Effect of Chlorination of Ground Rubber Tire on Its Compatibility with Poly(vinyl chloride): Dielectric Studies

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ABSTRACT: Dielectric analysis (DEA) of molded ground waste rubber tire (GRT) and its chlorinated derivatives (Cl-GRT) was undertaken. Dielectric spectra of Cl-GRT show formation of a biphasic structure consisting of the rubbery phase and a hard phase whose relaxation occurs in the high-temperature region. DEA of plasticized poly(vinyl chloride) (PVC) containing GRT and PVC containing Cl-GRT was also undertaken. It is observed that PVC containing Cl-GRT exhibits a higher loss factor in the high-temperature region than does the PVC compound containing GRT, due to enhanced interaction between Cl-GRT and PVC. While the activation energy for dielectric relaxation of PVC does not change when compounded with GRT, it does decrease when PVC is compounded with Cl-GRT due to dipolar interaction. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 993–1000, 2002; DOI 10.1002/app.10320

Key words: dielectric analysis; ground rubber tire (GRT); chlorinated GRT; poly(vinyl chloride); compatibility

INTRODUCTION

Disposal of waste tire rubber is a global problem. Recycling of waste rubber is necessary due to environmental and economic reasons. Worn-out tires are the major sources of waste rubber. Incorporation of ground rubber tire, commonly called GRT, as a filler into virgin polymer matrices, such as natural rubber (NR),[1] styrene–butadiene rubber (SBR),[2] and low-density polyethylene (LDPE),[3–5] and preparation of thermoplastic elastomeric blends based on GRT[6–8] are attractive routes for GRT recycling. However, GRT cannot be added to polar matrices like poly(vinyl chloride) (PVC) due to lack of compatibility. Compatibility of GRT with polar matrices can be enhanced by surface modification of GRT.[9–10] Waddell et al. reviewed the surface modification of rubbers.[11] Chlorination of polymeric surfaces is known to enhance the compatibility of nonpolar materials with polar substrates. Surface chlorination of GRT and the characteristics of chlorinated GRT were reported recently by Naskar et al.[12] Surface hydrophilicity of GRT was found to increase on chlorination.

Since chlorination of GRT generates permanent dipoles in polymer molecules, it is expected that chlorinated GRT (Cl-GRT) will be compatible with plasticized PVC. This makes it possible for the utilization of GRT in a broad spectrum of matrices. The present work aimed at understanding the effect of chlorination of GRT on its compatibility with PVC.

GRT can be chlorinated to different extents. In a previous communication, the physical properties of the plasticized PVC compounds containing Cl-GRT were reported.[10] The physical properties of the blends containing Cl-GRT were found to be superior to those of the blend containing GRT. This article reports the results of dielectric stud-

Table I   Description of the Materials Used

Material	Characteristics
Cryogenically GRT, obtained from Recovery Technology Inc. (Ontario, Canada)	Particle size: 160–205 μm, composition[13]: rubber %, 44; carbon black % 27; ash %, 17; acetone extractables %, 12
Plasticized PVC (K, 67) compound, obtained from Kalpana Plastics Ltd. (Calcutta, India)	PVC, 100 parts; plasticizer (dioctyl phthalate, chlorinated paraffin wax), 40 parts; stabilizer (Ba, Cd complex, Ca/Zn stearate), 6 parts; stearic acid, 0.5 parts
Trichloroisocyanuric acid (TCICA), obtained from the Sigma Aldrich foreign holding company (Bangalore, India)	97% pure
Methanol obtained from S.D. Fine Chem. Ltd. (Boisar, India)	A.R. grade, 99% pure

ies on plasticized PVC, GRT, Cl-GRT, PVC/GRT, and PVC/Cl-GRT blends.

EXPERIMENTAL

Materials

Details of the materials used are shown in Table I.

Chlorination of GRT

GRT particles were acetone-extracted for removal of extractable materials and then dried at 50°C for 24 h in an air-circulating oven. Next, the particles were immersed in a freshly prepared trichloroisocyanuric acid (TCICA) solution in methanol at three different concentrations (i.e., 1, 3, and 5% weight/volume) for 20 min at 25°C. The particles were then filtered, washed thoroughly under distilled water, and dried for 24 h at 50°C in the oven. Untreated GRT and GRT treated with 1, 3, and 5% TCICA solutions are designated as G_0, G_1, G_3, and G_5, respectively. The method used is the same as described earlier.[12] It was observed that the degree of chlorination follows the order $G_0 < G_1 < G_3 < G_5$.

PVC Compounding and Molding

GRT or Cl-GRT was mixed with plasticized PVC, at a fixed loading of 40 parts per hundred parts of PVC. Compounds were prepared in a Brabender Plasticorder PLE 330 at 170°C using a cam-type rotor. First, PVC granules were taken in the hot chamber (170°C) and allowed to soften for 2 min at 60 rpm. Then, GRT or Cl-GRT was added and allowed to mix until a constant torque was attained. The mix, while still hot, was taken out from the plasticorder and then sheeted out at 2-mm nip gap on a two-roll mill. The sheeted compound was subjected to compression molding in an electrically heated hydraulic press at 180°C for 2 min under 6 MPa pressure. The molded sheet was then cooled under pressure by water circulation through the hot mold.

Electrical Properties

The dielectric constant (ε') and the loss factor (ε'') of GRT, Cl-GRT, PVC, PVC/GRT, and PVC/Cl-GRT blends were measured in a dielectric analyzer DEA-2970 coupled with a temperature controller 2000 (TA Instruments Inc., USA) using compression-molded specimens of 0.3–0.6-mm thickness. The measurements were done in the frequency range of 1–10^5 Hz and at the heating rate of 3°C/min, using parallel-plate sensors.

RESULTS AND DISCUSSION

Electrical Properties of GRT and Cl-GRT

Variation of the dielectric constant (ε') and loss factor (ε'') against temperature, at a frequency of
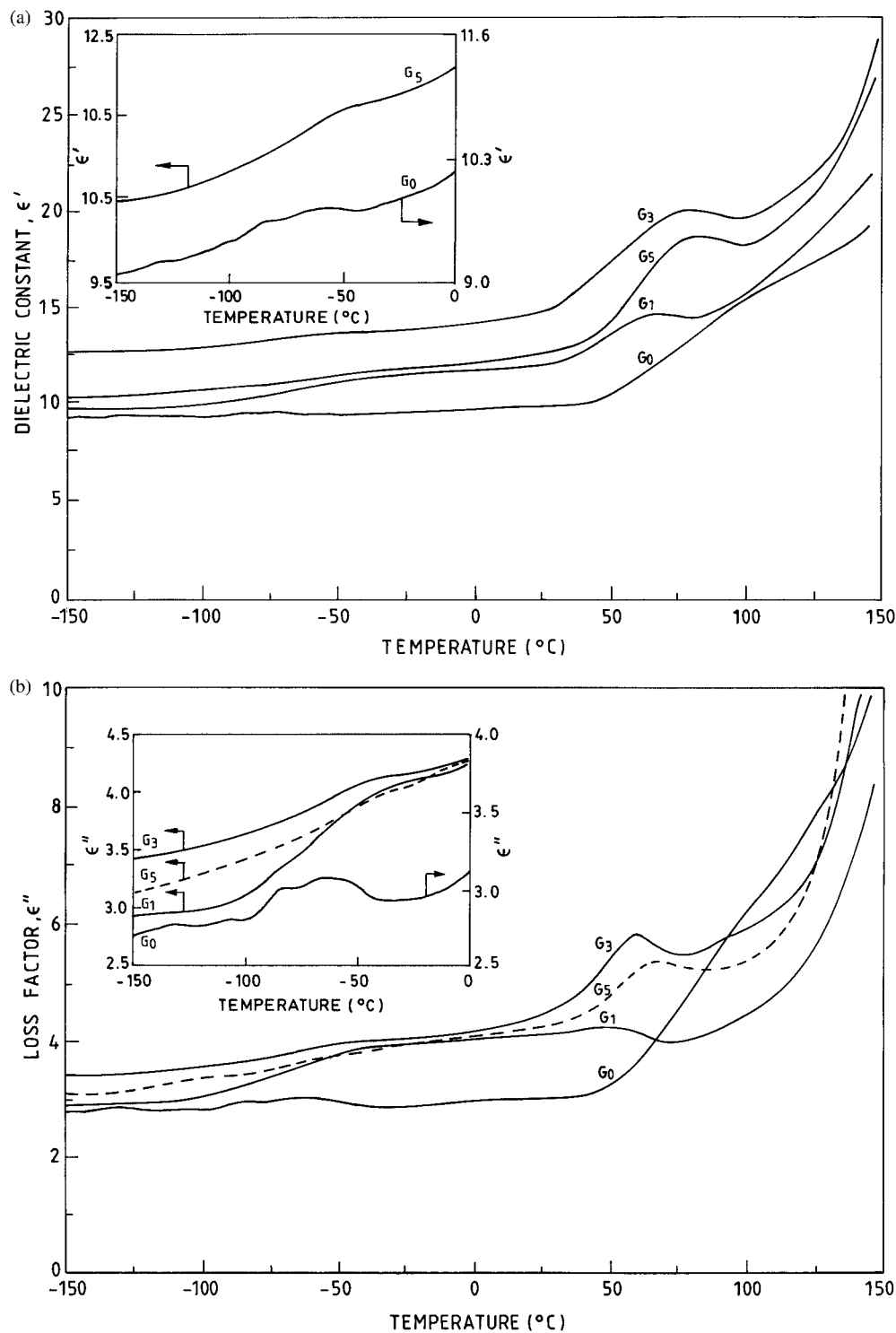
Figure 1   (a) Temperature dependence of dielectric constant (ε') at 10^5 Hz. (b) Temperature dependence of loss factor (ε'') at 10^5 Hz.

10^5 Hz, for G_0, G_1, G_3, and G_5 are shown in Figure 1(a,b), respectively. It is observed that the ε' and ε'' for G_0 show a broad multiple dielectric dispersion in the temperature range -100 to $-40°$C (shown in Fig. 1(a,b), inset) which are ascribed to glass–rubber transitions of different rubbers
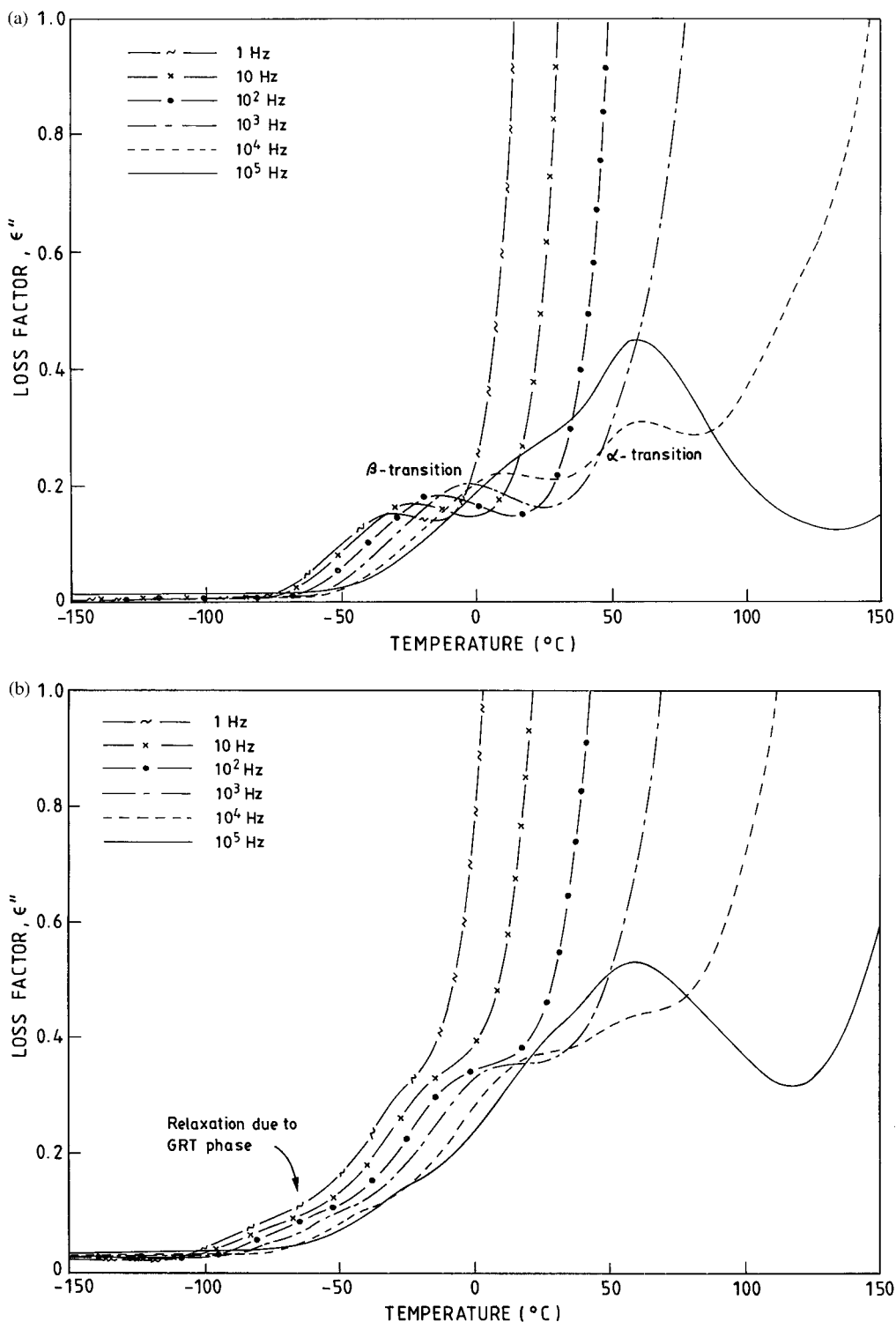
Figure 2 (a) Temperature dependence of loss factor (ε'') of plasticized PVC at different frequencies. (b) Temperature dependence of loss factor (ε'') of plasticized PVC compound containing unmodified GRT (G_0) at different frequencies. (c) Temperature dependence of loss factor (ε'') of plasticized PVC compound containing Cl-GRT (G_3) at different frequencies.
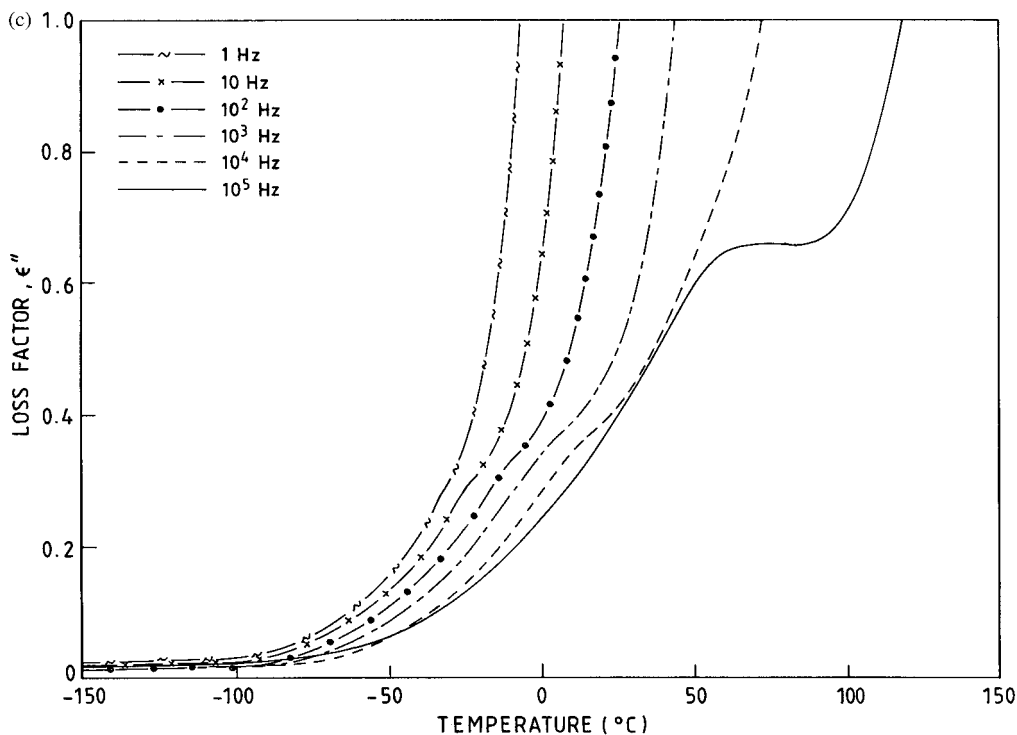
Figure 2 (*Continued from the previous page*)

present in the rubber blends used in tire making and, consequently, in GRT. G_0 is GRT consisting of primarily crosslinked rubber hydrocarbons filled with carbon black. In a previous communication, it was reported that the rubber components of GRT consists of NR, SBR, and polybutadiene rubber (BR).[13] The presence of carbon black in GRT contributes toward interfacial polarization, as a result of which the dielectric constant as well as the loss factor are significantly higher than are those for nonpolar rubber hydrocarbons even at lower temperature. Chlorination of GRT results in a broad dielectric relaxation [Fig. 1(a)] in the glass–rubber transition region instead of the multiple dispersion, as was observed in the case of G_0 [Fig. 1(b)]. The broad and weak loss maxima in the temperature range of -140 to $-110°C$, observed in G_0, which is due to a crankshaft motion of the linear hydrocarbon segments present in GRT, disappear on chlorination of GRT. Beyond the glass transition temperature (T_g), ε' and ε'' remain almost constant until an abrupt rise at around 50°C is observed due to softening of the polymer, which facilitates interfacial polarization and ionic conduction. Unlike G_0, the chlorinated GRT, however, displays a distinct high-temperature relaxation around 60°C

due to softening of the hard phase formed by the chlorination of GRT [Fig. 1(a,b)].

Dynamic mechanical studies also revealed the occurrence of a high-temperature relaxation of chlorinated GRT.[12] The formation of the hard phase is believed to be due to rigidity of the chlorinated rubber hydrocarbon chains arising out of dipole–dipole interactions. Thus, chlorinated GRT forms a biphasic structure consisting of the rubbery phase and a hard phase. As the test temperature approaches the relaxation of the hard phase, dipolar orientation is facilitated, resulting in an increase of ε' and ε''. But beyond a critical temperature, thermal motion in the softened mass randomizes the dipoles. Hence, ε' and ε'' show a decreasing trend [Fig. 1(a,b)] until an abrupt rise in the dielectric constant, and a loss factor is observed at still higher temperature (i.e., around 100°C) due to an increased contribution of interfacial polarization and ionic conduction. Since G_1, G_3, and G_5 are more polar than is G_0, increase in the loss factor and dielectric constant with increase in the temperature is higher for the chlorinated derivatives. It is interesting to note that the dielectric constant at any temperature follows the order $G_0 < G_1 < G_5 < G_3$. The higher polarity of G_3, as compared to G_5, is ascribed to

the fact that at a higher degree of chlorination random spatial orientation of the dipoles probably makes the resultant vector for G_5 lower than for G_3.[12]

Dielectric Properties of the PVC/GRT and PVC/Cl-GRT Compounds

Variation of the dielectric loss factor (ε'') of the plasticized PVC compound against temperature, at different frequencies, is shown in Figure 2(a). Plasticized PVC exhibits a transition below room temperature and the onset of a new relaxation process, which is, however, masked by ohmic conduction and/or interfacial polarization. The loss peak due to the second relaxation process at higher temperature appears at higher frequencies (10^4 and 10^5 Hz), when contributions of interfacial polarization and/or ohmic conduction are negligible. With increase in the frequency, the loss maximum shifts toward higher temperature. The occurrence of two loss maxima in plasticized PVC at a plasticizer level below 50 parts per hundred parts of rigid PVC was reported by Wurstlin.[14] Fitzgerald and Miller proposed that the appearance of a second loss peak in the high-temperature region of the loss factor spectrum of PVC plastisol is possibly due to a fraction of PVC, which has not been plasticized to the same extent as has the bulk of the material.[15] Dyson also made a similar observation of microphase separation.[16] With an increase in frequency, the low-temperature relaxation peak (β transition) broadens and partially masks the high-temperature peak (α transition), resulting in a very broad dielectric relaxation.

ε'' versus temperature plots of plasticized PVC containing 40 phr of GRT at different frequencies are shown in Figure 2(b). It is observed that the peaks due to relaxation of the plasticized PVC phase are broadened by the addition of GRT. The nature of the curve is slightly changed at low frequency due to high interfacial polarization and the loss maximum due to T_g of the plasticized PVC phase is blurred. However, loss peaks appear at higher frequencies, showing both α and β transitions at 10^4 Hz, due to the presence of an unplasticized segregated PVC phase in the bulk of plasticized PVC. The two transitions are again merged at 10^5 Hz, as observed in plasticized PVC. The loss spectrum of the PVC/GRT composite exhibits a hump between -70 and $-40°C$ due to the T_g of the rubber hydrocarbons present in GRT.

Figure 2(c) shows the variation of ε'' of the PVC compound containing Cl-GRT (i.e., G_3) at differ-
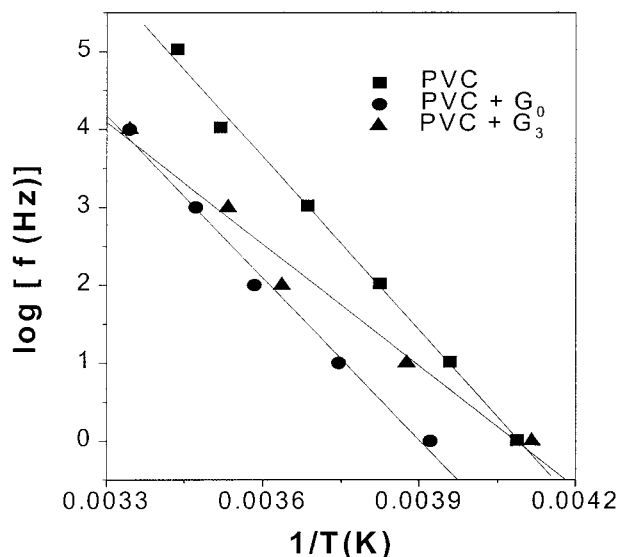

Figure 3 Plots of log f versus $1/T$.

ent frequencies. Here, interfacial polarization and/or ohmic conduction are so strong that the loss maxima due to dielectric relaxation are all masked. Only a hump due to the β transition, as defined earlier, is observed at higher frequencies. At 10^5 Hz, part of the loss peak around 70°C due to the α transition appears, whereas the β transition is suppressed and cannot be observed. This is indicative of an interaction between the plasticized PVC and Cl-GRT phases. The loss spectrum of the PVC/Cl-GRT blend does not show any peak due to the Cl-GRT phase, whereas a small and broad peak due to the GRT phase is observed in the PVC/GRT blend, indicating a lack of compatibility between the PVC and GRT phases.

The temperature dependence of the loss factor maxima at different frequencies can be used for the calculation of the activation energy for the dielectric relaxation process. The activation energy of the relaxation process is calculated from the slope of the linear plots of the reciprocal of the absolute temperatures corresponding to the maxima of the loss peaks against frequency (Fig. 3) using the Arrhenius equation[17]:

$$\log f = -E_a/(2.303RT) + \log K \qquad (1)$$

where T is the absolute temperature at which the loss maximum is observed at frequency f; R, the gas constant; K, the arbitrary constant; and E_a, the activation energy.

The activation energies of the compounds along with their relaxation temperatures at different

Table II Temperatures Corresponding to Dielectric Relaxation (T_d) of the PVC Compounds at Different Frequencies and Activation Energies of the Relaxation Process

Frequency (Hz)	Plasticized PVC		PVC Compound Containing 40 phr G_0		PVC Compound Containing 40 phr G_3	
	T_d (°C)	Activation Energy[a] (kcal/mol)	T_d (°C)	Activation Energy[a] (kcal/mol)	T_d (°C)	Activation Energy[a] (kcal/mol)
1	−29[a]		−18[a]		−30[a]	
10	−21[a]		−6[a]		−15[a]	
10^2	−12[a]	33.27[b]	6[a]	31.80[c]	2[a]	23.84[d]
10^3	−2[a]		15[a]		10[a]	
10^4	11,[a] 59[e]		26,[a] 57[e]		26[a]	
10^5	18,[a] 60[e]		—,[f] 60[e]		—,[f] 72[e]	

[a] Corresponds to β relaxation.
[b] Correlation of Arrhenius fit (−0.998).
[c] Correlation of Arrhenius fit (−0.996).
[d] Correlation of Arrhenius fit (−0.991).
[e] Temperature corresponding to α relaxation, observed only at high frequencies.
[f] Not observed.

frequencies are shown in Table II. It is observed that on incorporation of GRT the temperatures corresponding to the loss maxima is increased due to the filler action, but in the low-frequency range, the temperature corresponding to the loss maximum of the blend containing G_3 is closer to that of the neat PVC compound. This is possibly due to a higher degree of compatibility between the PVC and G_3 phases through dipolar interaction between them. The activation energy for the relaxation process of PVC and PVC compounded with nonchlorinated GRT are almost the same, indicating that the dielectric relaxation kinetics of the PVC phase is not influenced by the inclusion of GRT. However, in the presence of Cl-GRT, the activation energy of the dielectric relaxation of plasticized PVC decreases, presumably due to dipolar interaction between PVC and chlorinated GRT. Results of the dielectric studies are in agreement with the findings reported earlier on the mechanical properties of PVC filled with Cl-GRT.[10]

CONCLUSIONS

Surface chlorination of GRT enhances its dielectric constant. The dielectric constant of chlorinated GRT increases with increase in the level of chlorination and reaches a maximum at an optimum degree of chlorination, beyond which it decreases. Chlorinated GRT, when molded, forms a

biphasic morphology consisting of the rubbery phase and a hard phase, which is formed by the dipolar interaction. In spite of the very lossy nature of GRT and chlorinated GRT (as compared to the PVC compound), their blends with the plasticized PVC compound do not show a high dielectric loss factor. This indicates that the blends can be used as dielectric material. While the activation energy for the dielectric relaxation of the PVC phase is not influenced by the presence of GRT in the compound, the presence of chlorinated GRT lowers the activation energy, indicating a higher degree of compatibility through dipole–dipole interaction between PVC and chlorinated GRT.

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