Cure Kinetics and Sorption Characteristics of Neoprene-Based Rubber Ferrite Composites

K. H. Prema [a] [b] , Philip Kurian [a] , M. R. Anantharaman [c] & Vijutha Sunny [c]

[a] Department of Polymer Science and Rubber Technology , Cochin University of Science and Technology , Cochin, Kerala, India

[b] Department of Chemistry , S. D. College , Alappuzha, Kerala, India

[c] Department of Physics , Cochin University of Science and Technology , Cochin, Kerala, India
Published online: 28 Dec 2009.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Cure Kinetics and Sorption Characteristics of Neoprene-Based Rubber Ferrite Composites

K. H. Prema,[1,2] Philip Kurian,[1] M. R. Anantharaman,[3] and Vijutha Sunny[3]

[1]Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, Kerala, India
[2]Department of Chemistry, S. D. College, Alappuzha, Kerala, India
[3]Department of Physics, Cochin University of Science and Technology, Cochin, Kerala, India

Rubber ferrite composites were prepared by incorporating nickel ferrite in a neoprene rubber matrix. Kinetics of the cure reaction were determined from the rheometric torque values and found to follow first-order kinetics. Analysis of the swelling behavior of the rubber ferrite composites in toluene elucidates the mechanism of solvent penetration and sorption characteristics, and reveals the extent of the physical interaction of the ferrite particles with the neoprene rubber matrix. Mechanical properties of rubber ferrite composites were determined, which support the reinforcing nature of nickel ferrite to the neoprene rubber matrix. These results show that magnetic composites with the required processing safety can be prepared economically by incorporating higher amounts of nickel ferrite in the neoprene rubber matrix.

Keywords   cure kinetic, ferrites, rubber ferrite composites, sorption kinetics

INTRODUCTION

Polycrystalline ferrites are incorporated into elastomers to produce flexible magnets or rubber ferrite composites (RFCs) [1–4]. Appropriate selection of magnetic filler and matrix can result in RFCs with desired properties for various applications. Advantages of RFCs over their metallic and ceramic counterparts include light weight, low cost, resistance to corrosion, easy processability and high production rates [5,6]. Magnetic properties of these flexible magnets can be tailored by the selection of the appropriate type and amount of ferrites. Use of these materials as EMI shields and microwave-absorbing materials brings about their commercial applications [7,8].

The determination of processability and cure characteristics is indispensable for the evaluation of the physical and mechanical properties of RFCs. Physicomechanical properties of composites depend on the particle size of the filler and its interaction with the elastomers. Cure kinetics and sorption studies reveal the interaction of the filler particles with the elastomer matrix at the molecular level. The chemical influence of ferrite particles on cure reaction can be followed from cure kinetic studies. Processability, and thereby performance characteristics, are being assessed from cure characteristics. The mechanism of solvent flow through the composites can be analyzed from sorption studies that indicate the polymer/filler interaction.

In the present investigation, cure kinetics and sorption characteristics of neoprene-based nickel ferrite-filled RFCs are reported. Neoprene is a polar rubber, characterized by appreciable ozone, weather and flame resistance and by moderate oil resistance. Mechanical properties of neoprene-based vulcanizates are comparable with those of natural rubber-based composites. The choice of nickel ferrite as the magnetic filler for the preparation of RFCs is justified due to its high resistivity, low eddy current loss, high saturation magnetization and other magnetic characteristics [9]. The nickel ferrite used for the preparation of RFCs was synthesized by sol-gel method [10]. The precharacterized nickel ferrite is incorporated into the neoprene matrix for various loadings according to conventional methods. Cure characteristics and sorption studies were carried out as per the ASTM standards. The results were analyzed and correlated with the mechanical properties.

EXPERIMENTAL

Materials

Neoprene rubber used for the preparation of RFCs is W type, manufactured by M/s Du Pont, USA. Mooney viscosity [ML(1 + 4) at 100°C] is 47. Nickel ferrite nanoparticles used for the preparation of RFCs were

synthesized by sol-gel method and characterized by XRD [11]. Other chemicals used in this study were of AR grade.

Synthesis of Neoprene-Based RFCs

Precharacterized nickel ferrite was incorporated into W grade neoprene rubber according to the recipe given in Table 1. RFCs were prepared with the loading of ferrite ranging from 40 to 120 phr in steps of 20. A control compound was prepared without nickel ferrite. Mixing was carried out in a Brabender Plasticorder, Model PL 3S, at 50 rpm rotor speed and at 60°C, as per ASTM D3182-89 (2001). The mixed stock was homogenized using a two-roll mill at 0.8 mm nip gap and made into sheets of 3 mm thickness.

Determination of Cure Characteristics

Cure characteristics of the RFCs were determined using a rubber process analyzer (RPA 2000, Alpha Technology) at a temperature of 160°C. From the RPA result, optimum cure time, scorch time and maximum and minimum torque values were determined.

Cure Rate Index and Cure Kinetics of RFCs

The cure rate index (CRI) [12,13], a parameter which indicates the speed of the curing reaction, and rate constant of the cure reactions were determined from the rheometric data. CRI is calculated using the relation

$$CRI = 100/(cure\ time\text{-}scorch\ time) \tag{1}$$

The kinetics of a first-order chemical reaction can be expressed by the following equation [14–16]

$$\ln(a - x) = -kt + \ln a \tag{2}$$

Table 1: Recipes used for the preparation of NiFe$_2$O$_4$ filled RFCs^a.

Material	Loading (phr)
Neoprene	100
ZnO	5
MgO	4
Stearic acid	1
NiFe$_2$O$_4$	X
Naphthaneic oil	5% of X
NA22	0.5

^{a}Where X is 20, 40, 60, 80, 100 and 120 parts of nickel ferrite per hundred parts of neoprene rubber.

where, a is the initial concentration of the reactant, x is the concentration at any instant of time t and k is the reaction constant.

The vulcanization reaction of rubber can be considered as a first-order chemical reaction, and the rate of reaction can be monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of the rubber. The following substitutions in Eq. (2) are made:

$$(a - x) = M_h - M_t \tag{3}$$

$$a = M_h - M_0 \tag{4}$$

where, M_h is the maximum torque, M_0 is minimum torque and M_t is the torque at time t.

So that Eq. (2) can be rewritten as

$$\ln(M_h - M_t) = -kt + \ln(M_h - M_0) \tag{5}$$

If the plot of $\ln(M_h - M_t)$ against time is a straight line, then it indicates that the cure reaction follows first-order kinetics. The rate constant (k) of the cure reaction is directly obtained from the slope of the straight line.

Determination of Sorption Characteristics

In order to analyze the interaction between the components of the system, equilibrium swelling studies were carried out in toluene. Circular samples of diameter 20 mm were punched from the vulcanized sheet and were allowed to swell in toluene at room temperature. At different time intervals, the amount of solvent entering the sample was assessed gravimetrically until equilibrium was reached, as evidenced by the constant weight of the sample. The mole % uptake of solvent was calculated using the equation [16,17]

$$Q_t = \frac{\left(\frac{M_{c(m)}}{M_{r(m)}}\right) \times 100}{M_{i(s)}} \tag{6}$$

where $M_{c(m)}$ is the mass of solvent at a given time, $M_{r(m)}$ is the molecular weight of the solvent and $M_{i(s)}$ is the initial weight of the specimen. At equilibrium swelling, Q_t was taken as Q_∞, the mole % uptake at infinite time. Sorption curves were obtained by plotting mole % uptake against the square root of time. The effective diffusivity, D, of the elastomer-solvent system was calculated from the initial portion of the sorption curves using the equation:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \tag{7}$$

where θ is the slope of the initial portion of the sorption curve.

Another parameter, called sorption coefficient, S, was calculated from the equilibrium swelling using the relation

$$S = \frac{M_\infty}{M_0} \tag{8}$$

where M_∞ is the mass of the penetrant sorbed at infinite time and M_0 is the initial weight of the polymer sample. Sorption coefficient describes both initial penetration and dispersal of penetrant molecules inside the elastomer network.

The permeation coefficient, P, which is a characteristic parameter reflecting the collective processes of diffusion and sorption, was calculated using the equation [18].

$$P = DS \tag{9}$$

Evaluation of Mechanical Properties

Stress-strain properties, such as tensile strength, modulus and elongation at break, were determined using Shimadzu Universal Testing Machine model SPL 10 kN at a crosshead speed of 500 mm/min. Stress-strain measurements were carried out as per ASTM D 412-98a(2002). Tear resistance of the samples was tested as per ASTM D 624-2000 using test specimens having a 90° angle on one side and tab ends, punched out from the molded sheets along the mill grain direction.

RESULTS AND DISCUSSION

Cure characteristics of RFCs with various loadings of nickel ferrite were obtained from RPA results and are given in Table 2. Cure time of the compounds increases with loading of the nickel ferrite. As the ferrite loading increases, the curatives may get adsorbed over the surface of the ferrite

Table 2: Cure characteristics of RFCs.

Loading (phr)	Optimum cure time, t_{90} (minutes)	Scorch time, t_{10} (minutes)	Maximum torque, D_{max} (dNm)	Minimum torque, D_{min} (dNm)
0	12.75	1.01	2.98	0.29
40	16.97	1.86	4.24	0.29
60	16.99	2.28	4.48	0.28
80	17.51	2.34	5.08	0.34
100	20.03	2.49	5.12	0.39
120	23.29	2.76	5.27	0.47

particles and their effective concentrations may decrease. Consequently, the time required for the optimum cure increases. Scorch time of the compound increases with filler loading, which shows better processing safety.

Maximum and minimum torque values increase with increased ferrite concentration. An increase in maximum torque value with the addition of nickel ferrite indicates a better interaction of the filler particles with the elastomer matrix.

Kinetics of cure reactions of neoprene rubber-based RFCs with different loading of nickel ferrite were determined from the torque values. The plot of $\ln(M_h - M_t)$ versus time is shown in Figure 1. The linear nature of these graphs indicates that the cure reaction follows first-order kinetics, which indicates that curing reaction depends only on the concentration of one reactant species. Deviation from linearity is not observed with an increase in ferrite loading; thus ferrites have a negligible role in the curing reaction. Thus the cure reaction of RFCs is independent of the amount of ferrite present in the compound. From the slope of the straight lines, the rate constants of the cure reactions were determined and are shown in Figure 2. Variation of rate constants of the vulcanization reaction is similar to the variation of the cure rate index given in the same figure. The rate of curing reaction is found to be decreased on incorporation of 40 phr ferrite and increases on further addition of the ferrite. The rate of the cure reaction, which depends on the concentration of the rubber phase, is expected to decrease with filler loading.
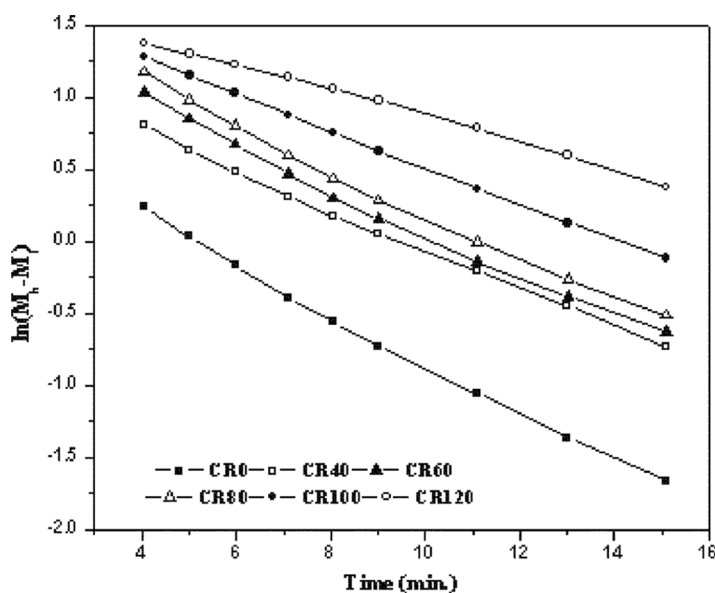

Figure 1: $\ln(M_h - M_t)$ vs. time for $NiFe_2O_4$ filled RFCs.
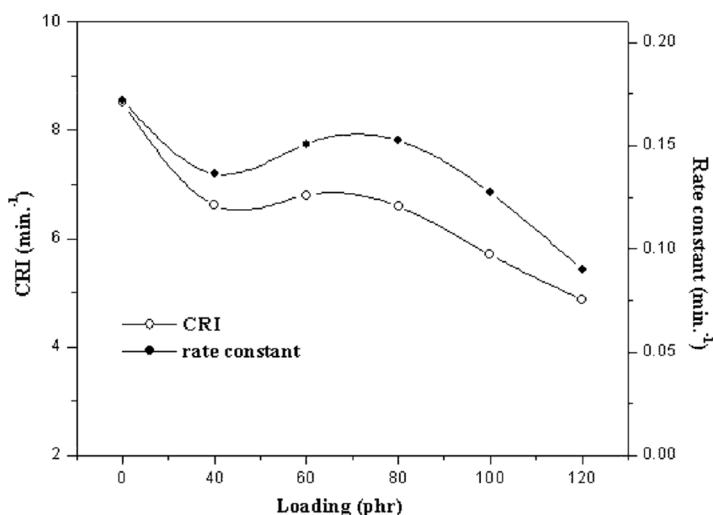
Figure 2: Cure rate index and cure rate constant of RFCs.

Swelling studies of the RFCs were carried out using toluene as the penetrant. The sorption parameters, like diffusion, sorption and permeation coefficients, were calculated according to Eqs. (7), (8) and (9). Room temperature sorption curves, expressed as percent penetrant uptake $Q_{(t)}$, versus square root of time $t^{1/2}$, are depicted in Figure 3. A perusal of the sorption curves indicates that the initial swelling rate of the samples is very high. This

Figure 3: Sorption curves of RFCs with different loading of $NiFe_2O_4$ (CRn stands for nickel ferrite filled neoprene-based RFCs).

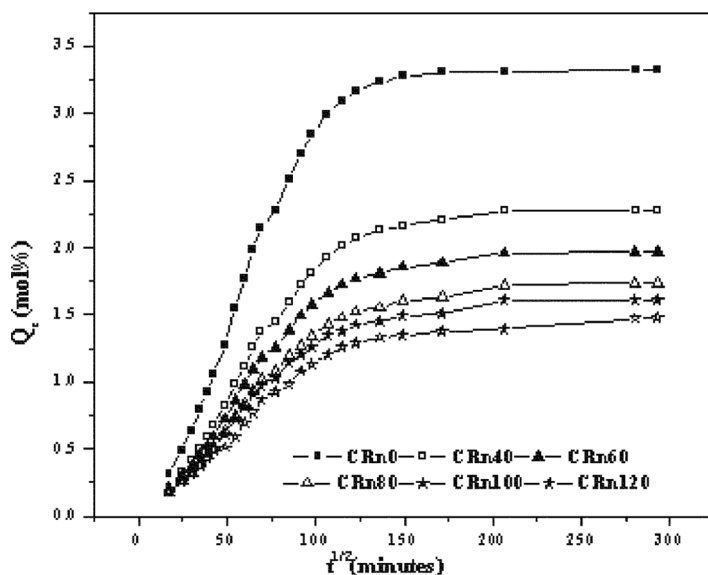is due to the large concentration gradient of the penetrant molecules at the initial stages of penetration. As the time increases, the swelling rate decreases and reaches an equilibrium where the solvent uptake become negligible. Equilibrium mole % uptake is found to decrease with increasing filler loading. This is due to the decrease in volume fraction of the elastomer with loading of the ferrite.

The mechanism of penetrant transport into the elastomer network can be analyzed using an empirical relation of the form [19]

$$\log Q_t/Q_\infty = \log k + n \log t \tag{10}$$

where, Q_t is the mole % uptake at time t, Q_∞ is the equilibrium mole % uptake and k is a constant. The value of n determines the mode of transport of solvent through the rubber compound, which depends upon many factors such as the chemical nature of rubber and vulcanizing agents [20], dimension and shape of the filler particles, rubber-filler compatibility and interfacial adhesion. The liquid diffusion can be Fickian, non-Fickian or anomalous, depending upon the value of 'n'. When n is 0.5, the mechanism is known as Fickian. Here, the rate of polymer chain relaxation is high compared to the diffusion rate of the penetrant. When $n = 1$, the transport process corresponds to a mechanism where chain relaxation is slower than liquid diffusion, which is expected for rigid polymers. When the value of n is in between 0.5 and 1, transport behavior is termed as anomalous, where rearrangement of polymer segments occurs at a comparable rate to that of the change of concentration [21,22].

The value of n for different loadings of nickel ferrite in neoprene-based RFCs is given in Table 3. Since the value of 'n' is between 0.5 and 1, the transport mechanism can be considered as anomalous where rearrangement of polymer chains occurs at a comparable rate to that of the change of concentration [23,24]. The time taken by the rubber chains to respond to the swelling stress and to rearrange themselves to accommodate the solvent molecules is responsible for the anomalous behavior of the sample. As the loading increases, the value of n decreases, which indicates that polymer relaxation increases compared to the rate of the diffusion of penetrant molecules.

Table 3: Sorption characteristics of RFCs with different loading of $NiFe_2O_4$.

Loading (phr)	'n'	$D \times 10^7$ (cm^{2}S^{-1})	S	$P \times 10^7$ (cm^{2}S^{-1})
0	0.68	7.66	3.0599	23.5
40	0.63	6.55	2.0949	13.7
60	0.61	6.27	1.8078	11.3
80	0.59	5.89	1.5912	9.37
100	0.58	5.83	1.4832	8.64
120	0.52	4.53	1.2269	5.55

Table 4: Mechanical properties of $NiFe_2O_4$ filled neoprene-based RFCs.

Loading (phr)	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Modulus at 300% elongation (MPa)
0	13.99	35.16	1165	1.51
40	19.19	35.55	1290	2.07
60	18.59	36.69	1218	2.34
80	17.76	39.26	1194	2.53
100	15.59	40.28	1143	2.63
120	13.52	41.50	1092	2.72

Diffusion, sorption and permeation coefficients of RFCs with different nickel ferrite loading are also given in Table 3. Diffusivity is a kinetic parameter, which depends on polymer segmental mobility. Sorption describes the initial penetration and dispersal of permeant molecules into the polymer matrix. The sorption coefficient is a thermodynamic parameter which depends on the strength of the interactions in the polymer- penetrant system. Stronger polymer-filler interaction reduces diffusion and sorption of the penetrant molecules through the system. Permeation is a combined effect of diffusion and sorption. Hence, the permeability of solvent molecules depends on both diffusivity and sorptivity. All these sorption characteristics were found to decrease with an increase in nickel ferrite content in RFCs. The decrease in diffusion and sorption coefficients strongly indicates that incorporation of nickel ferrite into a neoprene matrix reinforces the matrix. The decrease in sorption characteristics of these composites is due to the strong interaction of the filler with the matrix. Analysis of mechanical properties of the RFCs supports these observations [11]. Improved mechanical properties of neoprene-based RFCs are given in Table 4. RFCs were found to have better tensile strength, elongation at break, tear strength and modulus values than the gum vulcanizate. Improvement in mechanical properties of neoprene-based RFCs by the incorporation of nickel ferrite can be explained at the molecular level from the swelling studies of these composites.

CONCLUSIONS

Nickel ferrite-filled neoprene composites with improved mechanical properties can be prepared by shear mixing in an internal mixer. Evaluation of cure characteristics showed that conventional methods of curing can be employed for the preparation of RFCs. The cure reaction follows first-order kinetics and depends only on the concentration of the elastomer phase and not on the nature of the filler.

The mechanism of solvent penetration through the nickel ferrite-filled composites was analyzed. Sorption characteristics are decreased with an increase in ferrite content due to increased filler-polymer interaction. Thus, better physical interaction between ferrite particles and a neoprene matrix can be expected at the molecular level in these RFCs.

REFERENCES

[1] Malini, A., Mohammed, E. M., Sindhu, S., Joy, P. A., Date, S. K., Kulkarni, S. D., Kurian, P., and Anantharaman, M. R. *J. Mate. Sci.* **36**, 5551 (2001).

[2] Mohammed, E. M., Malini, K. A., Joy, P. A., Kulkarni, S. D., Date, S. K., Kurian, P., and Anantharaman, M. R. *Plastics, Rubber and Composites* **31**, 106 (2002).

[3] Anantharaman, M. R., Jagathesan, S., Sindhu, S., Malini, K. A., Chinnasamy, C. N., Narayanasamy, A., Kurian, P., and Vasudevan, K. *Plast. Rubber Compos. Process Appl.* **27**, 77 (1998).

[4] Soloman, M. A., Kurian, P., Anantharaman, M. R., and Joy, P. A. *Polymer-Plastics Technology and Engineering* **43**, 1013 (2004).

[5] Soloman, M. A., Kurian, P., Joy, P. A., and Anantharaman, M. R. *Int. J. Polym. Mater.* **53**, 565 (2004).

[6] Malini, K. A., Kurian, P., and Anantharaman, M. R. *Material Letters* **57**, 3381 (2003).

[7] Annadurai, P., Mallick, A. K., and Tripathy, D. K. *J. Appl. Poly. Sci.* **83**, 145 (2002).

[8] Barba, A. A., Lamberti, G., d' Amore, M., and Acierno, D. *Polymer Bulletin.* **57**, 587 (2006).

[9] Son, S., Taheri, M., Carpenter, E., Harris, V. G., and McHenry, M. E. *J. Appl. Phy.* **91**, 7589 (2002).

[10] Mathew, G., John, A. M., Nair, S. S., Joy, P. A., and Anantharaman, M. R. *J. Magn. Magn. Mater.* **302**, 190 (2006).

[11] Prema, K. H., Kurian, P., Joy, P. A., and Anantharaman, M. R. *Polymer-Plastics Technology and Engineering* **47**, 137 (2008).

[12] Blow, C. M., and Hepburn, C. (1985). *Rubber Technology and Manufacture*, Butterworths, London.

[13] Wazzan, A. A. *Int. J. Polym. Mater.* **54**, 783 (2005).

[14] Mathew, G., Nah, C., Rhee, J. M., and Singh, R. P. *Journal of Elastomers and Plastics* **38**, 43 (2006).

[15] Da Costa, H. M., Visconte, L. L. Y., Nunes, R. C. R., and Furtado, C. R. G. *Int. J. Polym. Mater.* **53**, 475 (2004).

[16] Mathew, G., Singh, R. P., Nair, N. R., and Thomas, S. *J. Mater. Sci.* **38**, 2469 (2003).

[17] Sheela, J., Kumaran, M. G., and Thomas, S. *Plastics, Rubber and Composites Processing and Applications* **27**, 82 (1998).

[18] Aminabhavi, T. M., Phayde, H. T. S., Ortego, J. D., and Vergnaud, J. M. *European Polymer Journal* **32**, 1117 (1996).

[19] Chiou, J. S., and Paul, D. R. *J. Polym. Eng. Sci.* **26**, 1218 (1986).

[20] Mathew, A. P., Packirisamy, S., Kumaran, M. G., and Thomas, S. *Polymer* **36**, 4935 (1995).

[21] Mateo, J. L., Bosch, P., Serrano, J., and Calvo, M. *European Polymer Journal* **36**, 1903 (2000).

[22] George, S., Varughese, K. T., and Thomas, S. *Polymer.* **41**, 579 (2000).

[23] Asaletha, R., Kumaran, M. G., and Thomas, S. *Polymers and Polymer Composites* **6**, 357 (1998).

[24] Geethamma, V. G., and Thomas, S. *Polymer Composites* **26**, 136 (2005).