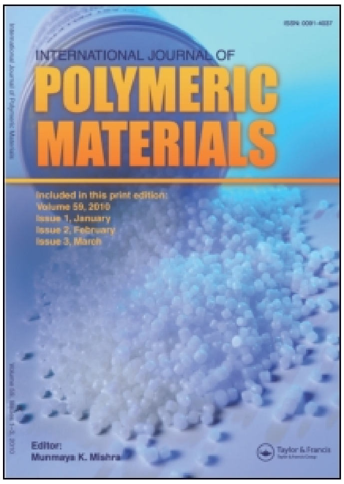

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DYNAMICALLY VULCANIZED THERMOPLASTIC ELASTOMER BLENDS OF NATURAL RUBBER AND POLYPROPYLENE

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Dynamic vulcanization of a soft grade of thermoplastic natural rubber (TPNR) was carried out using several concentrations of Hexamethylene N, N′ bis (tert-butyl peroxy carbamate) (HBTP). The blends were melt mixed in a Brabender plasticorder. The effectiveness of dynamic vulcanization was investigated using the Brabender plastograms, swelling index measurements, rheological behavior by means of a capillary rheometer, dynamic mechanical properties, and tensile testing. It was found that varying the HBTP concentration had a great influence on the rheological behavior as well as the dynamic and tensile properties of the material. The increase of HBTP dosage resulted in an increase of the extent of crosslinking and caused an increase of the elastic modulus and a reduction of the loss modulus. The ultimate tensile strength and elongation at break also increased with increasing HBTP loading. The rheograms indicated that the blends exhibit a pseudoplastic behavior.

Keywords: thermoplastic elastomers, dynamic vulcanization, natural rubber, polypropylene, hexamethylene N, N′ bis(tert-butyl peroxy carbamate)

1. INTRODUCTION

Thermoplastic elastomers (TPE's) are materials that combine the advantages of the processing of thermoplastics with the outstanding mechanical properties and elastic recovery of vulcanized rubbers [1].

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Various types of TPE's have been prepared and their morphology, mechanical and rheological properties have been studied [2–6].

Among the various TPE's, those which are prepared by physical melt mixing of a polyolefin and an elastomer have gained significant attention because of the simple preparation method and the ease of tailoring the properties required [7]. Addition of a small concentration of a crosslinking agent during melt mixing leads to the in situ vulcanization of the dispersed rubber particles [8]. This process, which is called dynamic vulcanization, is a route to new thermoplastic elastomers with good properties, such as reduced permanent set, improved ultimate mechanical properties, greater resistance to attack by fluids, and improved high temperature utility [9].

Thermoplastic Natural Rubber (TPNR) is a blend obtained by melt mixing Natural Rubber (NR) and Polypropylene (PP) [10]. Many crosslinking agents, including sulfur, sulfur donors, peroxides, and bismaleimides, have been used for the dynamic vulcanization of TPNR [11]. Additionally, the use of bisperoxy carbamates as crosslinking agents in single-phase rubbers such as natural rubber, styrene-butadiene rubber, silicone rubber, polychloroprene and epichlorohydrin rubber has been reported by Hepburn [12]. The objective of the present work was therefore to study the use of Hexamethylene N, N′ bis(tert-butyl peroxy carbamate) (HBTP) for the dynamic vulcanization of a soft grade of TPNR.

2. EXPERIMENTAL

2.1 Mixing

The two polymers used in this study were of commercial grade and were supplied by Entreprise Nationale des Plastiques et Caoutchoucs (ENPC, Algeria). Natural rubber was an SMR 20 grade with a density of 0.93 gr/cc. The polypropylene used was an injection grade with a density of 0.91 gr/cc and percent crystallinity of 42. HBTP was supplied by Janssen Chimica. The other additives, namely TMTD (Tetrametyl thiuram dissulfide), ZnO (Zinc oxide), MBT (Mercapto benzo thiazole) and stearic acid, were standard materials used in rubber formulations and were used as received.

In this study, all the NR/PP blends contained 70/30 rubber to plastic ratio. The compositions of the blends are shown in Table 1. Five different formulations were prepared and are designated H0, H1, H2, H3, and T1. The letter H designates a blend dynamically vulcanized with HBTP, and the number following this letter, as in H2, refers to the amount in Phr of this crosslinking agent. The letter T refers to the

TABLE 1 Composition of the Blends

	Designation				
Ingredient	H0	H1	H2	H3	T1
NR	70	70	70	70	70
PP	30	30	30	30	30
HTBP	0	1	2	3	–
TMTD	–	–	–	–	1
MBT	–	–	–	–	1
ZnO	–	–	–	–	5
Stearic acid	–	–	–	–	2

reference formulation based on TMTD and MBT. H0 is the unvulcanized blend.

Mixing of the different formulations was carried out in a Brabender Plasticorder (model PLE 331), using a cam-type mixer with a rotor speed of 60 rpm. Polypropylene was introduced first and melted for 2 minutes at 170°C. Then natural rubber was added and the two polymers were allowed to blend for 2 minutes before adding the curatives. Mixing continued then for 5 minutes. At the end of this mixing step, the blends were taken out and sheeted through a two-roll mill. The slabs were then cut into small pieces and remixed in the Brabender at 160°C for 2 minutes and finally sheeted out.

Samples for testing were stamped out from 2-mm–thick sheets prepared by compression molding at 150°C and under a pressure of 10 Mpa for 15 minutes.

2.2 Testing

2.2.1 Tensile Properties

Tensile testing was performed using an ADAMEL testing machine (model DY 25) following ASTM D412-80 test method at a cross-head speed of 500 mm/min.

2.2.2 Dynamic Mechanical Properties

The dynamic mechanical properties of the blends were investigated using a Rheometrics Solid Analyzer (model RSA II). Measurements of the storage modulus (E'), the loss modulus (E''), and the dissipation factor ($tan\,\delta$) were made over the temperature range of -80 to $+100$°C at a heating rate of 2°C/min. Samples were vibrated in tension mode at a frequency of 30 Hz and a strain amplitude of 0.2 mm.

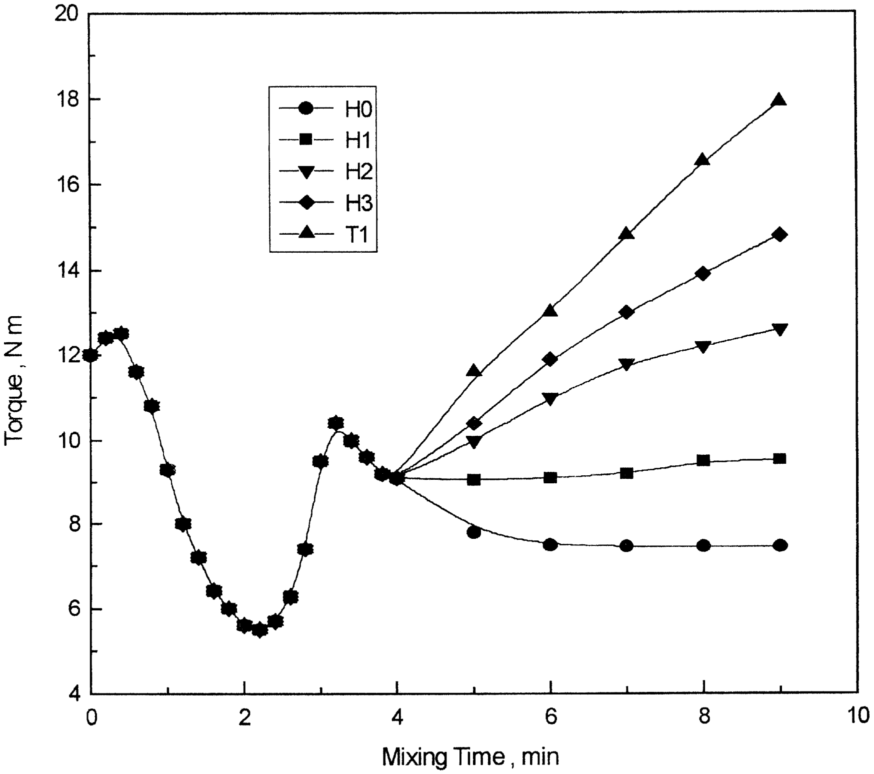

FIGURE 1 Variation of torque with mixing time for NR/PP blends at different crosslinking agent concentration.

2.2.3 Determination of the Swelling Index

In order to estimate the extent of crosslinking, the swelling index was measured by the immersion, in cyclohexane during 24 hours, of 2-mm–thick rectangular specimen of a length of 1.5 cm and a width of 1 cm. The swelling index was calculated as:

$$\text{Swelling Index} = \frac{\text{Swollen mass}}{\text{Initial mass}} \tag{1}$$

2.2.4 Rheological Behavior

Rheological measurements were performed at 175°C using an Instron capillary rheometer with a capillary of an L/D ratio of 40. The force required to move the plunger was recorded for different

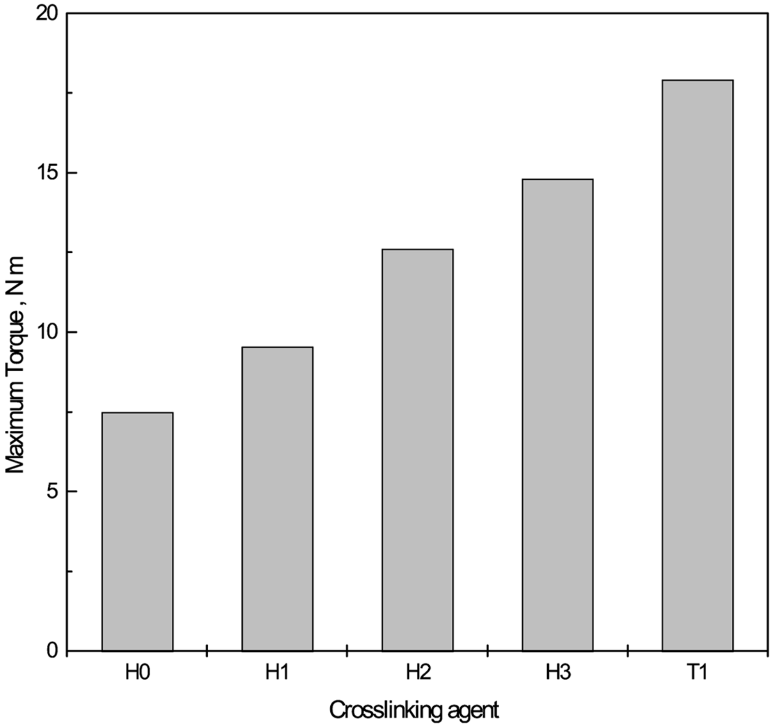

FIGURE 2 Variation of the value of maximum torque with crosslinking agent concentration for NR/PP blends.

cross-head speeds and the corresponding apparent shear stress and shear rate at the wall were calculated. The power law index was determined as the slope of the logarithmic plots of shear stress versus shear rate.

3. RESULTS AND DISCUSSION

3.1 Brabender Plastograms

The variation of the torque with mixing time by means of the Brabender Plasticorder is an appropriate way of monitoring the dynamic vulcanization. The plastograms of the different formulations are shown in Figure 1. These curves indicate that at first when PP is introduced into the mixer the torque is high. As the polymer is sheared inside the hot chamber, it starts to melt and consequently the torque decreases. When NR is added, the torque first increases and then shows a small drop as it melts before it finally levels off. But with

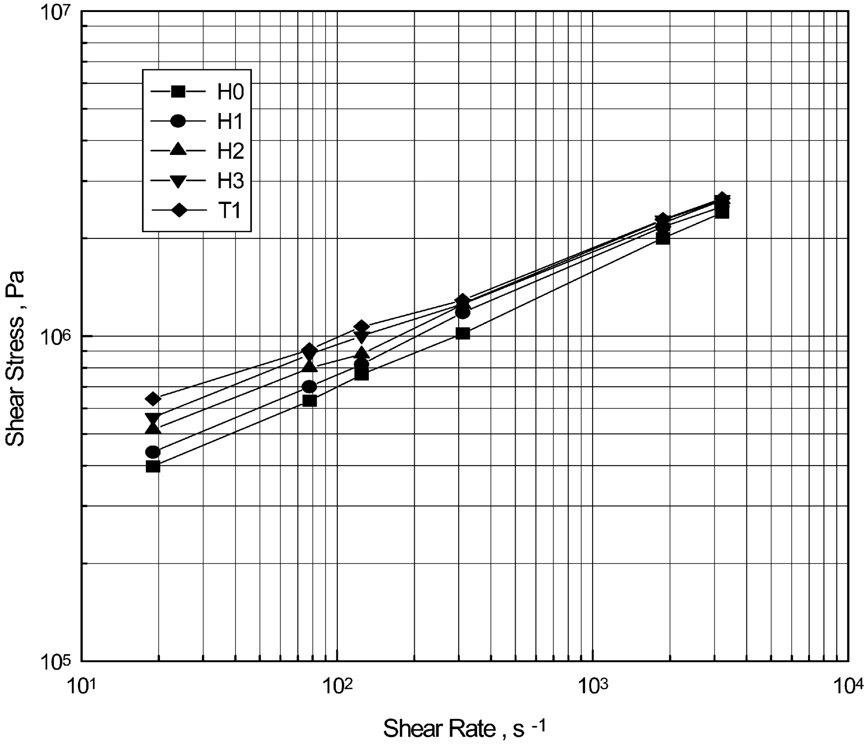

FIGURE 3 Variation of shear stress with shear rate for NR/PP blends at different crosslinking agent concentration.

blends containing HBTP there was a substantial increase in torque with increasing mixing time. This is due to the formation of crosslinks inside the rubber phase leading to greater resistance to rotation. Figure 2, which shows the variation of the value of the final torque with the amount of the crosslinking agent, indicates that the level of the torque in the Brabender Plasticorder increases linearly with the concentration of HBTP. It is also shown that a HBTP content of 1 Phr was not relatively high enough to cause important crosslinking compared to that achieved by the reference formulation. The blend crosslinked with TMTD and MBT exhibited higher torque levels indicating either a higher extent of crosslinking or stronger crosslinks.

3.2 Rheological Behavior

Thermoplastic elastomers are destined to be processed using techniques involving high shearing. It is therefore very important to

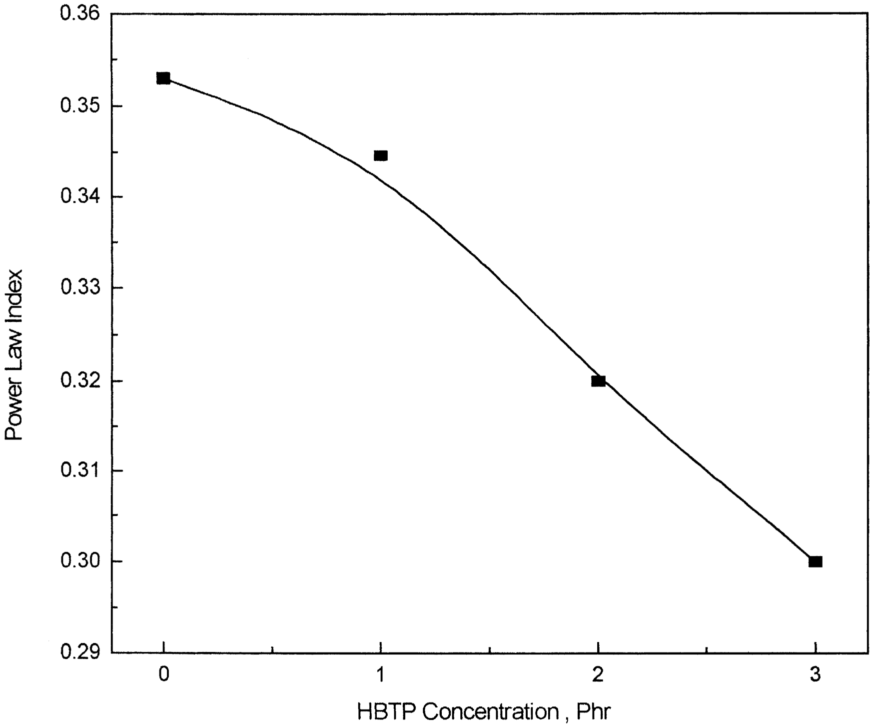

FIGURE 4 Effect of crosslinking agent concentration on the power law index of NR/PP blends.

examine the flow behavior of these materials under several shearing conditions. Figure 3 represents the capillary rheometer rheograms of the 70/30 blend of NR/PP blend dynamically vulcanized with different concentrations of HBTP. These flow curves show that the shear stresses increase linearly with shear rates indicating a characteristic pseudoplastic behavior. It is also shown that the rate of increase in shear stress depends on the concentration of the curative. This could be related to the effect of crosslinking and the formation of intermolecular linkages that increase the viscosity of polymer melts [13]. The slope of these flow curves can be used to estimate the value of the power law index (n′). The variation of n′ with HBTP concentration is shown in Figure 4. The values of the power law index (n′) decrease with increasing the crosslinking agent loading and are all less than 1, confirming the pseudoplastic nature of the material over the entire range of recorded shear rates.

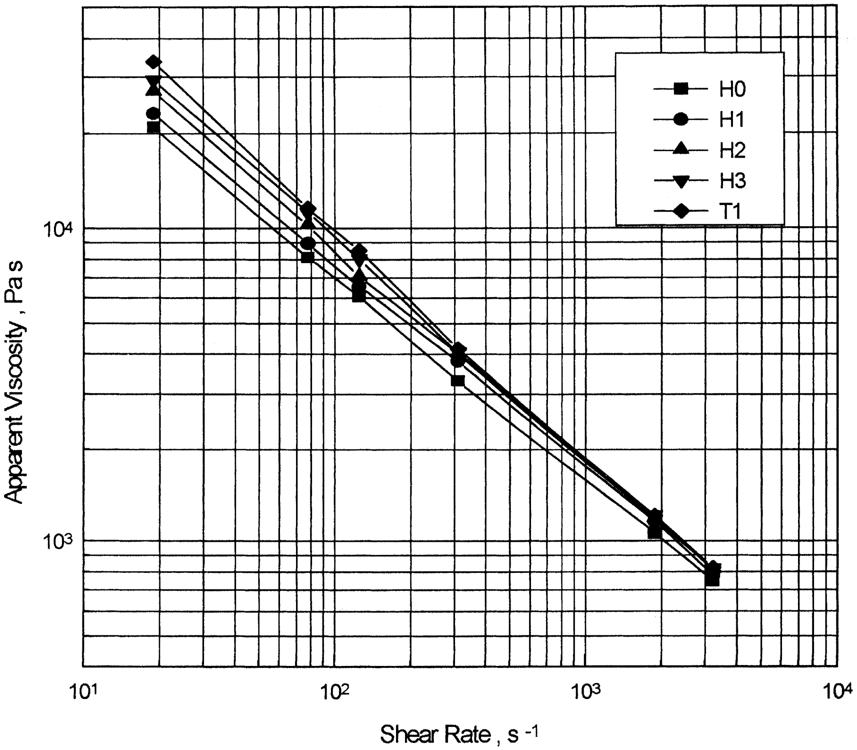

FIGURE 5 Variation of the apparent viscosity with shear rate for NR/PP blends at different crosslinking agent concentration.

Figure 5 shows the effect of shear rate on the viscosity of the mixes containing different amounts of the curatives. In all cases it is clear that the viscosity decreases with shear rate and increases with increasing concentration of HBTP. The increase in viscosity with the amount of the crosslinking agent is less pronounced at high shear values where the curves converge. Similar results have been reported for EPDM/PP blend systems [8]. Again these rheograms reflect the effect of the extent of crosslinking on the viscosity of the material. That is, the higher viscosity of the dynamically vulcanized NR/PP blends is the consequence of the intermolecular network formation, which is known to affect melt flow. It is to be noted, however, that even though the viscosity increases with HTBP dosage over the whole range of shear rates, the blend can still be processed like thermoplastics.

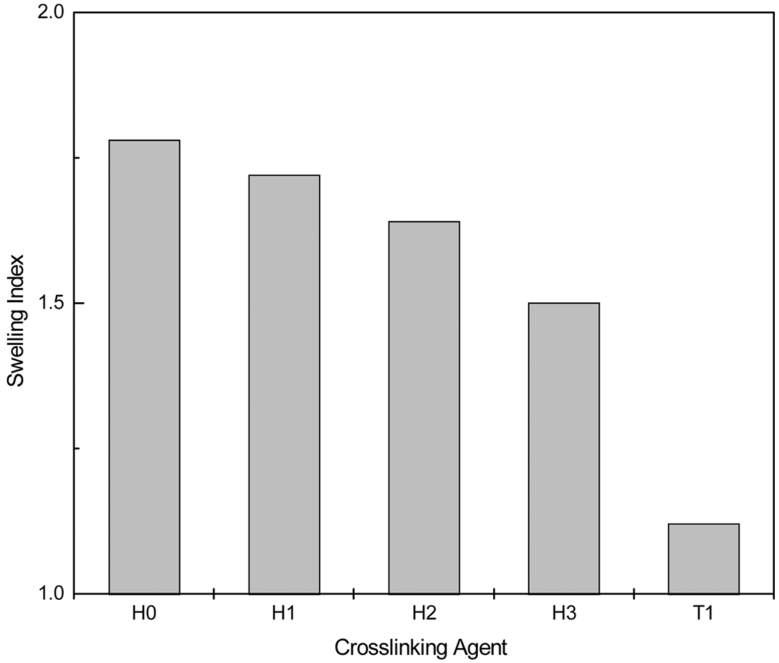

FIGURE 6 Effect of varying crosslinking agent concentration on the swelling index of NR/PP blends.

3.3 Swelling Index Measurements

The degree of crosslinking of the elastomer phase in the blends dynamically vulcanized by different amounts of HBTP can be estimated by measuring the swelling index. It is clear that, as shown in Figure 6, the swelling index decreases with increasing the concentration of the crosslinking agent. This result, which is consistent with a report by Mathew et al. [14] on PVC/NBR thermoplastic elastomer, indicates that the restriction to swelling of the material increases as the degree of crosslinking is increased by higher loading of HBTP.

3.4 Dynamic Mechanical Properties

Thermoplastic elastomers are frequently used in applications where they are subjected to cyclic stressing, which can generate heat. Their inability to tolerate elevated temperatures may pose a limitation on their application. It is therefore very important to study their dynamic

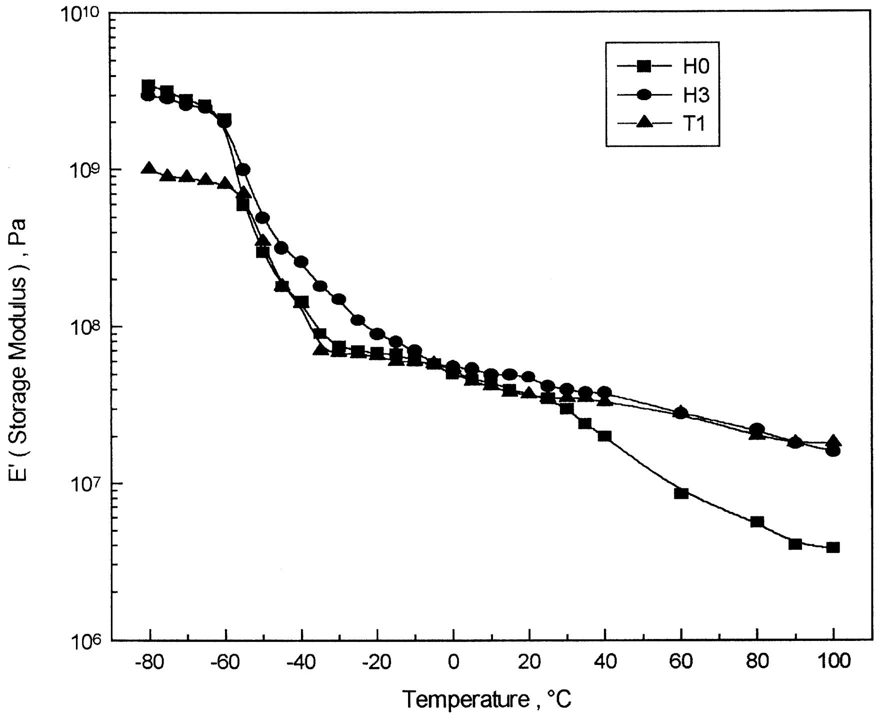

FIGURE 7 Variation of the elastic modulus with temperature for NR/PP blends H0: unvulcanized; H3: NR/PP/3HBTP; T1: NR/PP/TMTD.

mechanical properties. The variation of the elastic or storage modulus (E'), the loss modulus (E''), and the loss factor ($tan\ \delta$) with temperature are presented in Figures 7–9. The curves have three distinct regions: a glassy region, a transition region, and a rubbery region. In the first region, at low temperatures the molecular chains are frozen in a rigid network with a high value of the modulus. In the second region, as temperature is increased long range motion of chain segments starts to occur, leading to a decrease in the modulus. This decrease in stiffness due to the increase in temperature is very pronounced in the third region, the flow region, where the amorphous chains completely flow leading to a very low value of the modulus. It is shown in Figure 7 that the reduction in the modulus of the unvulcanized blend is large, whereas with the crosslinked blends the drop in the elastic modulus is relatively less and starts to occur at higher temperatures. It is also apparent that the plateau region of the dynamically vulcanized blends was extended towards larger temperature intervals. The plots of the

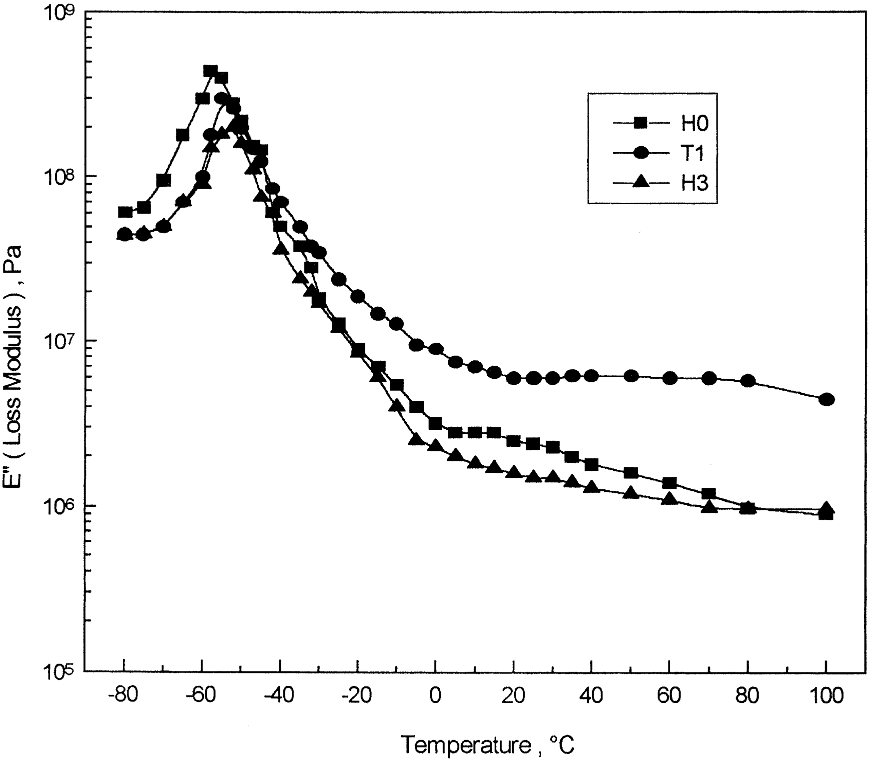

FIGURE 8 Variation of the loss modulus with temperature for NR/PP blends H0: unvulcanized; H3: NR/PP/3HBTP; T1: NR/PP/TMTD.

loss modulus (E'') and loss factor ($tan\,\delta$) against temperature are shown in Figure 8 and Figure 9, respectively. In these curves the Tg peaks for the three blends are distinct. The values of Tg obtained are given in Table 2. In Figure 8, it is seen that the loss modulus near the glass transition temperature of NR for the three blends is almost the same, but as the temperature is increased energy dissipation takes place and a corresponding peak is observed. As expected, the curves of the loss modulus (E'') show that crosslinking reduces damping [5]. In Figure 9, it is shown that there was a reduction in $\tan\delta$ peak of the dynamically vulcanized blends. This reduction was more important in the case of the TMTD/MBT-based formulation, confirming the results of the swelling measurements that the extent of crosslinking was higher. Moreover, the values of Tg suggest that crosslinking by means of HBTP was less compared to TMTD/MBT system. In other words, more interchain linkages were formed in the latter system leading to a

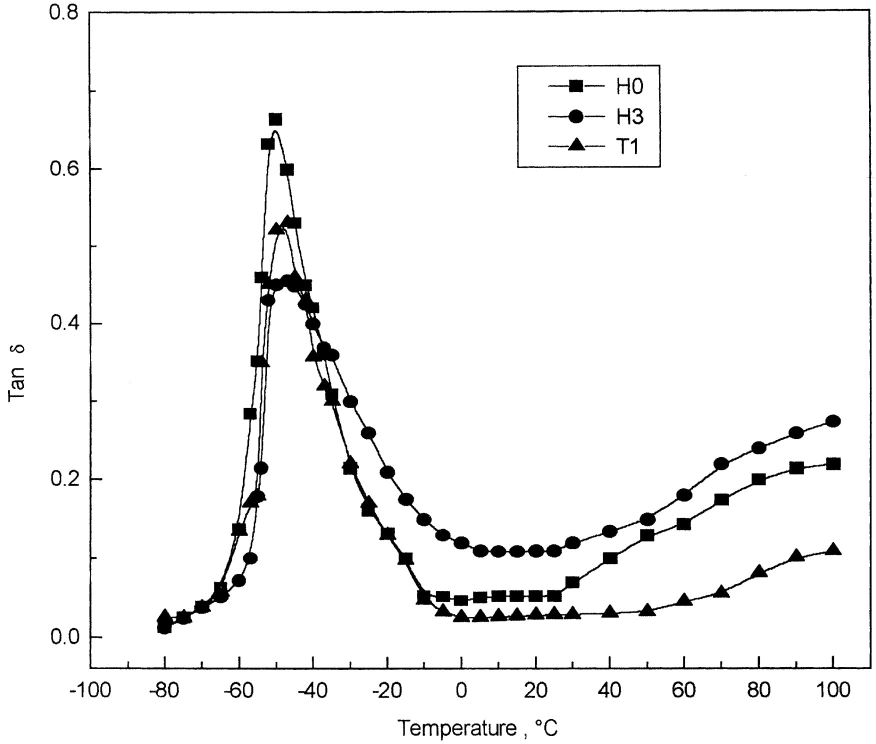

FIGURE 9 Variation of the dissipation factor with temperature for NR/PP blends H0: unvulcanized; H3: NR/PP/3HBTP; T1: NR/PP/TMTD.

TABLE 2 Glass Transition Temperature (Tg) and tan δ_{max} for NR/PP Blends

Blend designation	Tg, °C	tan δ_{max}
H0	− 50	0.665
H3	− 45	0.448
T1	− 47	0.530

higher shift of the glass transition temperature of NR, since the crosslinks reduce chain flexibility.

3.5 Tensile Properties

The effects of varying HBTP content on tensile strength and elongation at break are presented in Figure 10. It is apparent that the

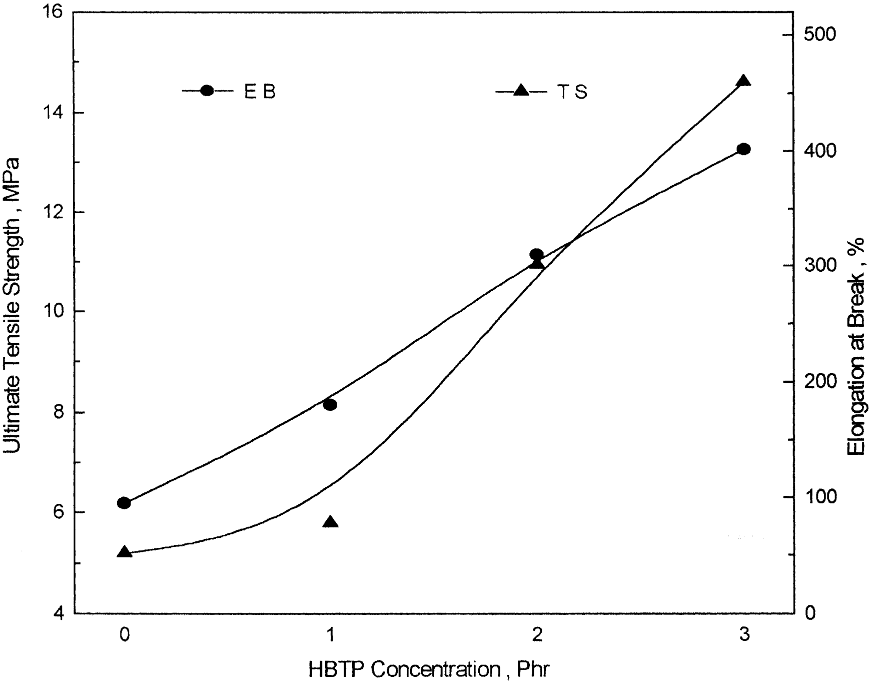

FIGURE 10 Effect of crosslinking agent on tensile strength (TS) and elongation at break (EB) of NR/PP blends.

ultimate tensile strength improves continuously as the amount of the crosslinking agent increases. The elongation at break shows the same trend. This is explained by the fact that in the unvulcanized formulation the two polymers are incompatible and the blend behaves like a weak and brittle material. Consequently, rupture occurs by a weak viscous mode. However, when the crosslinking agent is introduced during melt mixing the blend becomes tough because the rubber phase could undergo large deformation and the material can be elongated to larger extensions before failure.

4. CONCLUSION

Hexamethylene N, N′ bis(tert-butyl peroxy carbamate) (HBTP) was used for the dynamic vulcanization of a 70/30 blend of NR/PP. The blends were melt mixed in a Brabender Plasticorder. It was found that the values of torque obtained increased with an increase in curative concentration. Measurements of the swelling index revealed that the extent of crosslinking increases with HBTP loading. The rheological behavior of the blend was evaluated using a capillary rheometer. It was found that the viscosity of the thermoplastic elastomer decreases with increasing shear rate. The values of the power law index confirmed the pseudoplastic nature of the material. The dynamic mechanical properties of the blend were also examined and revealed that the increase in extent of crosslinking with increased HBTP dosage increased the elastic modulus and reduced the loss modulus. Tensile testing also showed that the ultimate tensile strength and elongation at break continuously increased as a result of increased HBTP content.

Overall, the degree of crosslinking by HBTP was found to be lower than that of the blend dynamically vulcanized by TMTD and MBT.

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