

Cure Characteristics and Physico-Mechanical Properties of Blends of Epoxidised Natural Rubber and Polystyrene

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Abstract. Studies in the processing characteristics and physico-mechanical properties of blends of epoxidised natural rubber (ENR) and polystyrene (PS) were carried out using various ratios of their compositions of (100:0, 95:5, 90:10, 85:15, 80:20, 75:25 and 70:30 w/w of epoxidized natural rubber). Epoxidised natural rubber (35% epoxide level) was obtained by reacting natural rubber with peroxyformic generated in situ, using formic acid and hydrogen peroxide. The 35% ENR obtained showed a lower scorch time and cure rates. The blends of ENR with PS (90:10 w/w) showed better physico-mechanical properties in terms of the: tensile strength, elongation at break, hardness, compression set, Plasticity Retention Index (PRI), Mooney viscosity while blends of ENR with PS (95:05 w/w) were very resistance to mineral oil and some organic solvents. However, substitution of ENR with more than 20% of PS showed deleterious effects on the cure characteristics and physico-mechanical behaviour of the vulcanisates.

Keywords: physico-mechanical properties, blends, epoxidised, natural rubber, polystyrene

Introduction

Natural rubber has long been recognized as a major raw material for the production of various consumer-rubber products, such as automobile tyres and tubes, latex-dipped goods like surgical gloves, hoses, and natural rubber foams, etc. (Okieimen *et al.*, 1991; UNIDO, 1989). The attainment of a good quality product from rubber material lie depends in the choice and characteristics of the raw materials used. (UNIDO, 1989). If the raw material is adulterated or inferior, the desirable characteristics are difficult to be attained. There is a need, therefore, to study and improve the procedures to modify natural rubber with other synthetic polymers. Polymers can be broadly grouped into natural or synthetics categories. Natural polymers include proteins, polysaccharides, gums and elastomers, while the synthetic polymers include plastics (thermo-plastics and thermosets), non-biological elastomers and fibres (Okieimen *et al.*, 1991). Plastics are the materials which deform under stress and retain the deformation when the stress is removed. An example of plastic is styrene ($\text{CH}_2 = \text{CHPh}$), which is a petrochemical-based polymer (Daniel *et al.*, 1989).

Technological innovations in rubber processing are increasing rapidly and a great deal of commercial interest is being placed on the blends of rubber that can combine improved processing characteristics with good solubility parameters in solvents (UNIDO, 1989). Modification of natural rubber (NR) by the inclusion of various additives to enhance the processability of the vulcanisate has been well established

Menon *et al.*, 1994; Nguyen *et al.*, 1993; Amin and Scott, 1974). The additives used are mostly from petrochemicals sources, which tend to modify the properties of the rubber. (Challioui-Gillet, 1994; Elhamdaoui, 1991). Perera *et al.* 1988) reported that some new generic family of polymers, obtained by modifying natural rubber through epoxidation has lesser solubility problems and good processing characteristics. Epoxidation, which is the formation of oxirane rings (epoxides) by the action of an organic peracid on a carbon-carbon double bond ($\text{C}=\text{C}$), can provide materials with added value that can give the desired properties for specific applications (Aigbiodion *et al.*, 2000).

This study is aimed at determining the processing and physico-mechanical properties of the vulcanisate made from combining a petrochemical-based polymer (polypropylene) with epoxidised natural rubber (ENR). The paper reports on the processing characteristics and physico-mechanical properties of blends of ENR and various ratios of polypropylene, with the expectation that the results will make NR to have more diverse applications and minimize the use of heavy equipment associated with NR processing.

Materials and Methods

Materials. The natural rubber latex (NRL) used was obtained from the NIG -804 clonal series of Rubber Research Institute of Nigeria. Crumb natural rubber, conforming to Standard African Rubber (SAR) grade 3, was obtained from the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City. Reagents used in the preparation and characterization of natu-

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ral rubber (NR) and epoxidised natural rubber (ENR) were of analytical grade, while the rubber compounding chemicals used were of commercial grades. Polystyrene (PS) was obtained from the Nigerian National Petroleum Corporation, Warri.

Production of crumb rubber. Crumb rubber was obtained by following the method described by the Professional Association of Natural Rubber in Africa (PANRA, 1998) with slight modification as reflected by Akinlabi (1996). In a typical procedure, the natural rubber latex was coagulated with formic acid, washed and cut into smaller units before drying in air-circulated oven at 100 °C for 3 h.

Production of ENR. The NR obtained as described above (production of crumb rubber) was epoxidised using *in situ* method (Aigbodion *et al.*, 2000; UNIDO, 1989). The temperature of the medium was about 5 °C. Formic acid (90%) was added to NR over a period of time with gentle stirring. Hydrogen peroxide (30%) was added dropwise while stirring. The reaction was left for further 3 h before raising the temperature of the medium to about 55 °C in order to coagulate the product. The ENR produced was washed with distilled water severally till acid-free and then dried at 70 °C.

The extent of epoxidation of NR was determined by titrating ENR solutions with a standard hydrogen bromide solution using violet as indicator. This method was found to achieve about 35% level of epoxidation.

Cure characteristics. The cure characteristics of the mixture were measured at 170 °C using an oscillating disk rheometer (Alpha ODR 2000) in accordance to ISO 3417 method (ISO 3417, 1998).

Measurement of plasticity. The initial plasticity (P^0) of the mixes and the plasticity after ageing in the plastimeter oven for 30 min (P^{30}) at 140 ± 2 °C were measured using Mark IV Wallace rapid plastimeter. The plasticity retention index (PRI) was calculated according to ISO 2930 (1998).

Mechanical properties. The test specimens were molded in an electrically heated hydraulic press (Tecno Loire) at 174 °C. Tensile properties of the vulcanisates 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 per ASTM method A (ASTM D-412-87, 1992).

Crosslinking density. The chemical crosslinking density of the vulcanisate was determined by following the procedure of equilibrium swelling in toluene (Okieimen and Akinlabi, 2002; Akinlabi *et al.*, 2000). The volume fraction of the rubber in swollen gel V_2 was calculated using the following expression.

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

where:

D = the deswollen mass of test piece

T = the mass of test piece after acetone extraction and drying

E = the mass fraction of acetone extractable material in the test piece

S = the swollen mass of test piece

F = the mass fraction of added non-rubber ingredients

ρ_{rh} = the density of the vulcanisate network

ρ_s = the density of the swelling liquid

The chemical crosslinking density was calculated using the Flory-Rhener equation (Flory and Rhener, 1943).

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

where:

ρ = the density of the rubber hydrocarbon

V_1 = the molar volume of the solvent

V_2 = the volume fraction of rubber in the swollen sample

Mc = the molecular weight between crosslinking and is related to the shear modulus (G) by the following expression (Okieimen and Akinlabi, 2002; Akinlabi *et al.*, 2000):

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

χ = the polar-solvent interaction parameter given as

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

Measurement of the Mooney viscosity. The Mooney viscosity of the sample was determined using the shearing disc viscometer according to ISO 289 (1998). The results were expressed in terms of ML (1 + 4) at 100 °C.

Solubility tests. The rates at which the mixes swell in solvents such as, toluene, carbon tetrachloride, acetone, ethanol and methanol were determined according to ASTM method (ASTM D-3610, 1992).

Results and Discussion

Preparation of ENR/PS blends. The blends of ENR/PS were prepared in a banbury mixer using the recipe as given in Table 1. The results of the cure characteristics of the mixes are shown in Table 2. It may be concluded from the results obtained that ENR had the least cure time of 4.22 min. it was also observed that as the level of polystyrene concentration in the mixtures increased, the cure time also increased. This shows that polystyrene increases the cure time of ENR vulcanisates. This observed trend could have resulted from the plasticising nature of polystyrene.

The results of the rheometry torque Table 2 show that blends with 10% polystyrene had the highest torque of 12.18 N.m. Higher concentration of polystyrene above the 20% concentration resulted in low rheometry torque. This observation gave an indication that mixtures with higher concentration (above 20% PS) may result in poor mechanical behaviour.

Results of the physico-mechanical properties of the mixes are shown in Table 3. It may be noted from the obtained results that the tensile strength ranged from 16.3 Mpa for mixture A to 9.4 Mpa for mixture G, showing a 42.3% decrease in the tensile strength of the mixture with increasing PS content. The 50% and 100% elongations were found to be decreasing as the concentration of PS in the mixtures increased. The results for the elongation at break also revealed that there was decrease with increasing PS concentration.

Table 1. Recipe for the preparation of epoxidised natural rubber polystyrene (ENR/PS) blends

Compound components (PPhr)	Sample mixture						
	A	B	C	D	E	F	G
35% ENR	100	95	90	85	80	75	70
PS	-	5	10	15	20	25	30
(ZnO)	6	6	6	6	6	6	6
Sulphur	2	2	2	2	2	2	2
Stearic acid	3	3	3	3	3	3	3
MBT	1	1	1	1	1	1	1
CB (HAF)	40	40	40	40	40	40	40
Flectol H	2	2	2	2	2	2	2

PPhr = parts per hundred; PS = Polystyrene; MBT = mercaptobenzothiazole; C B = carbon black; HAF = High abrasion furnace; Flectol H = polymerized 1, 2-dihydro-2,2,4-trimethyl quinolene.

Several workers (Aigbodion *et al.*, 2000; PANRA, 1998; Akinlabi, 1996; Perera *et al.*, 1988) have attributed this flexibility and elasticity of NR to the presence of double bonds in *cis*-1,4 polyisoprene. Thus, the high elongations observed for the mixtures with higher percentage of ENR were in accordance with the observations of previous workers.

The shear modulus, molecular mass between crosslinking and volume fraction of rubber in the swollen gel were found to reduce as the concentration of PS in the mixtures increased, while the crosslinking densities increased. The results for crosslinking density suggest that materials with higher concentration of ENR were more crosslinked. The result of the volume fraction of rubber confirms that mixtures with higher concentration of ENR have more rubber present in the vulcanisate. The results of the physical parameters, *viz-a-viz*, the plasticity, hardness, abrasion resistance and compression set shown in Table 3 were found to increase as the concentration of PS increased. This clearly shows that PS, being a plastic, has impacted some of its plasticity properties on the ENR thereby enhancing the physical parameters of the vulcanisate blends.

The solubility results in Table 3 show that vulcanisates with higher concentration of PS were more resistance to solvents. Generally, in the material selection, manufacturers and engineers always prefer using materials that have processing advantage in terms of cost reduction while still retaining the anticipated properties of the product(s) developed from the material. Bearing this in mind, it can be concluded that formulations B and C possessed good physico-mechanical properties in addition to their lower cure times. Their resistance to solvents were also encouraging. It can, therefore, be suggested that if a product is to be made from epoxidised natural rubber, consideration should be given, when selecting the

Table 2. Results of the oscillating disc rheometer

Mixture* (min)	Ts ¹ (min)	Ts ² (min)	Ts ¹⁰ (min)	Ts ⁵⁰ (min)	T ⁹⁰ (min)	ML (N.m)	MH (N.m)	RT (N.m)
A	0.46	0.60	0.47	1.28	4.22	4.16	12.60	11.76
B	0.51	0.58	0.46	1.37	4.44	4.34	12.84	11.99
C	0.47	0.94	0.49	1.40	4.63	4.24	13.06	12.18
D	0.50	1.19	0.51	2.19	5.06	4.61	12.95	12.12
E	0.98	2.54	0.96	2.98	5.12	4.54	12.01	11.26
F	0.48	2.11	0.48	2.54	5.26	4.63	11.00	10.36
G	0.50	2.43	0.50	2.02	5.39	4.44	11.41	10.71

* = refer Table 1 for the composition of the mixtures; Ts¹ = the time in minutes to an increase of 1 unit of torque above ML; Ts² = the time in minutes to an increase of 2 units of torque above ML; Ts¹⁰ = the time in minutes to an increase of 10 units of torque above ML; Ts⁵⁰ = the time in minutes to an increase of 50 units of torque above ML; T⁹⁰ = the cure time in minutes; ML = the minimum torque (N.m); MH = the maximum torque (Nm); RT = rheometry torque, which was calculated using the formula: $90(MH - ML) + ML/100$; N.m = newton meter.

Table 3. Physico-mechanical properties of vulcanised epoxidised natural rubber/polystyrene (ENR/PS) blends

Parameters	Mixtures						
	A	B	C	D	E	F	G
Tensile strength (MPa)	16.3	16.7	17.6	14.8	12.5	10.2	9.4
50% elasticity (MPa)	2.0	2.0	2.0	1.8	1.7	1.4	1.4
100% elasticity (MPa)	5.4	5.5	5.5	5.1	4.1	3.2	2.4
Elongation at B (%)	673	552	540	503	425	374	362
S. m.	0.371	0.376	0.365	0.354	0.325	0.320	0.300
C.L	1.6	1.5	1.5	1.3	1.3	1.2	1.2
Molecular mass.	5.6	5.4	5.4	5.3	5.0	4.6	4.2
Vol. fract. of rub. (V_2)	0.8	0.7	0.7	0.6	0.5	0.5	0.4
Plast. Ret. Ind. (PRI)	65	67	67	68	69	70	70
M. vis. ML at 100 °C	70	74	75	76	78	78	80
Hardness (IRHD)	50	53	53	55	58	58	60
Compression set	44	44	44	46	46	46	46
Abrasion resistance index	52	54	55	60	62	64	65
Solubility in chloroform	733	641	618	598	555	522	505
Solubility in toluene	356	331	302	290	263	251	236
Resistance in mineral oil	152	148	143	139	120	112	103

C.L dens. (ρ/M_c) $\times 10^{-4}$ = crosslinking; S.m (G) in MN/m^2 = shear modulus; molecular mass between crosslinking (M_c); MPa = mega pascal, B = Break; S.m = Shear modulus; C.L= crosslinking density; V_2 = vol. fraction of rubber in swollen gel; PRI = Plasticity retention index; M.vis = mooney viscosity; IRHD = International rubber hardness.

raw materials, not to blend epoxidised natural rubber with more than 15% of PS if such materials, are likely to have contact with chloroform, toluene or mineral oil.

Conclusion

This work has shown that *in-situ* epoxidation of NR, using performic acid at a temperature of 5 °C produces ENR, which is softer than PS and therefore of lower tensile strength. Blending of ENR with PS affects the processability and vulcanisate properties of the ENR. Blend ratio of 85 ENR : 15 PS were found to have the best physico-mechanical properties among all the mixtures studies, while blend with 5% PS concentration showed good resistance to mineral oil and some organic solvents. Above all, the gradual replacement of ENR with PS had shown that up to 20% ENR substitution with PS did not have any serious deleterious effect on the properties of the final product(s).

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