Bull. Chem. Soc. Ethiop. **2004**, 18(2), 229-234. ISSN 1011-3924
Printed in Ethiopia

SHORT COMMUNICATION

THERMODYNAMIC PARAMETERS OF ELASTICITY AND ELECTRICAL CONDUCTIVITY OF REINFORCED NATURAL RUBBER VULCA NIZATES

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(Received April 1, 2003; revised August 11, 2004)

ABSTRACT. The thermodynamic parameters (change in free energy of elasticity, ΔG_e; change in enthalpy of elasticity, ΔH_e; and change in entropy of elasticity, ΔS_e) and the electrical conductivity of natural rubber composites reinforced separately with some agricultural wastes have been determined. Results show that the reinforced composites are relatively more ordered and more spontaneous to elasticity than the unreinforced composite. These more ordered composites were observed to conduct electricity better than the unreinforced. The inclusion of the agricultural wastes examined in the formulation of natural rubber composite enhances the elasticity and the electrical conductivity of natural rubber.

KEY WORDS: Thermodynamic parameters of elasticity, Natural rubber, Electrical conductivity of natural rubber composites, Reinforced composites, Unreinforced composites

INTRODUCTION

Fibrous materials have found utility as industrial raw materials in the production of particle boards [1], wood particle-cement composites used as roofing sheets [2] and plastic composites used for autobody panels, microwave cook ware and satellite receptor antenna dishes [3].

The mechanical and rheological properties of filled natural rubber have been examined [4-7]. Coconut fibre has been reported to be a potential filler in natural rubber [8]. We have reported the mechanical and the rheological properties of natural rubber filled separately with cowbone, egg shell, maize shaft, banana peel, rice husk, mango seed skin, groundnut shell and been seed skin [9]. Results showed that it is advantageous to fill natural rubber with these agricultural wastes. In the present work we have examined the separate effects of locust leaf and the aforementioned agricultural wastes (except cowbone and egg shell) on the electrical conductivity and the thermodynamic parameters of elasticity of natural rubber. The aim has been to search for economic utility for these agricultural wastes.

EXPERIMENTAL

Filler preparation

Methods of natural rubber latex compounding were based on the formulation in Table 1. The composite compounding was based on the formulation in Table 2. Compounding and curing

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*Corresponding author. E-mail: olumayede@excite.com was done as reported elsewhere [9]. Sample meant for the determination of mechanical properties are used in this work for elasticity and electrical conductivity determinations.

Table 1. Latex compounding.

Natural rubber latex (cm^3)		250	250	250	250	250	250	250	250	250	250	250	250	250
(a)	Control (g)	-	-	-	-	-	-	-	-	-	-	-	-	-
(b)	Mango seed skin (g)	5	-	-	-	-	-	-	-	-	-	-	-	-
(c)	Banana peel (g)	-	5	-	-	-	-	-	-	-	-	-	-	-
(d)	Sweet potato leaf (g)	-	-	5	-	-	-	-	-	-	-	-	-	-
(e)	Rice husk (g)	-	-	-	5	-	-	-	-	-	-	-	-	-
(f)	Ground nut shell (g)	-	-	-	-	5	-	-	-	-	-	-	-	-
(g)	White cocoyam leaf (g)	-	-	-	-	-	5	-	-	-	-	-	-	-
(h)	Bean seed skin (g)	-	-	-	-	-	-	5	-	-	-	-	-	-
(i)	Maize shaft (g)	-	-	-	-	-	-	-	5	-	-	-	-	-
(j)	Locust leaf (g)	-	-	-	-	-	-	-	-	-	0.2	-	-	-
(k)	Locust leaf (g)	-	-	-	-	-	-	-	-	-	-	0.4	-	-
(l)	Locust leaf (g)	-	-	-	-	-	-	-	-	-	-	-	0.6	-
(m)	Locust leaf (g)	-	-	-	-	-	-	-	-	-	-	-	-	0.8

Table 2. Composite compounding formulation.

	A	B	C	D	E	F	G	H	I	J	K	L	M
Natural rubber	100+	100++	100++	100++	100++	100++	100++	100+	100+	100++	100++	100++	100++
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3	3	3	3	3	3
MBTS	1	1	1	1	1	1	1	1	1	1	1	1	1
Sulphur	3	3	3	3	3	3	3	3	3	3	3	3	3

MBTS = dibenzthiazyl disulphide. + = dried natural rubber without filler (control). ++ = dried natural rubber containing fillers as shown in Table 1. Quantities shown in Table 2 are in parts per hundred rubber (pphr).

Electrical conductivity

Measurement of electrical conductivity of natural rubber composite was done as reported by [10].

Measurement of changes in elasticity with temperature

An Ohaus Balance Model DIAL-O-Gram 310 g was used to perform this experiment following the procedure described by [11]. The balance was placed on a suitable level and a tall beaker (one litre) was placed on the left hand side of the balance. The lower circular part of the balance on which the tall beaker rested was raised to a suitable height so that the whole dumb-bell shaped sample was completely immersed inside the tall beaker. A 300 g standard weight was hung into the dumb-bell shaped sample through a hole bored on the rubber sample by means of a small weightless hook. The other end of the rubber sample with a similar hole was hung unto the hook on the balance. This arrangement caused a tension on the rubber sample. The pointer of the balance was adjusted to zero. Boiling water was poured into the tall beaker until the total length of the sample was completely immersed in the hot water throughout the experiment. As the temperature of the hot water was decreased the corresponding mass required to bring the balance to zero was recorded against a specific temperature.

TREATMENT OF DATA

The tension f was expressed as a function of absolute temperature by a proposed Arrhenius type equation [11] such that:

$$f = d\ (\exp)\ \Delta G_e/RT \qquad (1)$$

where d is the density of rubber in the composite. It is treated as a constant on the assumption that its variation with temperature is in significant. Rearranging equation (1), it becomes

$$\frac{f}{d} = (\exp)\ \Delta G_e/RT \qquad (2)$$

$$\text{But} \quad \Delta G = \Delta H - T\Delta S \qquad (3)$$

$$\text{Therefore} \quad \frac{f}{d} = (\exp)\frac{\Delta H_e}{RT} - \frac{\Delta S_e}{R} \qquad (4)$$

$$\text{i.e.}\ \log \frac{f}{d} = \frac{\Delta H_e}{2.303RT} - \frac{\Delta S_e}{2.303R} \qquad (5)$$

The linear plot of log (f/d) versus inverse absolute temperature I/T gives $\Delta H_e/2.303R$ as the slope and $\Delta S_e/2.303R$ as the intercept. Values of ΔG_e are then evaluated using equation (3).

RESULTS AND DISCUSSION

The thermodynamic parameters as evaluated by least square method are contained in Table 3. Examination of the entropy factor ΔS_e reveals that all composites studied shows negative values. The filled composites show more negative ΔS_e values than the unfilled gum stock. These observations are similar to those noted for the same composites when the thermodynamic equation of state for elastic materials was used. The entropy decreases when NR was filled connoting that the material tends to a more ordered state [11]. All the systems show positive change in free energy, ΔG_e suggesting that the composites would not stretch unless under tension. The magnitude of the change in free energy does not vary significantly for all systems. However, the change in free energy seems to decrease (becomes less positive) as the concentration of locust filler increases. This could be understood by recalling that the molecules become more ordered with increasing filler concentration and hence would be more spontaneous to elasticity at relatively high filler concentration where entanglement is least. The change in enthalpy ΔH_e follows the change in free energy trend being almost constant for all systems. But enthalpy change increases with increasing locust filler concentration. It appears that the more spontaneous to elasticity the composite becomes the more the heat change accompanying elasticity.

Table 3. Thermodynamic parameters of elasticity of the composites examined.

Filler	Change in entropy ΔS_e (kJK^{-1}) (x 10^4)	Change in enthalpy ΔH_e (kJ)	Change in free energy ΔGe (kJ) mole^{-1} at 313 K
Unfilled	-1.70	0.55	0.605
Sweet potato leaf	-2.15	0.54	0.607
Cocoyam leaf	-2.28	0.54	0.609
Banana peel	-2.04	0.55	0.613
Mango seed skin	-1.95	0.55	0.608
Bean seed skin	-2.48	0.53	0.608
Groundnut shell	-2.21	0.54	0.608
Rice husk	-2.17	0.54	0.611
Maize cob	-2.49	0.53	0.611
Locust leaf (0.2 g)	-1.30	0.56	0.604
Locust leaf (0.4 g)	-2.02	0.63	0.601
Locust leaf (0.6 g)	-2.01	0.63	0.598
Locust leaf (0.8 g)	-2.41	0.75	0.592

Electrical conductivity data are given in Table 4. It is observed from this table that the agricultural waste additives improve the electrical conductivity of the natural rubber composites. Natural rubber vulcanizate being a polymer in which all chemical bonding is of the covalent type is a non-conductor since shared valence electrons are unable to move out of their particular molecular orbital for conduction [12]. The increased conductivity of the composite could thus be said to be due to the conducting ability of the additives.

Table 4. Electrical conductivity (ohm^{-1} m^{-1}) of the composites examined as a function of temperature.

Filler	Temperature (K)				
	302	305	311	325	335
Unfilled	5.83	6.89	8.08	7.68	6.47
Sweet potato leaf	10.29	9.39	10.29	10.21	10.28
Cocoyam leaf	10.33	10.99	7.74	7.96	9.29
Banana peel	6.16	4.49	4.16	4.27	4.10
Mango seed skin	10.03	10.85	8.96	8.82	8.82
Bean seed skin	6.08	2.05	2.07	2.11	2.10
Groundnut shell	6.47	3.83	4.29	4.19	4.19
Rice husk	6.32	11.27	4.58	9.69	8.93
Maize cob	7.15	7.87	6.55	5.02	3.91

Electrical conductivity of the composites is also observed to generally decrease (after and initial increase for some) with increasing temperature. This behaviour is contrary to that of non-conductors whose electrical conductivity is expected to increase with temperature [12]. However, since the conducting ability of the natural rubber composites has been enhanced by the agricultural waste additives, the conducting ability of the reinforced composites could be viewed to be due solely to the intrinsic ability of the additives. The effect of the increase in temperature on the non-conducting natural rubber (whose electrical conductivity should increase with temperature) is more than compensated for by the effect the increase in temperature had on the electrical conductivity of the additives. This would have a resultant effect in favour of the conducting additives resulting in the decrease in electrical conductivity as the temperature is increased. This behaviour is similar to that of metals whose electrical conductivities increase as the temperature falls [13]. Since an electrical current is a flow of electrons amongst the positive ions in a metal crystal, this impedes movement and reduces conductivity. Thus an increase in temperature introduces greater thermal agitation as ions vibrate about their mean position. This obviously reduces the mean free path which electrons can follow and consequently their mobility resulting in a decrease in conductivity [12].

The activation energies of electrical conductance are given in Table 5. It is observed that the composite with relatively low activation energy for conductance conducts better than those with relatively high activation energy. The lower the activation energy, the greater is the number of electrons that would have the necessary energy to move and conduct electricity. Comparing the results of the thermodynamic parameters with the electrical conductivity results, the composites with additives are relatively more ordered and conduct electricity better than the unfilled composite.

Table 5. Activation energy for conductance of the composites examined.

Filler (0.2 pphr)	Activating energy (10^2) kJ mole^{-1}	Electrical conductivity at 302 K (ohm^{-1} m^{-1})
Unfilled	2.33	5.83
Maize cob (0.2 pphr)	2.11	7.15
Groundnut shell -	1.64	6.47
Banana peel -	1.69	6.16
Rice husk -	1.0	6.32
Bean seed skin -	0.96	6.08
Sweet potato leaf -	0.96	10.29
Mango seed skin -	0.95	10.03
Cocoyam leaf -	0.65	10.33

CONCLUSION

Thermodynamic results revealed that the composites reinforced with the agricultural waste examined are relatively more ordered and more spontaneous to elasticity than the reinforced composite. These more ordered composites are observed to conduct electricity better than the unreinforced composite. It appears that the inclusion of the agricultural wastes in the formulation of natural rubber composite enhances the elasticity and the electrical conductivity of natural rubber composite.

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