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THERMAL CHARACTERIZATION OF THERMOPLASTIC ELASTOMERIC NATURAL RUBBER–POLYPROPYLENE BLENDS

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ABSTRACT

The thermal behaviour of natural rubber–polypropylene (NR/PP) thermoplastic elastomeric blends has been studied by a number of different techniques, e.g. differential scanning calorimetry (DSC), thermogravimetry (TG) and dynamic mechanical analysis (DMA). The melting temperature (T_m) for polypropylene is 165 °C. DSC results show a drop in the T_m value with increasing rubber content. The effect of 20 parts of an interfacial agent, like ethylene–propylene diene rubber (EPDM) or chlorinated polyethylene (CPE), is similar. Heat of fusion (ΔH) values exhibit a similar trend indicating increasing isolation of the crystallizable component at high rubber content. There is a 79% drop in crystallinity with the incorporation of 70 parts of natural rubber. The glass transition temperature (T_g) of the rubber phase, can be detected by this technique. The T_g of the blends is higher than that of pure NR. The elevation of T_g coupled with the depression of T_m indicate the kinetic restriction on the crystallization process. The TGA shows that the onset of degradation for pure PP is delayed with the addition of rubber. Differential thermogravimetry (DTG) curves for the blends display two peaks. The highest thermal stability is attained with the addition of ethylene–propylene diene rubber to the NR/PP blend. Dynamic mechanical analysis shows the existence of two T_g values—one corresponding with the amorphous phase and the other with the polypropylene phase—indicating the incompatibility of the blends. The values of the elastic modulus also display a sharp change in magnitude in the vicinity of the glass transition temperature. The intensity of the damping (tan δ) peak is found to be governed by the overall blend crystallinity. A new method for calculation of crystallinity by DMA is also suggested.

INTRODUCTION

Thermoplastic elastomers (TPE), a novel class of polymers combining the outstanding dual characteristics of elastomers and thermoplastics, have been gaining importance in recent years, and are reported in various books [1–3]. The most spectacular results in the search for TPE have been achieved by blending rubbers and plastics. Among the various rubber–plastic blends [2],

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thermoplastic natural rubber is the most useful for natural-rubber-producing countries. Several studies have been made in this field regarding processability and rheological behaviour [4,5], mechanical properties, strength and failure behaviour [6,7], adhesion between the components of the blends [8,9], ageing behaviour [10], etc. With the great strides made in this field, the immense potential of these materials is increasingly understood. So far, these materials have been put to rather modest uses like automotive applications, wires and cables, footwear, hoses, tubing, flexible couplings, and sports goods. However, very few studies have been devoted to the evaluation of their thermal behaviour. This particular study is of immense importance because the materials could be used over a wide range of service temperatures (from the glass transition temperature T_g of the rubber phase to the melting temperature T_m of the plastic phase). Roy Choudhury et al. [11] highlighted the thermal characteristics of natural rubber–polyethylene blends with reference to interaction between components. Martuscelli et al. [12] reported the thermal behaviour of nylon 6–rubber blends. Thermoplastic natural rubber from NR and PP has been chosen for the present study.

EXPERIMENTAL

The formulations of the mixes are given in Table 1. Mixing and moulding were done as reported earlier [9]. EPDM and CPE were added as interfacial agents to NR/PP blends.

Thermal analysis of samples

Differential scanning calorimetry (DSC)

The thermal behaviour of the blends was investigated with the help of a Du Pont 910 thermal analyser. The samples were programme-cooled at $10\,^\circ C\ min^{-1}$ to $-150\,^\circ C$ with subsequent heating at $10\,^\circ C\ min^{-1}$ to $200\,^\circ C$ in a nitrogen atmosphere. The cycle was repeated with cooling and heating at the same rate for a second time. The T_g value was taken as the mid-point of the step in the scan. The peak maximum from the melting thermogram

TABLE 1

Formulations of mixes

Blend [a]	A	B	C	D	E	F	G
NR	90	70	70	70	50	50	–
PP	30	30	30	30	50	50	30
EPDM	–	–	20	–	–	20	70
CPE	–	–	–	20	–	–	–

[a] For abbreviations see text.

was considered to be the melting point. The melting enthalpy was determined from the area of the melting endotherm.

Thermogravimetry (TG)

Thermogravimetric analysis of the samples was carried out in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} in a Du Pont 9000 thermal analyser, with a constant weighed quantity of sample in all cases. Thermograms were recorded from room temperature to 600 °C. The onset of degradation and the residue left at 600 °C were estimated. The temperature at which the rate of mass loss is at a maximum (T_{max}) was evaluated from the differential thermogravimetry (DTG) curve.

Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were carried out on a dynamic mechanical analyser (Rheovibron DDV-III-EP) comprising a temperature programmer and a controller. The experiment was conducted in tension mode from -150 to $+200$ °C at a frequency of 11 Hz at 0.125% dynamic strain with a programmed heating rate of 3 °C min^{-1}. Liquid nitrogen was used to achieve sub-ambient temperature.

RESULTS AND DISCUSSION

DSC study

The melting phenomena of the blends were studied by measuring the equilibrium melting temperature (T_m), crystallinity and heat of fusion (ΔH) values. Figure 1 shows the DSC thermograms of different NR/PP blends. It is clearly evident from the figure that there is a shift in the T_m value of the blends from that of pure PP. Pure PP shows a melting temperature of 165 °C. With the incorporation of rubber (NR, EPDM or CPE) there is a gradual drop in melting temperature. Such a drop in T_m shows, in part, that the blends do not crystallize to the same extent as pure PP. This feature of melting point depression may be accounted for as a result of the diluent effect of the amorphous component [12]. In addition, in all the blends considered this drop in the T_m value is accompanied by a consistent decrease in the ΔH value. The total degree of crystallinity of the blends also decreases rapidly with the increase in the rubbery component. The drop in crystallinity is 74% for 70/30 NR/PP, 76% for 70/20/30 NR/EPDM/PP and 57% for 50/20/50 NR/EPDM/PP blends respectively, and these decreases are a result of reduction in the values of ΔH. A similar observation is made for natural rubber–polyethylene blends [11].

T_g values, as obtained from DSC thermograms, are reported in Table 2. Pure NR shows a transition at -70 °C, but the T_g of PP could not be

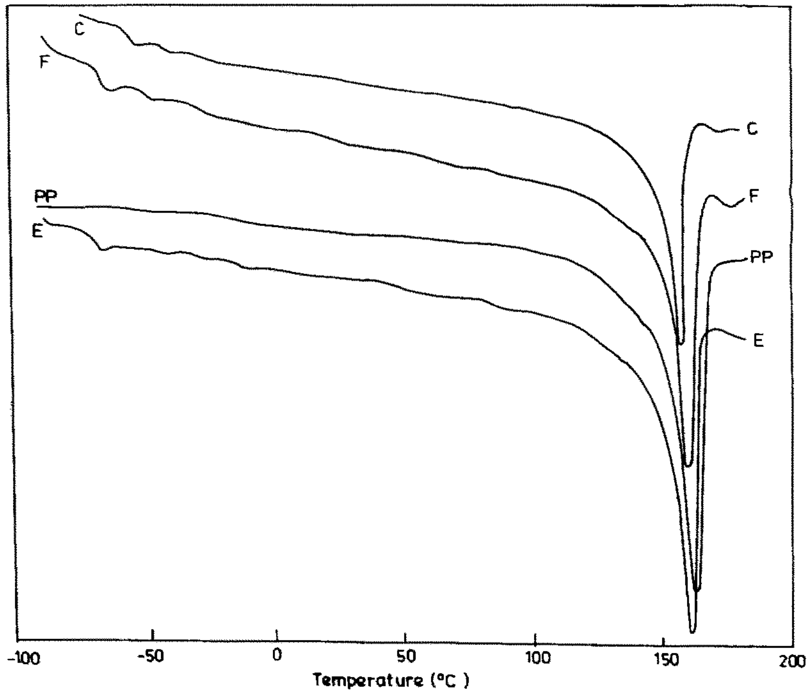

Fig. 1. DSC thermogram of different NR/PP blends and pure PP.

detected from the DSC plot. On blending PP (30 parts) with NR (70 parts) the T_g value of NR changes and a sharp value of T_g at $-64.4\,^\circ\mathrm{C}$ is observed. This elevation of T_g of NR is accompanied by a drop in T_m of PP (from 165 °C to 161 °C). Thus, the interval $(T_m - T_g)$ decreases, and this imposes a severe kinetic restriction on the crystallization process. With increasing rubber content (20 parts NR/EPDM/CPE) the T_g value remains relatively constant, but the transition broadens. NR/PE thermoplastic elastomeric blends displayed similar behaviour. As the T_g value of the NR phase in the blend does not undergo substantial variation, it may be assumed that the blends are thermally incompatible and the high crystallinity of PP complicates the detection of its T_g value in the blend.

TG analysis

Thermogravimetric curves of pure PP and different blends in a nitrogen atmosphere are shown in Fig. 2. The decomposition of PP in nitrogen starts at around 275 °C and 50% decomposition occurs around 375 °C, as is evident from the steep nature of the TG curve. The derivative curve (DTG) of PP shows one major T_{max}, i.e. the temperature at which the degradation rate is maximum. The main degradation occurs between 400 and 425 °C with T_{max} at 390 °C. Pure NR shows T_{max} at 410 °C.

TABLE 2

Thermal properties of blends

Sample reference [a]	PP	A	B	C	D	E	F	G	NR	EPDM	CPE
Parameters measured											
Peak temperature, T_m (°C)	165	160	161.2	160.5	160.9	163	162	–	–	–	–
Heat of fusion, ΔH ($J\ g^{-1}$)	84	18.8	22.2	18	21.8	44	36	–	–	–	–
Crystallinity (%)	61	13.6	16	13	15.8	32	26	–	–	–	–
Glass transition temperature, T_g (°C)	–	−64	−64.4	−64	−63	−63.5	–	–	−70	−56	–

[a] For designations see Table 1.

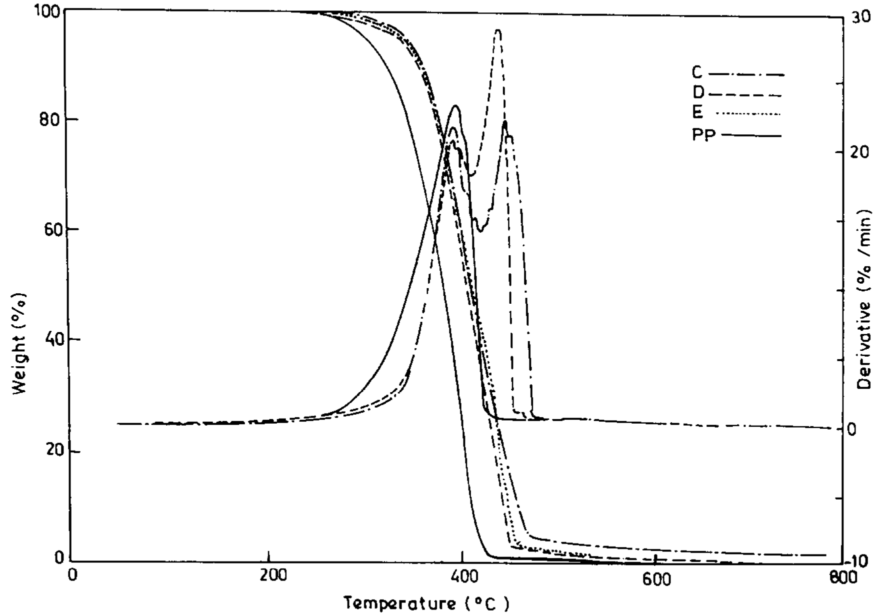

Fig. 2. TG and DTG curves of different NR/PP blends and pure PP.

The effect of blend ratio on the weight loss is also shown in Fig. 2. The onset of degradation for blends is delayed with the introduction of rubber. This means that the thermal stability of PP is enhanced by using the rubber, which may be due to retention of volatile PP degradation products by the elastomers or to delay in the decomposition of PP.

The DTG curve of NR/PP (90/30) blend (A) shows two peaks, one at 400 °C and another at 430 °C (Table 3). The second peak, a result of the

TABLE 3

Thermogravimetric analysis

Sample	T_{max}	
	1 (°C)	2 (°C)
Pure PP	390	–
Pure NR	410	–
A	400	430
B	400	440
C	400	450
D	400	445
E	400	440
F	400	462
G	400	460

NR phase, shows a shift towards the right on the temperature axis, which may be because of gel formation of rubber during preparation of the blend. With the addition of EPDM or CPE to NR/PP, two major T_{max} values are also observed. For a 70/20/30 NR/EPDM/PP blend (C) these two major T_{max} peaks (400 and 450 °C) are associated with two small satellite peaks 1 °C apart. This finding may be ascribed to the different degradation patterns and mechanisms in the two cases. However, it is apparent from the curves that, the stability of NR/PP is enhanced by the presence of EPDM or CPE (20 parts) in NR/CPE/PP and NR/EPDM/PP (Fig. 2). It was reported earlier [9] that EPDM or CPE enhances the adhesion between NR and PP by acting as an interfacial agent at the interface.

With the 50/50 NR/PP blends, a trend similar to that of 70/X/50 ($X = 0$ or 20 parts of EPDM or CPE) blends was observed. The major difference is that the first peak is broadened and the second peak is sharp with the change in blend ratio. The 50/20/50 NR/EPDM/PP blend (F) shows the higher T_{max} value (462 °C). Thus, it is clearly evident from the T_{max} values that EPDM increases the heat stability of the NR/PP blends in both 70/30 and 50/50 proportions. In all cases, the PP phase begins to degrade at a lower temperature than NR.

Dynamic mechanical properties

The dynamic mechanical properties of the blends shown in Figs. 3–5 represent the typical plots of the dynamic elastic (storage (E') and viscous (loss) (E'') moduli and damping (tan δ) of the blends vs. temperature. Figure 3 illustrates the E' spectra for the blends. In Fig. 3 the characteristic sigmoidal variation of the elastic modulus is observed with four distinct regions, e.g. glassy, transition, rubbery and high temperature regions (a, b, c and d). The E' values decrease with increasing temperature as usual, and over the transition region a large abrupt change in modulus of the blends (crystalline/amorphous) takes place due to transformation from the glassy to the rubbery state. In the glassy region the modulus values for the blends are comparable, as is evident from Table 4. This also compares the storage moduli of the blends and pure PP at three different temperatures (-125, -50 and $+50$ °C). The difference in E' values is small at low temperatures because short range segmental motions determine behaviour in the glassy state. At high temperatures, also, a similar trend is observed. However, the moduli values at -50 °C differ for different blends. The blends with higher PP content show higher modulus values (e.g. 50/20/50 NR/EPDM/PP).

Figures 4 and 5 represent the temperature dependence of E'' and tan δ for a few systems. The loss modulus and tan δ curves are similar for all the samples except for pure PP. Pure PP exhibits transition from 12.7 to 15 °C, and for pure NR the transition occurs at -53 °C. Each blend shows distinct peaks corresponding to the T_g value of NR, and transition due to PP

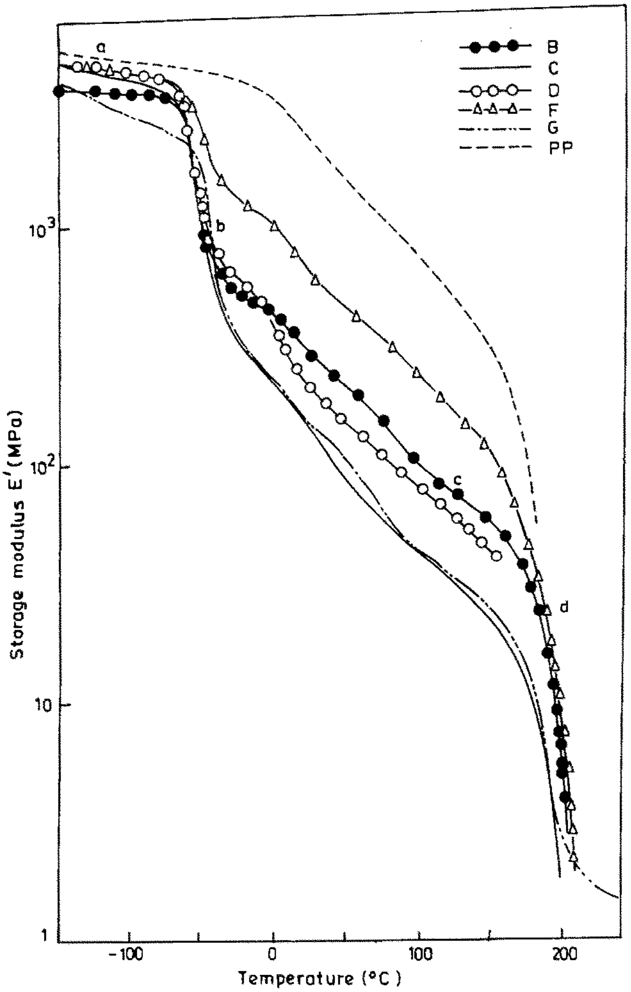

Fig. 3. Effect of temperature on storage modulus E' of different NR/PP blends and polypropylene.

appears as a shoulder. The intensity and location of these peaks from both tan δ and E'' are reported in Table 5.

It is interesting to note that there are two transitions, T_{g1} and T_{g2}, in the tan δ as well as in the E'' curves. Moreover, at low temperature, E'' peaks are at the same temperature as tan δ transitions for all the blends. For example, for the 70/30 NR/PP system the first transition (T_{g1}) occurs at around -57 °C (from both tan δ_1 and E_1''), but the second transition (T_{g2}) occurs at $+16$ °C (from tan δ_2) and 4.1 °C (from E_2''). The occurrence of the high temperature peaks (tan δ_2 and E_2'') at different temperatures results from the fact that E' is dependent on temperature. In the glassy region, E' remains relatively constant (as discussed earlier in Table 4); therefore, at low

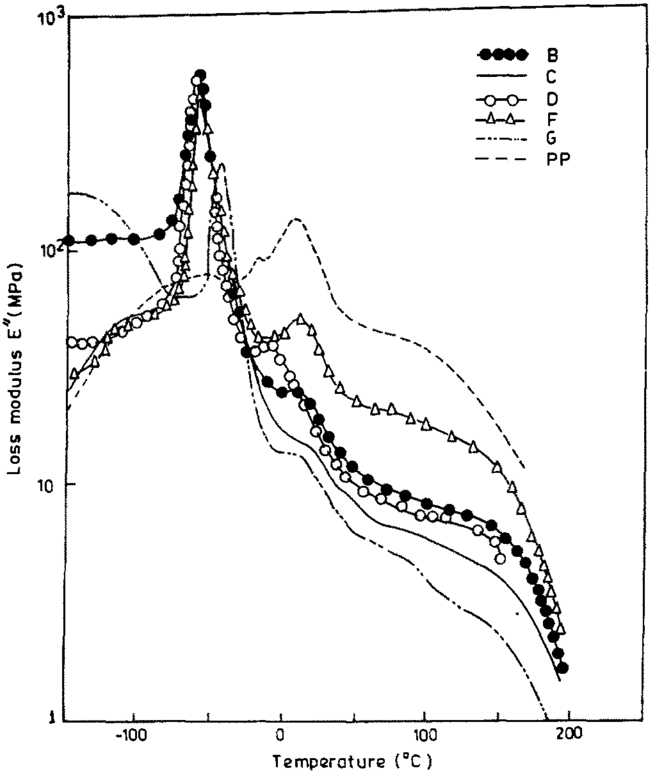

Fig. 4. Effect of temperature on loss modulus E'' of different NR/PP blends and polypropylene.

temperature, tan δ and E'' peaks occur at the same temperature. However, as the temperature increases, E' changes, and since these three parameters are related by tan $\delta = E''/E'$, so tan δ and E'' peak temperatures show marked variation in their locations. This is totally controlled by how much E' changes with temperature. However, the T_g values measured by DSC and DMA techniques display somewhat different results. The T_g of the rubber phase has only been detected by the DSC technique, whereas two transitions corresponding to the rubber and the plastic phases have been clearly displayed by the DMA spectra. The reason for this observation may be that the DSC thermograms involve longer range motions than the segmental micro-Brownian motions responsible for dynamic mechanical loss peaks. MacKnight and Karasz [13] also made a similar observation from DSC and DMA techniques for blends of poly(2,6-dimethyl-1,4-phenylene ether) with atactic polystyrene. The same was observed by Locke and Paul [14] for modification of blends from waste plastics.

The important and striking feature of pure PP is that both the damping and the E'' spectra consist of a number of peaks of various heights and widths and the sharpest of these occurs at T_g. The onset of glass transition is

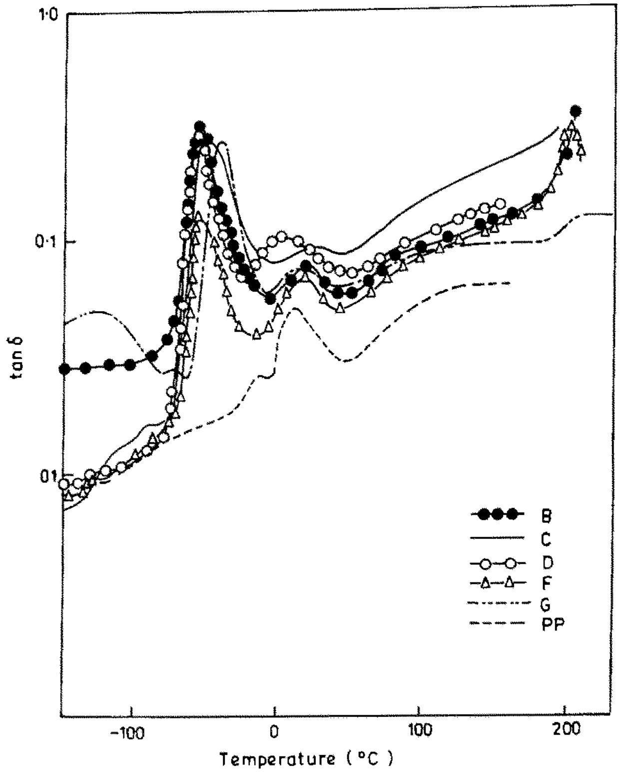

Fig. 5. Effect of temperature on damping (tan δ) of different NR/PP blends and polypropylene.

exhibited by a small hump at −4 °C. This may be ascribed to the presence of crystals of various sizes in PP. No such peak is observed for the blends. At still higher temperatures, when PP enters into the zone of thermal flow, further increase in the tan δ value is observed, and finally it starts flowing. However, in the blends, owing to the presence of the amorphous rubbery component (NR, EPDM or CPE), the bulk thermal flow is restricted to

TABLE 4

Comparison of the dynamic mechanical behaviour of NR/PP blends

	E' (dyn cm^{-2})		
	−125 °C	−50 °C	+50 °C
PP	5.2×10^{10}	3.5×10^{10}	7×10^{9}
NR/PP 70/30	4.5×10^{10}	1×10^{10}	2.2×10^{9}
EPDM/PP 70/30	4.5×10^{10}	6×10^{9}	1.2×10^{9}
NR/CPE/PP 70/20/30	5×10^{10}	1×10^{10}	1.3×10^{9}
NR/EPDM/PP 70/20/30	5×10^{10}	5×10^{9}	1.2×10^{9}
NR/EPDM/PP 50/20/50	5.1×10^{10}	2×10^{10}	4×10^{9}

TABLE 5

Dynamic mechanical properties

Sample	T_{g1} [a] (°C)	T_{g2} [b] (°C)	tan δ_1	tan δ_2	$E''1$ peak temp. (°C)	$E''2$ peak temp. (°C)
PP	–	12.7	–	0.051	–	6.7
NR/PP 70/30	−57	16	0.299	0.074	−58	4.1
NR/EPDM/PP 70/20/30	−59	16.2	0.267	0.096	−59.4	17
NR/EPDM/PP 50/20/50	−56	16.1	0.125	0.068	−56	10
NR/CPE/PP 70/20/30	−58.4	12	0.276	0.1	−59	−9
EPDM/PP 70/30	−41.3	13–18	0.259	0.075	−44.1	6.9

[a] T_{g1} is the glass transition temperature of the rubber phase.
[b] T_{g2} is the glass transition temperature of the PP phase.

some extent. The TG analysis also shows that the stability of PP increases on introduction of rubber.

Estimation of crystallinity by a DMA technique

A rapid method of estimation of crystallinity was evaluated by observing the drop in modulus (E') from an E' vs. temperature plot. The DMA spectra for a blend is considered to consist of two parts, the crystalline and amorphous regions. Thus, taking natural rubber to be fully amorphous, the degree of crystallinity was measured (from the modulus drop from glassy to melting region) by the following relation

$$X_c = \frac{E'_{T_g} - E'_{T_m}}{E'_{T_g}} \times 100$$

where E'_{T_g} and E' represent the storage moduli corresponding to the glassy and the crystalline regions. In order to study the parameters that govern the height of the mechanical peak, the crystallinity values so obtained were plotted against tan δ (tan δ_2 from Table 5) for various blends. It is interesting to note that, as the crystallinity increases, the tan δ_2 value decreases (Fig. 6). For example, pure PP (the crystallinity of which is 61%) shows the lowest tan δ_2 value (0.051). A similar observation was made by Greus and Calleza [15] while studying the effect of irradiation and annealing on polyethylene. According to them the crystalline morphology, and not the degree of branching as suggested by other authors [16], is the parameter

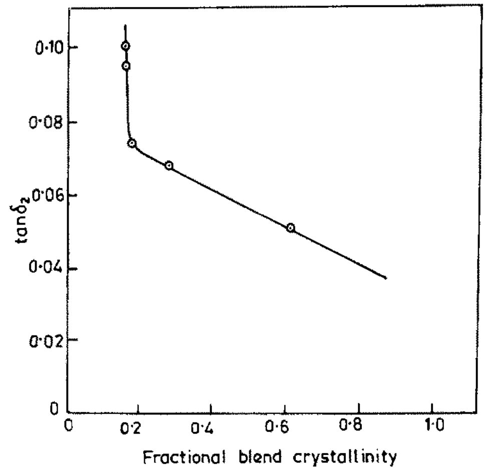

Fig. 6. Plot of damping factor ($\tan \delta_2$) vs. crystallinity of blends and pure polypropylene.

which governs the height of the relaxation peak. In the present investigation, the specific morphology of the different NR/PP blends, which was discussed in our earlier communication [9], is responsible for the different heights of tan δ peaks and hence for varying crystallinity and the relaxation phenomenon. Koleske and Lundberg [17] also made a similar observation that the height of the loss peak depends on the degree of crystallinity. It may be noted that the values of crystallinity of pure PP and blends measured by DMA techniques are in line with those of DSC measurements. The trend is also found to be similar in both cases.

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