Melt-Processable Rubber: Chlorinated Waste Tire Rubber-Filled Polyvinyl Chloride

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ABSTRACT: Chlorinated ground rubber tire (Cl-GRT) particles were used as filler in a plasticized polyvinylchloride (PVC) to develop a melt-processable rubber composition. Physical properties of the Cl-GRT-filled PVC compound showed improvement compared to the nonchlorinated counterpart. Interaction between Cl-GRT and PVC was examined on the basis of results of stress relaxation, dynamic mechanical thermal analysis, and solvent swelling studies. The Cl-GRT could be loaded upto 40 parts per hundred parts of PVC, and the composition still retains the elastomeric characteristics. The Cl-GRT-filled composite was found to be reprocessable like the unfilled PVC compound. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 622–631, 2002; DOI 10.1002/app.10352

Key words: poly(vinyl chloride); waste rubber; recycling melt processable rubber

INTRODUCTION

Disposal of waste rubber material is a global problem, and used tires constitute the largest volume of scrap rubber. Recycling of waste tires is essential due to economic and environmental reasons. Utilization of ground waste rubber has been reviewed recently.[1] Finely ground waste tire rubber (commonly called ground rubber tire, abbreviated as GRT) has been used as filler in rubbers[2–5] and in thermoplastics.[6] Physical properties and processability are reported to be adversely affected when large volumes of waste rubber is added to a rubber compound.[7] Baker and coworkers reported utilization of GRT in thermoplastic matrices.[8–11] Impact modification of polypropylene by blending it with waste rubber has also been reported.[12,13] Utilization of GRT in polar polymer matrices has not been successful due to surface energy mismatch, leading to incompatibility. Surface modification of GRT is nec-

essary to enhance compatibility. Bagheri et al.[14] used surface-oxidized GRT to toughen epoxy resin. Rodriguez[15] studied silane treatment of GRT to improve mechanical properties of GRT-filled unsaturated polyester resin.

Chlorination has been reported to be a very effective way to modify the GRT surface and make it polar.[16–22] Oldfield et al.[16] studied chlorination of vulcanized rubber surface using trichloroisocyanuric acid (TCICA). Naskar et al.[23] chlorinated the GRT surface using TCICA and characterized the modified GRT. Molded sheets based on GRT treated with 3% TCICA solution in methanol, exhibit optimum combination of surface and tensile properties. Kim et al.[24] reported that chlorinated crumb rubbers are compatible with nitrile rubber (NBR) and the chlorinated crumb/NBR blend shows greater physical properties than the unmodified crumb/NBR blend. Addition of nitrile rubber-based printing roller waste powder in rigid polyvinylchloride has been reported to improve the impact resistance and flex properties of the plastic.[25] The present article reports the results of studies on utilization of chlorinated GRT as filler in the plasticized poly-

Table I   Description of the Materials Used

Material	Characteristics
Cryogenically ground rubber tire (GRT), obtained from Recovery Technology Inc. Ontario, Canada.	Particle size: 160–205 μm, Composition[3]: rubber %, 44; carbon black% 27; ash%, 17; acetone extractables %, 12
Plasticized PVC (K, 67), 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 Sigma Aldrich foreign holding company, Bangalore, India.	97% pure
Methanol and Nitric acid, obtained from S.D. Fine chem. Ltd. Boisar, India	A.R grade, 99% pure

vinylchloride (PVC) compound. Studies include measurement of physical properties, stress relaxation, dynamic mechanical properties, swelling behavior, and morphology of chlorinated GRT-filled PVC.

EXPERIMENTAL

Materials

Details of the materials used are shown in Table I.

Chlorination of GRT

The method used is the same as described earlier.[23] 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 TCICA solution in methanol for 20 min. The particles were then filtered, washed thoroughly under tap water, and dried for 24 h at 50°C in the oven. The GRT treated with TCICA solution is designated as Cl-GRT. Characterization of the Cl-GRT has been reported recently.[23]

Formulations

Compositions based on PVC filled with different loadings of GRT and Cl-GRT are given in Table II.

Mixing and Molding

Compounds of PVC and GRT were prepared in a Brabender Plasticorder PLE 330 at 170°C using a

Table II   Physical Properties of Plasticized PVC Compound Containing GRT and Cl-GRT[a]

Physical Properties	Composition (PVC/Filler)[b]					
	100/0	100/10	100/20	100/40	100/60	100/80
Tensile strength (MPa)	13.4	8.4 (8.3)	7.5 (6.9)	7.1 (5.3)	6.1 (3.8)	5.7 (3.5)
Elongation at break (%)	424	230 (238)	192 (188)	132 (136)	96 (91)	74 (72)
Young's modulus (MPa)	6.0	6.1 (5.8)	7.9 (6.0)	10.8 (8.2)	13.7 (8.5)	15.6 (9.2)
100% modulus (MPa)	5.5	5.3 (5.1)	5.4 (4.8)	6.7 (4.9)	—	—
Toughness (J/m^2) ($\times 10^{-3}$)	15.42	5.50 (5.42)	4.20 (3.56)	3.12 (2.21)	1.82 (1.18)	1.32 (0.80)
Tear strength (kN/m)	52.8	43.2 (41.1)	39.4 (34.6)	39.0 (30.0)	28.8 (22.9)	24.8 (17.2)
Hysteresis loss ratio at 100% elongation	0.730	0.730 (0.735)	0.757 (0.777)	0.746 (0.830)	—	—
Tension set (%) at 100% elongation	12	12 (12)	12 (14)	12 (16)	—	—
Hardness (shore A)	55	56 (55)	60 (57)	68 (58)	70 (60)	72 (62)

[a] Values in the parentheses indicate properties of corresponding unmodified GRT filled compound.
[b] Parts by weight.

cam-type rotor. First PVC granules were added 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 value was attained. The blends, while still hot, were taken out from the Plasticorder and were then sheeted out at a 2-mm nip gap on a two-roll mill.

The sheeted out compounds were compression molded in an electrically heated hydraulic press at 180°C for 2 min at 6 MPa pressure and then cooled under pressure by water circulation through the hot platens of dimension 18×12 cm.

Measurement of Physical Properties

Dumbbell-shaped tensile specimens and unnicked 90° angle test pieces for tear testing were punched out from the molded sheets. Tensile strength, modulus, elongation at break, and tensile set at 100% elongation were measured, according to ASTM D412-98a specification, in a Zwick Universal Testing Machine (UTM) model 1445 at a strain rate of 500 mm/min at 25°C. Tear strength was measured according to ASTM D 624-98 in the Zwick UTM. Hysteresis loss at 100% elongation was measured at 25°C by subtracting the area under the force–retraction curve from the area under the force–deformation curve (up to 100% elongation). Hysteresis loss ratio was calculated as the ratio of hysteresis loss to the area under the force–deformation curve. Toughness was measured from the area under the stress–strain curve. Hardness of 10 mm-thick specimens was measured using shore A Durometer.

Stress Relaxation

Stress relaxation behavior of the compounds was studied in the Zwick UTM at 25°C. Dumbbell specimens were stretched to predetermined lengths (applied strain corresponding to 0.105, 0.295, and 0.540) at 500 mm/min, and the stress readings were recorded against time.

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical spectra of the blends were obtained using a dynamic mechanical thermal analyzer (DMTA, MK II) of Polymer Laboratory (UK). Sample specimens of dimension $43.5 \times 12.5 \times 1.5$ mm were analyzed in dual cantilever bending mode at a constant frequency of 1 Hz, peak-to-peak displacement of 64 μm, and in the temperature range from -120 to 150°C. The heat-ing rate was 2°C/min. The temperature corresponding to the peak in tan δ vs. temperature plot was taken as the glass-to-rubber transition temperature (T_g).

Morphology

Morphology of the molded compositions was examined under the scanning electron microscope (JEOL JSM 5800) by fracturing the specimens in liquid nitrogen and then etching out the GRT or Cl-GRT in boiling concentrated nitric acid (115°C) for 30 min. The samples were washed with water and dried at room temperature. Etched out samples were gold coated and then examined under the SEM.

Swelling

Circular test pieces of radius of about 10 mm were die cut from the molded sheets (1.5 mm thick), then weighed accurately and immersed in acetone at room temperature (25°C). After equilibrium swelling, the specimens were removed from the solvent, blotted, and weighed quickly. Volume swelling (%) for a specimen was estimated as

$$\text{Volume swelling } (\%) = (W_2/W_1 - 1)\rho_c/\rho_s \times 100 \tag{1}$$

where W_1 and W_2 are specimen weights before and after swelling, respectively, ρ_c and ρ_s are the density of the compound and solvent, respectively.

Reprocessability

Reprocessability of the selected compound was done by remixing and remolding of the failed test specimens after 2 months of aging at room temperature, followed by measuring the physical properties. The process was repeated twice.

RESULTS AND DISCUSSION

Physical Properties

Physical properties of the compositions are summarized in Table II. Stress–strain curves of the compounds are shown in Figure 1. It is observed that incorporation of GRT in PVC matrix decreases the tensile strength, toughness, elongation at break, and tear strength of PVC. But GRT increases the Young's modulus and hardness, al-

though the effect is pronounced at high loading (≥40 phr). Furthermore, GRT causes increase of hysteresis loss ratio and tension set. Properties of the chlorinated GRT-filled PVC are also shown in Table II. Chlorination of GRT improves toughness, Young's modulus, 100% modulus, and hardness, but reduces hysteresis loss ratio and tension set of the composite, when compared with the nonchlorinated counterpart. It is also evident that Cl-GRT-filled composition in general displays higher physical properties than the GRT counterparts. The enhancement in properties by Cl-GRT is believed to be due to the dipole–dipole interaction between PVC and the chlorinated GRT. At low loading of GRT (e.g., at 10 phr), the effect of chlorination is not pronounced. However, at high loading of GRT (e.g., 60, 80 phr), the enhancement in properties of the PVC/GRT compositions due to chlorination of GRT is significant. The blends exhibit characteristics of the melt processible rubber up to 40 parts of Cl-GRT per 100 parts of PVC, beyond which the ultimate elongation is reduced drastically. The decrease in ultimate elongation at high loading of GRT is due to inextensibility of the GRT particles, and hence, the strain experienced by the PVC matrix is higher. It is interesting to note that the ultimate elongation of both modified and unmodified GRT-filled compounds at fixed GRT loading is the same. It seems that the adhesive bonding between matrix and the filler fails before tensile failure; in other words, dewetting takes place prior to tensile failure. Dipole–dipole interaction
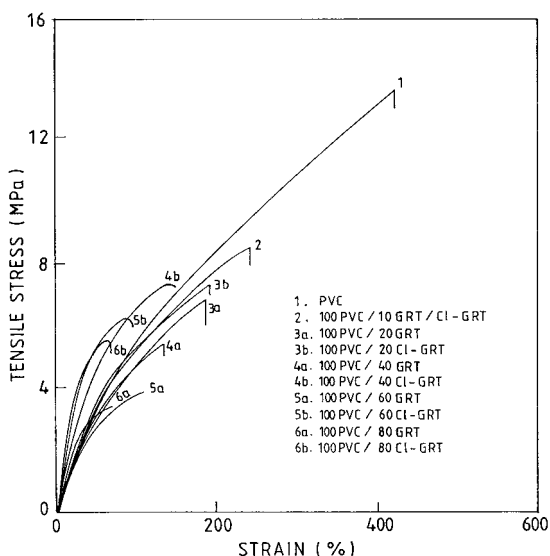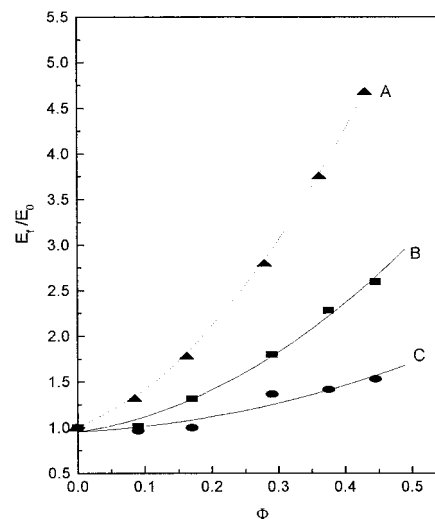

Figure 2 Plot of Young's modulus ratio of filled to unfilled compound against volume fraction of filler. (A) Guth-Gold plot (calculated); (B) Plot for PVC/Cl-GRT compositions; (C) Plot for PVC/GRT compositions.

between Cl-GRT and PVC causes an increase in the tensile strength in the case of Cl-GRT-filled compound. Figure 2 shows the plots of ratio of Young's moduli of filled to unfilled compounds (E_f/E_0) against volume fraction of GRT or Cl-GRT (ϕ). The variation of moduli with filler loading could be fitted into the following equations:

$$\text{For GRT: } E_f/E_0 = 1 + 0.36\phi + 2.20\phi^2 \quad (2)$$

$$\text{or, } \Delta E/E_0 = (E_f - E_0)/E_0 = E_1 = 0.36\phi + 2.20\phi^2 \quad (2a)$$

$$\text{For Cl-GRT: } E_f/E_0 = 1 + 1.07\phi + 6.30\phi^2 \quad (3)$$

$$\text{or, } \Delta E/E_0 = (E_f - E_0)/E_0 = E_2 = 1.07\phi + 6.30\phi^2 \quad (3a)$$

It is evident from eqs. (2a) and (3a) that

$$E_2 \approx 3E_1 \quad (4)$$

Coefficients of the equation representing the variation of $\Delta E/E_0$ against volume fraction of Cl-GRT is found to be three times higher than that of the GRT. Equation (3) is closer to the calculated Guth-Gold equation (shown in Fig. 2), which can be expressed as,

$$E_f/E_0 = 1 + 2.5\phi + 14.1\phi^2 \quad (5)$$

Figure 1 Stress–strain curves of different blends.

$$\text{or, } \Delta E/E_0 = (E_f - E_0)/E_0 = 2.5\phi + 14.1\phi^2$$

$$(5a)$$

Equation (5) is valid for rigid reinforcing fillers in a polymer matrix, where filler–matrix adhesion is believed to be high. In the present study fillers are soft and the adhesion is not strong, and hence, the deviation of the experimental plots from the calculated Guth-Gold plot. Chlorination of GRT increases its modulus.[23]. Furthermore, an increase in adhesion between the filler and the matrix in the case of Cl-GRT makes the variation of Young's moduli with filler concentration closer to the Guth-Gold plot (Fig. 2).

Morphology

SEM photomicrographs of the cryo-fractured surface where from rubber particles have been etched out by boiling nitric acid are shown in
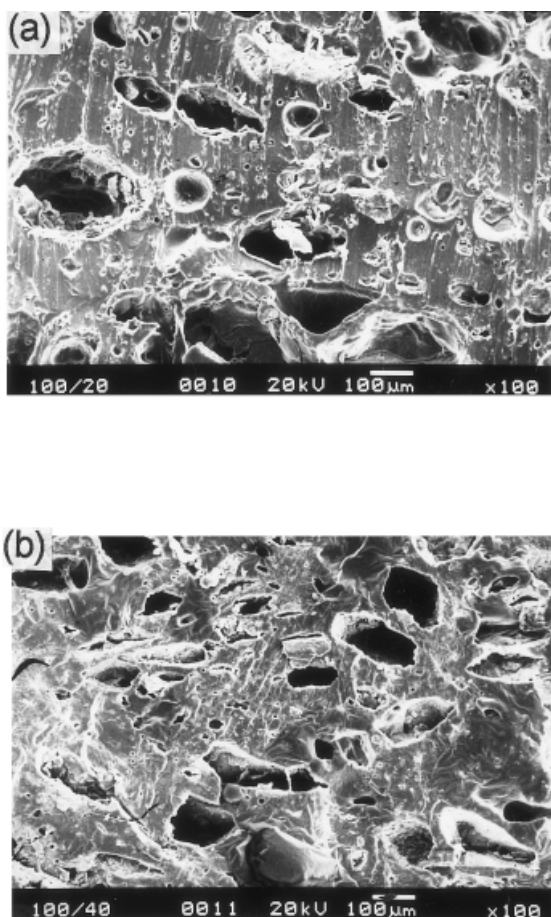
Figure 3 SEM photomicrographs of PVC/Cl-GRT compositions where from Cl-GRT phase has been etched out; (a) 100/20; (b) 100/40.
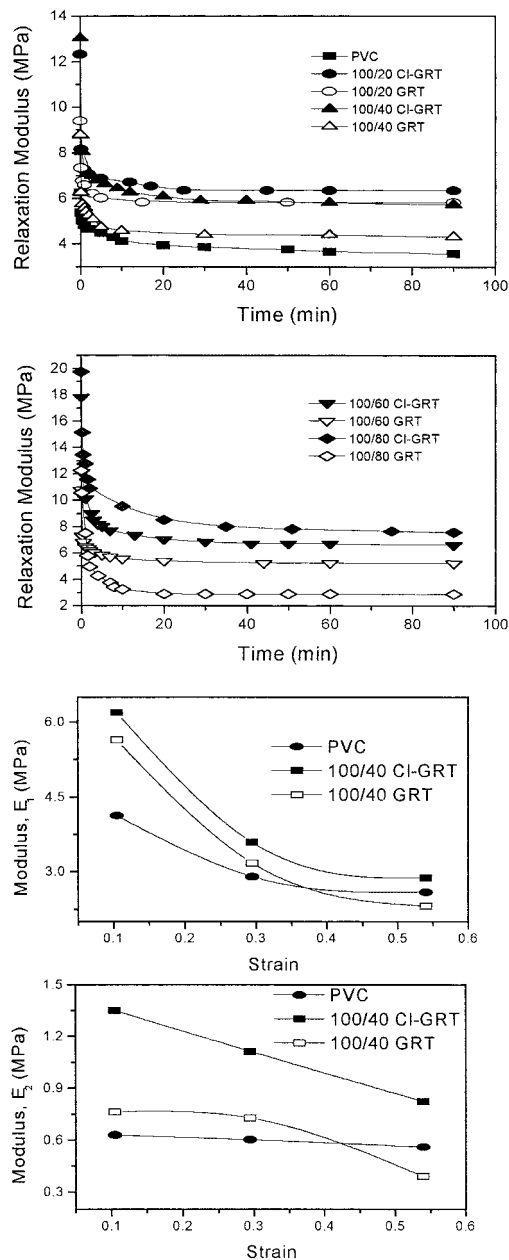
Figure 4 (a) Plot of relaxation moduli of compositions against time; (b) Plot of E_1 and E_2 against applied strain.

Figure 3(a)–(b). The holes indicate the domains of GRT particles. It is clear that the rubber particles are dispersed in the PVC matrix.

Stress Relaxation

Relaxation modulus of the compositions at a strain of 0.105 against time is shown in Figure 4(a). It is observed that the relaxation modulus of

Table III Relaxation Times and Moduli of PVC/Cl-GRT Composites from Stress Relaxation Study[a]

Composition (PVC/Filler)[b]	Strain Applied	E_1 (MPa)	τ_1 (s)	E_2 (MPa)	τ_2 (s)
100/0	0.105	4.12	35	0.63	1980
	0.295	2.95	35	0.60	1920
	0.540	2.59	30	0.56	1900
100/20	0.105	5.65 (5.63)	30 (30)	0.91 (0.61)	900 (1190)
100/40	0.105	6.19 (5.35)	30 (35)	1.35 (0.76)	870 (1080)
	0.295	3.59 (3.17)	30 (40)	1.11 (0.73)	960 (1190)
	0.540	2.88 (2.31)	30 (30)	0.82 (0.39)	1140 (1260)
100/60	0.105	6.85 (5.13)	40 (35)	1.65 (0.97)	930 (760)
100/80	0.105	7.81 (3.44)	50 (60)	3.39 (1.66)	1010 (615)

[a] Values in the parentheses refer to the corresponding GRT filled compound.
[b] Parts by weight.

the filled composites, at a particular time, increases with an increase in filler loading, and at a particular loading, the Cl-GRT-filled composition exhibits higher relaxation modulus than the GRT-loaded compound. With an increase in filler loading at a particular strain the true strain experienced by the matrix increases due to inextensibility of the particulate fillers. This causes an increase in relaxation modulus with an increase in filler loading. At a particular loading, Cl-GRT-filled composition yields higher modulus due to improved matrix–filler interaction. The stress relaxation process in a polymeric material may be assumed to consist of orientation of chain units and slippage of chain segments along with dewetting of fillers from the matrix. The stress decay of the unfilled compound is very fast initially and very slow in the long-time region. A quantitative representation of the stress relaxation process (at room temperature, within an experimental time limit) can be made with a model consisting of two Maxwell elements and one spring, all in parallel. Then tensile modulus of the material at time t may be expressed as:[26]

$$E(t) = E_e + E_1 e^{-t/\tau_1} + E_2 e^{-t/\tau_2} \qquad (6)$$

where E_i and τ_i represents the tensile moduli and relaxation times of the elements, respectively. The stress relaxation data have been analyzed by the method described by Sabia and Eirich.[26] The moduli and relaxation times (at specific strain) of the compositions are shown in Table III. It is observed that E_1 increases with increase in Cl-GRT loading but it deceases in the case of GRT-filled composites. This indicates that good adhe-

sion between Cl-GRT and PVC takes place, whereas dewetting occurs by the application of strain in the case of GRT-filled composites and the effect is more pronounced at higher filler loading. Previously it has been reported that chlorination enhances the surface energy of GRT by an increase in the polar contribution.[23] Hence, the extent of interaction between Cl-GRT and PVC is likely to be higher than that of GRT and PVC. The τ_1 is found to be very short (less than a minute). E_2 for the compositions increases with an increase in filler loading. E_2 for the Cl-GRT-filled compound is always higher than the corresponding GRT-filled composite. τ_2 for PVC compound is very high. With incorporation of 20 parts of Cl-GRT, τ_2 drops drastically from 1980 s (for unfilled compound) to 900 s. With further increase in Cl-GRT loading, τ_2 does not change significantly. But τ_2 for the GRT filled composites gradually decreases with increase in filler loading.

The reciprocal of relaxation time $(1/\tau)$ may be treated as kinetic rate constant, if the process is assumed to be first order.

$$E(t) = E_0 e^{-t/\tau} \quad \text{or} \quad E(t) = E_0 e^{-kt} \qquad (7)$$

where $k = 1/\tau$, which resembles first order rate constant. Therefore, the higher the τ, the slower the relaxation process. Thus, a decrease in τ_2 with an increase in loading of GRT suggests that faster relaxation takes place through a dewetting or filler–matrix separation process.

Stress relaxation study of the unfilled and filled PVC compositions with 40 parts of GRT and Cl-GRT was also carried out at a strain level of 0.295 and 0.540. It is observed that both E_1 and

E_2 decrease with increase in strain. The decrease in E_2 is marginal in the case of unfilled compound. Both E_1 and E_2 drastically reduce in the case of GRT filled compound at higher strain (0.540) [Fig. 4(b)]. A higher degree of dewetting is believed to be the reason for this behavior. Relaxation time τ_2 is found to be almost independent of the applied strain.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical loss tangent spectra of plasticized PVC, sheeted out ground rubbers (GRT and Cl-GRT), and their composites at 100/40 and 100/80 PVC/filler compositions are shown in Figure 5(a). GRT exhibits a glass–rubber transition at −30°C. On chlorination of GRT, the $(\tan \delta)_{max}$ is lowered from 0.430 to 0.243, without a shift in glass–rubber transition temperature (T_g). Cl-GRT also exhibits a high temperature relaxation (62°C), which is due to the softening of the hard phase formed by dipole–dipole interaction of the chlorinated segments of rubber hydrocarbon of GRT.[23] Plasticized PVC shows T_g at 11°C. The composites of PVC and GRT/ Cl-GRT are found to exhibit two relaxation transitions, the one around −40°C is due to the glass–rubber transition of the elastomeric phase and the other in the range of 20–40°C is due to the PVC phase. Results of loss tangent plots are given in Table IV. Incorporation of GRT into PVC shifts the T_g of both phases, while T_g of GRT or Cl-GRT is lowered from −30°C to around −41°C, and that of the PVC phase is raised from 11°C to 20–40°C, depending on the composition. This is probably due to the migration of the plasticizer from the PVC phase to the GRT or Cl-GRT phase. 100/40 PVC/filler compositions show a shift of T_g of the PVC phase to 25°C for GRT and 23°C for Cl-GRT. At this composition $(\tan \delta)_{max}$ for the PVC phase is lowered from 0.528 (for unfilled compound) to 0.466 for the GRT-filled and to 0.450 for the Cl-GRT-filled compound. For 100/80 PVC/filler composition, the T_g of the PVC phase is observed at 38°C with $(\tan \delta)_{max} = 0.457$ for the GRT-filled compound and at 32°C with $(\tan \delta)_{max} = 0.423$ for the Cl-GRT-filled compound. The lower $(\tan \delta)_{max}$ and less shift in T_g of the PVC phase in the PVC/Cl-GRT composition are indicative of enhanced compatibility between Cl-GRT and PVC. Although the transition temperature of the elastomeric phase does not change with an increase in the Cl-GRT loading, the corresponding tan δ peak height increases. Furthermore, as loading of Cl-GRT in-
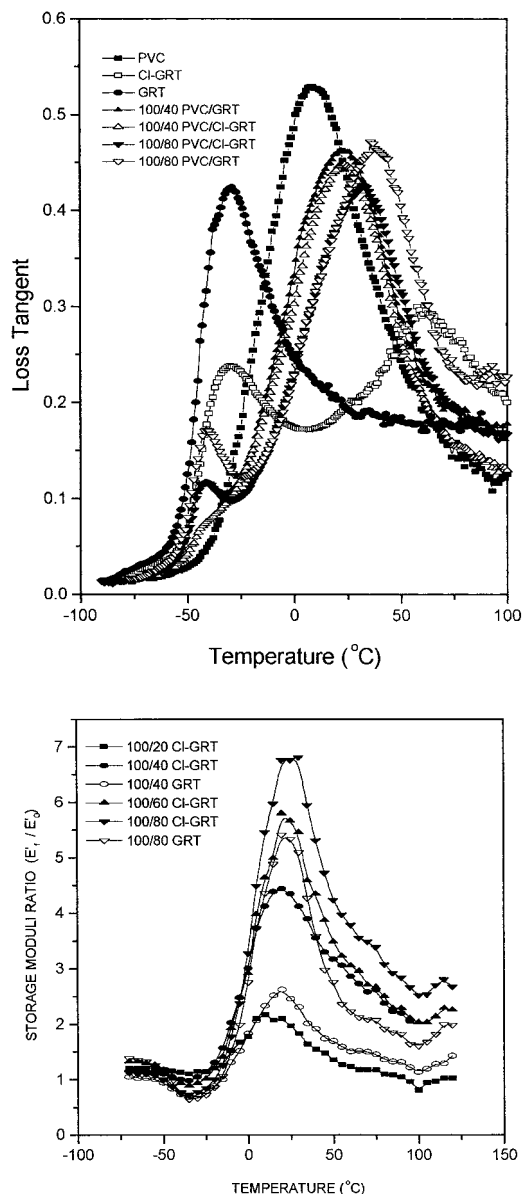
Figure 5 (a) Loss tangent plots of the composites and their neat components; (b) Plots of relative moduli (E'_f/E'_0) of composites against temperature.

creases, the tan δ peak due to the PVC phase is shifted towards higher temperature and the peak height is gradually lowered. Variation of $(\tan \delta)_{max}$ for the PVC phase vs. volume fraction of the filler in the composites for both GRT and Cl-GRT can be expressed by the following equations:

$$\text{For GRT: } (\tan \delta)_{max} = 0.53 - 0.16\phi \qquad (8)$$

$$\text{For Cl-GRT: } (\tan \delta)_{max} = 0.53 - 0.23\phi \qquad (9)$$

Table IV   Results of Dynamic Mechanical Studies on PVC/Cl-GRT Composites[a]

Composition (PVC/Filler)[b]	Rubber Phase		PVC Phase	
	T_g (°C)	$(\tan \delta)_{max}$	T_g (°C)	$(\tan \delta)_{max}$
0/100	−30	0.425	—	—
0/100	−30	0.243	—	—
100/0	—	—	11	0.528
100/20	—	—	22	0.491
100/40	−42 (−41)	0.074 (0.119)	23 (25)	0.450 (0.466)
100/60	−41	0.112	26	0.444
100/80	−42 (−41)	0.118 (0.171)	32 (38)	0.423 (0.457)

[a] Values in the parentheses refer to the corresponding GRT filled compound.
[b] Parts by weight.

It is clear that the negative slope is higher for Cl-GRT than that of GRT. Because the slope is believed to be a measure of the interaction between the filler and the matrix,[27–29] it is evident that the interaction between Cl-GRT and PVC is greater than that between GRT and PVC.

Storage moduli spectra also provide information about the matrix–filler interaction. Figure 5(b) shows the plot of relative modulus (ratio of storage modulus of composite to the matrix) against temperature. The nature of the curve is found to be same for all the composites. It is observed that below −50°C the changes in relative modulus with incorporation of the filler is insignificant. Relative modulus decreases with an increase in filler loading in the temperature range −50 to −20°C, because of the glass–rubber transition of the filler phase. At a particular loading, the GRT-filled composite exhibits lower relative modulus than the Cl-GRT-filled compound. Around T_g the relative modulus of the filled compound is found to be maximum. Up to T_g, the adsorbed and immobilized polymer matrix on the particle surface makes the composite a single rigid unit although the neat matrix becomes rubbery at this temperature range. As the temperature further rises beyond T_g, the matrix cannot withstand the dynamic force, and the rigid composite breaks into smaller units. At this stage particle–particle motion dominates as the immobilized softened matrix undergoes slippage at the interface during deformation of the material.[30] Slippage is also caused by the mismatch of coefficients of thermal expansion of the filler and the matrix. Thus, beyond T_g the relative modulus decreases and this is true for any kind of filled system.[30] However, the relative modulus of the composites of a specific composition beyond T_g is dependent on the degree of interaction between the filler and the matrix, and the modulus of the filler. Upon chlorination modulus of the GRT increases.[23] At constant filler loading, higher modulus of the filler and good adhesion with the matrix cause the composites containing Cl-GRT to display higher relative modulus than those containing GRT even at an elevated temperature.

Solvent Swelling

Results of equilibrium swelling studies of the composites in acetone provide information about the filler–matrix interaction.[31] The volume swelling (%) of the composites is plotted against volume fraction of the filler for both GRT and Cl-GRT (Fig. 6). Figure 6 shows that swelling (%) of the composite having low volume fraction of filler
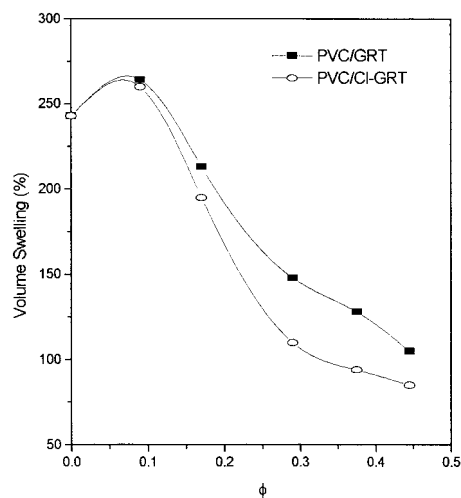
Figure 6   Volume swelling (%) of composites against volume fraction of filler.

Table V   Results of Reprocessability Studies

Properties	PVC			100/40 PVC/Cl-GRT		
	First Cycle	Second Cycle	Third Cycle	First Cycle	Second Cycle	Third Cycle
Tensile strength (MPa)	13.4	11.9	10.9	7.1	6.7	6.2
Ultimate elongation (%)	424	367	302	132	123	125
Young's modulus (MPa)	6.0	6.1	6.6	10.8	10.7	10.9
100% modulus (MPa)	5.50	5.58	5.76	6.70	6.3	5.90
Toughness $(J/m^2)(\times 10^{-3})$	15.42	11.21	9.84	3.12	2.92	2.86
Tear strength (kN/m)	52.8	52.2	52.0	39.0	38.2	37.0

(e.g., $\phi = 0.09$ or 10 phr filler loading) is higher than that of the unfilled compound. At low loading there is no interaction between the filler and matrix, and during swelling the shear force experienced by the polymer desorbs the matrix from the filler surface and opens up small vacuoles.[31] However, at higher loading of filler the volume swelling of the composite is lower than that of the unfilled compound, because fillers do not swell in acetone. A higher degree of the filler–matrix interaction makes the physical bonds at the interface to withstand the shear force caused by swelling of the matrix. It is clear from the plot (Fig. 6) that at fixed filler loading, swelling (%) of the composite containing Cl-GRT is always less than that of the GRT-filled compound. As discussed earlier, the dipole–dipole type of interaction at the interface of Cl-GRT and PVC restricts volume swelling of the compound.

Reprocessability

Mechanical properties of the composites indicate that plasticized PVC could be loaded with Cl-GRT up to 40 phr when the composition displays characteristics of a melt-processible rubber. The 100/40 PVC/Cl-GRT composition and the unfilled PVC compound were reprocessed by remixing and remolding of the waste specimens from laboratory failure testing, followed by 2 months storage at room temperature. The mechanical properties of the recycled compositions are shown in Table V. It is observed that the 100/40 PVC/Cl-GRT composite shows greater retention of tensile strength, ultimate elongation, and toughness even after three times reprocessing of the compound. Like the unfilled compound, the tear strength and Young's modulus are not significantly changed in the filled composition. Only 100% modulus of the filled compound is slightly reduced on reprocess-

ing. Thus, the 100/40 PVC/Cl-GRT composition can be reprocessed like a melt-processible rubber.

CONCLUSIONS

Chlorinated ground rubber tire powders (Cl-GRT) can be used as filler in a plasticized PVC compound. Maximum 40 phr of Cl-GRT may be loaded, beyond which physical properties like tensile strength, ultimate elongation, and tear strength are adversely affected. SEM photomicrographs indicate that filler particles are dispersed in the PVC matrix. Stress relaxation study of the compositions shows improved adhesion between PVC and Cl-GRT, which restricts dewetting at the interface by the application of strain. Results of DMTA and solvent swelling studies provide evidence for enhanced interaction between PVC and Cl-GRT compared to PVC–GRT interaction. The PVC/Cl-GRT composite also exhibits reprocessability characteristics of a melt-processable rubber.

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