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Effect of Part Replacement of Mercaptobenzothiazole with Locust Bean Cake on the Thermal and Electrical Conductivities of Natural Rubber Vulcanizates

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Abstract. The effect of part replacement of mercaptobenzothiazole (MBTS) with locust bean cake (LBC) on the thermodynamic parameters, thermal and electrical conductivities of natural rubber (NR) composite, was examined. Generally, all the thermodynamic parameters, the thermal conductivity and the electrical conductivity of the NR vulcanizates were altered on the inclusion of the MBTS/LBC mix in the formulations of the composites. The degree of alteration of these properties increased with increasing LBC contents in the MBTS/LBC mix. It appears that upto 50/50, MBTS/LBC mix, the lower the entropy change of the molecules of the composite, the higher was the crosslink density of the composite, and the better was the ability of the composite to conduct heat and electricity. It is, therefore, advantageous to replace MBTS with LBC upto 50% in the formulations of NR composites for improved thermal and electrical insulation.

Keyword: mercaptobenzothiazole, locust bean cake, natural rubber, thermodynamic parameters, rubber vulcanizates

Introduction

Locust bean, which is common in Nigeria particularly in the Northern and South-Western parts, has been studied extensively (Adewumi, 1997). It has been found to contain 39-40% oil, 31-40% protein, and 11.7-15.4% carbohydrates (Oladele *et al.*, 1985). The oil has been reported to be suitable for the manufacture of soap (Owoyale *et al*.,1986). It has also been established that the leaves of the locust tree are rich in nitrogen, which are used as livestock feed and as a manure. The fermented products of locust bean are used as food condiments all over Nigeria (Adewumi, 1997). Recently, Olaofe *et al.* (1998) have reported on the chemical composition and functional properties of the locust bean.

The properties of natural rubber composites accelerated with mercaptobenzothiazole (MBTS) have been studied (Adeosun *et al.*, 1997; Adu and Adeosun, 1997; Elliot, 1987; Bristow, 1986). The effect of addition of locust bean cake on the properties of natural rubber composite accelerated with MBTS have also been studied. These studies have shown that at relatively low locust bean cake concentration of ≤ 0.3 in the locust bean cake/MBTS admixture, the tensile strength and modulus of natural rubber composite improved over the conventional MBTS composite. Also, the degradation resistance of the raw rubber, before compounding for vulcanization, and the reversion resistance of the resultant natural rubber compound were noted to improve on the addition of locust bean cake.

These observations on the positive effects of locust bean cake on the properties of natural rubber have aroused interest to examine the thermodynamics of elasticity, and the electrical and thermal conductivities of natural rubber composite accelerated with locust been cake in the admixture with the conventional MBTS accelerator.

Materials and Methods

Preparatory and analytical procedures. Filler preparation, latex compounding, dry rubber composite compounding formulation (Table 1), and curing procedures were followed as reported already (Adeosun and Olaofe, 2005; Adeosun *et al.*, 1997). The determination of thermodynamic parameters of elasticity was done as described by Adeosun *et al.* (1999). The measurement of electrical conductivity was done as reported earlier (Oyeleke, 2000). Thermal conductivity measurements were done by Lee's disc apparatus. The sample thickness was determined by micrometer screw gauge. After the determination of the steady state temperature of the lower plate it was heated directly to nearly 100 ^{0}C. The sample was then placed on the plate and the temperature monitored at intervals of thirty seconds. Data obtained were used to plot the cooling curve. The gradient of the curve at the steady state temperature of the lower plate was evaluated and used in the Fourier's equation.

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Table 1. Compounding formulation of the natural rubber composites examined

Constituents	Sample code*						
	P_1	P_2	P_3	P_4	P_5	P_6	P_7
Natural rubber	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Steanic acid	3	3	3	3	3	3	3
Sulphur	1	0.8	0.6	0.5	0.4	0.2	-
MBT [a]	-	0.2	0.4	0.5	0.6	0.8	1
LBC [b]							

*constituents as ratio by parts in different compounding formulations; [a] mercaptobenzothiazole (MBT); [b] locust bean cake (LBC)

Data treatment. (a) The thermodynamic equation of the state for elastic materials was used in the form shown in equation (1) below (Das and Behera, 1983):

$$f = \left(\frac{dH}{dL}\right)_{T.P} + T\left(\frac{df}{dT}\right)_{L.P} \quad (1)$$

When the elastic material under tension f was extended by an amount dL, the plot of tension f versus absolute temperature T showed linearity (Fig. 1) with slope $\left(\frac{df}{dT}\right)_{T.P}$, and intercept $\left(\frac{dH}{dL}\right)_{T.P}$ $\left(\frac{dS}{dL}\right)_{T.P}$ was evaluated using equation (2) (Das and Behera, 1983; Wall, 1942).

$$\left(\frac{dH}{dL}\right)_{T.P} = -\left(\frac{dS}{dL}\right)_{L.P} \quad (2)$$

and $\left(\frac{dG}{dL}\right)_{T.P}$ was evaluated using equation (3):

$$\left(\frac{dG}{dL}\right)_{T.P} = \left(\frac{dH}{dL}\right)_{T.P} - T\left(\frac{dS}{dL}\right)_{T.P} \quad (3)$$

values of $\left(\frac{df}{dT}\right)_{L.P}$, $\left(\frac{dS}{dL}\right)_{T.P}$, $\left(\frac{dG}{dL}\right)_{T.P}$ and $\left(\frac{dH}{dL}\right)_{T.P}$ are shown in Table 2.

(b) Thermal conductivity was evaluated using equation (4) (Bird *et al.*, 1960):

$$K = \frac{Q}{A\,(T_1 - T_2)\,L} \; (Wm^{-1}K^{-1}) \quad (4)$$

where:
K = thermal conductivity
Q = heat flow
A = area of conducting material
L = thickness of conducting material
ΔT = change in temperature between surface within which the conducting material was enclosed

Results and Discussion

Values of $\left(\frac{df}{dT}\right)_{L.P}$, $\left(\frac{dH}{dL}\right)_{T.P}$, $\left(\frac{ds}{dL}\right)_{T.P}$ and $\left(\frac{dG}{dL}\right)_{T.P}$ of the composites examined, as evaluated by the least square method, are given in Table 2. The linear plots of tension f versus absolute temperature, using equation (1) for the composite are shown in Fig 1. The crosslink densities from the previous work on the components (Adeosun *et al.*, 1999) are also shown in Table 2.

For highly elastic rubber-like materials, $\left(\frac{df}{dT}\right)_{L.P}$ had a large positive value and the term $T\left(\frac{df}{dT}\right)_{L.P}$ predominated over the $\left(\frac{dH}{dL}\right)_{T.P}$ (equation 1). The $\left(\frac{df}{dT}\right)_{L.P}$ was, however, small and negative for materials such as steel (Das and Behera, 1983). It may be observed from Table 2 that the rubber-like nature of the natural rubber composite deteriorated steadily, reaching a minimum at 50/50 MBTS/LBC, and then improved as the concentration of LBC increased. At relatively low LBC concentration (0.2 to 0.5 parts per 100 rubber), elasticity decreased with increasing LBC concentrations, but at relatively high LBC concentrations (0.6 to 1.0 parts per 100 rubber), elasticity improved with increasing LBC concentration.

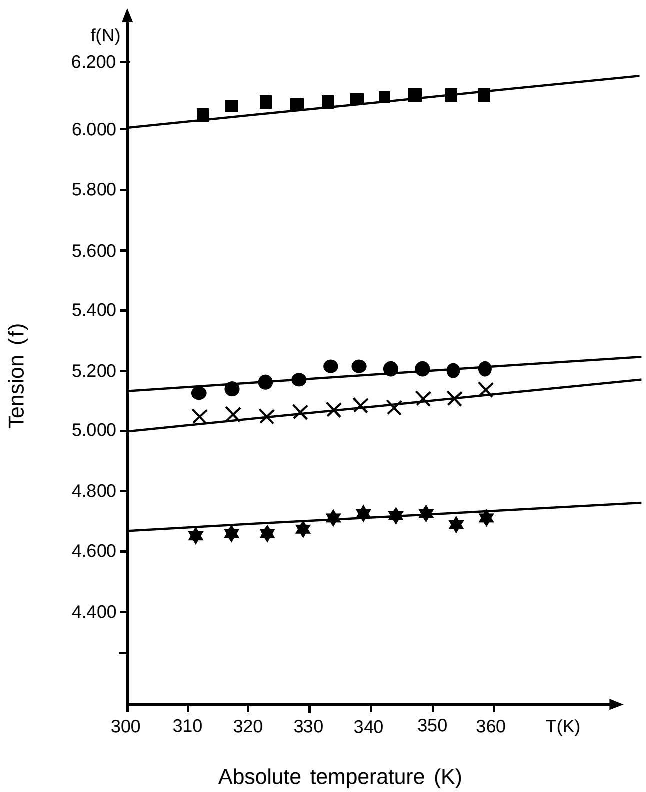

Fig. 1. Graph of tension f as a function of absolute temperature.

Table 2. Thermodynamic parameters of elasticity and thermal conductivities of the composites examined

Composite sample*	Locust bean cake : MBTS (pphr)	Elasticity $\frac{df}{dT}$ x 10^4 (J/mol)	Free energy $\frac{dG}{dL}$ x 10^4 (J/mol)	Enthalpy $\frac{dH}{dL}$ x 10^4 (J/mol)	Entropy $\frac{dS}{dL}$ x 10 (J/mol)	Crosslink density
P1	0:1.0	2.88	5.10	5.12	-2.88	5.76
P2	0.2:0.8	2.24	5.02	4.35	-2.24	5.25
P3	0.4:0.6	1.72	5.14	4.63	-1.72	5.32
P4	0.5:0.5	1.68	5.17	4.67	-1.68	3.65
P5	0.6:0.4	1.74	4.65	4.13	-1.74	5.45
P6	0.8:0.2	1.84	4.60	4.05	-1.84	5.65
P7	1.0:0	2.36	4.84	4.13	-2.36	3.55

*refer Table 1 for constituents of the composite samples; pphr: parts per hundred rubber; MBTS: mercaptobenzothiazole

Considering the entropy factor, $\left(\frac{ds}{dL}\right)_{T,P}$ results show negative values for all the composites. This is not surprising as entropy decreased (tends to a more orderly state) as the composite was extended. This happens due to the uncoiling of the long chain polymer molecules in the direction of stretching when the length was extended (Das and Behera, 1983). The change in entropy of elasticity becomes more positive as LBC concentration increased, reaching a maximum and then decreased progressively. The molecules of the natural rubber composites containing only the conventional MBTS accelerator seem more orderly than the composites containing MBTS/LBC mix. This orderliness decreased to a minimum at 50/50 composition of MBTS/LBC and then the molecules became progressively more orderly with increasing LBC concentrations. A cursory look at the change in free energy of elasticity revealed that values at relatively low LBC concentrations are observed to be more positive than at high LBC concentrations. A closer look revealed that the change in free energy increased with increasing LBC contents in the MBTS/LBC admixture, reaching a maximum at 50/50 mix and dropped thereafter. This connotes that as the LBC contents increased, the composite became progressively less spontaneous to elasticity–until the composites became more spontaneous after reaching 50/50 composite. The change in enthalpy of elasticity generally follows the same trend as the change in free energy of elasticity. The heat accompanying the composites under stress seems to increase as the spontaneity of elasticity decreased.

The variation of thermal conductivity of the composites as a function of LBC concentration is presented in Table 3. It may be observed that the thermal conductivity of the conventional composite drastically decreased from 6.07 W/m/K to 3.37 W/m/K on the introduction to the mix containing 0.2 parts per hundred rubber LBC. Also, the thermal conductivity decreased progressively, reaching a minimum and then increased as LBC concentration was further increased (but still inferior to the conventional composites in respect of conductivity). This trend connotes that the ability of the NR composites to insulate heat increased on the introduction of the MBTS/LBC mix, reaching a maximum and deteriorated thereafter. The composites containing the mix are, therefore, better heat insulators than the conventional composites with the 50/50 mix exhibiting the best ability to insulate heat.

Table 3. Thermal and electrical conductivities of the composites examined

Composite sample*	LBC: MBTS ratio (pphr)	Thermal conductivity (10) (W/m/k)	Electrical conductivity (10^4) (Ω/m)
P1	0:1.0	6.07	4.97
P2	0.2:0.8	3.37	3.39
P3	0.4:0.6	2.92	4.00
P4	0.5:0.5	2.27	3.75
P5	0.6:0.4	3.47	3.75
P6	0.8:0.2	2.73	4.12
P7	1.0:0	2.68	4.09

*refer Table 1 for constituents of the composite samples; pphr: parts per hundred rubber; LBC: locust bean cake; MBTS: mercaptobenzothiazole

The data on electrical conductivity are also presented in Table 3. It may be observed that the composite containing only the conventional MBTS accelerator had the highest ability to conduct electricity. On the introduction of the MBTS/LBC mix, electrical conductivity dropped and decreased progressively as the concentration of LBC in the mix increased, reaching a minimum and thereafter increased with further increase in LBC contents in the MBTS/LBC mix. This trend observed for electrical conductivity agrees with the thermal conductivity trend, though they showed minima at slightly different MBTS/LBC ratio. When the crosslink densities of the composition were compared to their thermal and electrical conductivities it appeared that the higher the crosslink density, the higher was the ability of the composite to conduct heat and electricity.

Conclusion

Generally, all the thermodynamic parameters, the thermal conductivity and the electrical conductivity of the natural rubber composites deteriorated on the inclusion of the MBTS/LBC mix in the formulation of the composites. The degree of deterioration increased with increased LBC concentration in the MBTS/LBC mix. It appears that up to 50/50, MBTS/LBC mix, the less orderly is the molecule of the composite, the less is the crosslink density of the composite and the less is the ability of the composite to conduct heat and electricity. Hence, the higher is the possibility of utilizing the composite as thermal and electrical insulators. It is, therefore, advantageous to include MBTS/LBC in the formulation of natural rubber composites for improved thermal and electrical insulation.

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