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Properties of Natural Rubber Composites Activated with Unsaturated Systems

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The mechanical and rheological properties of natural rubber composites activated with the conventional saturated ZnO/ stearic acid pair have been studied extensively (Bristow 1986; Elliot 1986; Barker 1987). The mechanical and rheological properties of natural rubber composites activated with ZnO/ unsaturated carboxylic acid have been reported (Bristow 1987). The effect of cure temperature on the mechanical properties of natural rubber activated wit ZnO/saturated carboxylic acid has also been reported (Barker 1987; Adeosun *et al* 1998). The thermodynamics of stretching and the thermal conductivity of the systems ZnO/saturated carboxylic acid have however not been given much attention as their mechanical and rheological properties. In this work, the thermal conductivities and the thermodynamic parameters of these systems have been examined alongside their mechanical and rheological properties.

Zinc oleate was prepared by the method of metathesis which has been described elsewhere (Ubbelohde 1973; Akanni and Adeosun 1989). The test compounds were prepared using the formulations in Table 1, at the Dunlop Nigeria Plc Laboratory Ikeja, Lagos.

Mixing was done on a water cooled 6" laboratory two-roll mill which was carefully controlled and made to attain a maximum temperature of 70°C. The maximum speed of the fast roll was 24rpm.

The rheological properties of the compounds were determined using monsanto Rheometer model 100 at 185°C. The tensile stress – strain properties were determined using Instron Universal testing machine model 4301. Method for the determination of the thermal conductivity and thermodynamic parameters have been reported by Adeosun *et al* (2000).

Treatment of Data

(a) mechanical properties: The data were used as measured by the Instron machine.

(b) The rheometer plots (rheographs) were analysed as follows:

(i) Scorch time used as recorded by the rheometer; (ii) Cure time used as recorded by the rheometer; (iii) Crosslink density measured as the difference between the maximum and the minimum torque; (iv) Reversion resistance was evaluated as recommended by Bristow (1986).

(c) Thermodynamic parameters of stretching:

The change in free energy ΔG, change in enthalpy ΔH and the change in entropy ΔS of stretching were evaluated from equations 1,2 and 3 respectively (Bird *et al* 1960; Mearns 1973; Das and Behera 1983).

$$\log F = \log A + \Delta G/2.303\,RT \quad (1)$$

$$\log F/d = -\Delta H/2.303RT \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

(d) Thermal conductivity K, was evaluated using equation (4) (Higgin 1997).

$$K = \frac{MC\ RL}{A(Q_1-Q_2)}$$

where K = thermal conductivity; A = cross-sectional area of sample; (Q_1-Q_2) = change in temperature between the faces of the plates; L = thickness of sample; M = mass of brass plate

C = specific heat capacity of brass plate

R = gradient of the cooling curve at Q_2

Data are presented in Table 2 for the mechanical properties of the natural rubber composites activated with the systems ZnO/Stearic acid, ZnO/Oleic acid and Zinc Oleate/Stearic acid. It is observed from the table that tensile strength, modulus and resilience of the conventional ZnO/stearic acid sys-

Table 1

Compound formulation (Cure temperature 14O°C)

Composite	Parts	Per hundred	Rubber (pphr)
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	3	-	3
Oleic acid	-	3	-
Zinc oleate	-	-	5
MBT	1	1	1
Sulphur	3	3	3

Table 2

Mechanical properties of the system examined (cured at 413°K)

System	Tensile Strength (KNm^{-2})	Modulus 100% (KNm^{-2})	Modulus 300%	Elongation break (%)	Resilience (%)	Hysteresis	Hardness (IHRD)
ZnO/Stearic Acid	6.264	1.076	2.515	455.5	91.72	.0109	45.0
ZnO/Oleic Acid	5.341	0.961	2.174	477.1	88.49	.0113	41.8
Zinc Oleate/ Stearic Acid	1.932	0.551	0.939	592.8	79.49	.0125	46.8

Table 3
Rheological properties of the systems examined

System	Cure time (min)	Scorch time (min)	Crosslink density	Reversion resistance tR5/t95	TR10/90
ZnO/Stearic acid	1.11	0.64	6.45	2.60	2.27
ZnO/Oleic acid	1.05	0.60	5.55	2.30	2.17
ZnOleate/ Stearic acid	0.92	0.76	3.29	2.11	2.10

Table 4
Thermal conductivity and thermodynamic parameters for the composites examined

System	Thermal conductivity; K (Wm-1K^{-1})	Change in free energy; ΔG (J)	Change in enthalpy ΔH (J)	Change in entropy as at 300k (j.K^{-1})
ZnO/Stearic acid	0.38	-.26	1.08	4.5×10^{-3}
ZnO/Oleic acid	0.21	-.10	1.16	4.2×10^{-3}
Zinc Oleate/ Stearic acid	0.22	-.27	0.96	4.1×10^{-3}

tem are superior to those of the unsaturated systems ZnO/ Oleic acid and Zinc Oleate/Stearic acid. The heat build up and elongation at break of the conventional systems are however relatively lower than for the unsaturated systems. The rheological properties of all systems are presented in Table 3. The conventional system is observed to have superior reversion resistance and crosslink density compared to the unsaturated systems.

The thermodynamic parameters of stretching of the systems are presented in Table 4. The change in entropy of stretching of the natural rubber composites follows the decreasing trend ZnO/stearic acid, ZnO/Oleic acid and zinc Oleate/stearic acid. A decrease in entropy connotes that the material tends to a more ordered state as it is extended (Das and Behera 1983). The present result suggests that the unsaturated systems are relatively more responsive to stretching than the saturated system.

The thermal conductivity of the systems are contained in Table 4. It is observed that the saturated system conducts heat better than the unsaturated systems. It appears that higher entropy leads to increased lattice vibration resulting in higher heat conductance.

The results of the present work, have shown conclusively that the conventional saturated system ZnO/stearic acid shows superiority to the unsaturated systems ZnO/Oleic acid and Zinc Oleate/Stearic acid in tensile strength, mo dulus, resilience, hysteresis (the lower the better), crosslink density and reversion resistance. The unsaturated systems also show inferiority to the saturated conventional system in thermal conductivity which makes them better thermal insulators.

Key words: Unsaturated system, Mechanical properties, Rheological properties, Thermal conductivity, Insulator.

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