

# Thermal Aging Properties and Chemical Resistance of Blends of Natural Rubber and Epoxidized Low Molecular Weight Natural Rubber

A. K. Akinlabi,<sup>1</sup> F. E. Okieimen,<sup>2</sup> A. I. Aigbodion<sup>1</sup>

<sup>1</sup>Rubber Research Institute of Nigeria, PMB 1049 Benin City, Nigeria

<sup>2</sup>Chemistry Department, University of Benin, Benin City, Nigeria

Received 17 September 2004; accepted 4 February 2005

DOI 10.1002/app.22314

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Studies into solvent resistance and aging properties of blends of natural rubber and epoxidized low molecular weight natural rubber were carried out. Vulcanization of the blends using the semi-efficient vulcanization (semi-EV) system was found to have curing advantages over conventional vulcanization (CV) and efficient vulcanization (EV) systems. The rheological properties (cure time,  $t_{90}$ , and scorch time,  $t_2$ ), solvent resistances, and aging properties of the vulcanizates were found to improve as the level of

epoxidized low molecular weight natural rubber in the blends increases. The mechanical properties of the blends were also found to be within the accepted level for NR vulcanizates. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1733–1739, 2005

**Key words:** blends; mechanical properties; rheology; vulcanization

## INTRODUCTION

Commercial interests of rubber users in having rubber materials that can combine improved processing characteristics with better resistance to solvents has greatly enhanced innovations in rubber technology.<sup>1</sup> Some of the limitations suffered by natural rubber in areas like poor resistance to oxygen and ozone, high permeability to gases, and so forth have made scientists find ways of improving and modifying these limitations.<sup>2,3</sup> It was in the light of this that Perera and colleagues<sup>4</sup> reported on a new generic family of polymers with lesser solubility problems and good processing characteristics. Epoxidation, which involves the formation of oxirane rings (epoxides) by the action of an organic peracid on a carbon–carbon double bond, has also often been documented as a way of modifying NR.<sup>5</sup> As natural rubber is epoxidized, its chemical and physical properties change according to the extent (mol %) to which modification is introduced, with the properties being more akin to those of synthetic rubbers than to NR.<sup>6</sup>

In NR compounding, various additives are added to enhance the processability of the vulcanizate<sup>7–10</sup>; the additives are mostly from petrochemical sources.<sup>11–13</sup>

The recent development about the use of modified rubbers has shown epoxidized rubbers being used as a copolymer with NR during compounding.<sup>10,14</sup> Epoxidized rubbers have been documented as having influence in segment packing density of polymers,<sup>10,15</sup> and it is hoped that the blending of NR with epoxidized low molecular weight natural rubber might increase interactions in the polymer chain segments and segment packing density of the rubber matrix, thereby affecting the transport system of the new material. This article, therefore, reports on the solvent resistance and aging properties of the blends of natural rubber with epoxidized low molecular weight natural rubber.

## EXPERIMENTAL

### Materials

Natural rubber latex from NIG 804 clone having the characteristics shown in Table I was obtained from the estates of the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City; while the crumb rubber conforming to Standard African Rubber (SAR) grade 3 having the characteristics given in Table II was also obtained from the RRIN. The reagents used in the preparation and characterization of natural rubber (NR), low molecular weight rubber (LMWNR), and epoxidized low molecular weight rubber (ELMWNR) were of analytical grades, and the rubber compounding chemicals were of the commercial grades.

Correspondence to: A. K. Akinlabi, <sup>1</sup>CIRAD-CP TA 80/16, 73 rue J-F Breton, 34398, Montpellier, France (akakinlabi@yahoo.com).

**TABLE I**  
**Properties of RRIN's NIG804 Latex Clone**

Parameters	
Total solid content, TSC (%)	45.0
Dry rubber content, DRC (%)	38.5
Mechanical stability, MST (sec)	550
Volatile fatty acids (%)	0.17

## Methods

### Production and characterization of LMWNR samples

The method described by Okieimen and Akinlabi<sup>10</sup> was adopted with slight modification, using nitrobenzene as the depolymerizing agent; the extent of depolymerization was determined by size exclusion chromatography (SEC)<sup>16</sup> and viscosity measurement using a Ubbelohde viscometer.<sup>2,10</sup> The SEC used was designed by MILLIPORE consisting of a Waters 717 plus Auto sampler, a Waters 600E system controller, a Waters 510 HPLC pump—an automatic injector, a Waters 486 UV Tunable Absorbance Detector (220nm), a Waters R1410 refractometer, and two PLGEL 30cm mixed columns with a porosity of 20 $\mu$ m. The installation was computer controlled by special software (baseline). The column temperature was fixed at 55°C. The cyclohexane flow rate was 0.81 mL/min, the injected volume 100 $\mu$ L (at a concentration of 0.2mg/mL), for the LMWNR samples, and 25 $\mu$ L for the standard solutions. Calibration was carried out with synthetic poly(*cis*-isoprene) with molecular weights of 3660, 7000, 33,900, 68,500, 108 000, 293,000, 590,000, 963,000, and 3.0 million (expressed in g/mol). Prior to injection, the solutions were filtered (porosity of 0.45 $\mu$ m).

### Production of ELMWNR

The *in situ* epoxidation method was used with formic acid (90%) and hydrogen peroxide (30%) at a reaction medium of 5°C, as described by Okieimen and Akinlabi<sup>14</sup> with slight modification to obtain about a 35% level of epoxidation. The extent of epoxidation of LMWNR was determined by titrating ELMWNR solutions with a standard hydrogen bromide solution using violet as the indicator.

### Compounding of the mixes

Recipes used for the different vulcanization systems are shown in Table III, while Table IV shows the recipe used for the blends of natural rubber and epoxidized low molecular weight natural rubber. Mixings were carried out using a laboratory two-roll mill in accordance with the method described by the American Society for Testing and Materials (ASTM) D-3184–80.

### Cure characteristics

The cure characteristics of the mixes were measured at 170°C using an Oscillating Disk Rheometer (ALPHA ODR 2000) in accordance with the ISO 3417 method. The respective cure times as measured by  $t_{90}$ , scorch times, torque, and cure rates were determined from the rheograph.

### Measurement of the Mooney viscosity

The Mooney viscosity of the sample was determined using the shearing disc viscometer model type Wallace MK III, according to ISO 289. The results were expressed in terms of ML (1 + 4) at 100°C.

### Compression set measurement

A Wallace compression set machine (Model/Ref no C2; Hz 50) was used. The compression set was designed to evaluate the extent by which the specimen fails to return to its original thickness when subjected to a standard compression load (1N) for a given period of time (24 h) at a given temperature (100°C). The difference between the original thickness and the recovered thickness was expressed as a percentage of the original thickness. This was expressed mathematically as:

$$\text{Compression set (\%)} = \frac{(t_o - t_r)100}{t_o} \quad (1)$$

where  $t_o$  = initial thickness and  $t_r$  = recovered thickness.

### Hardness test

The hardness test of rubber is the relative resistance of a surface to indentation by an indicator of a specified dimension under a specified load.<sup>17</sup> The hardness of the vulcanizate was determined by adopting the standard dead load method described in BS 903 Part A26. The standard dead load method of measurement cov-

**TABLE II**  
**Properties of Standard African Rubber (SAR) 3**

Parameters	
Dirt content retained on 45 $\mu$ m sieve (%)	0.02
Ash content (%)	0.32
Volatile matter (%)	0.40
Nitrogen (%)	0.23
Initial plasticity (P0)	36
Plasticity after aging for 30 min at 140°C (P30)	24
Plasticity retention index (PRI)	67
Mooney viscosity ML (1+4), 100°C	70

**TABLE III**  
Recipe for Three Different Vulcanization Systems

Compound component	(phr) <sup>a</sup>	(phr) <sup>b</sup>	(phr) <sup>c</sup>
Natural rubber	70	70	70
ELMWRN (30% epoxide)	30	30	30
Zinc oxide (ZnO)	5.0	2.0	3.0
Carbon black (HAF)	40	40	40
Sulphur	2.5	0.5	1.5
Stearic acid	0.7	1.5	1.0
Dibenzothiazyl disulphide (MBTS)	-	-	1.5
CBS	0.5	2.5	-
TMTM	-	1.0	-
Flectol H (antioxidant)	2.0	2.0	2.0

<sup>a</sup> Conventional vulcanization system (CV).

<sup>b</sup> Efficient vulcanization system (EV<sub>2</sub>).

<sup>c</sup> Semi-efficient vulcanization system (semi-EV).

CBS = N-cyclohexylbenzothiazole-2-sulphenamide.

TMTM = Tetramethylthiuram monosulphide.

Flectol H = Polymerized 1,2 dihydro-2,2,4-trimethyl quinolene.

ers rubbers in the range of 30 to 85 International Rubber Hardness Degrees (IRHD).

#### Abrasion resistance

A Wallace Akron abrasion tester was used in accordance with the BS method.<sup>18,19</sup> The angle between the test specimen and the wheel was adjusted to an angle of 15°. The abrasion was carried out for four 1000 revolutions, and the material loss for each run was noted. The specimen was re-weighed between each test run. From the mean of the five runs, the volume of rubber loss per 1000 revolutions of the abrasive wheel was calculated.

The results were expressed as:

$$\text{Abrasion resistance index} = \frac{[S]100}{T} \quad (2)$$

where S = volume loss per 1000 revolutions of abrasive wheel, calculated from the mean of 5 runs on standard rubber, and T = volume loss per 1000 revo-

lutions of abrasive wheel, calculated from the mean of 5 runs on the sample rubber.

#### Mechanical properties

The test specimens were molded in an electrically heated hydraulic press (TECHNO LOIRE) at 164°C for 4 min by using the cure time,  $t_{90}$ , obtained from the rheograph. Tensile properties of the vulcanizates were measured with a Mosanto Tensile Tester Model (1/M) at a crosshead speed of 500mm/min using a dumbbell test specimen (Type II) as contained in ASTM D-412-87 (method A).

#### Swelling experiments

The resistance of the vulcanizates in toluene, carbon tetrachloride, acetone, ethanol, methanol, and *n*-hexane were determined by using the methods described in ASTM D3610<sup>20</sup> with slight modification, while the resistance of vulcanizates in mineral oil was determined by using the method described by De and De.<sup>21</sup>

**TABLE IV**  
Recipe for Preparation of Blends of NR/ELMWRN Using Semi-EV Vulcanization System

Compound component (phr)	Samples			
	A	B	C	D
Natural rubber	100	90	80	70
ELMWRN (30% epoxide)	-	10	20	30
Zinc oxide (ZnO)	3.0	3.0	3.0	3.0
Carbon black (HAF)	40	40	40	40
Sulphur	1.5	1.5	1.5	1.5
Stearic acid	1.0	1.0	1.0	1.0
Dibenzothiazyl disulphide (MBTS)	1.5	1.5	1.5	1.5
Flectol H (antioxidant)	2.0	2.0	2.0	2.0

Flectol H = Polymerized 1,2 dihydro-2,2,4-trimethyl quinolene.

TABLE V  
Results of the Oscillating Disc Rheometer

Vulcanization systems	$t_1$ (m)	$t_2$ (m)	$t_{90}$ (m)	$M_L$ Nm	$M_H$ Nm	ODRT Nm	CR (%/min)
CV	0.52	1.05	5.26	4.30	13.33	12.43	23.75
EV	0.48	0.59	4.46	4.58	13.16	12.30	25.84
Semi-EV	0.50	1.25	4.03	4.60	7.73	7.42	35.97

$t_1$  is the time in minutes to an increase of 1 unit of torque above  $M_L$ .

$t_2$  is the time in minutes to an increase of 2 units of torque above  $M_L$ .

$t_{90}$  is the cure time in minutes. This corresponds to the torque obtained.

$M_L$  is the minimum torque N.m.

$M_H$  is the maximum torque N.m.

ODRT is the Oscillating Disc Rheometer Torque and calculated using the formula:  $90(M_H - M_L) + M_L 100$ .

Cure rate is calculated using the formula  $100/(t_{90} - t_2)$  (%/min).

Three different shapes of the cured sample (triangle, square, and rhombus) were cut from the 1mm thickness mold and weighed before submerging each sample in its respective solvent in airtight bottles maintained at 25°C for 72h. Experiments were carried out in triplicate. At the end of the swelling, the sample was removed from the solvent and carefully blotted to remove excess liquid on the surface; the weights were immediately taken. Thereafter, the sample was further dried to a constant weight. The percentage increases in weight of the sample were calculated as the swelling, while the percentage loss in weight after drying to a constant weight was calculated as the solubility.

$$\% \text{ Swelling} = \left( \frac{W_2 - W_1}{W_2} \right) \times 100 \quad (3)$$

$$\% \text{ Solubility} = \left( \frac{W_1 - W_3}{W_1} \right) \times 100 \quad (4)$$

where  $W_1$  is the initial weight of the sample,  $W_2$  is the weight after swelling, and  $W_3$  is the weight after drying to a constant weight.

#### Crosslink density

The chemical crosslinking density ( $\rho RT/Mc$ ) was calculated from the shear modulus ( $G$ ), while the molecular mass between crosslinks was calculated using the Flory–Rehner equation:<sup>22</sup>

$$\ln(1 - V_2) + V_2 + \chi V_2^2 + \rho V_1 V_2^{1/3} / Mc = 0 \quad (5)$$

where  $\rho$  was the density of the rubber hydrocarbon,  $V_1$  was the molar volume of the solvent,  $V_2$  was the volume fraction of rubber in the swollen sample,  $Mc$  was the molecular weight between crosslinking, and  $\chi$  was the polar–solvent interaction parameter given as ( $\chi = 0.44 + 0.18V_2$ ).

$$\text{Crosslinking densities } (\rho/Mc) = G/RT \quad (6)$$

#### Aging properties of the vulcanizates

An air-oven aging testing was carried out in a precision oven with forced circulating air at the required temperature (30, 40, 50, 60, and 70°C) for 48h in accordance with the modified ASTM D-1870.<sup>23,24</sup> Test samples used for tensile-mechanical properties were cut from the dumbbell specimen. Properties measured on the fresh samples were also measured on the aged samples.

## RESULTS AND DISCUSSION

The rheological characteristics of the three vulcanization systems highlighted in Table III are given in Table V. The higher cure rate results observed in the semi-EV system might have been enhanced by the formation of rubber-bound intermediates and their conversion to crosslink. This same phenomenon has been documented as having a significant role in the efficiency of semi-EV systems at high vulcanizing temperatures.<sup>25</sup> In natural rubber processing, low cure time ( $t_{90}$ ) and high scorch time ( $t_2$ ) systems are considered based on the processing advantages in time gained.

The higher cure time values observed in the conventional vulcanization system could have resulted from the reaction of the sulfur, from the additives (oxidation of sulfides) with the epoxides causing ring openings of the epoxide groups, which might have led to ether crosslinks and consequently have resulted in the material having a high cure time and high ODR torque. This observation was very similar to the findings of some previous researchers.<sup>6,26,27</sup> Baker and coworkers<sup>6</sup> earlier suggested that besides the predominantly polysulphidic crosslinks, the high sulfur vulcanizates harden rapidly due to the acidic byproducts containing sulfur, resulting in an increase in cure time.

The semi-EV system showed the smallest ODR torque with the highest cure rate, while the conventional vulcanization system showed the highest ODR



TABLE VI  
Physico-Mechanical Properties of the Vulcanizates

Parameters	A	B	C	D
Tensile strength (Mpa)	15.7	14.0	13.2	13.0
Modulus at 50% elongation (MPa)	2.2	1.8	1.5	1.4
Modulus at 100% elongation (MPa)	6.0	4.6	4.3	4.1
Elongation at break (%)	890	910	950	987
Crosslink density ( $\times 10^{-4}$ )	1.3	1.4	1.6	1.6
Hardness (IRHD)	58	54	54	54
Compression set (%)	42	42	42	42
Abrasion resistance (%)	61	58	56	56
Mooney viscosity ML (1 + 4) at 100°C	82	76	75	72

torque values and the smallest cure rates, and the efficient vulcanization system was in between the CV and semi-EV.

The physicomechanical properties of the vulcanizates compounded with the recipes in Table IV are shown in Table VI. The tensile strength varies from 15.7Mpa for mix A to 13.0Mpa for mix D, which shows a decrease in the value of tensile result as the composition of ELMWNR in the blend increases. The modulus at 50% elongation and the 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 least values. The result of the elongation at break was opposite to what was observed in the tensile result. The smallest value observed was for base mix A and the highest value observed was for mix D, implying that ELMWNR must have enhanced the elasticity of the vulcanizate.

The crosslinking density result was found to increase as the composition of ELMWNR in the blends increases. The hardness and abrasion resistance values of mix A were found to be the highest, giving an indication that ELMWNR has not impacted any hardening properties on the vulcanizates; rather, it has had a plasticizing effect. Effects of plasticizers on natural rubber mix have been earlier documented by some researchers,<sup>28-30</sup> where it was mentioned that plasticizers enhance uniform distribution and dispersion of filler in the rubber matrix. This was in line with the crosslink density result and the result of the compression sets, which show nearly the same values for all the vulcanizates.

The swelling results in Table VII show that the vulcanizates have more affinities for toluene and carbon tetrachloride, followed by acetone and *n*-hexane, but showed slight solubility in ethanol and methanol. Mix A (NR) swells most in all the solvents with the trend reducing as the concentration of the ELMWNR increases, that is, from mix A to mix D, suggesting that ELMWNR improved the resistance of the blends to solvents through uniform distribution and dispersion of fillers in the rubber matrix, giving rise to a well crosslinked vulcanizate. Swelling of natural rubber has been documented to be influenced by various

factors, such as crosslink type and density, amount and type of filler, and type of elastomer.<sup>10,31</sup> The swelling results shown in Table VII reduce with an increase in the level of ELMWNR, suggesting an ether crosslink resulting from the ring-opening of epoxide groups from the ELMWNR. The results shown in Table VII are in line with the previous works<sup>14,26,31,32</sup> on epoxides, confirming that epoxides offer unique properties, such as good oil resistance, low gas permeability, improved wet grip, and rolling resistance, coupled with high strength. In fact, the oil resistance of ENR (50% epoxide) was reported to approach that of medium-acrylonitrile-content nitrile rubber (NBR) and surpass that of chloroprene rubber.<sup>26,31</sup> It is worth mentioning that swelling the samples for longer periods (96h and above) in toluene and carbon tetrachloride showed vulcanizates A and B turning into slurry, which could have still been caused by low crosslinking as compared to vulcanizates C and D.

#### Aging results

The aging results are presented as percentage change in the properties of the vulcanizates, using the expression below:

$$\text{Extent of aging} = \left[ \frac{[O - A]}{O} \right] \times 100 \quad (7)$$

where O is the original value for the fresh sample and a is the value after aging.

The results of the physicomechanical properties of the vulcanizates after aging at 70°C for 48h were compared with their unaged results and are presented in Table VIII. The aging results at 30, 40, 50, and 60°C were not discussed because of marginal changes in the values when compared with the unaged.

The aging results shown above indicate that as the concentration of the epoxidized low molecular weight natural rubber in the blends increases, the aging properties improve. It can be seen that the percentage aging values for parameters with higher compositions of ep-

TABLE VII  
Swelling Results

Solvents	Samples	$W_1$	$W_2$	$W_3$	% swelling	% solubility
Toluene	A	0.34120	0.40978	0.31919	20.10	6.45
	B	0.38610	0.45869	0.36212	18.80	6.21
	C	0.37240	0.43347	0.35598	16.40	4.41
	D	0.35160	0.39977	0.33817	13.70	3.82
Carbon tetrachloride	A	0.31240	0.38144	0.29194	22.10	6.55
	B	0.38800	0.46327	0.36460	19.40	6.03
	C	0.34810	0.40658	0.33129	16.80	4.83
	D	0.36730	0.42019	0.35169	14.40	4.25
Acetone	A	0.35210	0.41164	0.33235	16.91	5.61
	B	0.36620	0.41871	0.34782	14.34	5.02
	C	0.35460	0.39144	0.34393	10.39	3.01
	D	0.37160	0.40285	0.36116	8.41	2.81
Ethanol	A	0.34170	0.38431	0.32280	12.47	5.53
	B	0.36240	0.40339	0.34287	11.31	5.39
	C	0.34010	0.36568	0.32911	7.52	3.23
	D	0.31990	0.33586	0.31049	4.99	2.94
Methanol	A	0.35520	0.40027	0.33705	12.69	5.11
	B	0.37270	0.41045	0.35447	10.13	4.89
	C	0.34620	0.37050	0.33744	7.02	2.53
	D	0.33310	0.35045	0.32541	5.21	2.31
n-Hexane	A	0.35640	0.39754	0.33666	11.54	5.54
	B	0.38240	0.42073	0.36317	10.02	5.03
	C	0.36910	0.40104	0.36028	8.65	2.39
	D	0.37210	0.39240	0.36440	5.46	2.07
Mineral oil	A	0.37940	0.39049	0.36831	2.92	1.32
	B	0.36480	0.37531	0.35429	2.88	1.15
	C	0.39130	0.39733	0.38527	1.54	0.94
	D	0.38840	0.39301	0.38379	1.19	0.89

$W_1$  is the weight after extraction.

$W_2$  is the weight after swelling at 25°C for about 6 hrs.

$W_3$  is the weight after drying in a vacuum to a constant mass.

oxidized low molecular weight natural rubber were found to be the lowest, and this increases as the composition of ELMWNR in the blends reduces. The observed trend suggests epoxidized low molecular weight natural rubber to have good aging properties, which is an improvement over the aging limitations of natural rubber.

## CONCLUSIONS

The results of this study have shown that solvent resistance and aging properties of natural rubber have

been improved by blending NR with 30phr of ELMWNR (35% epoxide). In addition, there were improvements in the rheological properties of the vulcanizate with blends of ELMWNR. Above all, the physicochemical characteristics of the vulcanizate blends were well compared with natural rubber (mix A).

The authors are grateful to the authorities of the French Embassy in Nigeria for funding part of this project; and to the Center de Cooperation Internationale en Recherche Agronomique pour le Development (CIRAD)-CP, Montpellier.

TABLE VIII  
Aging Results of Blends of Natural Rubber with Epoxidized Low Molecular Weight Natural Rubber at 70°C for 48h  
(% of original sample values)

Parameters	A (%)	B (%)	C (%)	D (%)
Tensile strength (Mpa)	6.8	6.1	4.2	3.4
Modulus at 50% elongation (MPa)	5.9	5.2	4.0	3.4
Modulus at 100% elongation (MPa)	5.7	5.5	4.8	3.8
Elongation at break (%)	10.9	9.2	8.6	7.4
Hardness (IRHD)	4.0	3.0	3.0	3.0
Compression set (%)	3.0	3.0	3.0	3.0
Abrasion resistance (%)	7.4	6.3	4.4	4.2
Mooney viscosity ML (1 + 4) at 100°C	8.8	7.5	6.4	5.8

lier, France, and the Rubber Research Institute of Nigeria, Benin City, Nigeria, for the use of their laboratory facilities.

## References

1. UNCF. Report on Quality Control and Quality Improvement of African Natural Rubber; United Nations Common Fund for Commodities: Abidjan, 1996.
2. Okieimen, F. E.; Wepuaka, A.; Akinlabi, A. K. *Nigerian J Appl Sci* 1991, 9, 113.
3. Abraham, D.; Geroge, K. E.; Francis, D. J. *Polymer* 1998, 39, 117.
4. Perera, M. C. S.; Elix, J. A.; Bradbury, J. H. *J Polym Sci* 1988, 26, 637.
5. Aigbodion, A. I.; Menon, A. R. R.; Pillai, C. K. S. *J Appl Polym Sci* 2000, 77, 1413.
6. Baker, C. L. S.; Gelling, I. R.; Newell, R. *Rubber Chem Technol* 1985, 58, 67.
7. Amin, M. U.; Scott, G. *Eur Polym J* 1974, 10, 1019.
8. Menon, A. R. R.; Pillai, C. K. S.; Nando, G. B. *J Appl Polym Sci* 1994, 51, 4033.
9. Nguyen, V. B.; Levon, T.; Marin, M. *J Appl Polym Sci* 1993, 56, 845.
10. Okieimen, F. E.; Akinlabi, A. K. *J Appl Polym Sci* 2002, 85, 1070.
11. Aigbodion, A. I.; Bakare, I. O.; Okieimen, F. E.; Akinlabi, A. K. *Indian J Chem Technol* 2001, 8, 1.
12. Cole, O. D. *Natural Rubber: Introduction to Rubber Technology*; Morton, M., Ed.; Reinhold Publ. Corp.: New York, 1966, 66.
13. Lu, G.; Li, Z.-F.; Li, S.-D.; Xie, J. *J Appl Polym Sci* 2002, 85, 1736.
14. Okieimen, F. E.; Akinlabi, A. K.; Aigbodion, A. I.; Bakare, I. O., *J Polym Mat* 2003, 20, 403.
15. Siddaramaiah, S.; Roopa, S.; Premakumar, U. *Polymer* 1998, 39, 3925.
16. Bonfils, F.; Koman Achi, A.; Sainte Beuve, J.; Sylla, X.; Allet Don, A.; Laigneau, J. C. *J Nat Rubber Res* 1995, 10, 143.
17. British Standards-903, Determination of Natural Rubber Hardness, Manual for Natural Rubber Testing Methods, Part 26A, British Standard Organization, Ed.; London: England, 1995.
18. Wallace, W. H.; Abrasion Resistance Manual In Wallace Test Equipment Manual R12; Wallace & Co.: Croydon, England, 1981.
19. British Standards-903, Determination of Abrasion Resistance, In Manual for Natural Rubber Testing Methods, Part A9; British Standard Organization, Ed.; England, 1988.
20. American Standard Testing Methods-D3610, Special Technical Bulletin for Swelling, In Annual Book of ASTM Standard Section, ASTM Standard Section, Ed.; West Conshohocken, PA, Vol. 9, 1989.
21. De, P. P.; De, S. K.; Alex, K. *J Polym Sci Part C* 1989, 27, 361.
22. Flory, P.; Rehner, J. *J Chem Phys* 1943, 11, 521.
23. American Standard Testing Methods-D1870, Special Technical Bulletin for Swelling, In Annual Book of ASTM Standard Section, ASTM Standard Section, Ed.; West Conshohocken, PA, Vol. 9, 1989.
24. Buzaré, J. Y.; Silly, G.; Emery, J.; Boccaccio, G.; Rouault, E. *Eur Polym J* 2001, 37, 85.
25. Morison, N. J. *Rubber Chem Technol* 1984, 57, 86.
26. Gelling, I. R.; Porter, M. In *Natural Rubber Science and Technology*; Roberts, A. D., Ed.; Oxford University Press: Oxford, 1988; p 359.
27. Amu, A.; Dulangali, S.; Gelling, I. R. Latest Developments in Epoxidized Natural Rubber, Singapore PLAST 1986, 37, 85.
28. Tang, F.; Dizhen, W.; Dongshan, L. *China Rubber Industry* 1998, 45, 711.
29. Thomas, G. V.; Gopinathan, N. M. *R. J Appl Polym Sci* 1998, 64, 785.
30. Nair, N. R.; Mathew, N. M.; Thomas, V.; Chatterjee, P.; Sidiqi, M. A. *J Appl Polym Sci* 1998, 68, 53.
31. Ismail, H.; China, H. H. *Eur Polym J* 1998, 34, 1857.
32. Bac, C. L. S.; Mihailov, M.; Terlemezyan, M. *Eur Polym J* 1991, 27, 557.