

# Thermoplastic Elastomers from Reclaimed Rubber and Waste Plastics

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**ABSTRACT:** Thermoplastic elastomeric compositions from reclaimed rubber and scrap plastics were prepared. The physical properties, dynamic mechanical properties, rheological behavior, and phase morphology of the blends were studied. A 50:50 rubber/plastic ratio was found to be the best for processability, ultimate elongation, and set properties. A sulfur-accelerator system was found to be better than a peroxide system for dynamic crosslinking. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2035–2042, 2002

**Key words:** thermoplastic elastomers; reclaimed rubber; waste plastics

## INTRODUCTION

The emergence of thermoplastic elastomers bridges the gap between conventional elastomers and thermoplastics. They have the performance characteristics of crosslinked elastomers at room temperature and enjoy the beauty of processing of thermoplastic materials. Thermoplastic elastomers have been described in several recent books.<sup>1–3</sup> Chowdhury and Bhowmick described the preparation and properties of several thermoplastic elastomeric natural rubber (NR)–plastic blends in earlier communications.<sup>4,5</sup> It was observed that the mechanical properties of the blends (i.e., the tensile strength or elongation at break) are inferior to either plastics or vulcanized rubbers. The morphology of the rubber–plastic blends was inferred to play a dominant role in deciding the properties of these blends. It is with this understanding that an investigation was undertaken to generate the morphology using recycled rubber and waste plastics. The properties of these blends were then compared with those of

the pure polymers. The results for NR and polyethylene (PE) are reported here.

The rubber and plastics industry faces a major challenge in this decade to find a satisfactory way to deal with an enormous quantity of waste rubber goods, particularly tire and waste plastics, which are an environmental hazard. A significant review of the reprocessing of vulcanized rubbers was published by Markarov and Drodzowski.<sup>6</sup> Krane et al.<sup>7</sup> reported disposal of vulcanized rubbers whereas research work on rubber reclaiming was reported by Smith<sup>8</sup> and Klingensmith.<sup>9</sup> Klingensmith and Baranwal<sup>10</sup> also recently reviewed the subject. Waste polybutadiene rubber grafted with ethyl acrylate was shown to substitute virgin polyacrylic rubber.<sup>11</sup> For example, Luo and Isayev<sup>12</sup> studied ground rubber tire (GRT)/polypropylene (PP) composites using 1,2-polybutadiene, polybutadiene–maleic anhydride adduct, 1,2-polybutadiene in dispersed calcium silicate, and maleic anhydride grafted PP as compatibilizers. Bagheri et al.<sup>13</sup> investigated toughened epoxies with carboxy-terminated butadiene and GRTs. *In situ* reactive compatibilization of GRTs in a PE matrix was attempted by Duhaime and Baker.<sup>14</sup> A blend of 40 wt % ethylene acrylic acid (EAA) coated GRT particles with

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**Table I Formulation of Mixes**

Sl No.	Mix No.	Composition (Rubber/Plastic/Additive <sup>a</sup> )
1	A	50 RRHC/50 LDPE
2	A <sub>1</sub>	50 RRHC/50 LDPE/1.0 DCP
3	A <sub>2</sub>	50 RRHC/50 LDPE/1.0 S, 0.25 TMTD, 1.0 MBT, 3.0 ZnO, 0.7 stearic acid
4	A <sub>3</sub>	50 RRHC/50 LDPE/3.0 maleic anhydride, 0.1 DCP
5	A <sub>4</sub>	50 RRHC/50 LDPE/5.0 EVA (28% VA)
6	A <sub>5</sub>	50 RRHC/50 LDPE/5.0 SEBS
7	B	40 RRHC/60 LDPE
8	C	60 RRHC/40 LDPE
9	D	35 RRHC/65 LDPE
10	N	50 NR/50 LDPE
11	N <sub>2</sub>	50 NR/50 LDPE/1.0 S, 0.25 TMTD, 1.0 MBT, 3.0 ZnO, 0.7 stearic acid

<sup>a</sup> Additive dosage in parts per hundred of rubber (phr); RRHC, reclaimed rubber hydrocarbon.

linear low density PE (LDPE) was shown to have high impact and tensile strength. Poor mechanical properties were obtained with high density PE.<sup>15</sup> Rajalingam and Baker<sup>16</sup> also observed that EAA acts as an interfacial coupling agent, such as carbon black, metal oxide, or other polar species, on the GRT surface. Plastic recycling is also a topic of many articles and reviews.<sup>17,18</sup> However, there was no report until now on the development of thermoplastic elastomers from waste rubber and waste plastics, although polymer compositions containing waste rubber or waste plastics are known.

## EXPERIMENTAL

Compositions were prepared from reclaimed NR (15.7% acetone extract, 35.9% organic fillers,

11.4% inorganic fillers, 37% rubber hydrocarbon, and 12.8% ash) and scrap grade LDPE (3.9% acetone extract, 0.1% ash, and 96% plastic), which were both obtained from Bengal Waterproof Limited (Calcutta, India).

The blends of reclaimed NR and scrap LDPE were prepared over a wide range of compositions from 70:30 to 30:70. For comparison, blends of pure NR (molecular weight =  $5 \times 10^5$  g/mol) and pure LDPE (melt flow index = 2.0 g/10 min at 190°C/2.16 kg, density = 0.920 g/mL) were evaluated wherever required. Dicumyl peroxide (DCP, containing 40% active ingredient) and sulfur and accelerators were used as curing systems to study the effect of vulcanization. In the blends the interaction between the heterogeneous rubber and polyolefin phases was varied by incorporating physical and chemical compatibilizers. The names of these ingredients and the formulations are given in Table I.

The blends were prepared on an open two-roll mill at a high temperature using steam. The rolls were initially heated at 110°C and the scrap LDPE was fed. When LDPE formed a sheet on the roll, the rolls were cooled using water. At 70°C reclaimed rubber was added to the LDPE on the rolls and the two polymers were mixed thoroughly to achieve uniform dispersion. The additives, if required, were added at 50–55°C and thoroughly dispersed. Finally, sheets were drawn out at a nip gap of 2–4 mm, depending on the characteristics of the blend ratio.

The sheeted out sample was compression molded between aluminum foils for 5 min at 150°C and a pressure of  $30 \times 10^5$  N/m<sup>2</sup> in an electrically heated press to get slabs with dimensions of 15 × 13 × 0.2 cm. After completion of the molding and still under compression, the sample was immediately cooled in water to avoid possible degradation of the rubber phase under high tem-

**Table II Blends of Rubber and Plastics, and Their Mixing Behavior**

Sl No.	Code No.	RRHC Content	LDPE Content	Remark
1	—	70	30	Very poor strength even at slightly elevated temperature, sheets cannot be drawn out
2	C	60	40	Sheets can be drawn out, further testing can be done
3	A	50	50	Appears to be best of lot, chosen for initial further testing
4	B	40	60	Further testing can be done
5	D	35	65	Appears to be more brittle than earlier samples, further testing can be done
6	—	30	70	Very brittle, further testing cannot be done

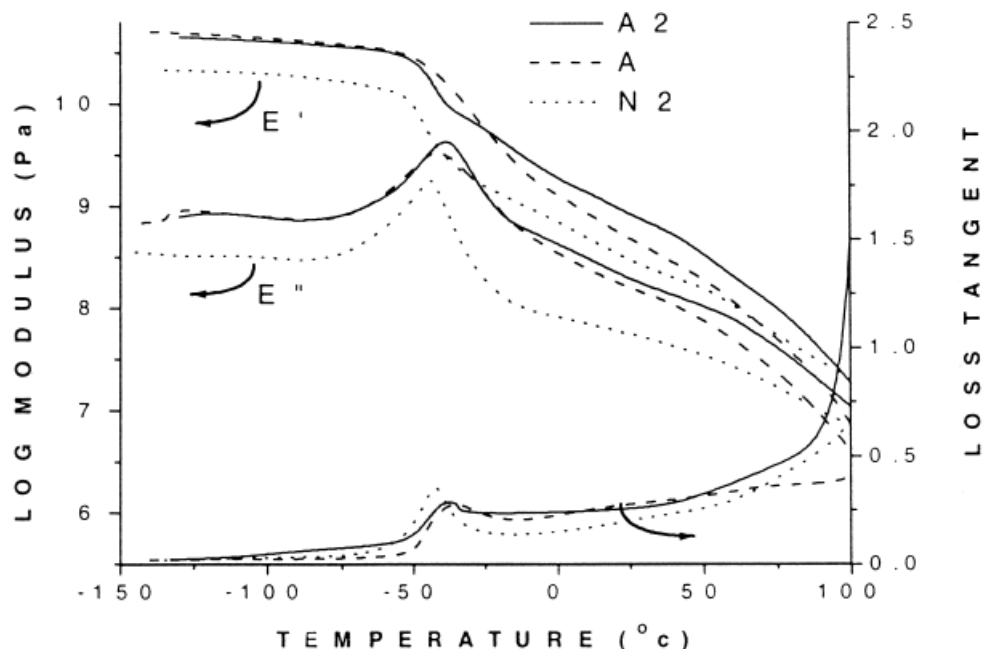


Figure 1 The dynamic mechanical properties of the blends.

perature exposure and to maintain the overall dimensional stability of the blend.

## Measurements

### Mechanical Properties

The determination of the modulus, tensile strength, and elongation at break was carried out on a Zwick universal testing machine (model 1445) according to the ASTM D 412-98a method using dumbbell-shaped test pieces. The tear resistance was tested according to ASTM D 624-98 using unnicked 90° angle test specimens along the grain direction. The hardness was measured via the ASTM D 2240-97 test method using a Shore A type durometer. The results reported here are the averages of three samples.

### Dynamic Mechanical Properties

The dynamic mechanical measurements were carried out using a Viscoelastometer DMTA (model MKII). The experiment was conducted in bending mode from -150 to +100°C at a frequency of 3 Hz and strain amplitude of 64 μm (peak to peak displacement) with a programmed heating rate of 2°C/min.

### Morphology

For studying the morphology, the reclaimed rubber-PE blend and NR-LDPE blend, both unvul-

canized and dynamically vulcanized, were etched with concentrated nitric acid at room temperature for 72 h. The samples were then washed thoroughly with water and dried. The samples were kept in an undisturbed condition and a dust-free environment. The samples were sputter coated with gold and SEM photographs were taken using a Philips model 500 scanning electron microscope at an accelerating voltage of 20 kV.

### Rheology

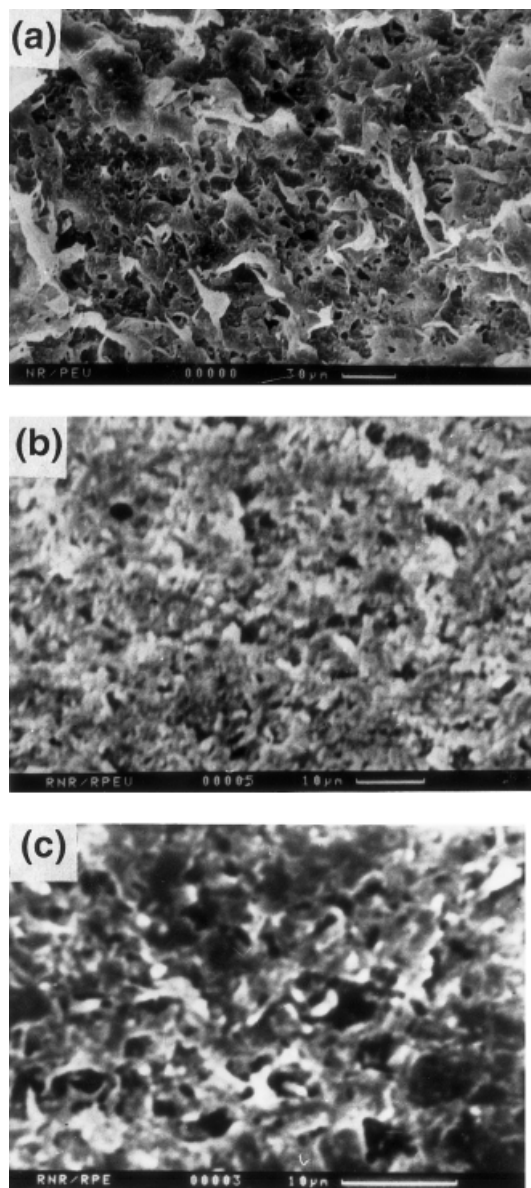
The rheological characteristics of the blends were measured by a Monsanto Processability Tester with a capillary length to diameter ratio of 30 (30:1 mm) and entrance angles of 45° and 60° (compound). The preheat time of each sample was 5 min at the processing temperature. The studies were carried out at 80, 100, and 120°C. The wall shear stress ( $\tau_w$ ), wall shear rate ( $\dot{\gamma}_w$ ), and shear viscosity ( $\eta$ ) were calculated using the following equations:

$$\tau_w = d_c \Delta P / 4l_c \quad (1)$$

$$\dot{\gamma}_w = [(3n' + 1)/4n'] \dot{\gamma}_{w,a} \quad (2)$$

$$\dot{\gamma}_w = 32Q / \pi d_c^3 \quad (3)$$

$$\eta = \tau_w / \dot{\gamma}_w \quad (4)$$



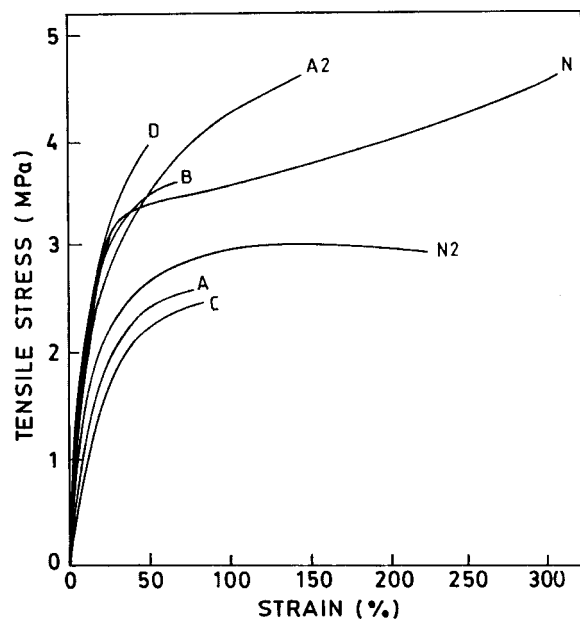
**Figure 2** SEM photomicrographs of blends with the rubber phase etched out: (a) N<sub>2</sub>, (b) A<sub>2</sub>, and (c) A.

where  $\Delta P$  is the pressure drop across the length of the capillary;  $d_c$  and  $l_c$  are the diameter and length of the capillary, respectively;  $Q$  is the volumetric flow rate;  $\gamma_{w,a}$  is the apparent wall shear rate; and  $n'$  is the uncorrected flow behavior index. The relaxed die swell was measured as  $(d_f - d_c)/d_c \times 100\%$ , where  $d_c$  and  $d_f$  are the diameters of the capillary used and the extrudate measured after 24 h of extrusion, respectively.

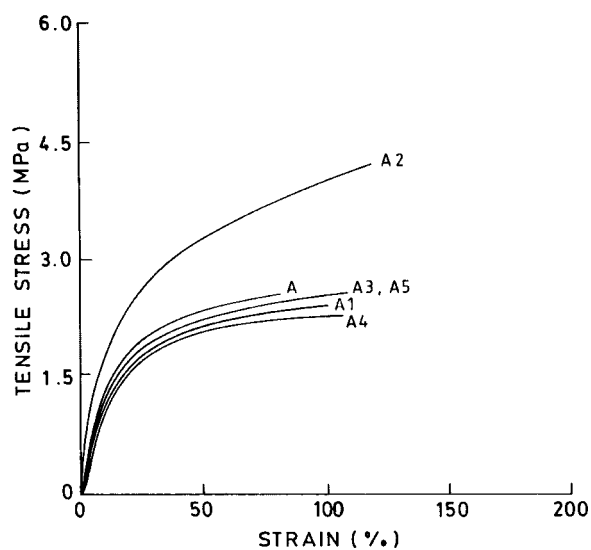
## RESULTS AND DISCUSSION

The formulations of the mixes are given in Table I. A wide range of blend ratios was prepared for

the study. However, we observed that at a very high rubber content it becomes increasingly difficult to process the material (Table II). It becomes sticky and the strength is poor. On the other hand, at higher plastic content the blend becomes brittle and loses the thermoplastic elastomeric



(a)



(b)

**Figure 3** Stress-strain curves of blends showing the effects of (a) crosslinking and the rubber/plastic ratio and (b) crosslinking and compatibilizers. Bar diagrams showing the variations of the (c) tensile strength, (d) elongation at break, (e) tear strength, and (f) Shore A hardness in different blends.

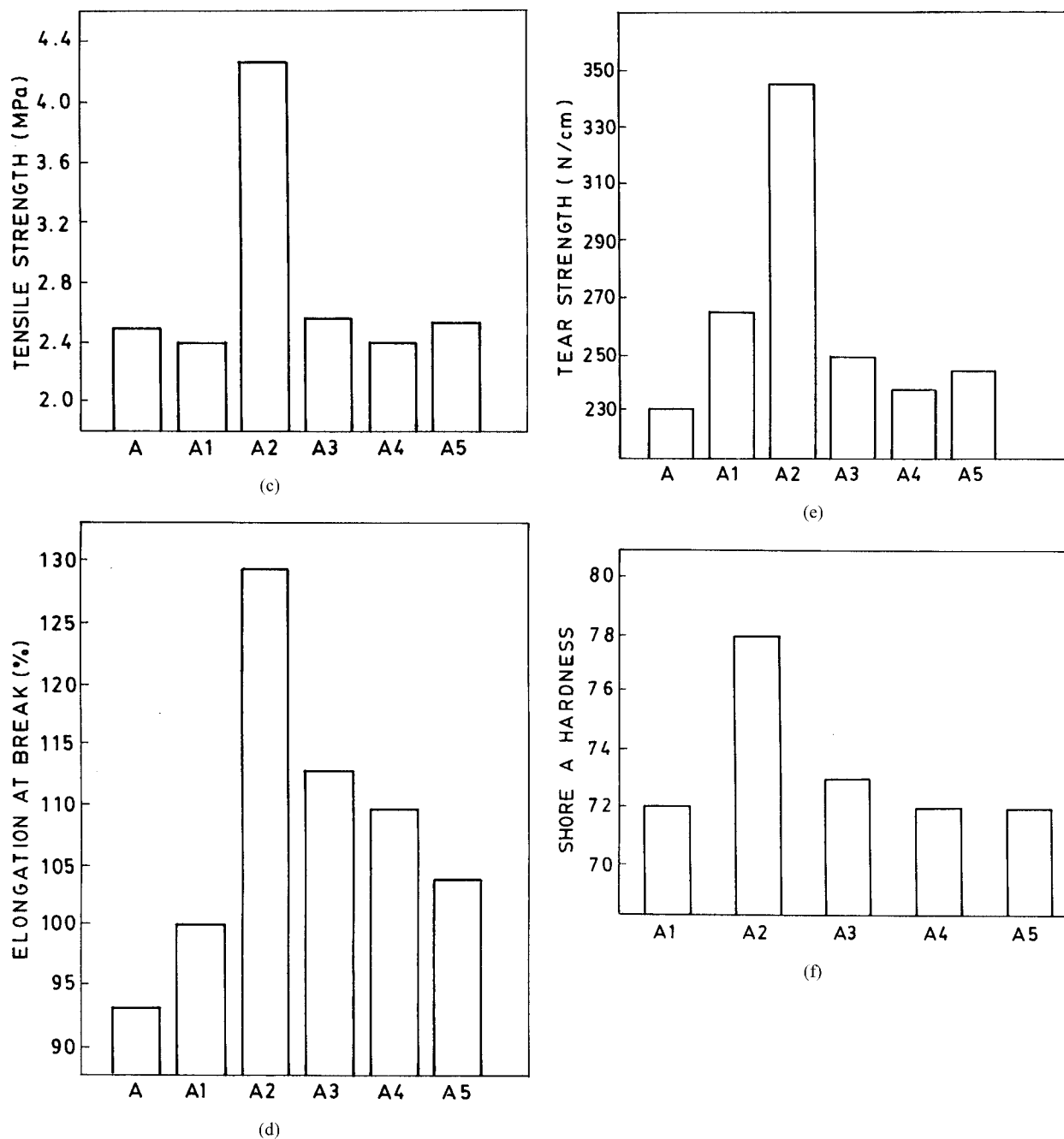


Figure 3 (Continued from the previous page)

behavior in terms of elongation and set. The 50 : 50 blend appears to be the best of the lot and is chosen for further investigation. The crosslinked 50:50 composition exhibits more than 100% elongation at break and a 5% tension set at 50% elongation.

#### Dynamic Mechanical Thermal Analysis

Figure 1 shows the dynamic mechanical properties of NR-LDPE systems. In the reclaimed rub-

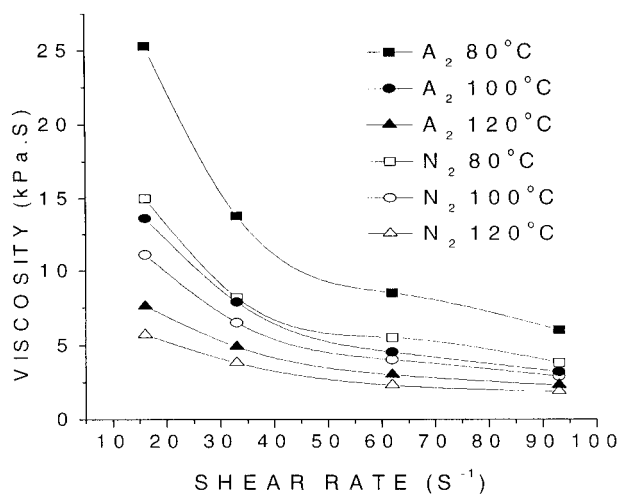
ber-PE blends, the low temperature transition due to PE is not so prominent. In fact, some authors reported earlier that in NR-PE blends the glass-transition temperature of PE is masked by its crystallinity, and suppression of the secondary relaxation due to the interaction of the blend components was also observed.<sup>19,20</sup> In comparing the uncrosslinked and crosslinked samples of reclaimed rubber-PE blends, both show a not so prominent transition due to PE at very low tem-

peratures, although the transition due to rubber is clear. However, at high temperature the uncrosslinked sample does not show any transition and seems to be disintegrated. A similar trend is observed in the NR-PE blend.

When comparing a reclaimed rubber-LDPE crosslinked blend with a NR-LDPE crosslinked blend, it is apparent that, although the trends are similar, the transition of the rubber is very well defined in the NR-PE blend with a sharp rise and fall of the  $\tan \delta$  value. However, the storage modulus of the reclaimed rubber-waste plastic system is higher over the whole range of temperatures, which is possibly due to the contribution from the filler. The peak  $\tan \delta$  value of the same system is lower as a result.

### Phase Morphology of Blends

The phase morphology of unvulcanized and vulcanized reclaimed rubber-scrap PE blends was studied. Similar studies were also carried out on the NR-PE blends for the purpose of comparison. The blend morphology of the NR-PE (50:50) system is shown in Figure 2(a-c). The morphology study was carried out by removing the surface rubber with concentrated nitric acid (etching) as explained earlier. It is clear from the morphology that the components are incompatible and a heterogeneous phase results [Fig. 2(a-c)]. The white portions of the micrographs in Figure 2 consist of LDPE and the dark voids are the areas where the rubber resided prior to extraction by etching. Dispersed domains of the rubber in a continuous



**Figure 4** The viscosity versus the shear rate plot for 50:50 blends at different temperatures.

**Table III** Flow Behavior Index Values

Samples	Flow Behavior Index		
	80°C	100°C	120°C
A	0.21	0.22	0.30
A <sub>2</sub>	0.20	0.24	0.33
N	0.33	0.33	0.34
N <sub>2</sub>	0.17	0.20	0.30
B	0.22	0.22	0.24
B <sub>2</sub>	0.15	0.15	0.27
C	0.24	0.25	0.25
C <sub>2</sub>	0.20	0.24	0.40
D	0.18	0.21	0.27
D <sub>2</sub>	0.17	0.21	0.37

The subscript 2 indicates that the sample is crosslinked.

plastic matrix are observed. A morphology similar to that of the NR-PE blend is observed in the reclaimed rubber-PE blends (50:50). However, the size of the unvulcanized rubber particles [about 5–6  $\mu\text{m}$ , Fig. 2(c)] is much larger compared to that observed in the crosslinked sample [Fig. 2(b)].

### Mechanical Properties of Reclaimed Rubber-LDPE Blends

The stress versus strain curves for various blends are shown in Figure 3(a). With the increase in plastic content, the stress at break increases while the elongation at break decreases. Figure 3(a,b) demonstrates the effects of crosslinking and the compatibilizers on the stress-strain curves. The values of the tensile strength and elongation at break are shown in the form of a bar graph to demonstrate the effects of crosslinking [Fig. 3(c,d)]. Both of the parameters are improved on crosslinking, the highest being achieved with the sulfur crosslinking. This may be attributable to the difference in the crosslinking density of the rubber by the two crosslinking systems and also a possible reduction of the crystallinity of PE by the peroxide curing system. The tear strength and Shore A hardness indicate similar enhancement with the crosslinked system [Fig. 3(e,f)]. The improvement of the tensile strength and tear strength may be attributed to the higher stored energy and energy dissipation due to crosslinking. For example, the area under the stress-strain curve for sample A<sub>2</sub> is much higher than that of sample A [Fig. 3(a)]. Even crosslinked

sample A<sub>2</sub> displays higher strength than its counterpart control NR-PE (N<sub>2</sub>), although in the uncrosslinked state the latter blend is better [Fig. 3(a)]. It is found that the tear strength and elongation at break of 50:50 blends are both better and the tensile strength of this blend, although less than that of 40:60 and 35:65 rubber/plastic ratios, is acceptable. A blend with a 50:50 blend ratio was prepared in a Brabender to compare it with the one prepared in an open two-roll mill. There is no increase in the properties of the blend prepared in the Brabender.

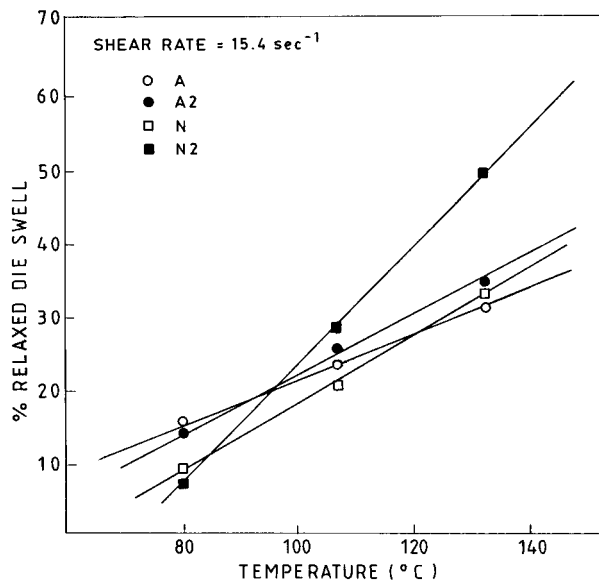
Physical compatibilizers like ethylene vinyl alcohol (EVA) and styrene-ethylene-butylene-styrene (SEBS) and chemical compatibilizers like maleic anhydride were used to study the effect of compatibilization on the mechanical properties of the reclaimed rubber-LDPE blend [Fig. 3(b)]. As can be inferred from Figure 3(c-f), not much change in the mechanical properties was observed when these compatibilizers were incorporated. This may be explained as being due to the high filler content in the system. As a result, the effect of compatibilizers on the rubber-filler system and the plastic-filler system becomes insignificant. Because the compatibilizers do not enhance the interaction in the rubber-filler or plastic-filler systems, the overall effect of these compatibilizers is not appreciated because of high filler content in the reclaimed rubber.

### Rheology

The rheological properties of NR-LDPE were also studied at a 50:50 blend ratio for comparing the properties with those of reclaimed rubber-LDPE blends of the same blend ratio. In both cases the viscosity decreases with an increase in the shear rate at a fixed temperature and also decreases with an increase in the temperature at a fixed shear rate (Fig. 4). It is also observed that the NR-LDPE blend has lower viscosity than the reclaimed rubber-LDPE blend at a particular shear rate and temperature. This is due to the high filler content (~47%) in the reclaimed rubber, which results in an increase in viscosity. The blend like most viscoelastic materials follows the Power law equation or the Ostwald de Waale equation:

$$\tau = k'(d_V/d_Y)^n \quad (5)$$

where  $\tau$  is the shear stress,  $d_V/d_Y$  is the shear rate,  $k'$  is the flow consistency index, and  $n$  is the flow behavior index.



**Figure 5** The relaxed die swell of 50:50 rubber-plastic blends as a function of the temperature.

The flow behavior indexes for different blend ratios with and without crosslinking and at three different temperatures are reported in Table III. The blend shows pseudoplastic behavior ( $n < 1$ ) and is thus non-Newtonian in character. The value of the flow behavior index increases with the increase in temperature. With crosslinking its value decreases at lower temperatures but increases at higher temperatures. The relaxed die swell of the reclaimed rubber-PE blends with a 50:50 blend ratio is shown as a function of temperature in Figure 5. The die swell increases with the temperature.

### CONCLUSIONS

Thermoplastic elastomers from reclaimed rubber and waste PE were developed. The properties of various compositions were studied and compared with the same derived from virgin polymers. The 50:50 blend with sulfur vulcanization displays the best properties. The rheological behavior and morphology of the blends are quite comparable to the blends of NR-PE. Hence, this material can replace the NR-PE blend in certain applications. The similarity to properties of NR-PE blends combined with the economics and the fact that this material can be mixed in open roll mills and can be processed like a plastic in existing machinery make it a very viable option for practical use.

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