

# Studies on the Dynamically Vulcanized Polypropylene (PP)/Butadiene Styrene Block Copolymer (SBS) Blends: Melt Rheological Properties

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**ABSTRACT:** Unvulcanized and dynamically vulcanized blends of isotactic polypropylene (PP) and butadiene–styrene block copolymer (SBS), in the composition range of 10–40 wt % SBS content are prepared in an internal mixer and the vulcanization process is investigated through time–torque curves. Study of melt rheological properties of these blends are reported, and results show the effects of blend composition and shear rate on melt viscosity and melt elasticity. Blending of PP with SBS increases melt viscosity and decreases extrudate distortion. Dynamically vulcanized blends show higher melt viscosity and lower melt elasticity than corresponding unvulcanized blends with no melt fracture in the studied range. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2703–2713, 1997

**Key words:** polypropylene; butadiene styrene block copolymer; melt viscosity; melt elasticity; melt fracture

## INTRODUCTION

The poor impact strength of polypropylene, especially at low temperature, has been overcome by melt blending with different elastomers and rubbers such as ethylene–propylene diene rubber (EPDM), polyisobutylene (PiB), and styrene–butadiene block copolymer (SBS).<sup>1</sup> An approach to further improve the performance of rubber-modified PP is to develop dynamically vulcanized thermoplastic elastomeric blends.<sup>2–6</sup> These blends have important technical advantages because they can be processed by such methods as extrusion and molding, even though

they possess a crosslinked elastomer as one component.

Most research has been directed to reveal the mechanical and physical properties of PP/SBS blends,<sup>7,8</sup> and works have been published on the rheological and mechanical properties of dynamically cured EPDM and polyolefin blends,<sup>9–12</sup> but not much work has been reported on systematic investigation of the effect of shear conditions on the rheological properties of unvulcanized and dynamically vulcanized PP/SBS blends.

In this article we present a comparative study of the mixing torque values and melt rheological properties of unvulcanized and dynamically vulcanized PP/SBS blends. Melt rheological data are used to obtain shear stress versus shear rate relationship, melt viscosity, effect of shear rate and temperature on melt viscosity, and melt elasticity param-

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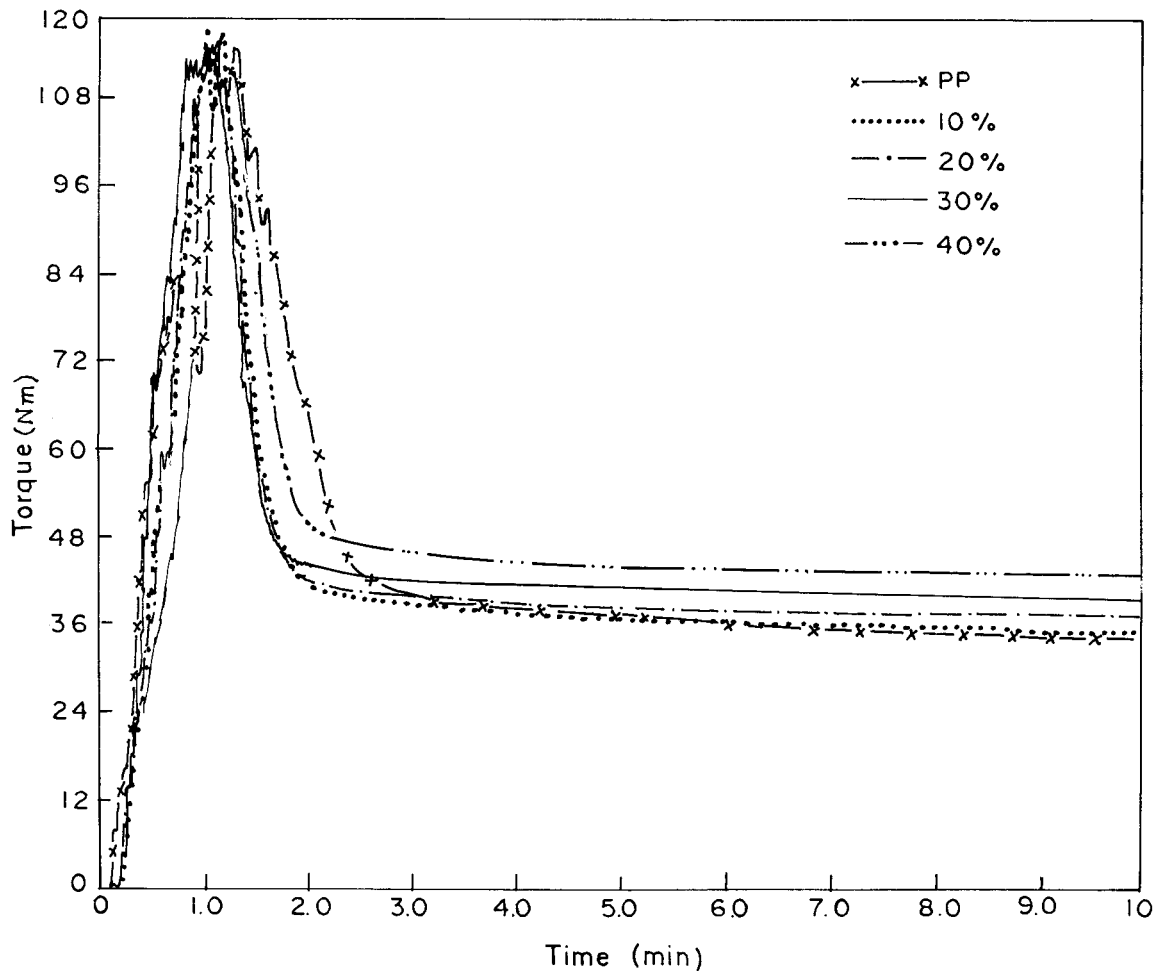


Figure 1 Time-torque curves for unvulcanized PP/SBS blends.

ters of PP/SBS blends at various compositions. Variation of extrudate distortion with blend composition is also illustrated.

## EXPERIMENTAL

### Materials

Isotactic polypropylene (PP), Koylene S-3030 (MFI—3 g/10 min at 230°C and 2.16 kg/cm<sup>2</sup>) supplied by Indian Petrochemicals Corporation Ltd. and Butadiene styrene triblock copolymer (SBS), Cariflex-1101 supplied by Shell Chemical Co. were used in this work. A modified phenolic resole resin, Hylak HR-6415 from Bakelite Hylam, India, and zinc oxide (LR) from Qualigens

were used as a curing agent and accelerator, respectively, for vulcanization.

### Preparation of Blends

The unvulcanized PP/SBS blends of compositions 10, 20, 30, and 40 wt % SBS content were prepared by melt mixing at 180°C for 10 min in the internal mixer of a torque rheometer, HAAKE RHEOCORD RC-90 using roller rotors. The charge weight taken was 200 g. The corresponding dynamically vulcanized blends were also prepared under identical conditions except that after initial mixing for 5 min, a mixture of curing agent and accelerator (10% and 1%, respectively, on the basis of SBS content in the blend) was introduced in the cavity of the mixer while mixing, which was

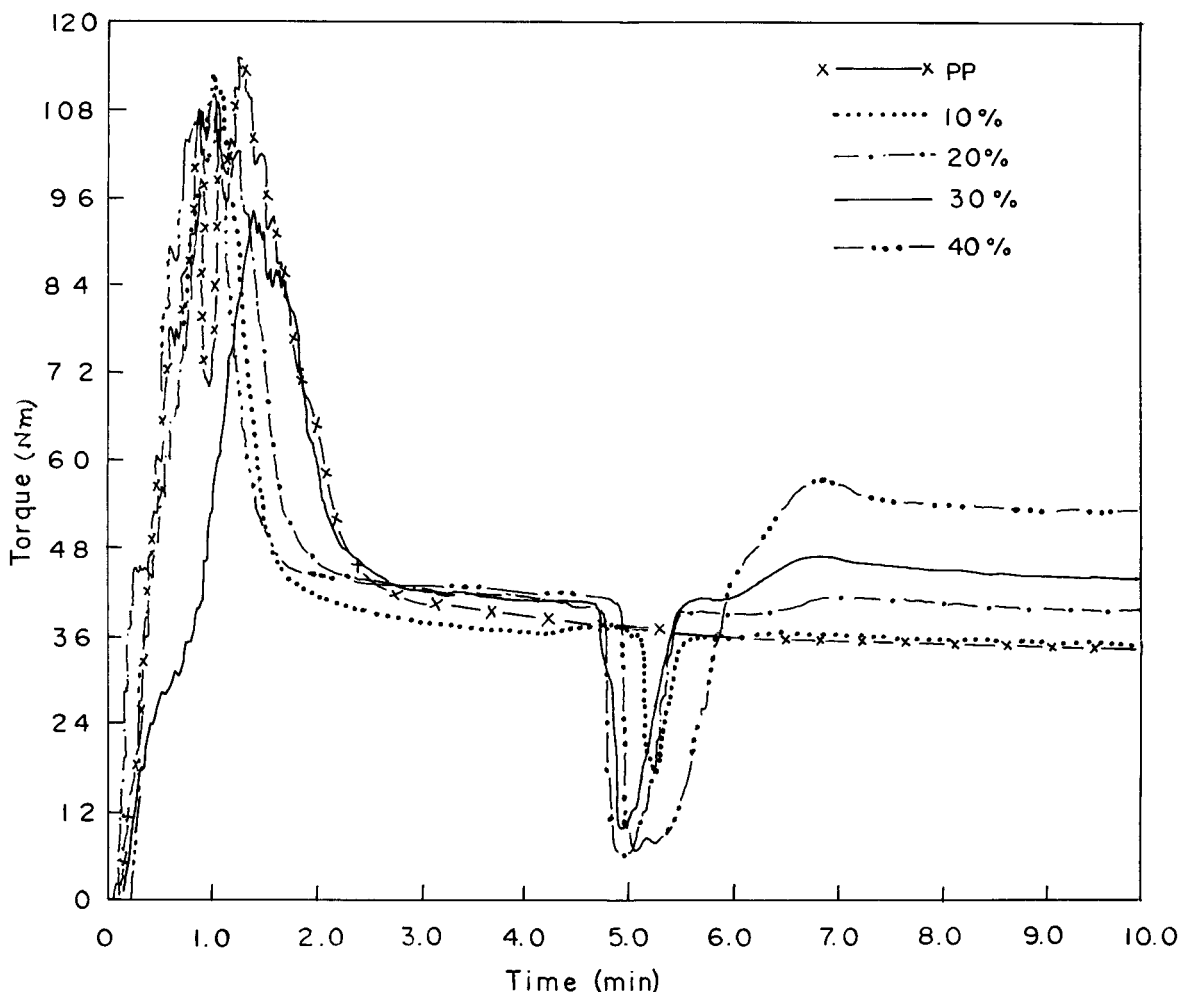


Figure 2 Time-torque curves for dynamically vulcanized PP/SBS blends.

further continued for 5 min until an equilibrium torque is reached after curing. The molten mass from the mixer was cut into fine granules after cooling.

#### Measurements

The rheological measurements were carried out in Kayness Galaxy V- rheometer, which is a piston-type capillary rheometer having a circular die of length/diameter ratio of 80. The measurements were made at three different temperatures viz. 190, 200, and 210°C in the shear rate range of  $0.9 \times 10^2$  to  $4 \times 10^3 \text{ s}^{-1}$ . The data on apparent shear stress [ $\tau_{w(\text{app.})}$ ] and apparent shear rates [ $\dot{\gamma}_{\text{app}}$ ] were obtained (end correction term has been ne-

glected). The apparent melt viscosity [ $\eta_{\text{app}}$ ] was evaluated as eq. (1).

$$\eta_{\text{app}} = \tau_{w(\text{app.})} / \dot{\gamma}_{\text{app}} \quad (1)$$

## RESULTS AND DISCUSSION

### Time-Torque Curves

The time-torque curves of unvulcanized and dynamically vulcanized PP/SBS blends are shown in Figures 1 and 2, respectively. Equilibrium torque values, which are indicative of melt viscosity at that temperature, increase with increasing SBS content in the blend, and this increase is

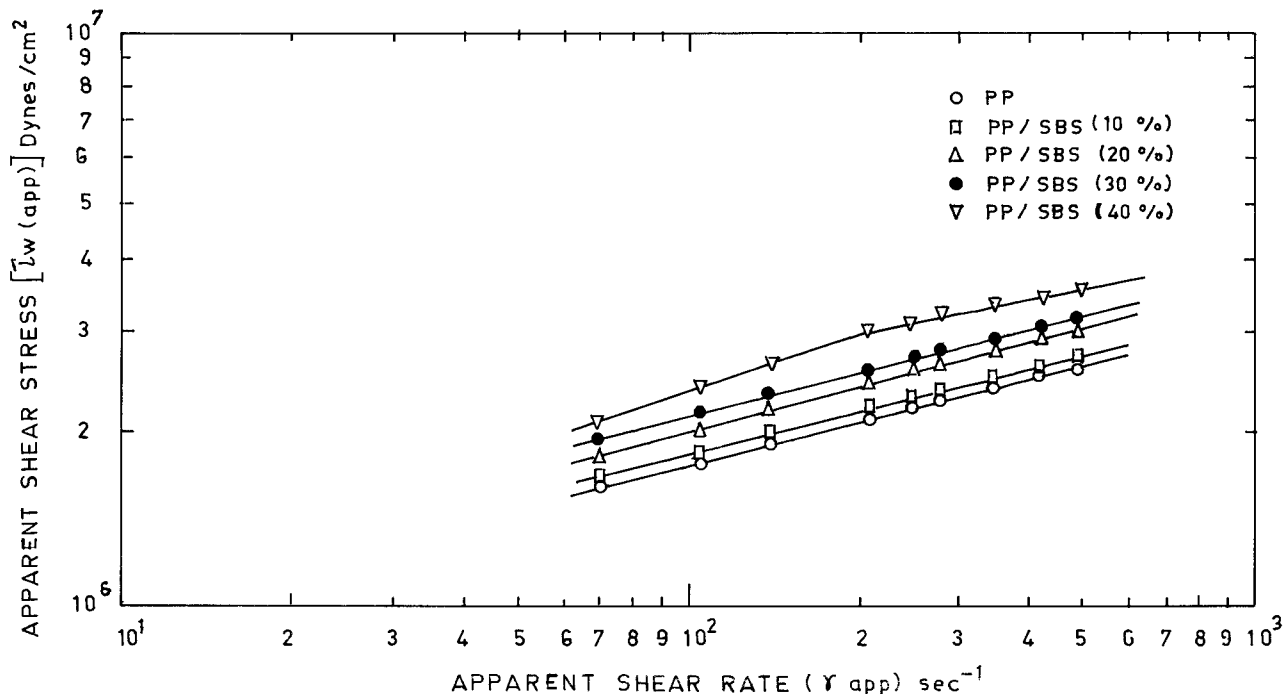


Figure 3 Shear stress–shear rate curves of unvulcanized PP/SBS blends at 190°C.

more conspicuous in dynamically vulcanized blend systems. This means that higher energy input is required for melt processing of dynamically

Table I Values of Power Law Exponent ( $n$ ) and Activation Energy for Viscous Flow ( $\Delta E$ ) for PP/SBS Blends

SBS Content (wt %)	$n$			$\Delta E$ (kJ/mol)
	190°C	200°C	210°C	
Unvulcanized Blend System				
0	0.26	0.25	0.23	26.99
10	0.25	0.23	0.21	30.42
20	0.25	0.21	0.21	33.87
30	0.25	0.21	0.21	33.87
40	—	0.23	0.22	37.34
Dynamically Vulcanized Blend System				
10	0.27	0.22	0.23	30.42
20	0.27	0.21	0.20	33.87
30	0.28	0.19	0.21	37.34
40	—	0.21	0.21	40.83

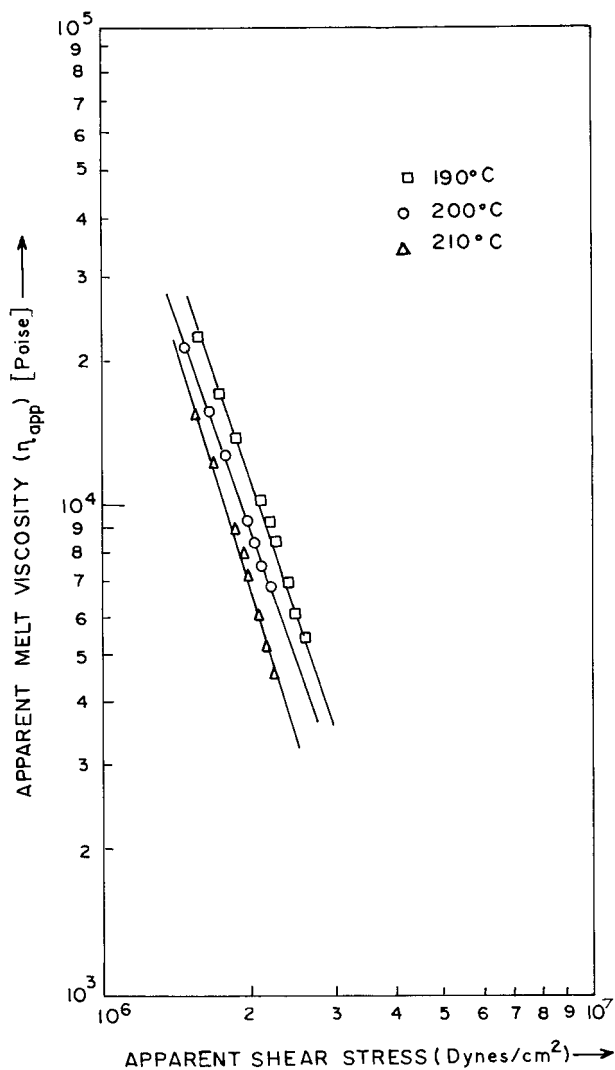
vulcanized blends than corresponding unvulcanized blends. As is reported in the literature,<sup>13</sup> the crosslinking of SBS in dynamically vulcanized blends is indicated by the increase in the torque value after the addition of a curing agent, which is insignificant at low SBS content and becomes prominent at higher SBS content. This indicates that the degree of crosslinking increases with increasing the SBS content in the blend.

#### Shear Stress–Shear Rate Curves

The variations of apparent shear stress [ $\tau_{w(\text{app.})}$ ] versus apparent shear rate [ $\dot{\gamma}_{\text{app.}}$ ] of PP/SBS blends in log–log scale were quite linear in general over the range studied and show that these fluids follow the power law relationship<sup>14</sup> given by eq. (2).

$$\tau_{w(\text{app.})} = K\dot{\gamma}_{\text{app.}}^n \quad (2)$$

except for composition having high SBS content (i.e., 40 wt %) at lower temperature (i.e., 190°C) where a slight deviation from the power law relationship is observed. The  $\tau_{w(\text{app.})}$  versus  $\dot{\gamma}_{\text{app.}}$  curves for the unvulcanized blends at 190°C is



**Figure 4** Variation of apparent melt viscosity ( $\eta_{app.}$ ) with shear stress for PP at various temperatures.

shown in Figure 3 as an example of these data. Values of the exponent  $n$  of the power law relation derived from these data for various samples are shown in Table I. Values of  $n$  lower than unity indicates a pseudoplastic behavior of the melts, and pseudoplasticity increases inappreciably with blend composition as is indicated by insignificant variation of  $n$ .

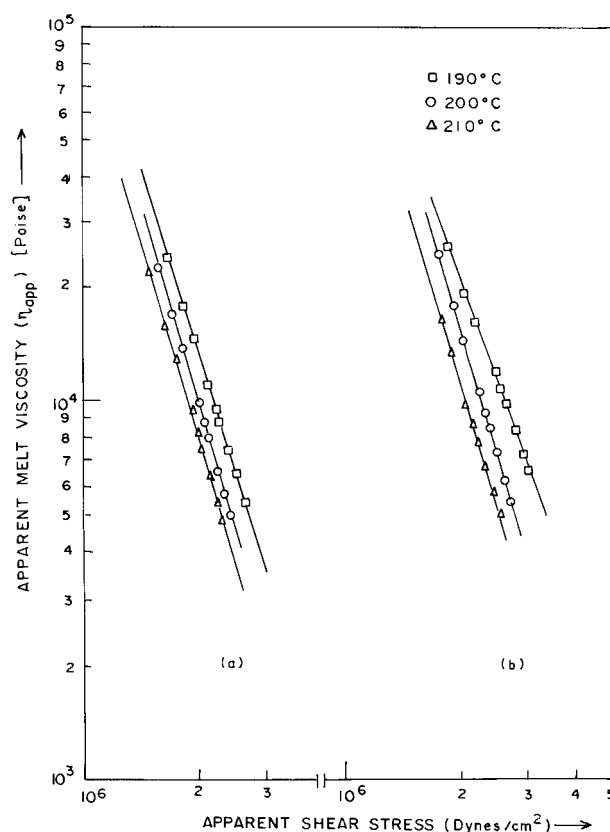
### Melt Viscosity

Variation of  $\eta_{app.}$  with  $\tau_{w(app.)}$  at three temperatures of measurement for PP and PP/SBS blends are shown in Figures 4–8 in the log-log scale. The

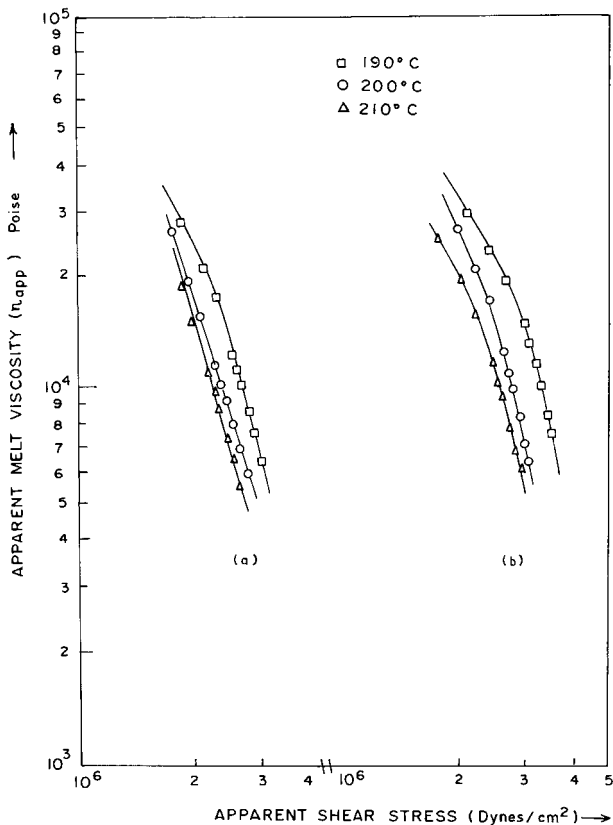
general trend of decrease of  $\eta_{app.}$  with increase in  $\tau_{w(app.)}$  is observed by these blend samples at all the blending ratios and temperatures. The decrease of  $\eta_{app.}$  with increasing  $\tau_{w(app.)}$  is quite linear in general with few exceptions, obeying the following form of the power law relationship [eq. (3)] for pseudoplastic fluids.<sup>14</sup>

$$\eta_{app} = K^{1/n} [\tau_{w(app.)}]^{(n-1)/n} \quad (3)$$

In unvulcanized blends, compositions having 30 wt % SBS at 190°C and 40 wt % SBS at all the studied temperatures, the rate of decrease in  $\eta_{app.}$  with an increase in the shear stress in the lower shear stress region is slow. At high SBS content, the droplet size is larger, as is evidenced in SEM studies (see companion article) and at low shear stress, coalescing of SBS droplets is more predominant than droplet breakup, resulting in resis-



**Figure 5** Variation of apparent melt viscosity ( $\eta_{app.}$ ) with shear stress for unvulcanized PP/SBS blends (a) at 10 wt % SBS, (b) at 20 wt % SBS, at various temperatures.

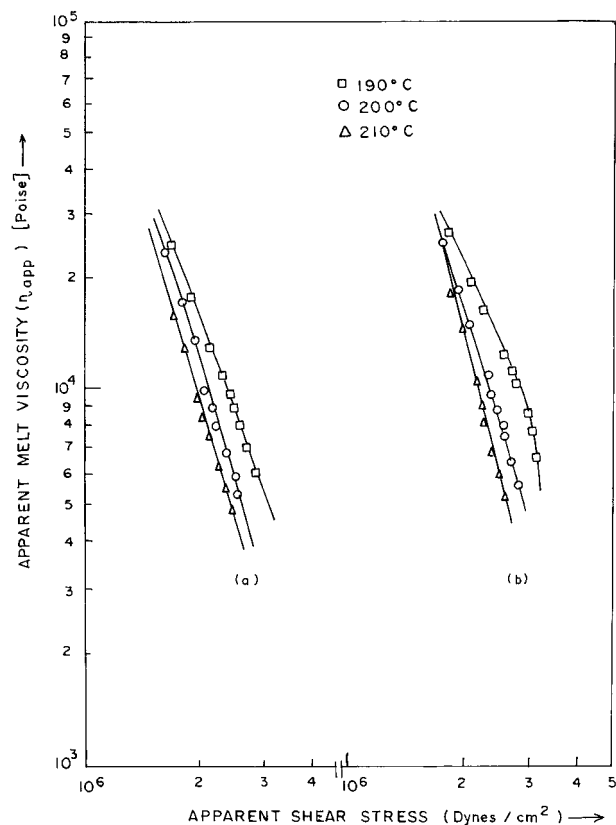


**Figure 6** Variation of apparent melt viscosity ( $\eta_{app}$ ) with shear stress for unvulcanized PP/SBS blends (a) at 30 wt % SBS, (b) at 40 wt % SBS, at various temperatures.

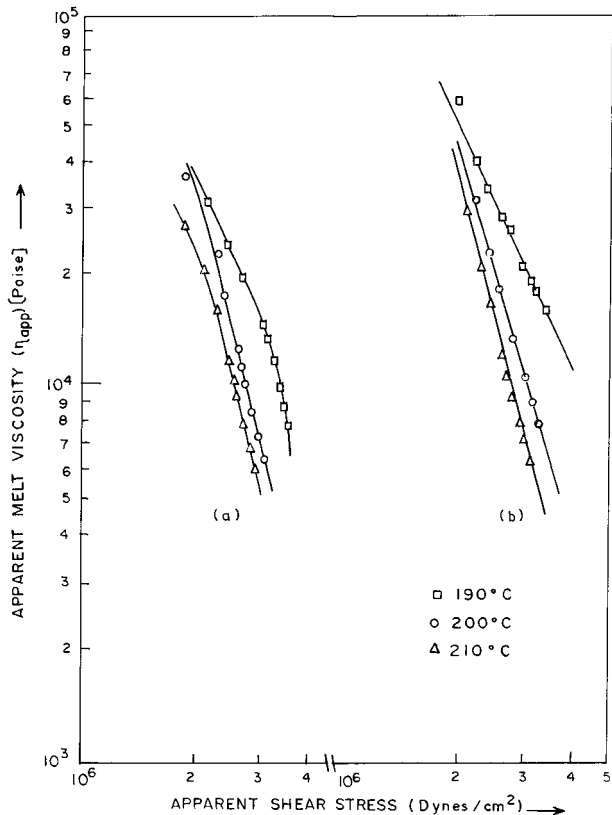
tance to flow or higher melt viscosity. As the shear stress increases, smearing of rubber droplets takes place faster than their ability to associate, causing a rapid decrease in melt viscosity. A similar explanation has been given for polymer deformation in shear<sup>15</sup> and for dispersed systems.<sup>16</sup> In dynamically vulcanized blends there is a network structure and intermolecular slippage, and disruption of overlapping chains are restricted especially at low flow rates, i.e., at compositions having 20–40 wt % SBS at 190°C, resulting in a slow decrease in melt viscosity with shear stress. The shear induced droplet breakup and intermolecular slippage becomes predominant at a higher shear stress, which further depends on the degree of crosslinking. As the degree of crosslinking is increasing with increasing SBS content, so is the critical shear stress at which the rapid decrease in melt viscosity takes place.

The temperature dependence of  $\eta_{app}$  of PP/SBS blends are shown in Figures 9 and 10 as Arrhenius plots,  $\log \eta_{app}$  versus  $1/T$ . The activation energy ( $\Delta E$ ), calculated from the slopes of these plots (Table I), increases with increasing the content of SBS in both the blend systems. The dynamically vulcanized blends having a higher loading of SBS and degree of crosslinking, show higher values of activation energy.

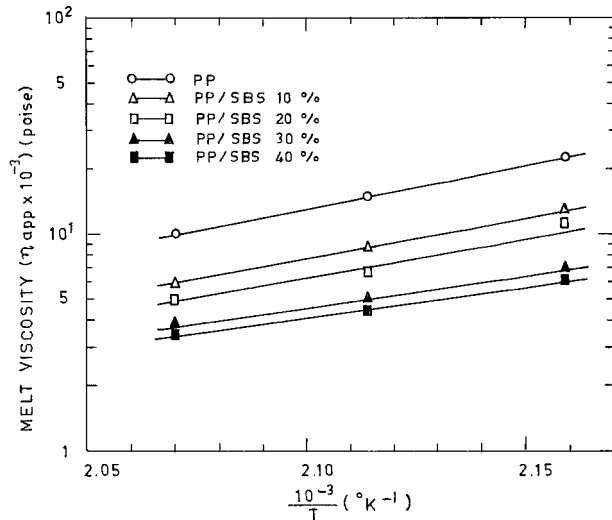
The variation of  $\eta_{app}$  with blend composition at 190 and 210°C at constant shear stresses are shown in Figures 11 and 12, respectively. There is a gradual increase in  $\eta_{app}$  with increasing the SBS content in both blend systems, with a sharp rise in the composition range of 30–40 wt % SBS in the unvulcanized blend system and in the range of 20–30 wt % SBS in the dynamically vulcanized blend system, which suggest a change in morphology at these composition ranges, as evi-



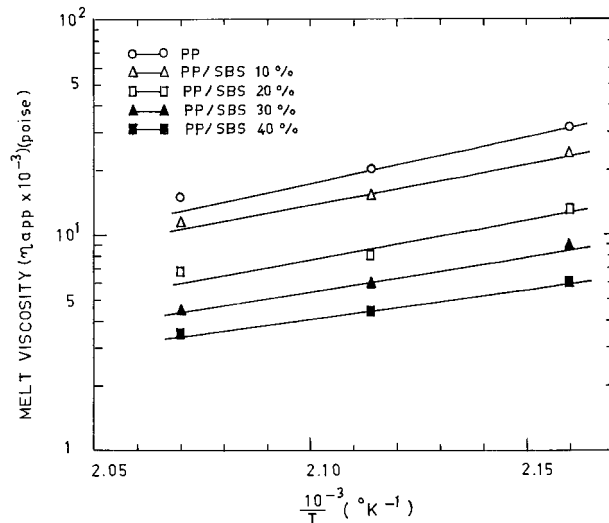
**Figure 7** Variation of apparent melt viscosity ( $\eta_{app}$ ) with shear stress for dynamically vulcanized PP/SBS blends (a) at 10 wt % SBS, (b) at 20 wt % SBS, at various temperatures.



**Figure 8** Variation of apparent melt viscosity ( $\eta_{app.}$ ) with shear stress for dynamically vulcanized PP/SBS blends (a) at 30 wt % SBS, (b) at 40 wt %, at various temperatures.

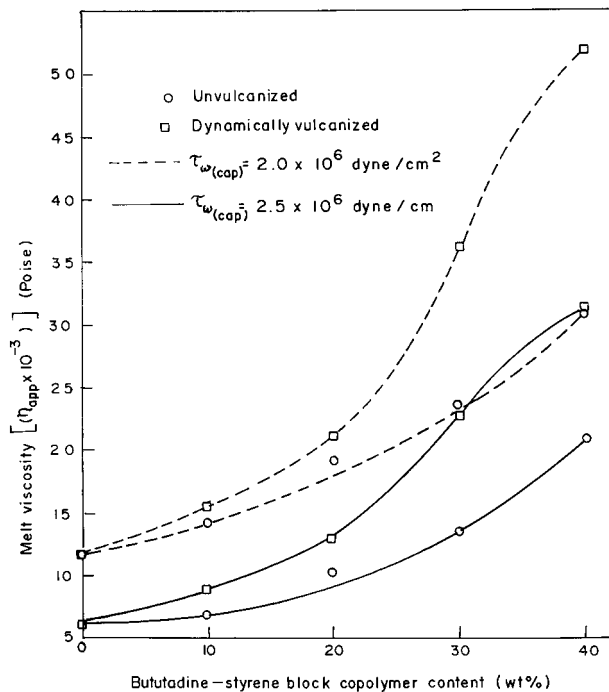


**Figure 9** Arrhenius plots,  $\log \eta_{app.}$  versus  $1/T$  for PP and unvulcanized PP/SBS blends at constant shear stress [ $\tau_{w(app.)} = 2.5 \times 10^6$  dynes/cm<sup>2</sup>].

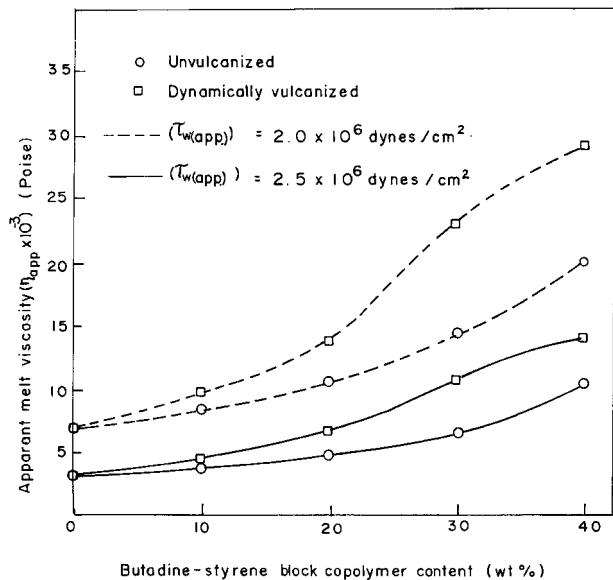


**Figure 10** Arrhenius plots,  $\log \eta_{app.}$  versus  $1/T$ , for PP and dynamically vulcanized PP/SBS blends at constant shear stress [ $\tau_{w(app.)} = 2.5 \times 10^6$  dynes/cm<sup>2</sup>].

denced in the SEM studies of the unvulcanized blends (refer to comparion article). The increase in melt viscosity on addition of an elastomeric



**Figure 11** Variation of apparent melt viscosity ( $\eta_{app.}$ ) with blend composition for PP/SBS blends at 190°C at different shear stresses.



**Figure 12** Variation of apparent melt viscosity ( $\eta_{app.}$ ) with blend composition for PP/SBS blends at 210°C at different shear stresses.

component is quite expected and reported in the literature.<sup>17</sup> As free volume is less and intermolecular slippage is restricted in a crosslinked structure, the dynamically vulcanized blends show higher melt viscosity than the corresponding un-

vulcanized blends at constant shear stresses, which is more conspicuous at higher SBS loading having a higher degree of crosslinking.

The increase in  $\eta_{app.}$  with blend composition and vulcanization is minimal at higher shear rates and temperature and, hence, it is easier to process such blends at these conditions.

### Melt Elasticity

From the measured value of the extrudate swell ratio  $Di/D$  at 200°C, where  $Di$  and  $D$  are the diameters of the extrudate and the die, respectively, various parameters characterizing the melt elasticity, viz. first normal stress difference ( $\tau_{11} - \tau_{22}$ ), recoverable shear strain ( $\gamma_R$ ), and the apparent shear modulus ( $G$ ) were calculated according to the following relationships<sup>1,14,18</sup>:

$$\tau_{11} - \tau_{22} = 2\tau_{w(app.)}[2(Di/D)^6 - 2]^{1/2} \quad (4)$$

$$\gamma_R = (\tau_{11} - \tau_{22})/2\tau_{w(app.)} \quad (5)$$

$$G = \tau_{w(app.)}/\gamma_R \quad (6)$$

The data of extrudate swell ratios ( $Di/D$ ) and various melt elasticity parameters at various shear rates for the unvulcanized and dynamically vulcanized blend systems are given in Tables II and III, respectively. Variation of ( $\tau_{11} - \tau_{22}$ ) as a

**Table II** Values of the Melt Elasticity Parameters for the Unvulcanized PP/SBS Blends at Various Shear Rates

SBS Content (wt %)	$\gamma_{app.}$ ( $s^{-1}$ )	$\tau_{w(app.)} \times 10^{-6}$ (dynes/cm <sup>2</sup> )	Di/D	$(\tau_{11} - \tau_{22}) \times 10^{-7}$ (dynes/cm <sup>2</sup> )	$\gamma_R$	$G \times 10^{-5}$ (dynes/cm <sup>-2</sup> )
0	69.4	1.49	1.75	2.21	7.44	2.00
	208.3	1.96	1.88	3.64	9.90	1.77
	486.1	2.43	2.07	6.05	12.83	1.43
10	69.4	1.58	1.70	2.15	6.8	2.32
	208.3	2.05	1.82	3.45	8.40	2.44
	486.2	2.44	2.00	5.48	11.22	1.96
20	69.4	1.71	1.63	2.04	5.96	2.87
	208.3	2.18	1.73	3.128	7.18	3.03
	486.1	2.64	1.90	5.07	9.59	2.75
30	69.4	1.79	1.53	1.74	4.86	3.68
	208.3	2.30	1.61	2.63	5.73	3.99
	486.1	2.64	1.77	4.23	7.71	3.67
40	69.4	1.97	1.33	1.19	3.01	6.54
	208.3	2.54	1.38	1.75	3.42	7.42
	486.1	3.02	1.44	2.40	3.98	7.58



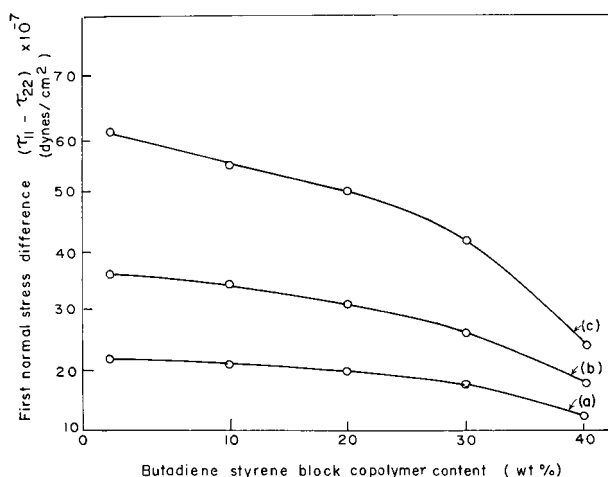
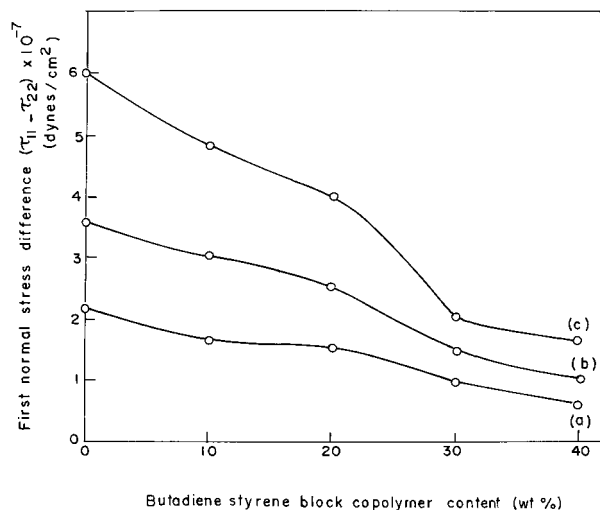
**Table III** Values of the Melt Elasticity Parameters for the Dynamically Vulcanized PP/SBS Blends at Various Shear Rates

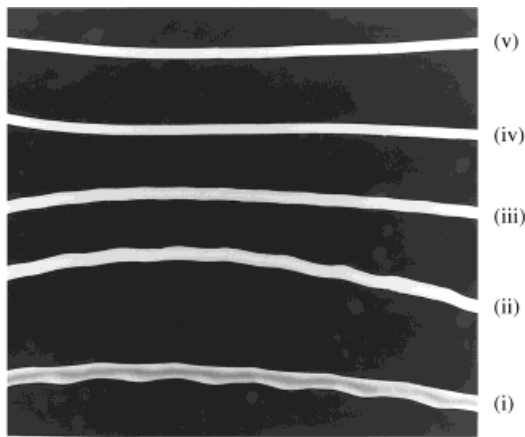
SBS Content (wt %)	$\gamma_{app.}$ ( $s^{-1}$ )	$\tau_{w(app.)} \times 10^{-6}$ (dynes/cm <sup>2</sup> )	Di/D	$(\tau_{11}-\tau_{22}) \times 10^{-7}$ (dynes/cm <sup>2</sup> )	$\gamma_R$	$G \times 10^{-5}$ (dynes/cm <sup>-2</sup> )
10	69.4	1.62	1.57	1.71	5.28	3.06
	208.3	2.08	1.74	3.04	7.31	2.84
	486.1	2.50	1.91	4.87	9.75	2.56
20	69.4	1.74	1.49	1.57	4.51	3.85
	208.3	2.27	1.60	2.55	5.61	4.04
	486.1	2.73	2.00	4.07	7.45	3.66
30	69.4	2.15	1.25	1.00	2.34	9.18
	208.3	2.60	1.32	1.52	2.92	8.90
	486.1	3.05	1.41	5.07	3.70	2.75
40	69.4	2.20	1.14	0.68	1.55	14.23
	208.3	2.78	1.19	1.07	1.91	14.49
	486.1	3.39	1.27	1.71	2.53	13.40

function of blend composition at several constant shear rates for PP/SBS blends are shown in Figures 13 and 14. At a constant shear rate there is a gradual decrease in melt elasticity with increasing SBS content in both the blend systems, with a sharp decrease in the composition range of 30–40 wt % SBS in the unvulcanized blend system and in the range of 20–30 wt % SBS in the dynamically vulcanized blend system. The total decrease in first normal stress difference was by a factor of 1.31–1.44 in the unvulcanized blend system and 1.53–1.64 in the dynamically vulcanized

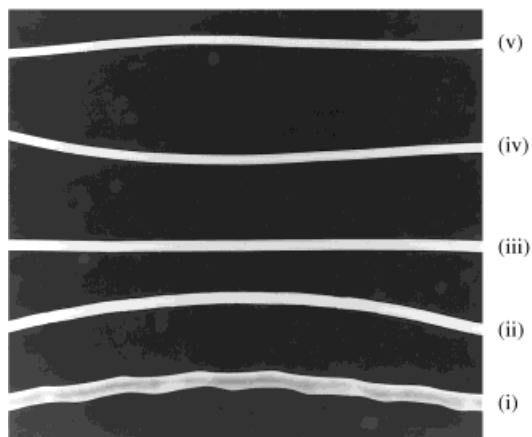
blend system in the studied range of blend composition, depending upon the shear rate, indicating that dynamically vulcanized blends have lower melt elasticity than corresponding unvulcanized blends. At any constant shear rate,  $\gamma_R$  decreases and  $G$  increases with increasing the SBS content in the blend.

The above observations indicate that a sharp decrease in melt elasticity takes place in the composition range where a sharp increase in melt viscosity takes place.

**Figure 13** Variation of first normal stress difference ( $\tau_{11}-\tau_{22}$ ) with blend composition for the unvulcanized PP/SBS blends at various shear rates ( $s^{-1}$ ): (a) 69.4, (b) 208.3, (c) 486.1.**Figure 14** Variation of first normal stress difference ( $\tau_{11}-\tau_{22}$ ) with blend composition for dynamically vulcanized PP/SBS blends at various shear rates ( $s^{-1}$ ): (a) 69.4, (b) 208.3, (c) 486.1.



(a)



(b)

**Figure 15** Distortion of extrudates at a constant shear rate [ $\dot{\gamma}_R = 104 \text{ s}^{-1}$ ]: (a) in unvulcanized, and (b) dynamically vulcanized PP/SBS blends at compositions (i) 0 wt % SBS, (ii) 10 wt % SBS, (iii) 20 wt % SBS, (iv) 30 wt % SBS, (v) 40 wt % SBS.

### Melt Fracture

Melt fracture behavior of PP is considerably affected by blending with SBS. Photographs of the extrudates of PP and its blends at a constant shear rate are presented in Figure 15 to show the effect of blend composition on the distortion of extrudate surfaces. At a constant shear rate the tendency of extrudate distortion decreases with increase in the SBS content in the unvulcanized blends so much so that in compositions having 30–40 wt % SBS almost no distortion of extru-

dates were observed. In the dynamically vulcanized blends no melt fracture was observed in the studied range and uniform extrudates, whose smoothness increases with increasing the SBS content, were obtained. For any given composition extrudate distortion was found to occur only when shear stress exceeded a certain critical value. The critical shear stress, above which the extrudate distortion start appearing in these blends increased with increasing the SBS content. The effects of blend composition on the extrudate distortion are quite consistent with the melt elasticity behavior of these blends. The above observations suggest that the processing behavior of the dynamically vulcanized blends are better than the corresponding unvulcanized blends.

### CONCLUSION

PP/SBS blends show a pseudoplastic non-Newtonian behavior. Incorporation of SBS into PP increases the melt viscosity with a steep rise in the composition of 30–40 wt % SBS in unvulcanized blends and 20–30 wt % SBS in dynamically vulcanized blends, suggesting a change in morphology at these composition ranges.

The rubber content in the blends and extent of dynamic crosslinking has a profound influence on the viscosity of blends at lower shear stress. The increase in  $\eta_{app}$  with the blend composition and vulcanization is minimal at higher shear rates and temperature and, hence, it is easier to process such blends at these conditions.

There is a decrease in melt elasticity and melt fracture with increasing SBS content in the blends. These effects are more pronounced in dynamically vulcanized blends, which indicate better processability of these blends than the corresponding unvulcanized blends.

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