Processing Characteristics and Physicomechanical Properties of Natural Rubber and Liquid Natural Rubber Blends

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ABSTRACT: Investigations into the processing characteristics and physicomechanical properties of natural rubber (NR) modified with liquid natural rubber (LNR) were carried out. Liquid natural rubber samples (of different molecular weights) were first produced by depolymerization of natural rubber latex (NRL), using nitrobenzene as the depolymerizing agent to lower molecular weight rubbers. The LNRs produced were then mixed with natural rubber in various proportions. The NR/LNR blends showed better processing characteristics by having higher scorch time and lower cure rate, higher molecular mass between crosslinking resulting from the lower volume fraction of the LNR, and good solubility properties; and marginal differences in shear modulus, crosslinking densities, Mooney viscosity, plasticity, and the plasticity retention index compared to properties of an unmodified NR. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1070–1076, 2002

Key words: natural rubber; natural rubber latex; liquid natural rubber; processability; physicomechanical properties

INTRODUCTION

Natural rubber (NR) is a high molecular weight compound, which has accounted for its use in some applications such as tires, tubes, and the like.[1,2] In recent times, there has been a great deal of commercial interest in blends of rubber that have better solubility in solvents than natural rubber because of its high molecular weight. In 1982 Schultz et al.[3,4] reported a new generic family of polymers with fewer solubility problems as a result of their cyclic ether units that were bonded together along the main chain.

The processing of rubber that requires heavy equipment and high-power input has brought about the need for rubber to be available in a physical form that is capable of being handled in liquids, fluids, and solids.[2] Availability of natural rubber in this form will increase its competitiveness in relation to synthetic rubbers, thereby increasing the benefit to manufacturers of rubber products and improving the future of natural rubber.[5,6] This will also provide materials with higher added value and give the desired combinations of properties for specific and demanding applications.[7]

Modification of elastomers with additives is a widely accepted practice to improve the processability of mixes and to impart desired properties to the vulcanizates.[8–11] Many of the additives

Table I Typical Characteristics of SAR 3

Parameter	
Dirt content retained on 45 μm sieve (%)	0.02
Ash content (%)	0.32
Volatile matter	0.40
Nitrogen (%)	0.23
Initial plasticity (P_0)	36
Plasticity after aging for 30 min at 140°C (P_{30})	24
Plasticity retention index (PRI)	67
Mooney viscosity ML(1+4), 100°C	70

Adapted from Standard African Rubber (SAR) Manual No. 2.[20]

presently used are based on petrochemical sources.[1,8] Reports on the use of liquid natural rubber (LNR) as a processing aid or modifier of NR vulcanizate properties are scanty,[12–14] although Meeker[15] did report the use of liquid synthetic rubber in facilitating the processing flexibility and performance attributes of rubber and adhesive compounds.

LNR, which is usually obtained by the partial depolymerization of NR, was previously found to have most of the natural components that produce the color, appearance, and performance of NR.[2,15] Not only this, LNR has the same monomer as the rubber 1,4-isoprene unit. This similarity of LNR to NR provided the basis for this study, to examine the processability and physicomechanical properties of NR modified with LNR.

EXPERIMENTAL

Materials

NR conforming to Standard African Rubber (SAR) grade 3, having the characteristics given in Table I, was obtained from the Rubber Research Institute of Nigeria (RRIN; Iyanomo, Benin City). The natural rubber latex (NRL) used was also obtained from the NIG804 clonal series of RRIN, having the characteristics given in Table II. Reagents used in the preparation and characterizations of LNR were analytical grade, whereas the rubber compounding chemicals were commercial grade.

Methods

Production of LNR Samples of Different Molecular Weights

Natural rubber latex was diluted to 20% dry rubber content (DRC) by adding distilled water and

Table II Typical Characteristics of RRIN's NIG804 Latex Clonal Series

Parameter	
Total solid content (TSC) (%)	45.0
Dry rubber content (DRC) (%)	38.5
Mechanical stability (MST) (s)	550
Coagulum content (%)	0.05
Sludge content (%)	0.10
Volatile fatty acids	0.17

From Akinlabi et al., 2001.[22]

the latex was stabilized with 2% nonionic surfactant. The latex was reacted with various concentrations of nitrobenzene, ranging from 0.5, 1.0, 1.5, 2.0, and 2.5 wt % of the DRC of the latex, to yield products of different molecular weights. The reaction was allowed to proceed for various periods of time (up to 10 h) at 30 ± 1°C under oxygen with continuous stirring (60 rpm). The resultant product was coagulated with 2% formic acid. The extent of depolymerization was determined by viscosity measurement using a Ubbelohde-type viscometer.

Preparation of NR/LNR Blends

The blends of NR/LNR were prepared in a Banbury mixer using the recipe in Table III.

Measurement of Plasticity

The initial plasticity (P_0) of the mixes in Table I and the plasticity after aging in the plastimeter

Table III Recipe for Preparation of NR/LNR Blends

Compound Component (phr)	Sample			
	A	B	C	D
Natural rubber	100	70	70	70
LNR (MW 26,600)	—	30	—	—
LNR (MW 18,500)	—	—	30	—
LNR (MW 8600)	—	—	—	30
Zinc oxide (ZnO)	6.0	6.0	6.0	6.0
Carbon black (HAF)	40	40	40	40
Sulfur	2.0	2.0	2.0	2.0
Stearic acid	2.5	2.5	2.5	2.5
Mercaptobenzothiazole (MBT)	0.5	0.5	0.5	0.5
Flectol H	2.0	2.0	2.0	2.0

Table IV   Results of Oscillating Disc Rheometer Measurements

Mix	T_{s1}[a] (min)	T_{s2}[b] (min)	T_{s10}[c] (min)	T_{s50}[d] (min)	T_{s90}[e] (min)	ML[f] (kg-cm)	MH[g] (kg-cm)	RT[h] (kg-cm)
A	0.52	1.05	0.51	2.14	5.26	4.30	13.33	12.43
B	0.48	0.59	0.46	1.40	4.46	4.58	13.16	12.30
C	0.59	1.31	0.47	1.32	4.08	4.01	8.03	7.63
D	2.17	3.56	1.14	3.09	4.03	4.60	7.73	7.42

[a] T_{s1} is the time (in min) to an increase of 1 unit of torque above ML.
[b] T_{s2} is the time (in min) to an increase of 2 units of torque above ML.
[c] T_{s10} is the time (in min) to an increase of 10 units of torque above ML.
[d] T_{s50} is the time (in min) to an increase of 50 units of torque above ML.
[e] T_{s90} is the cure time (in min). This corresponds to the torque obtained.
[f] ML is the minimum torque (N · m).
[g] MH is the maximum torque (N · m).
[h] RT, the rheometry torque, is calculated using the formula: [90(MH − ML)]/100 + ML.

oven for 30 min (P_{30}) at 140 ± 2°C were measured using a Mark IV Wallace Rapid Plastimeter. The plasticity retention index (PRI) was calculated using the procedures described in ISO 2930.

Cure Characteristics

The cure characteristics of the mixes were measured at 175°C using an oscillating disk rheometer (ODR; Alpha 2000) according to the ISO 3417 method, the results of which are shown in Table IV.

Mechanical Properties

The test specimens were molded in an electrically heated hydraulic press (Techno Loire) at 174°C. Tensile properties of the vulcanizates were measured with a Monsanto tensile tester (model 1/M; Monsanto, St. Louis, MO) at a crosshead speed of 500 mm/min using a dumbbell-shaped test specimen (type II), as detailed in ASTM D-412-87 (method A).

Crosslinking Density

The chemical crosslinking density of the vulcanizate was determined by following the procedure of equilibrium swelling in toluene.[16–18] The volume fraction of the rubber in swollen gel V_2 was calculated using the following expression[17]:

$$V_2 = \frac{[D - T(1 - E)^{-1}(F - E)]\rho_{rh}}{[D - T(1 - E)^{-1}(F - E)\rho_{rh} + (S - D)\rho_s} \quad (1)$$

where D is the deswollen mass of test piece (g); T is the mass of test piece after acetone extraction and drying (g); E, which is the mass fraction of

acetone extractable material in the test piece, is calculated from $[(t_u - T)/t_u]$ (g), where t_u is the mass of the unextracted test piece (g); S is the swollen mass of test piece (g); F is the mass fraction of added nonrubber ingredients (g); ρ_{rh} is the density of the vulcanizate network; and ρ_s is the density of the swelling liquid (g/m^3).

The chemical crosslinking density was calculated using the Flory–Rhener equation[16]

$$\ln(1 - V_2) + V_2 + \chi V_2^2 + \rho V_1 V_2^{1/3}/M_c = 0 \quad (2)$$

where ρ is the density of the rubber hydrocarbon, V_1 is the molar volume of the solvent, V_2 is the volume fraction of rubber in the swollen sample, and M_c is the molecular weight between crosslinking and is related to the shear modulus (G) by the following expression[1,8]:

$$G = \rho RT/M_c \quad (3)$$

and χ is the polar–solvent interaction parameter, given as[19]

$$\chi = 0.44 + 0.18V_2 \quad (4)$$

Measurement of the Mooney Viscosity

The Mooney viscosity of the sample was determined using the shearing disc viscometer according to ISO 289.[20,21] The results were expressed in terms of ML(1+4) at 100°C, where ML is the Mooney units obtained using the large rotor as signified by (L); 1 is the preheating period in minutes (1 min); 4 is the duration of the test once

Table V   Solubility Results

Solvent	Sample	W_1[a]	W_2[b]	W_3[c]	Solubility (%)
Toluene	A	0.3434	0.3915	0.3100	14.01
	B	0.3019	0.3504	0.2834	16.06
	C	0.2920	0.3490	0.2510	19.50
	D	0.2919	0.3498	0.2603	19.84
Carbon tetrachloride	A	0.3420	0.3889	0.3316	13.72
	B	0.3391	0.3934	0.3286	16.03
	C	0.3357	0.3975	0.3235	18.41
	D	0.3179	0.3784	0.3004	19.03
Acetone	A	0.3318	0.3627	0.3165	9.30
	B	0.3465	0.3841	0.3245	10.85
	C	0.3170	0.3573	0.3006	12.71
	D	0.3580	0.4064	0.4370	13.51
Ethanol	A	0.2977	0.3150	0.2826	5.80
	B	0.3194	0.3407	0.2954	6.67
	C	0.3296	0.3560	0.3166	8.01
	D	0.3490	0.3797	0.3317	8.80
Methanol	A	0.3325	0.3511	0.3244	5.60
	B	0.3279	0.3491	0.2991	6.47
	C	0.3185	0.3446	0.3005	8.20
	D	0.2899	0.3145	0.2967	8.49

[a] W_1 is the weight after extraction.
[b] W_2 is the weight after swelling at 25°C for about 6 h.
[c] W_3 is the weight after drying in a vacuum to a constant mass.

the motor is turning, in minutes; and 100°C is the test temperature.

Solubility Tests

The rates at which the mixes swell in solvents such as toluene, carbon tetrachloride, acetone, ethanol, and methanol were determined in accordance with ASTM D3610 (Table V). Three different shapes (triangle, square, and rhombus) were cut from each of the test samples. The weights of each were recorded before subjecting them to extraction for about 2 h to extrude out any unwanted substance. The samples were later dried in a vacuum chamber and reweighed before swelling in different solvents in a water bath at 25°C for about 6 h, after which the weights were recorded. Another redrying in a vacuum chamber until a constant weight was recorded followed this.

RESULTS AND DISCUSSION

It will be seen in the depolymerization results that the initial average molecular weight of the

NRL was 35,000 and with different concentrations of nitrobenzene as the depolymerizing agent, reacted for various times in the presence of pure oxygen, it was possible to produce LNR of about 21% of the NRL's initial average molecular weight. There was no marginal difference in the average molecular weight results obtained for the 2.0 and 2.5% concentrations of nitrobenzene. This can be seen in Table VI and is graphically represented as Figure 1.

The rheographs of the mixes are shown in Figure 2. The calculated rheometry torque (in kg-cm) was highest for mix A, with a value of 12.43, followed by mix B with 12.30, mix C with 7.63, and the lowest was mix D with 7.42. These values decrease as the concentration of LNR in the mixes decreases, which signifies the effect of LNR on NR. The cure time (in min) for all the mixes also decreases as the concentration of LNR decreases, with mix A having 5.26; mix B, 4.46; mix C, 4.08; and mix D, 4.03, as the vulcanizate with the lowest cure time.

The physicomechanical properties of the mixes are given in Table VII. The tensile strength varies from 14.4 MPa for mix A to 10.6 MPa for mix D,

Table VI   Effect of Nitrobenzene Concentration on the Extent of Depolymerization of NRL

Time (h)	Concentration of Nitrobenzene (%)				
	0.5	1.0	1.5	2.0	2.5
0	35,000	35,000	35,000	35,000	35,000
0.5	35,000	35,000	35,000	32,000	31,000
1.0	28,000	26,600	24,000	23,400	22,300
1.5	19,900	19,600	18,500	17,000	15,000
2	14,700	14,300	14,200	12,000	12,000
4	11,000	10,000	10,200	10,200	10,000
6	9,400	9,400	8,000	8,600	8,500
8	9,400	9,000	8,000	8,600	8,300
10	8,800	8,600	7,800	7,400	7,400

which shows a decrease in the value of tensile strength as the molecular weight of LNR decreases. The modulus at 50% elongation and modulus at 100% elongation follow the same trend as the tensile result with base mix A having the highest values and mix D having the lowest values. The result of the elongation at break was opposite to what was observed in the tensile result. The lowest value observed was for base mix

A and the highest value observed was for mix C. This phenomenon can be attributed to the fact that the LNR, which is a low molecular mass material, has affected not only the strength but also the elongation and elasticity of the vulcanizate.

The shear modulus (G), the plasticity, the Mooney viscosity, the crosslinking densities, and the volume fraction of the rubber in the swollen
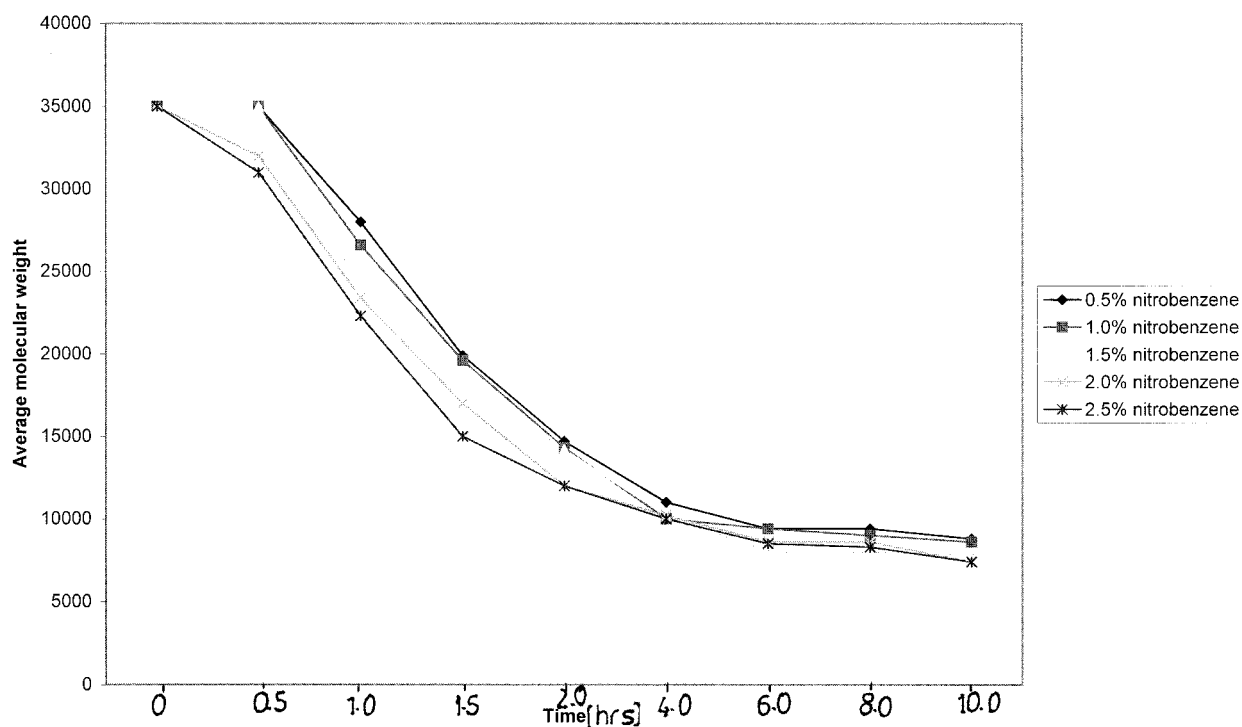
Figure 1   Variation of average molecular weight against time using different concentrations of nitrobenzene.
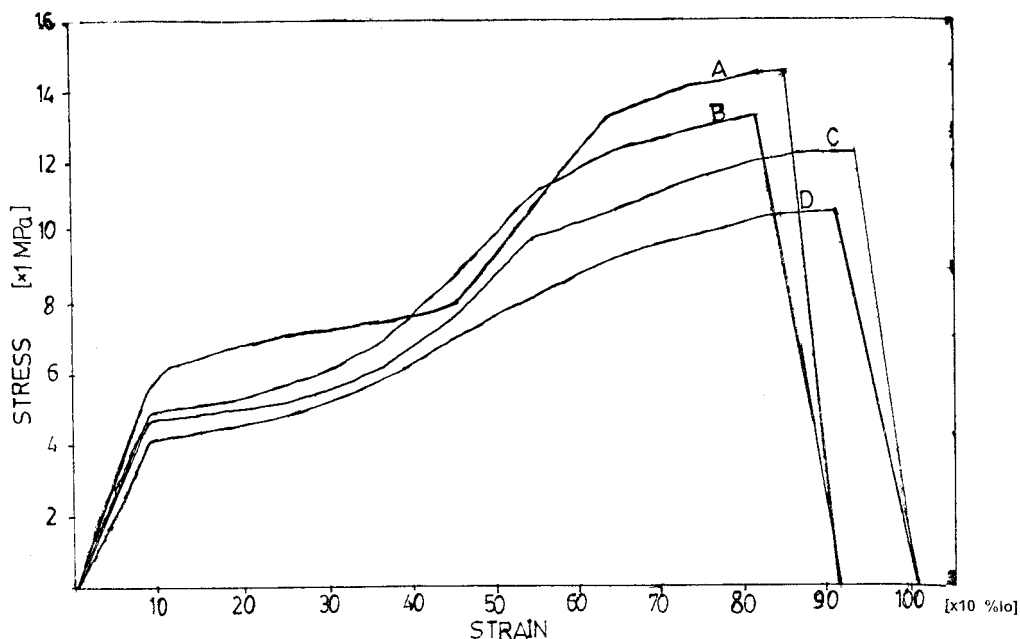
Figure 2 Stress–strain curves for the vulcanizates.

gel (V_2) all decrease as the molecular weight of LNR decreases. The molecular mass between crosslinking (M_c) increases from base mix A to mix D, implying that the vulcanizates with LNR are characterized by increased crosslinking. However, the parameters that were observed have not shown any of the vulcanizates to be inferior, despite the variation of LNR in the mixes.

The solubility results shows that the samples dissolve more readily in toluene and carbon tetrachloride than in acetone, but are sparingly soluble in ethanol and methanol. The 8600 MW LNR shows more solubility in all the solvents followed

by the 18,500 MW LNR, whereas the 26,600 MW LNR and the NR were only fairly soluble. This solubility result indicates that toluene and carbon tetrachloride swell the LNR more than they swell NR. The extent of solubility of the vulcanizates decreases from acetone to ethanol and methanol. It was also noticed that after swelling the samples for 6 h and redrying them in a vacuum chamber, the weights recorded were lower than the original weight of the samples, which could be attributable to some samples possibly having gone into solution. Surprisingly, maintaining the samples in toluene and carbon tetrachloride longer than

Table VII   Physicomechanical Properties of the Vulcanizate

Parameter	A	B	C	D
Tensile strength (MPa)	14.4	13.1	12.4	10.6
Modulus at 50% elongation (MPa)	2.0	1.6	1.2	1.4
Modulus at 100% elongation (MPa)	6.0	4.9	4.7	4.1
Elongation at break (%)	830	880	950	920
Shear modulus (G) in MN/m^2	0.4350	0.4240	0.4228	0.4010
Crosslinking density ($\rho/M_c) \times 10^{-4}$	1.6	1.5	1.5	1.4
Molecular mass between crosslinking (M_c)	5.50	5.90	5.80	6.10
Volume fraction of rubber (V_2)	0.8	0.7	0.7	0.6
Initial plasticity (P_0)	43	40	38	37
Plasticity after aging for 30 min (P_{30})	34	29	28	25
Plasticity retention index (PRI)	79.06	72.50	73.68	67.57
Mooney viscosity ML(1+4) at 100°C	84	79	77	72

6 h turns the solution to slurry, which could have been caused by the extent of crosslinking in the vulcanizates.

CONCLUSIONS

This work has established that the average molecular weight of natural rubber latex can be reduced to as low as 21% of its original average molecular weight by using nitrobenzene as the depolymerizing agent. These lower average molecular weight rubbers were found to be readily soluble in solvents such as carbon tetrachloride and toluene. It was also found that at concentrations of 2.0 and 2.5% nitrobenzene, changes in the depolymerization rate of the NRL to LNR were not very significant. In addition, the blended rubber does not show any inferior properties in terms of its processability characteristics in relation to the Mooney viscosity, plasticity, plasticity retention index, shear modulus, molecular mass between crosslinking, and the crosslinking densities compared to properties of an unmodified mix.

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