

# Dynamic Mechanical Properties of Thermoplastic Elastomers from Polypropylene-Natural Rubber Blend

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## Synopsis

The dynamic mechanical properties of thermoplastic elastomers from polypropylene natural rubber blends have been evaluated with special reference to the effect of blend ratio and extent of dynamic crosslinking of the elastomer phase. The effects of HAF black and silica fillers have also been studied. It has been found that increasing the proportion of elastomer phase reduced the storage modulus and increased the loss tangent values of the blends. The effect of dynamic crosslinking was found to be more prominent in blends containing higher proportion of elastomer phase. The improvement in storage modulus and decrease in loss tangent values were quite remarkable with increase in extent of crosslinking in these blends. The 70:30 NR:PP blend was found to exist as a two-phase system, both the components forming continuous phases of the blend.

## INTRODUCTION

Thermoplastic elastomers (TPEs) are materials having the processing characteristics of thermoplastics and the technical properties of vulcanized elastomers. Among the different types of TPEs, those prepared by the physical blending of a polyolefin and an elastomer, have gained considerable attention due to the simple method of preparation and easy attainment of the required technical properties. Addition of a small quantity of crosslinking agent during melt mixing (dynamic crosslinking) of the polyolefin and the elastomer improves the elastomeric properties of the thermoplastic elastomer. In polyolefin-elastomer blends, the effects of characteristics of the components, blend ratios and dynamic crosslinking of the elastomer phase on the technical properties, processing characteristics and failure mechanism of the resulting thermoplastic elastomers have already been reported.<sup>1-14</sup> One of the main disadvantages of TPEs is the lower maximum service temperature, which is dependent on the crystalline melting point or glass transition temperature of the polyolefin component. Cyclic stressing during service generates heat and hence, the study of the dynamic mechanical properties of the TPEs becomes important. The effects of degree of crosslinking and type of crosslinking on the viscoelastic properties of elastomers had been reported by Studebaker.<sup>15</sup> Medalia<sup>16-18</sup> and Ulmer et al.<sup>19,20</sup> have reported the effects of carbon black filler on the dynamic mechanical properties of different elastomers. The effects of composition and

morphology on the dynamic mechanical properties of heterogeneous polymer blends had been described by Brancaccio et al.<sup>21</sup> and Dickie.<sup>22</sup> The changes in viscoelastic properties with crosslinking of one of the components in polymer blends had been reported by Nakajima et al.<sup>23</sup> and Dickie et al.<sup>24</sup> In this paper we report on the dynamic mechanical properties of thermoplastic elastomers from natural rubber-polypropylene blends. The effects of blend ratios, extent of dynamic crosslinking of the elastomer phase and addition of carbon black and silica filler on storage modulus ( $E'$ ) loss modulus ( $E''$ ) and loss tangent ( $\tan \delta_E$ ) at different temperatures have been studied.

## EXPERIMENTAL

### Preparation of the Blends

The basic characteristics of the PP and NR used in this study are given in Table I. The compositions of the blends are given in Table II. The blend ratios are denoted by B, D, and F. Succeeding letters U, D, M, and S denote blends containing no cross-linking agent and those containing dicumyl peroxide (DCP), mixed and sulfur cure systems, respectively. H and Si denote the presence of HAF black and silica filler, respectively. Thus, blend BMH indicates that NR:PP ratio is 30:70 and that it contains mixed cure system and 50 phr HAF black filler. The ratios of the components were chosen such that the blend shows the properties of a thermoplastic elastomer. The blends of NR and PP were prepared in a Brabender Plasti-corder model PLE 330 using cam-type mixer at a temperature of 180°C and a rotor speed of 80 rpm. After four minutes blending the curatives were added in the master batch form. At the end of 7 minutes, the blend was taken out and sheeted through a laboratory mill at 2.0 mm nip setting. It was cut into small pieces and remelted in the Plasti-corder for one minute and finally sheeted out to ensure uniform dispersion of the ingredients. Samples of the blends were compression moulded in an electrically heated hydraulic press at 200°C for 2 min in a specially designed mould so that the mould could be cooled immediately after the moulding time, keeping the sample still under compression. Detailed blending and moulding procedures have already been reported.<sup>12</sup>

TABLE I  
Characteristics of the Base Polymers

Characteristics		NR	PP
Molecular weight	$\bar{M}_n$	—	1,06,000
	$\bar{M}_w$	7,80,000	5,30,000
Molecular weight distribution	$\bar{M}_w / \bar{M}_n$	—	5.0
Wallace plasticity	Po	59	—
Melt flow index (230°C, 2.16kg)	MFI	—	10.0
Brittle point, °C		—	5

TABLE II  
Composition of the Blends

Ingredient	B	D	F
PP <sup>a</sup>	70	50	30
NR <sup>b</sup>	30	50	70
Curatives <sup>c</sup>	U, D, M, S	U, D, M, S	U, D, M, S
HAF black <sup>d</sup>	—	—	H
Silica <sup>e</sup>	—	—	Si

<sup>a</sup> Isotactic polypropylene, Koylene MOO3O received from M/s Indian Petrochemical Corporation Ltd., Vadodara, Gujrat.

<sup>b</sup> Natural Rubber, ISNR 5 grade, received from the Rubber Research Institute of India, Kottayam, Kerala 686 009.

<sup>c</sup> U = Uncrosslinked system.

D = Blends containing 1.0 phr, 40% DCP, based on rubber phase only.

M = Blends containing 1.0 phr, 40% DCP, zinc oxide 5.0, stearic acid 2.0, CBS 1.0, TMTD 1.25 and sulfur 0.15 phr, based on rubber phase only.

S = Blends containing zinc oxide 5.0, stearic acid 2.0, CBS 2.0, TMTD 2.5 and sulfur 0.30 phr, based on rubber phase only.

<sup>d</sup> Blends containing 50 phr HAF black, based on rubber phase only.

<sup>e</sup> Blends containing 20 phr silica, Vulcasil S, based on rubber phase only.

### Measurement of the Dynamic Mechanical Properties

The dynamic mechanical properties of the blends were measured using a Rheovibron DDV III-C at a strain amplitude of 0.0025 cm and a frequency of 35 Hz. Moulded samples of dimensions  $7 \times 1 \times 0.5$  cm<sup>3</sup> were used for testing. The temperatures of testing were in the range of 26–100°C since the service temperatures of these types of TPEs are mostly in this range. The heating rate of the samples was 1°C rise in temperature per minute. Corrections for yielding of the samples in the clamps were made in the readings as suggested by Voet and Morawski.<sup>25</sup>

### Swell Measurements

The extent of crosslinking of the elastomer phase was determined by measuring the  $V_r$  (volume fraction of rubber in the solvent swollen vulcanizate) values. The swell measurements of the natural rubber vulcanizates having the same dosages of cross-linking agents as contained in the blend, were made using the method described by Ellis and Welding.<sup>26</sup> The  $V_r$  values were calculated using Flory-Rehner equation and the values obtained were 0.073, 0.136, and 0.172, respectively, for the DCP, mixed, and sulfur-cured rubber vulcanizates. The  $V_r$  values of the dynamically cross-linked 70:30 NR:PP blends were also measured using the method described above. The values obtained were 0.120, 0.210, and 0.249, respectively, for the DCP, mixed, and sulfur-cured blends. The higher  $V_r$  values of the blends, compared with those of the rubber vulcanizates, may be due to the restriction imposed by the PP phase for the swelling.

### Morphology Studies

The morphological studies of the NR-PP blends were made using the uncross-linked blends. Moulded pieces of the blends were cut using a rotary retracting microtome at -90 to -80°C so as to avoid any deformation of the

rubber phase during cutting. The cut edge of the sample was kept immersed in benzene at 40°C for 7 days, for extracting the rubber phase. The solvent was changed after every 12 h. The solvent extracted samples were dried at 40°C for 24 h. The extracted edge of the dried sample was sputter coated with gold and examined using a Philips 500 model scanning electron microscope (SEM), keeping the tilt at 30°. The SEM photographs of the blends BU, DU, and FU are shown in Figures 2, 3, and 4, respectively.

## RESULTS AND DISCUSSION

### Effects of Blend Ratio

The changes in  $E'$ ,  $E''$  and  $\tan \delta$  of the blends BU, DU, FU, and polypropylene with increase in temperature are shown in Figure 1. The storage modulus and loss modulus decrease with increase in temperature and proportion of elastomer phase in the blend. The loss tangent values initially decrease and then increase with increase in temperature. The increase in  $\tan \delta$  and decrease in moduli are quite remarkable when the proportion of rubber phase in the blend exceeds 50%. In blend BU, the rubber phase remains as dispersed particles, in the PP matrix, which is observed as the black spots in Figure 2. These black spots are formed due to the extraction of the rubber phase from the blend. As the rubber content is increased to 50%, the rubber phase also tends to form a continuous phase and this is clearly evident from Figure 3. In 70:30 NR:PP blend, both the phases form continuous phases as shown by continuous, narrow white layers followed by thick black layers in Figure 4.

When the elastomer phase becomes continuous in nature, this phase contributes a major share in the viscous deformation since the molecules are in the uncross-linked state. This results in progressive decrease in storage modulus and increase in loss tangent values from blend BU to FU. The initial decrease in  $\tan \delta$  values of the blends is due to a transition in the state of PP which has a brittle point of 5°C. This is evident from Figure 9 also.

### Effects of Crosslinking

The effects of crosslinking of the elastomer phase in 30:70 NR:PP blend on  $E'$ ,  $E''$  and  $\tan \delta$  are shown in Figure 5. The decrease in storage modulus and loss modulus with increase in temperature is more prominent in the uncross-linked blend (BU) than in the cross-linked blends. The effect of crosslinking of the elastomer phase on  $E'$  and  $E''$  is not prominent in the 30:70 NR:PP blend. The degradative action of DCP on PP, in addition to its cross-linking action on the dispersed NR phase, is evident from the lower storage modulus and higher loss tangent values of the blends BM and BD compared to those of BS and BU. The same trend can be observed in 50:50 NR:PP blend also (Fig. 6). The higher  $E'$  and lower  $\tan \delta$  values of the blend DU compared with those of DM and DD show that the degradative effect of DCP on PP dominates over its cross-linking action on the rubber phase. The effects of extent of crosslinking of the elastomer phase on  $E'$ ,  $E''$  and  $\tan \delta$  are most clearly observable in 70:30 NR:PP blend (Fig. 7). The storage

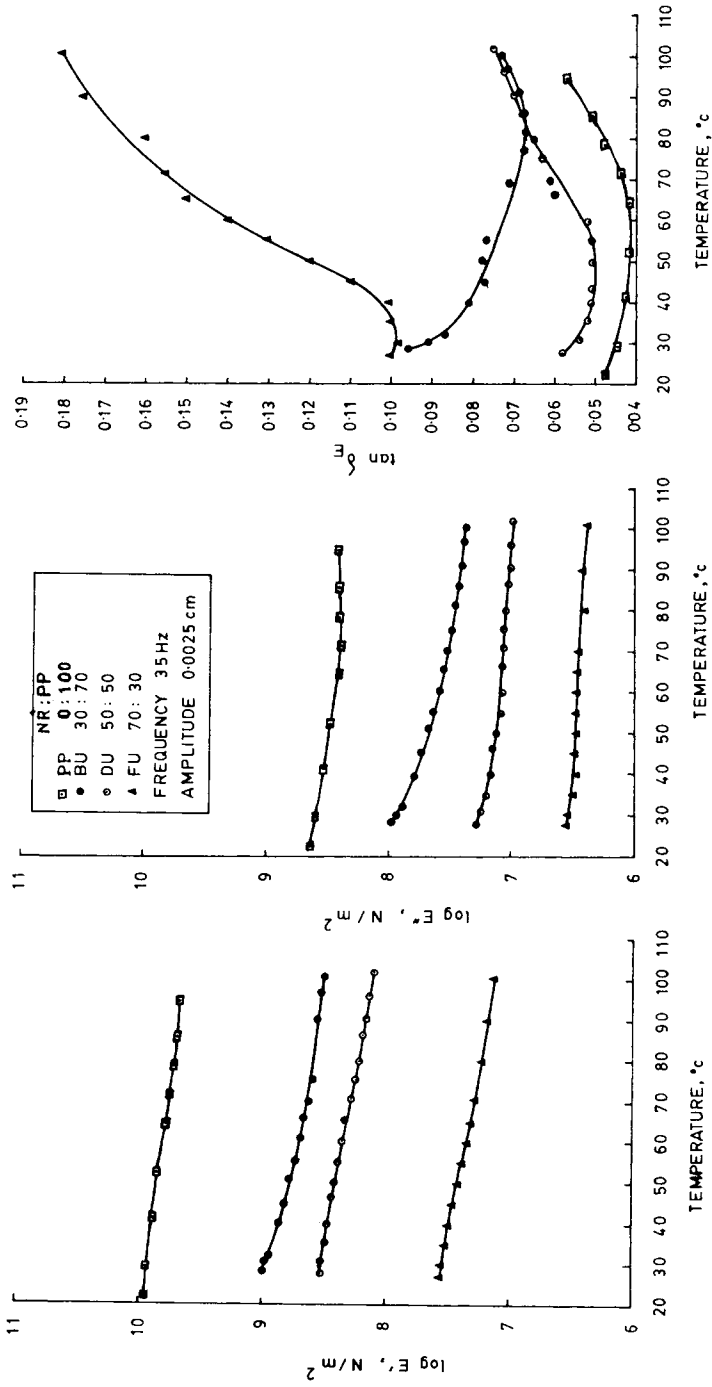


Fig. 1. Effect of blend ratio on  $E'$ ,  $E''$ , and  $\tan \delta_E$  of NR:PP blends.

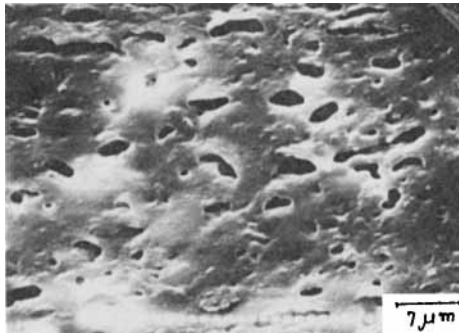


Fig. 2. SEM photograph of blend BU after extraction of the rubber phase.

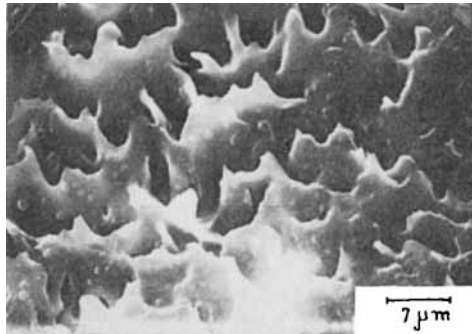


Fig. 3. SEM photograph of blend DU after extraction of the rubber phase.

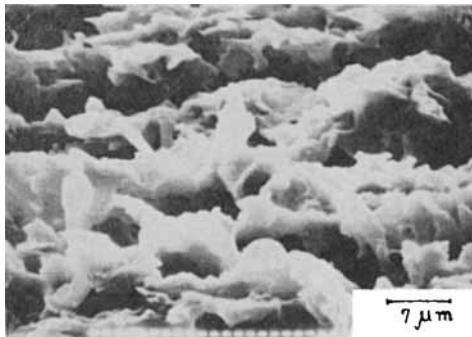


Fig. 4. SEM photograph of blend FU after extraction of the rubber phase.

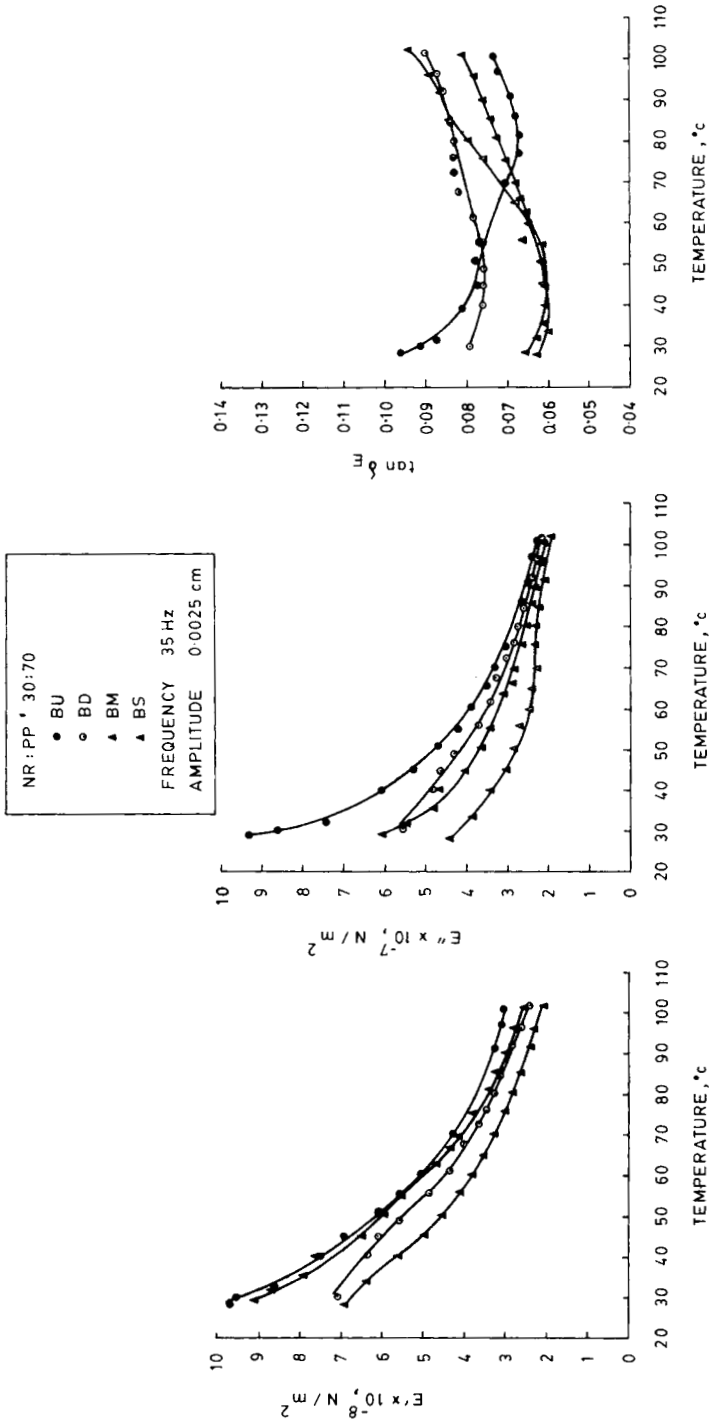


Fig. 5. Effect of dynamic crosslinking on  $E'$ ,  $E''$ , and  $\tan \delta$  of 30:70 NR:PP blend.

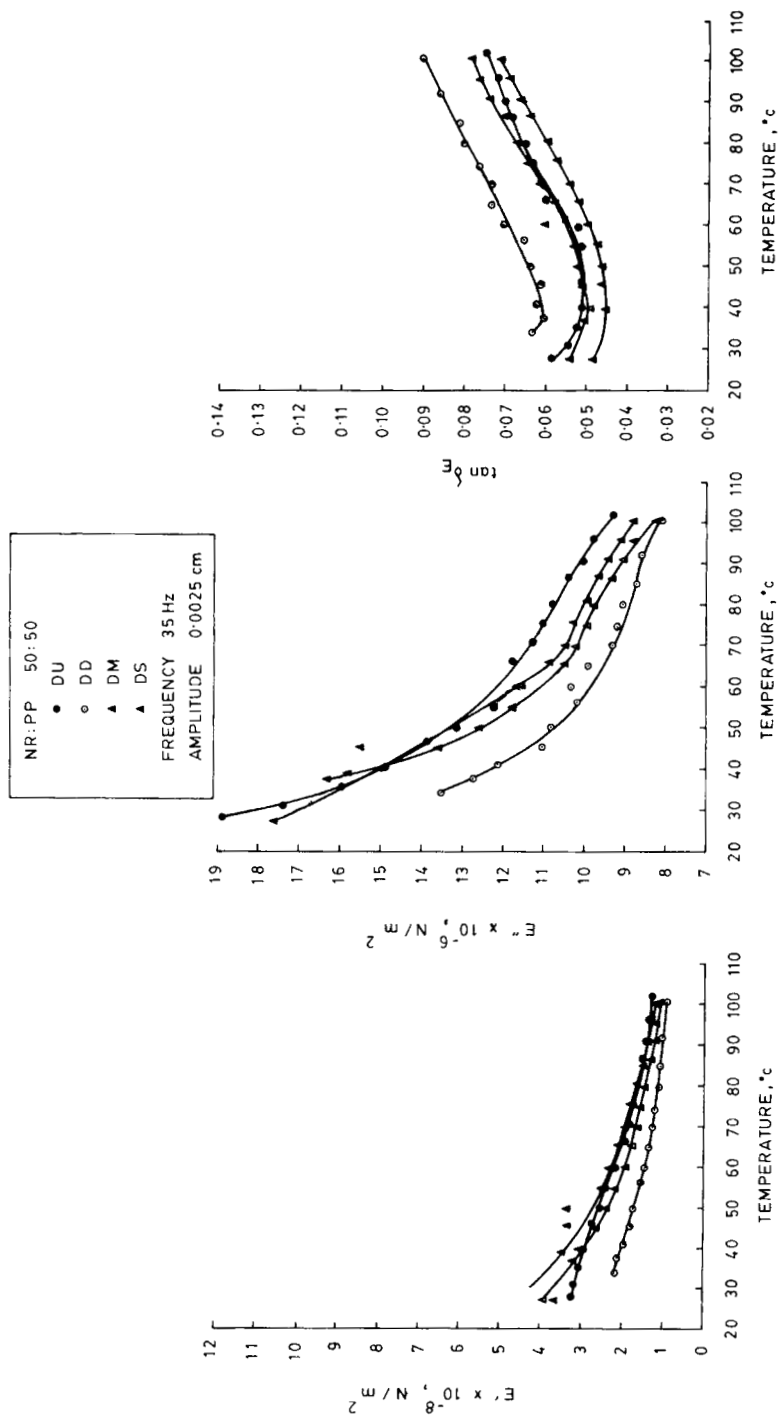


Fig. 6. Effect of dynamic crosslinking on  $E'$ ,  $E''$ , and  $\tan \delta$  of 50:50 NR:PP blend.



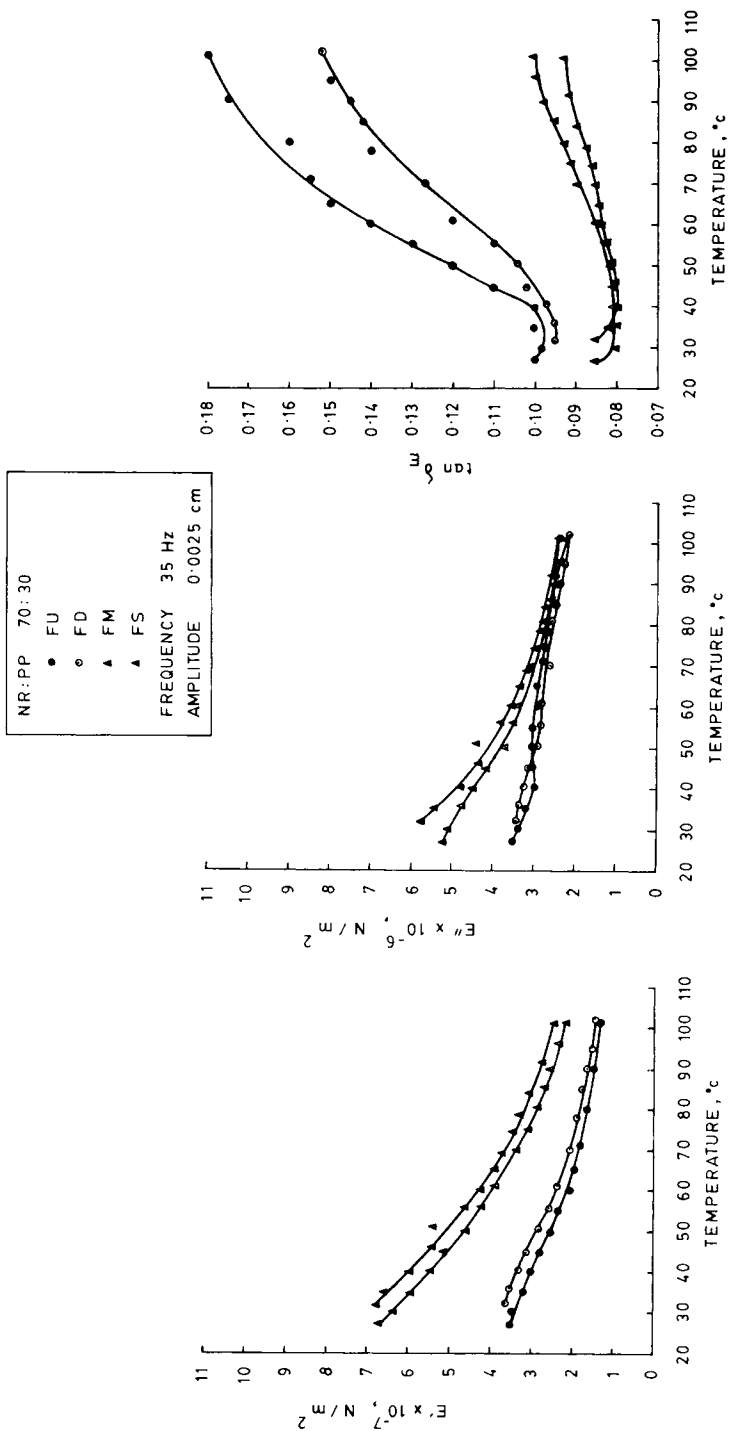


Fig. 7. Effect of dynamic crosslinking on  $E'$ ,  $E''$ , and  $\tan \delta$  of 70:30 NR:PP blend.

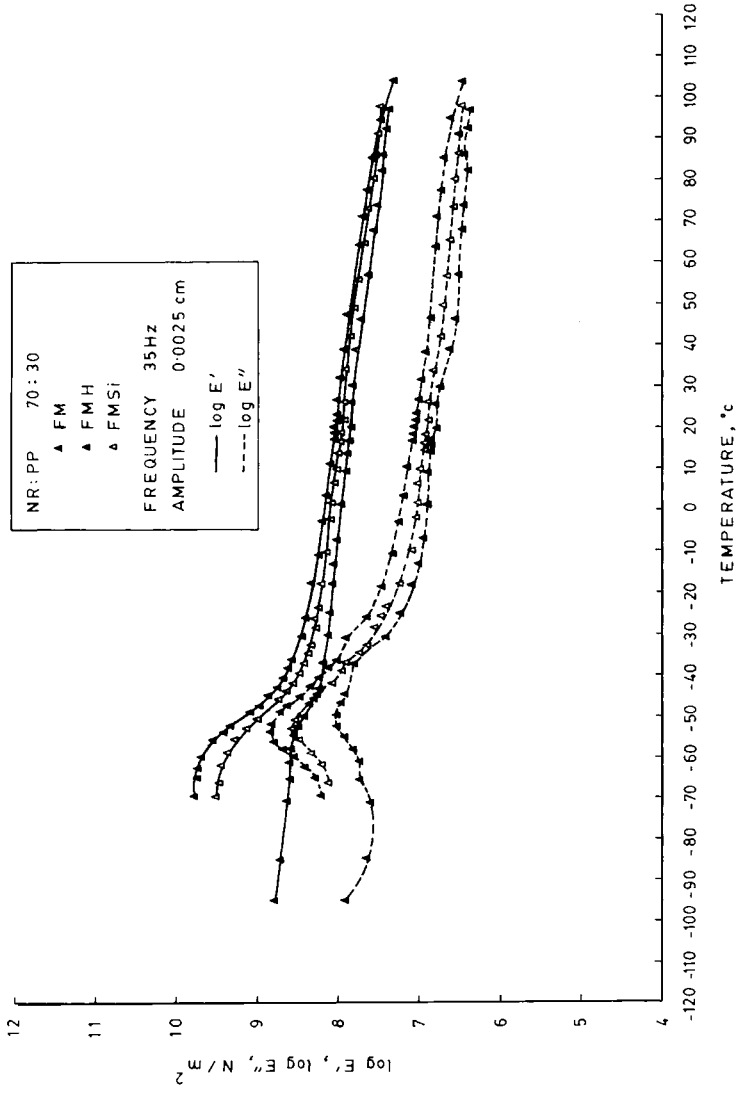


Fig. 8. Effect of HAF black and silica fillers on  $E'$  and  $E''$  of 70:30 NR:PP blend.

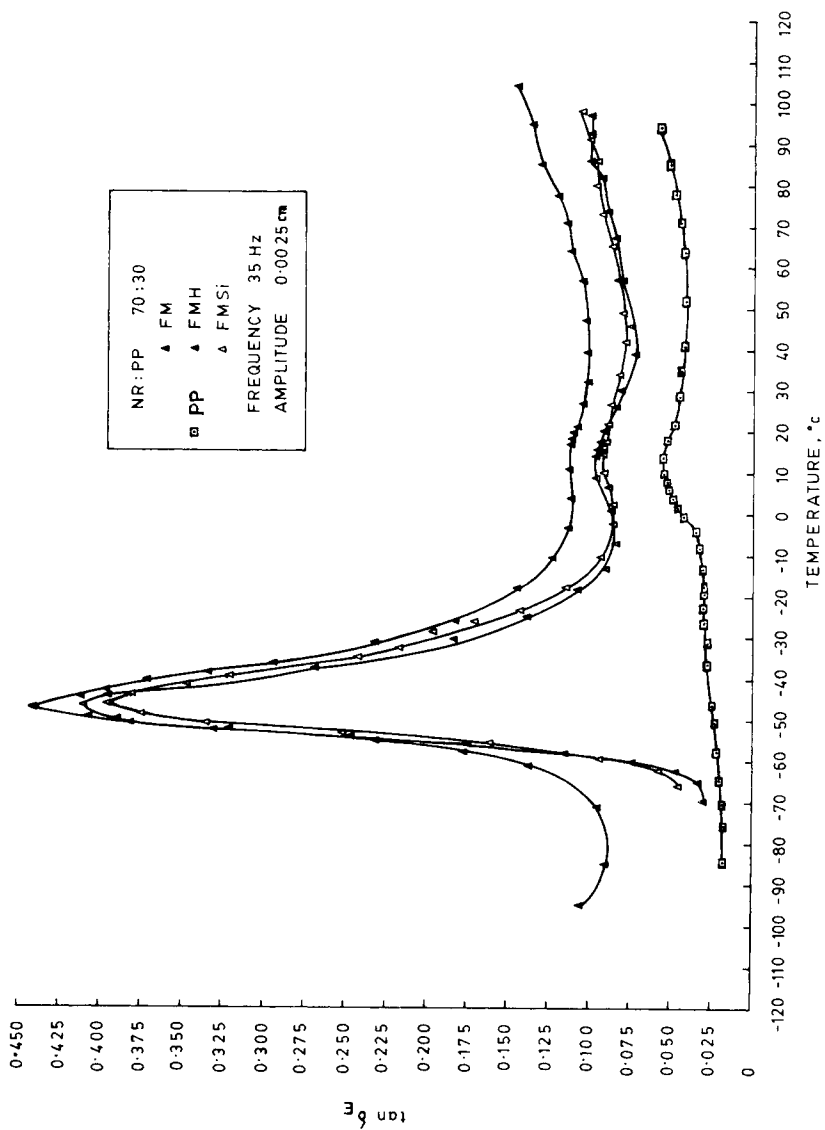


Fig. 9. Effect of HAF black and silica fillers on  $\tan \delta_g$  of 70:30 NR:PP blend.

modulus increases steadily with extent of crosslinking (FS > FM > FD > FU) and the increase is proportional to the degree of crosslinking of the elastomer phase. The loss tangent values decrease with extent of crosslinking of the elastomer phase and the effect of temperature becomes less prominent as the degree of crosslinking increases. It is well known<sup>27</sup> that the effect of any modification in one of the homopolymers of a polymer blend will tend to show up more clearly when that particular component becomes continuous or dominant phase than when it is the discontinuous phase. At higher proportions of the elastomer phase, the cross-linking agent, especially the sulfur cure system, has its action mainly on the elastomer phase.<sup>4</sup> As the effect of crosslinking agents is quite remarkable in 70:30 NR:PP blend, it is evident that the rubber phase also becomes continuous in nature in this blend. Thus, crosslinking of this phase leads to higher extents of recoverable deformation under cyclic straining of the blends, resulting in lower  $\tan \delta$  and higher  $E'$  values with higher extents of crosslinking.

### Effects of Reinforcing Fillers

The effect of reinforcing fillers, HAF black and silica, on the dynamic mechanical properties of 70:30 NR:PP blend containing mixed cure system are shown in Figures 8 and 9. Both HAF black- and silica-filled blends show higher  $E'$  and  $E''$  values than the unfilled blend. The peaks in  $E''$  and  $\tan \delta$  values and the sharp decrease in  $E'$  values in the temperature around  $-50^\circ\text{C}$  indicate the glass transition state of the NR phase. In the  $\tan \delta$  vs. temperature plot (Fig. 9) another peak can be observed in the temperature around  $+10^\circ\text{C}$ . This is due to the transition in the PP phase which has a brittle point of  $+5^\circ\text{C}$ . The presence of two peaks in this plot indicates the existence of two separate phases in the 70:30 NR:PP blend. The two phases may be existing as an interpenetrating network system, due to higher proportion of the NR phase and lower melt viscosity of the PP phase.

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Received November 20, 1984

Accepted July 24, 1985