and de Livonniere.[1] Photochemical degradation of NR in the presence of H_2O_2 resulted in hydroxy-terminated LNR and was reported by Raveendran et al.[2] Pautrat and Martaeu[3] used 4-methyl benzenesulfininic acid and hydrogen peroxide to prepare oligomers of low molecular weight. The use of solar energy for the preparation of LNR has been reported by Tillekeratne et al.[4] Depolymerized NR for the present study was prepared by a combination of mechanical and thermal energies aided by a peptizer, activated pentachlorothiophenol. For the thermal depolymerization, conditions such as peptizer dosage, temperature, and heating time were selected as reported by Claramma et al.[5] Liquid elastomers are used in a wide range of products like moisture-resistant sealants for filling voids, self-adhesive tapes, binder for grinding wheels, and rocket propellants.[6]

Improvements in flow properties imparted by LNR when used as a plasticizer in nitrile rubber compounds have also been reported.[7,8] In applications of LNR, such as castings, the property of most interest is its pourability and flowability. Preliminary studies on the rheological behavior of LNR have been reported by Radhakrishnan Nair et al.[9] Rheology of elastomers is affected by the viscoelastic behavior common to all polymeric materials; in addition, the morphology of rubber compounds, resulting from elastomer filler interaction, has a significant effect on the flow mechanisms and induces different behavior.

In the present article, viscosity studies were carried out on a series of LNRs of different molecular weights using a rotational-type viscometer, Rheomat 30, which could record a continuous plot of shear

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Table I Viscosity of LNR Samples

	Sample No.				
	LNR 1	LNR 2	LNR 3	LNR 4	LNR 5
Brookfield viscosity at 38°C (cps)	52,000	70,000	112,000	268,000	492,000

rate against shear stress, and the measurements were made at different temperatures.

EXPERIMENTAL

LNR samples were prepared by depolymerization of Indian Standard Natural Rubber (ISNR-5) under the influence of mechanical, chemical, and thermal energies. The parameters such as temperature and duration of heating were so chosen as to obtain LNR samples of different viscosities in the low, medium, and high ranges.

The samples were identified based on the their viscosity values measured using a Brookfield viscometer (Model RVT, spindle 6, 5 rpm) at 38°C, as given in Table I. These were characterized by NMR and IR spectroscopy. The ^{1}H-NMR spectrum was recorded with a Bruker 400 MHz instrument with $CDCl_3$ as the solvent. The IR spectrum was obtained with a Perkin-Elmer 16 PC spectrometer with a thin film on a KBr cell. Gel permeation chromatographic studies were carried out using a Waters GPC fitted with a Polymer Laboratories gel 10 microns mixed 600 × 7.5 mm column and two detectors (UV and refractometer). Measurements were performed at 25°C with tetrahydrofuran as the solvent (throughput 0.5 mL/min). A calibration curve was established with standard polystyrene samples and polystyrene data were calculated as suggested by Subramaniam[10]:

$$\text{Log } Mpi = 0.093 + 0.950 \log Mps. \quad (1)$$

where *Mpi* is the molecular weight of *cis*-polyisoprene, and *Mps*, the molecular weight of polystyrene.

Viscosity measurements were done using a Rheomat 30 viscometer manufactured by Contraves AG, Switzerland. It is a multispeed rotational-type viscometer separating two individual variables, shear rate and shear stress, which dictate the flow behavior of substances. The measuring system consists of a rotor and a stator with the test object lying between them. The shear stress and shear rate at the middle of the gap are recorded by an *X–Y* plotter. The multispeed instrument has an electronically controlled drive system. The drive system was programmed to change the rate of shear continuously so that the flow behavior of the material was plotted automatically as a rheogram (shear stress vs. shear rate). The measurement of shear rate–shear stress for different LNR samples was carried out over a wide range of temperatures from 20 to 40°C. Suitable cups were used and the rpm ranges from 1 to 15 and to 30 were selected. Accordingly, appropriate multiplication factors were used to convert the readings into actual shear rates that ranged from 0.215 1.975 S^{-1}. Viscosity was calculated as

$$\text{Viscosity (PaS)} = \text{shear stress (Pa)/shear rate } (S^{-1}) \quad (2)$$

RESULTS AND DISCUSSION

Characterization of LNR

The depolymerized LNR samples were pourable liquids in the viscosity range from 52,000 to 4,92,000 cps at 38°C. For spectroscopic characterization, LNR 1 was used, it being the sample that has undergone maximum depolymerization and other sible side reactions. Figure 1 is the NMR spect of LNR 1. The spectrum exhibited three chemical shifts of protons (δ methyl) at 1.54 ppm, (me ene) at 2.00 ppm, and (ethyl) at 5.1 ppm. Their respective interpretations are characteristic of *cis*-1,4-polyisoprene. The above protons on the chain end groups were not detectable. Figure 2 is the infrared spectrum of LNR 1, which shows absorption bands at 836, 1376, 1448, and 1662 cm^{-1}, typical of CH adjacent to C=C, CH_3 deformation, CH_2 bending, and C=C stretching, respectively, of the polyisoprene structure. A broad but weak band was also observed at 3500 cm^{-1}, indicative of formation of small amounts of side reaction products bearing —OH and —NH groups during the depolymerization process. Table II gives the physical and chemical properties of LNR. The brown color of the samples was due to the formation of small amounts of char

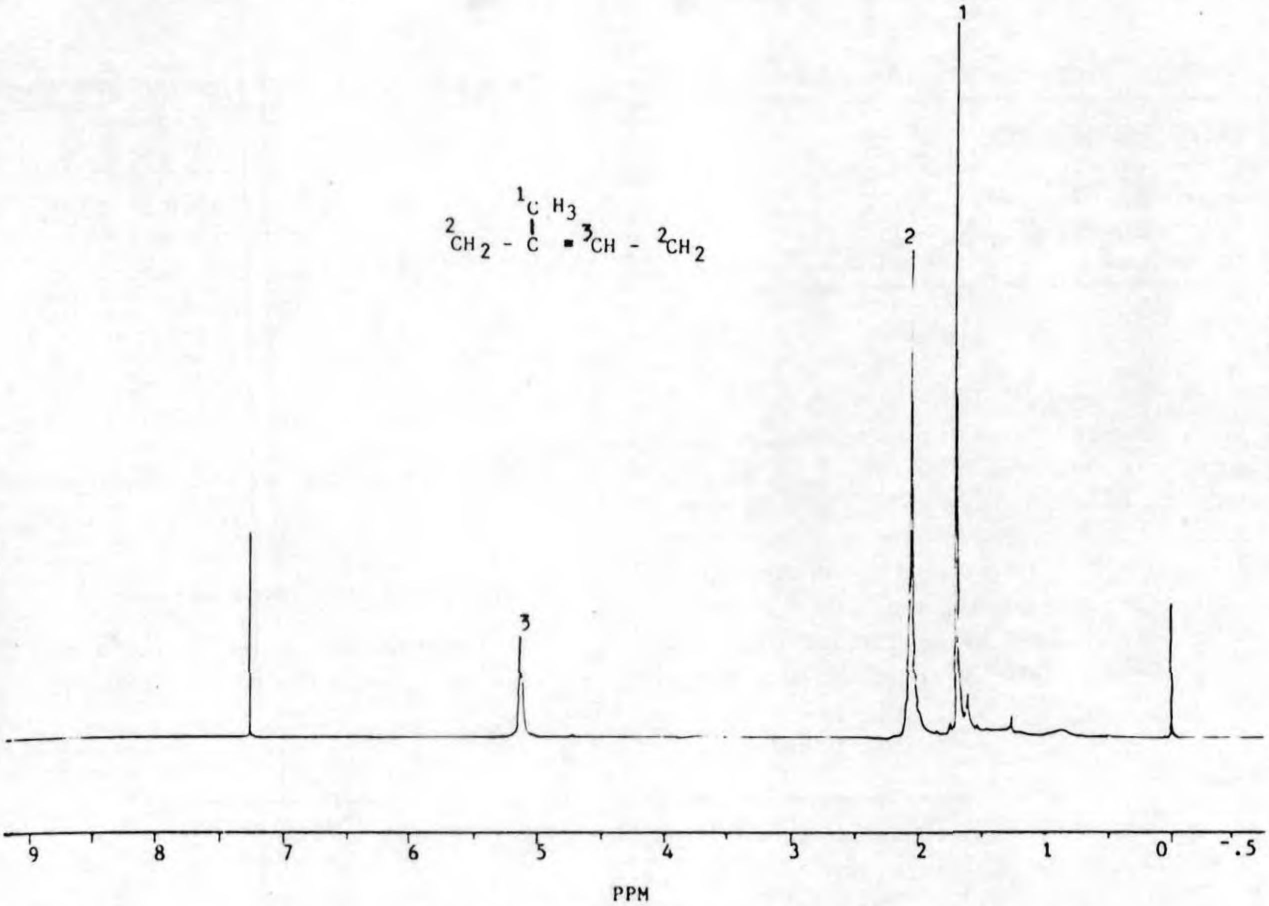

Figure 1 ^{1}H-NMR spectrum of LNR 1.

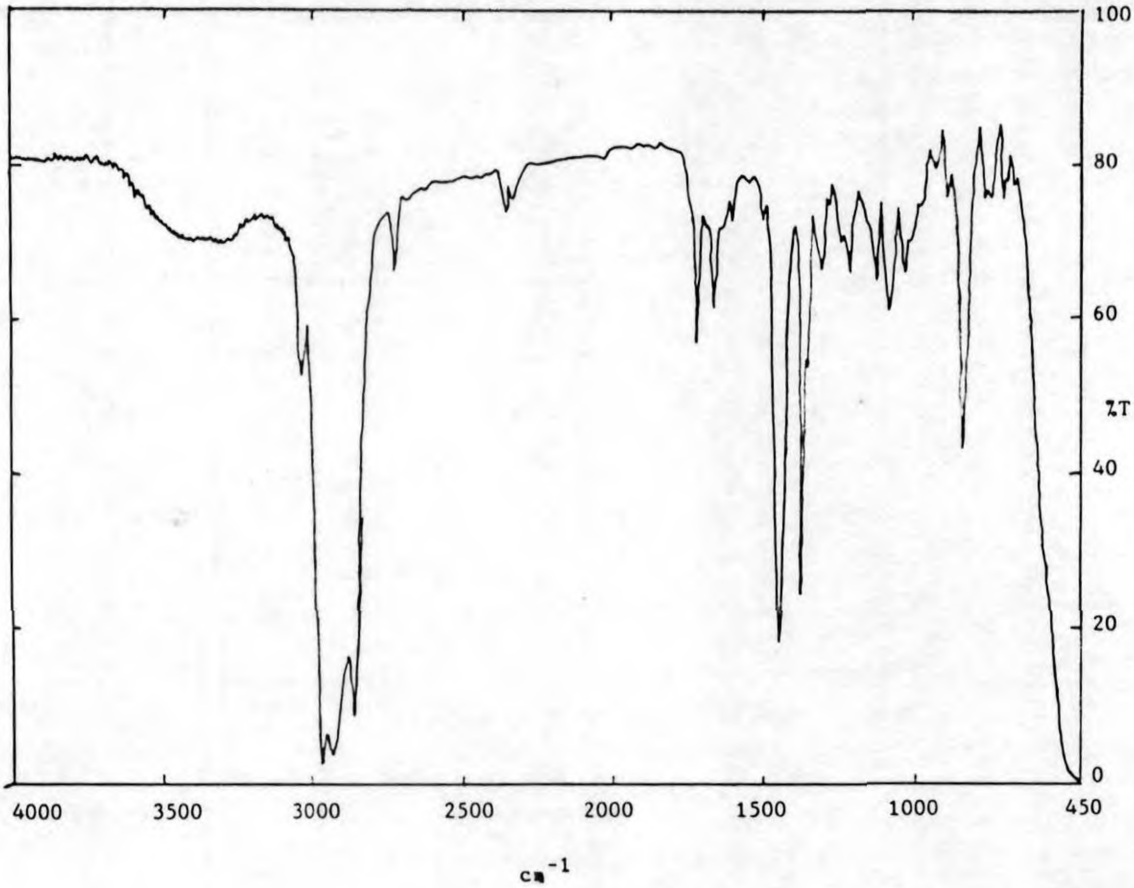

Figure 2 IR spectrum of LNR1.

Table II Properties of LNR

Specific gravity at 25°C	0.92
Color	Light brown in thin films
Ash content (%)	0.6
Volatile matter (%)	0.1
Iodine value	305

during the thermal depolymerization. The iodine value measured on the sample was 305, comparable to that of NR, and indicative of no appreciable quantity of addition products. Table III gives the number- and weight-average molecular weights. Polydispersity indices ($\bar{M}_w/\bar{M}_n$) of different LNR samples are also given in the table. The molecular weight distribution values ranging from 6.35 to 6.81 showed a relatively large dispersion range. The

Table III Molecular Weights of LNR Samples

	Sample				
	LNR 1	LNR 2	LNR 3	LNR 4	LNR 5
$\bar{M}_n$	3918	5113	5929	6461	8474
$\bar{M}_w$	30,900	32,490	44,210	54,420	72,960
$\bar{M}_w/\bar{M}_n$	7.89	6.35	7.46	8.42	8.61

GPC chromatograms of the samples are given in Figure 3.

Shear Rate–Shear Stress Relationship

The shear rate–shear stress relationship for th samples at 50°C is compared in Figure 4. It gives

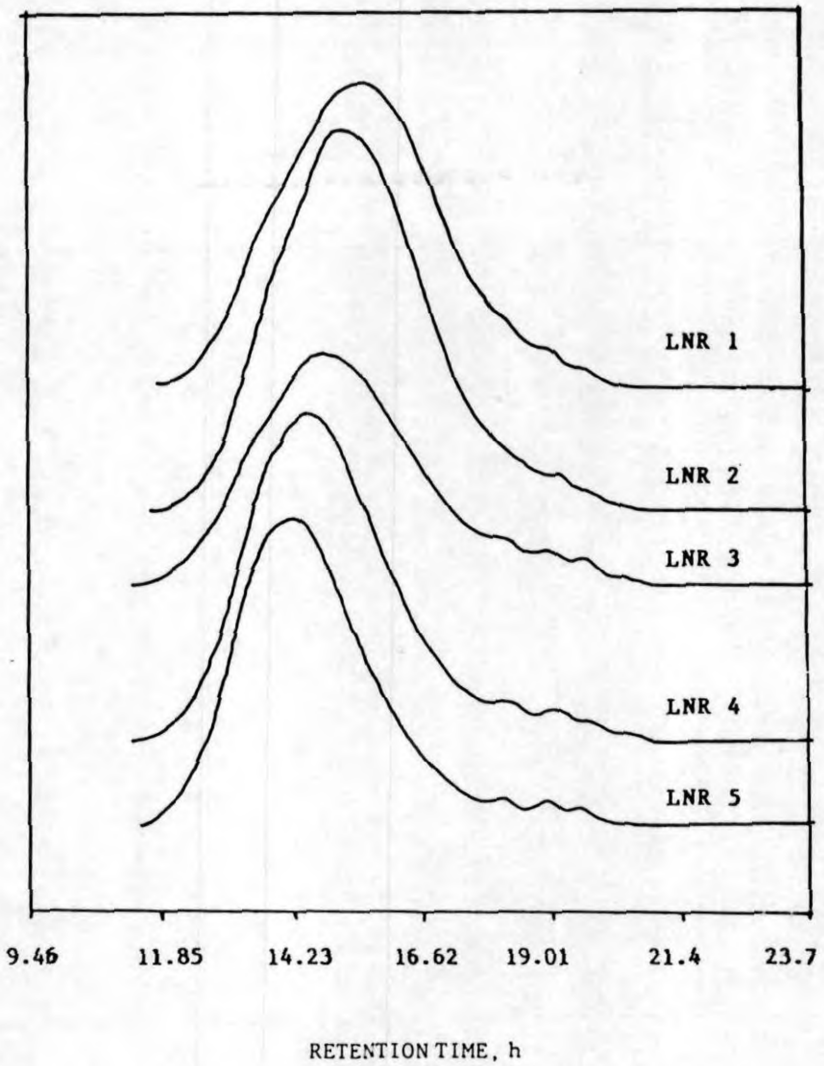

Figure 3 GPC chromatograms of LNR samples.

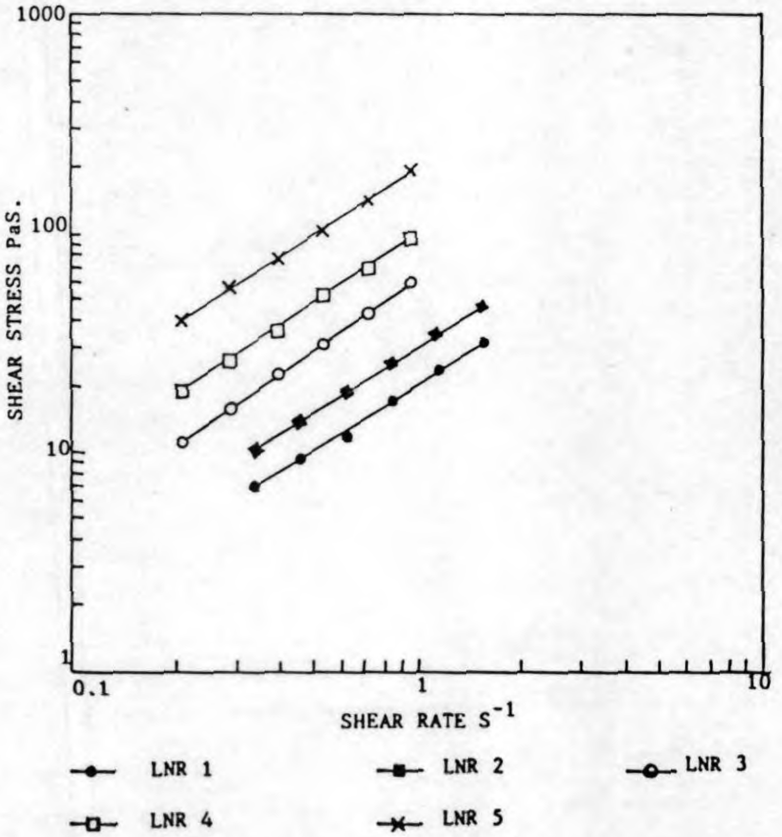

Figure 4 Shear stress vs. shear rate.

plot of logarithm of shear rate (γ) vs. shear stress (τ). With increase in the shear rate, shear stress increases linearly for all the samples. As the slope of the lines are close to 1, it can be inferred that the samples' behavior is almost Newtonian. The mathematical expression relating shear stress (τ) and shear rate (γ) for Newtonian liquids is given by the power law equation

$$\eta = K\gamma^n \tag{3}$$

where K is the consistency factor, and n, the flow behavior index. The values of K and n were calculated by regression analysis. It can be noticed that the value of n is around 1 for the low molecular weight sample. The high molecular weight sample exhibits more pseudoplastic behavior, as evidenced by the lower values of n. This may be attributed to the fact that at high temperatures the interparticle or intermolecular interactions will be weak, and, therefore, the molecules of the high molecular weight samples will be oriented in the line of shear. In general, with the decrease in molecular weight, the Newtonian behavior increases. Figure 5 gives the pseudoplasticity index of the samples at different temperatures. The high molecular weight sample showed a lower index at low temperature.

Effect of Shear Rate on Viscosity

Variations of shear rate with viscosity at 20°C for different LNR samples are given in Figure 6. In the case of LNR 1, 2, and 3, as the viscosity is independent of shear rate, the samples exhibit perfect Newtonian behavior. In the case of high molecular weight samples, LNR 4 and LNR 5, a marginal reduction in viscosity with increasing shear rate is observed, which may be attributed to the effect of molecular orientation. In liquid polymers of high molecular weight, the molecules are substantially entangled, giving rise to non-Newtonian behavior. In the case of low molecular weight liquid polymers, the entanglement between molecules is low, so that coupling is a weak phenomenon.

Effect of Molecular Weight on Viscosity

Figure 7 is a plot of viscosity vs. weight-average molecular weight of LNR samples at 50 and 80°C. In both cases, the viscosity increases with increase in molecular weight. This is due to the effect that, as the molecular weight increases, the entanglement and interaction between polymer chains also increase. It is also interesting to note that the increase

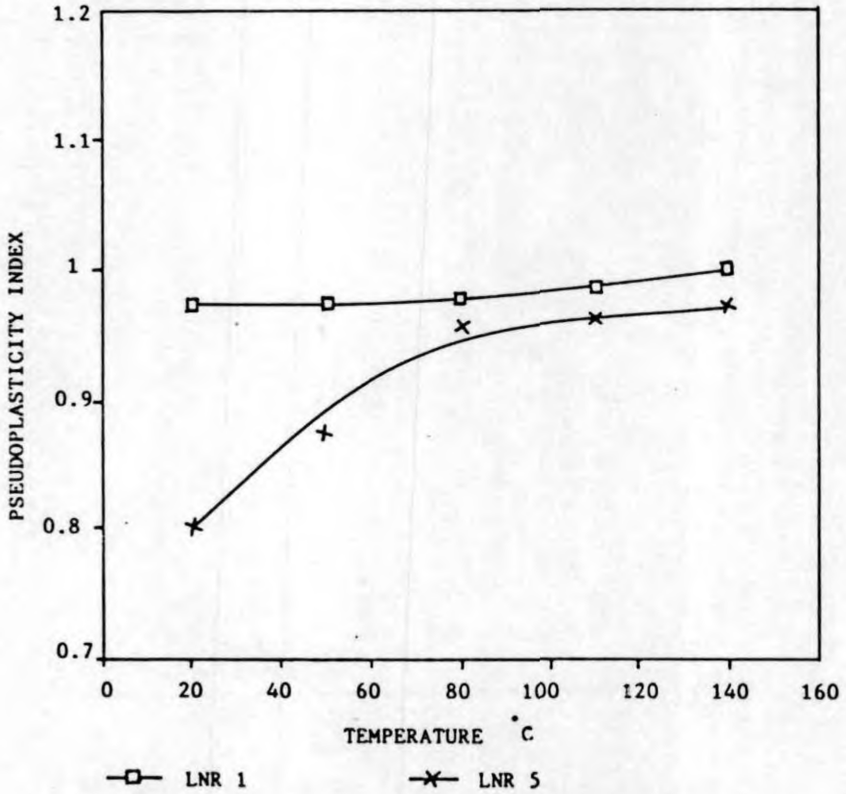

Figure 5 Variation of pseudoplasticity index with temperature.

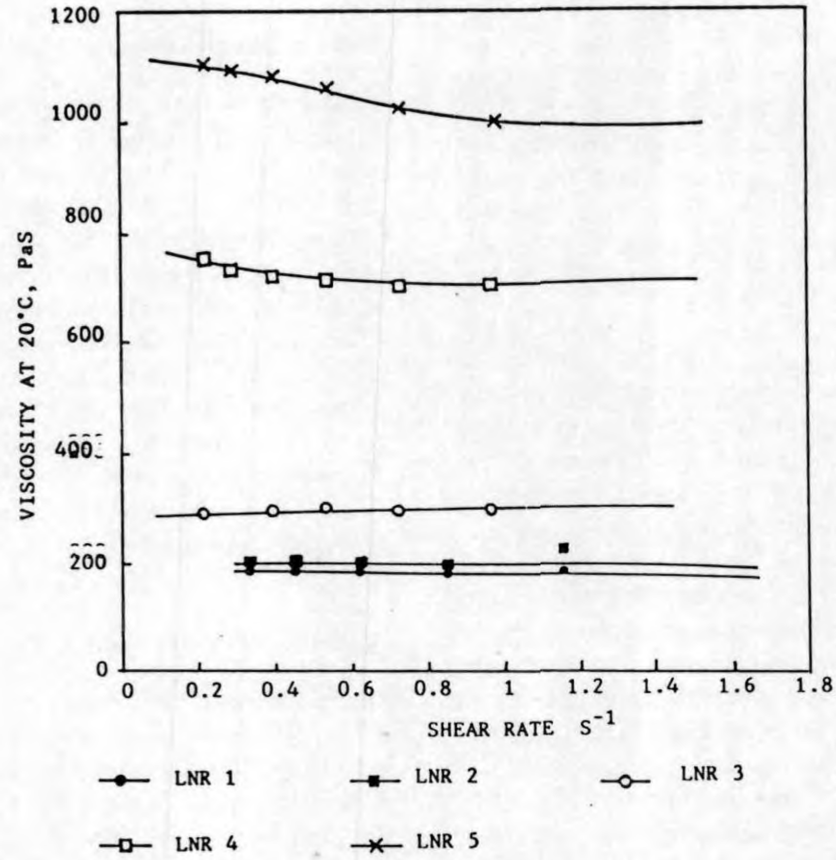

Figure 6 Viscosity vs. shear rate.

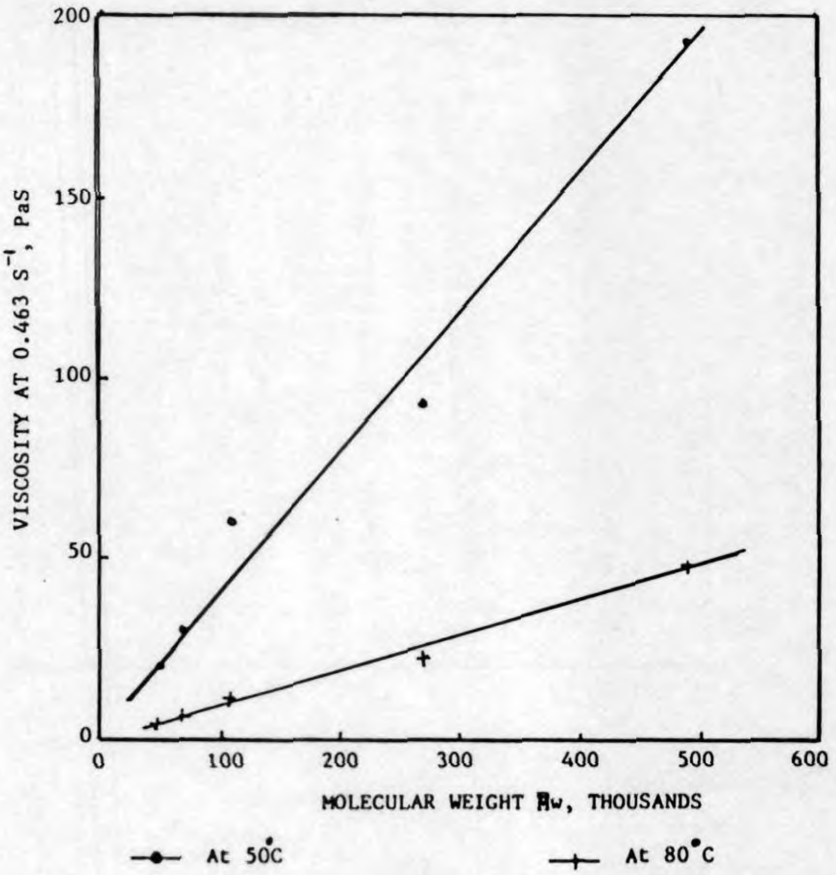

Figure 7 Effect of molecular weight on viscosity.

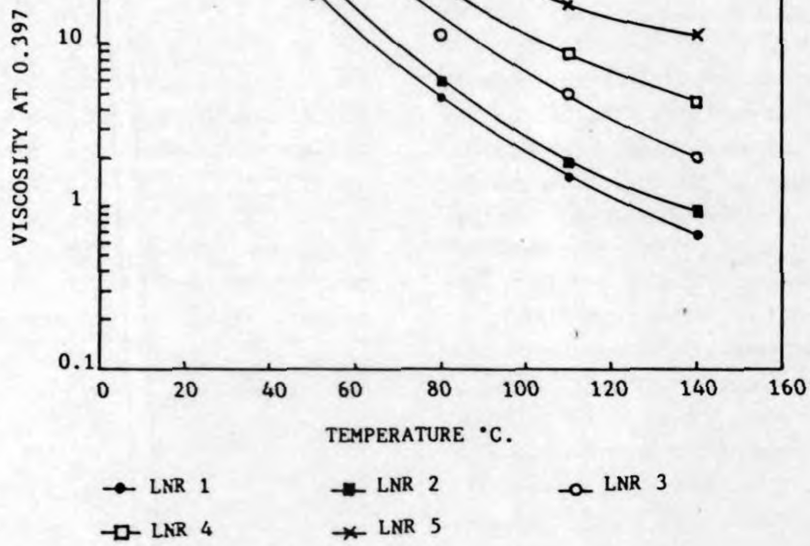

Figure 8 Influence of temperature on viscosity.

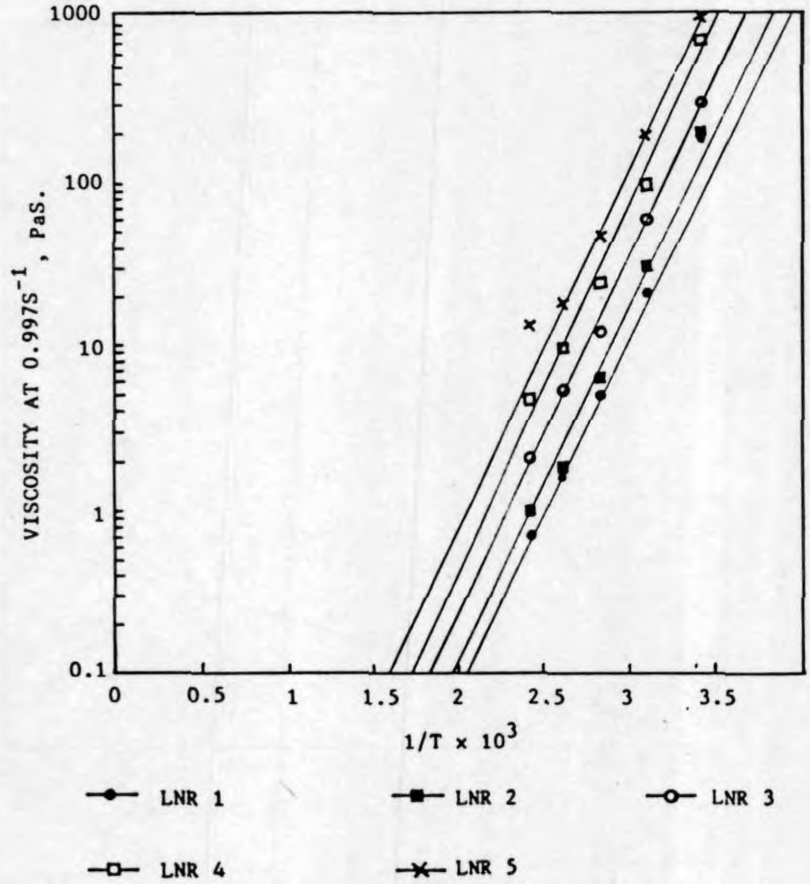

Figure 9 Plot of viscosity vs. 1/*T*.

in viscosity with molecular weight is more prominent at low temperatures. At high temperature, the intermolecular interaction decreases. This minimizes the effect of molecular weight on viscosity.

Effect of Temperature on Viscosity

Viscosities of the samples at different temperatures were plotted at a shear rate of 0.3973 S^{-1} and are given in Figure 8. In all cases, viscosity increases with increase in temperature. However, due to increased thermal motion and free volume, the viscosity difference among the samples shows greater divergence at high temperatures, indicating that the low molecular weight material becomes more fluid than do the high molecular weight samples. Thus, the viscosity range widens at higher temperatures. This may be attributed to the free Brownian movement of low molecular weight polymer chains under the influence of thermal energy. In the case of high molecular weight samples, the extra chain length restricts the molecular motion. A comparison of viscosities of different samples shows that the reduction in viscosity is around 100-fold for a 120°C increase in temperature. Thus, warming of LNR makes i possible for even high viscosity samples, which ar difficult to transfer at low temperature, to flo Variation of flow properties with temperature is o great interest in engineering applications. Viscosit at elevated temperatures is governed by the Ar rhenius equation

$$\eta = Ae^{-E/RT}$$

where E is the activation energy of flow, and T, th absolute temperature. The activation energy of flo at a particular shear rate can be obtained from th

Table IV Activation Energy of Flow

Sample	Activation Energy (kcal/mol
LNR 1	1176
LNR 2	1209
LNR 3	1262
LNR 4	1331
LNR 5	1363

slope of the line obtained by plotting log η vs. $1/T$. Plots of the above parameters were made at a shear rate of 0.997 S^{-1} and are given in Figure 9. The slopes of the lines were calculated and the activation energies of flow were determined. The activation energy values of different samples are given in Table IV. The activation energy was found to marginally increase with increase in molecular weight.

CONCLUSIONS

The present investigation indicates that the flow behavior of liquid natural rubber (LNR) is influenced by shear rate, temperature, and molecular weight. The properties governed by the above parameters are as follows:

1. Low molecular weight samples exhibit perfect Newtonian behavior.
2. High molecular weight samples show a pseudoplastic tendency, especially at low temperatures and shear rates.
3. Increase in temperature causes significant reduction in the viscosity of LNR samples in general. At high temperatures, low molecular weight samples behave more like fluids.
4. Activation energy of flow is only marginally influenced by molecular weight of the samples and shows an increasing trend with increasing molecular weight.

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