

Carbon-Black-Reinforced Natural Rubber/Polystyrene Full Interpenetrated Polymer Networks: Synthesis and Properties

Seyed Hamid Heidary, Iraj Amiri Amraei, Arash Payami

Composite Research Center, Malek Ashtar University of Technology, Lavizan, Tehran, Iran

Received 17 April 2008; accepted 28 January 2009

DOI 10.1002/app.30117

Published online 24 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis and properties of carbon-black-reinforced natural rubber/polystyrene full interpenetrated polymer networks were studied in detail. The interpenetrated polymer networks were prepared with the sequential method. The natural rubber was reinforced with 30 phr carbon black and crosslinked with 4 phr dicumyl peroxide. In all cases, natural rubber was the dominant phase in the interpenetrated polymer networks. When the polystyrene content of the interpenetrated polymer networks was increased to 12%, a good improvement in the tensile properties was observed, and the strength dropped with greater polystyrene content. Dynamic mechanical thermal analysis showed that when the tensile strength improved, there was a single phase, and a broad glass-transition temperature peak was observed in a plot of the loss factor versus the temperature. On the contrary, when the tensile strength dropped, there was phase separation,

and two glass-transition temperature peaks were observed in a plot of the loss factor versus the temperature. In fact, there was a good relation between the static properties and dynamic properties, so we could predict static properties such as the tensile strength by an analysis of the dynamic properties. It was revealed that the phase separation of natural rubber and polystyrene depended on the component ratio and carbon black content. Also, the presence of carbon black reduced the miscibility of natural rubber and polystyrene. Thermogravimetric analysis showed that the interpenetrated polymer networks, regardless of their composition, had better thermal properties than the corresponding homopolymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2143–2149, 2009

Key words: interpenetrating polymer networks (IPN); natural rubber; polystyrene

INTRODUCTION

Interpenetrated polymer network (IPN) synthesis can be considered a unique way of mixing two crosslinked polymers intimately.¹ During the synthesis of IPNs based on an elastomer and a plastic, many products can be synthesized by the manipulation of three process variables: the crosslink density of the elastomer, the crosslink density of the plastic, and the elastomer/plastic ratio.^{2,3} Depending on the elastomer/plastic ratio, a rubber-reinforced high-impact plastic or reinforced elastomer will result during the synthesis of IPNs from glassy polymers and an elastomer.⁴

Some researchers have studied toughening and improving the properties of polystyrene (PS) with the interpenetration technique. Natural rubber (NR)/PS IPNs can be considered examples of combinations of natural and synthetic polymers. NR/PS full IPNs possess higher tensile strength, modulus,

and tear strength than corresponding semi-IPNs, whereas the latter exhibit higher toughness and elongation than full IPNs.⁵ It has been proved that the base matrix (NR) which forms initially plays a vital role in controlling the mechanical properties. Also, increasing the crosslink density makes properties such as the tensile strength, modulus, and tear strength increase.⁵ The tensile strength, tear strength, and hardness of NR/PS full IPNs increase with increasing PS content; the elongation at break decreases with increasing PS content, and the mechanical performance improves with increasing PS crosslinking. Morphology studies of NR/PS IPNs have revealed that the phase distribution depends on the blend ratio, crosslinker level, and initiating system.⁶ The impact behavior of NR/PS semi-IPNs and full IPNs shows that as the PS crosslinker level increases up to 4%, the impact strength increases. Moreover, in moderately crosslinked IPNs, an IPN composition with 70% PS shows the maximum impact strength values.⁷

In this study, we performed the synthesis of elastomer/plastic IPNs based on carbon-black-reinforced NR and PS in which NR was the dominant phase. The IPNs were prepared with the sequential

Correspondence to: S. H. Heidary (composite_engineer@yahoo.com).

TABLE I
Characteristics of NR

Property	Value
T_g (°C)	-72
Density (gr/cm ³)	0.97
Volatile matter maximum (%)	0.50
Ash maximum (%)	0.40

method. The mechanical properties, dynamic mechanical thermal features, and thermal stability of the IPNs were investigated. Also, the effects of the component ratio and presence of carbon black on the aforementioned properties were studied.

EXPERIMENTAL

Materials

NR

The NR used was SMR-20 grade (Standard Malaysia Rubber, Lee Rubber Co., Malaysia). The physical properties of NR are presented in Table I.

Styrene monomer

The styrene monomer for IPN synthesis was supplied by Merck (Darmstadt, Germany). The monomer was made inhibitor-free by washing with a 1% NaOH solution before use.

Dicumyl peroxide (DCP)

DCP (40% active) was used as a vulcanizing agent for NR. It was supplied by Merck.

Benzoyl peroxide (BPO)

BPO was obtained from Merck and was used as an initiator for styrene polymerization.

Divinyl benzene (DVB)

DVB was used as a crosslinking agent for styrene. It was supplied by Merck.

Carbon black

The carbon black (Luqman Trading LLC, Dubai, United Arab Emirates) was N-330 grade.

IPN preparation

The IPN was prepared by a sequential technique. The NR was crosslinked first with DCP, and this was followed by swelling in styrene monomer and then polymerization and crosslinking of the PS phase.

Crosslinking of the NR phase

The following different series of vulcanized NRs were prepared.

Series I: Carbon-black-reinforced NR. NR was masticated in a two-roll mill at room temperature for 3–4 min to reduce the molecular mass of the rubber. Carbon black and DCP in doses of 30 and 4 phr, respectively, were added and mixed well with the masticated rubber. A rheograph of the mixture was taken on a Monsanto rheometer (Monsanto, USA), and the optimum cure time was determined. The mixture was vulcanized at 160°C on a hydraulic press to get a crosslinked NR sheet.

Series II: Nonreinforced NR. NR was masticated in a two-roll mill at room temperature for 3–4 min. DCP in a dose of 4 phr was added and mixed well with the rubber. A rheograph of the mixture was taken on a Monsanto rheometer, and the optimum cure time was determined. The mixture was vulcanized at 150°C on a hydraulic press to get a crosslinked NR sheet.

Polymerization and crosslinking of the PS phase

The vulcanized NR sheets were weighed and immersed in inhibitor-free styrene monomer containing 1% BPO as an initiator and 4% DVB as a crosslinker for the PS phase. The NR sheets were swollen for different times to obtain various weight percentages of PS. The swollen samples were kept at 0°C for a few hours to achieve an equilibrium distribution of the styrene monomer in the matrix. Each swollen NR sheet was put into an aluminum mold. A silicone rubber seal was placed between the aluminum plates, which were held together with some screw. The sealed mold was heated at 80°C for 6 h and at 100°C for 2 h to complete the polymerization and crosslinking of the styrene monomer. Then, the hardened sheets were kept in a vacuum air oven to free them of unreacted styrene. The final weight of the IPN was taken, and the composition of the sample was determined. The IPNs were coded on the basis of their composition. The nomenclature of the IPNs is given in Table II.

TABLE II
Nomenclature of the IPNs

Sample code	Carbon black content (phr)	DCP content (phr)	BPO content (%)	DVB content (%)	NR/PS ratio
N ₉₃	0	4	1	4	93/7
N ₈₉	0	4	1	4	89/11
N ₈₄	0	4	1	4	84/16
CN ₉₄	30	4	1	4	95/6
CN ₈₈	30	4	1	4	88/12
CN ₈₆	30	4	1	4	86/14
CN ₈₁	30	4	1	4	81/19

TABLE III
Gel Contents of the IPNs

Sample	N ₉₃	N ₈₉	N ₈₄	CN ₉₄	CN ₈₈	CN ₈₆	CN ₈₁
Gel content (%)	99.1	99	98.8	98.6	98.4	98.3	98.1

Gel content test

To estimate the gel content, known weights of the samples were Soxhlet-extracted with toluene at 110°C for 30 h. After extraction, the samples were dried in an oven and weighed. The percentage of insoluble matter was taken as the gel content.

Tensile test

The tensile strength and elongation at break (EB%) were measured with a tensile testing machine at a crosshead speed of 500 mm/min. The tensile testing was performed with dumbbell specimens at room temperature per the FED-STD-4111 test method.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical properties of the IPNs and crosslinked carbon-black-reinforced NR were determined with a model 2980 dynamic mechanical thermal analyzer supplied by TA Instruments (United States). The shape of each test sample was rectangular (30 mm long, 15 mm wide, and 2 mm thick). The single-cantilever mode of deformation was used under the test temperature range of -100 to +150°C at a heating rate of 5°C/min; the test amplitude and frequency were 15 A and 1 Hz, respectively. The cooling process was achieved with liquid nitrogen. The results were presented in terms of the loss factor ($\tan \delta$) and glass-transition temperature (T_g). Here, $\tan \delta$ was the ratio of the loss modulus (E'') to the storage modulus (E') whereas T_g was obtained from the E'' peak.

Thermogravimetric analysis (TGA)

A Perkin Elmer Pyris Diamond-S2 (Boston, MA) thermogravimetric analyzer was used for TGA of the IPN samples. A small amount (1–3 mg) of each sample was taken for the analysis, and it was heated from 25 to 525°C at a rate of 10°C/min in nitrogen. TGA and differential thermogravimetry (DTG) curves were drawn for each sample.

RESULTS AND DISCUSSION

Gel content

The gel contents of the IPNs are listed in Table III. The gel content of the IPNs is higher than 98% in all cases, showing the occurrence of crosslinking in

both phases. It is a known fact that as the crosslinker content increases, the gel content increases. This may be due to the increased crosslinking, which restricts chain mobility.

As the PS content is increased, not much difference in the gel content can be observed. Also, the IPNs containing carbon black exhibit less gel.

Tensile properties

The tensile strength, elongation at break, and average modulus of the IPNs are listed in Table IV. In the IPNs containing carbon black (filled IPNs), the tensile strength increases as the PS content increases from 5 to 12%, and with greater PS content, the strength drops. The increase in the tensile strength is due to the interpenetration and interlocking of NR and PS networks, which result in the reinforcement of the NR phase. The decrease in the tensile strength is due to the phase separation of NR and PS. In this case, PS acts as a rigid filler, and the result is that the tensile strength drops. In the IPNs without carbon black (unfilled IPNs), the trend of tensile strength enhancement with an increase in the PS content continues at least to 16% PS. Here, the increase in the tensile strength is due to the interlocking of NR and PS networks. It is clear that the IPNs without carbon black have less tensile strength than the IPNs containing carbon black with similar compositions. For example, sample CN₈₈ has a tensile strength equal to 12.32 MPa, and sample N₈₉ has a tensile strength equal to 4.15 MPa; sample CN₉₄ has a tensile strength equal to 10.94 MPa, and sample N₉₃ has a tensile strength equal to 3.25 MPa. This is probably due to the presence of carbon black.

Generally, as the PS content increases, the stress-strain curves show a decrease in the elongation at

TABLE IV
Tensile Properties of the IPNs

Sample code	Tensile strength (MPa)	Average modulus (MPa)	Elongation at break (%)
CN ₉₄	10.988	6.675	298
CN ₈₈	12.318	8.940	227
CN ₈₆	5.896	5.467	155
CN ₈₁	1.796	2.119	20
N ₉₃	3.252	2.332	223
N ₈₉	4.148	2.600	397
N ₈₄	5.378	4.274	306

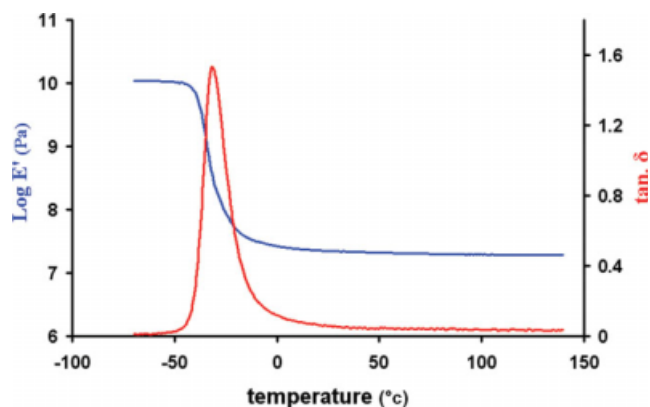


Figure 1 DMTA spectra of crosslinked carbon-black-reinforced NR containing 30 phr carbon black and 4 phr DCP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

break. This is due to the plastic nature and lower elongation of PS in comparison with NR.

Dynamic mechanical properties

DMTA is a common and useful technique for studying the T_g values and thus phase separation of IPNs,⁸ provided that the individual components of the IPNs have clearly defined and well-separated T_g values. The dynamic mechanical properties of the sequential IPNs were characterized with E' , E'' , and $\tan \delta$, and these parameters were functions of temperature and frequency. Dynamic mechanical plots of the crosslinked carbon-black-reinforced NR and the IPNs are shown in Figures 1–4.

As shown in Figure 1, as the temperature increases, the material goes through three regions—a glass region, a glass-transition region, and a rubbery region—and $\tan \delta$ goes through a maximum in the glass-transition region and then decreases in the rubbery region. $\tan \delta$ is low below T_g because the chain

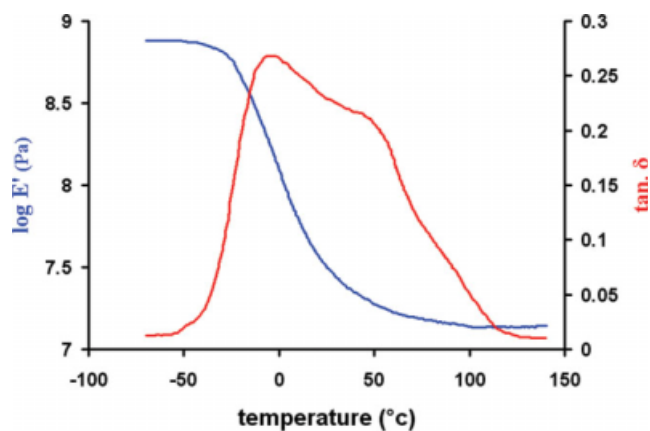


Figure 2 DMTA spectra of sample CN₉₄. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

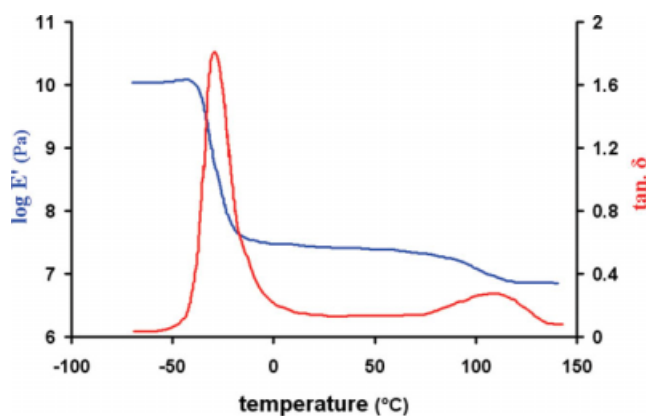


Figure 3 DMTA spectra of sample CN₈₁. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

segments are frozen; the molecular motions are primarily changes of the bond length and bond angle, and the deformations are mainly elastic. Above T_g , $\tan \delta$ is low because the molecular chains obtain enough energy, and the molecules are free to move. $\tan \delta$ is high in the glass-transition region because the chain segments begin to move, but they do not move freely because of the high system viscosity. The $\tan \delta$ maximum of crosslinked carbon-black-reinforced NR is 1.53, and T_g is -31.6°C . The peak of the glass-transition region is narrow and sharp.

In Figure 2, a DMTA plot of sample CN₉₄ is presented. The DMTA plot of the CN₉₄ IPN evidently shows that both the carbon-black-reinforced NR and PS polymers produce a semimiscible system, as can be seen from the inward shifts and broadening of the component transitions.^{9–11} One prominent characteristic feature of IPNs is the existence of glass transitions for each phase, which generally leads to a broad glass-transition region. The intensity of each transition is clearly related to the overall composition and phase continuity, whereas shifts and broadening of the transition indicate the extent of molecular mixing.^{12,13} A DMTA plot of sample CN₈₁ (Fig. 3) shows two glass-transition peaks, the sharp peak of NR and the short peak of PS. The presence of these two discrete peaks indicates the phase separation of NR and PS. In comparison with the NR homopolymer with a T_g of -31.6°C , a shift to -29.1°C is shown by the NR in sample CN₈₁. A DMTA plot of sample N₈₄ is presented in Figure 4. There is a single broad transition spanning the region between the T_g values of the component polymers (NR and PS). Phase separation does not exist here.

A simultaneous investigation of tension tests and DMTA indicates that when an IPN possesses a broad peak of $\tan \delta$, it exhibits reinforced mechanical properties; when two discrete peaks can be seen

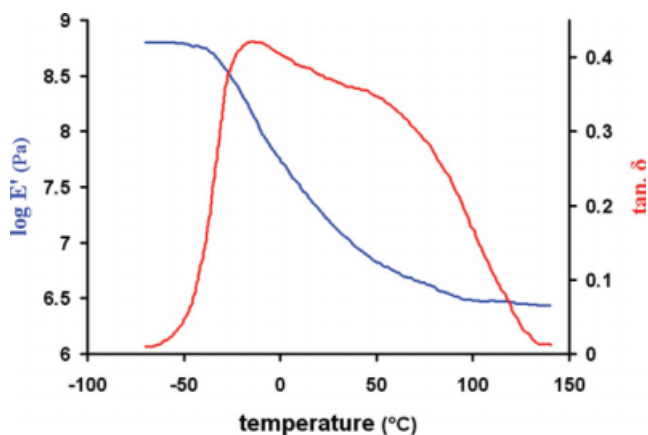


Figure 4 DMTA spectra of sample N₈₄. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the $\tan \delta$ plot, the mechanical properties are weak or drop. It can be said that the enhanced mechanical properties are due to considerable entanglement formed at the molecular level in the networks. In fact, there is a direct relation between the dynamic properties and static properties, so we can predict mechanical properties such as tensile properties from an analysis of the dynamic properties. Also, the extent of phase separation can be evaluated from static properties. A comparison of DMTA plots of carbon-black-filled IPNs and an unfilled IPN shows that in the filled IPNs, when the PS content increases up to 19%, phase separation results. From the tensile properties, it can be concluded that phase separation occurs when the PS content is higher than 12%. In the unfilled IPNs, phase separation does not occur at least up to 16% PS. It seems that the presence of carbon black decreases the miscibility of NR and PS, and the resulting phase separation occurs with less PS content.

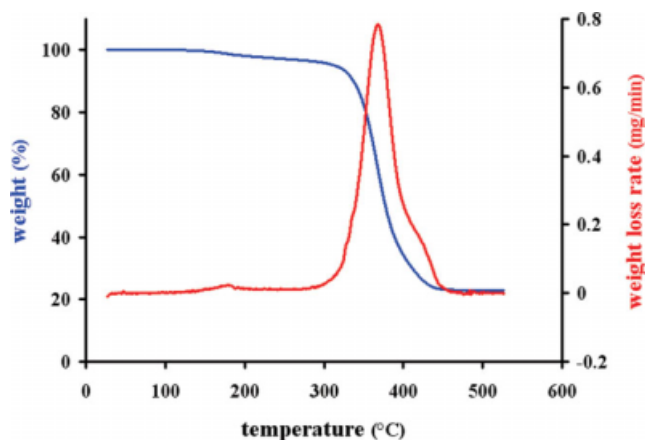


Figure 5 TGA and DTG curves of crosslinked carbon-black-reinforced NR (containing 4 phr DCP and 30 phr carbon black). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

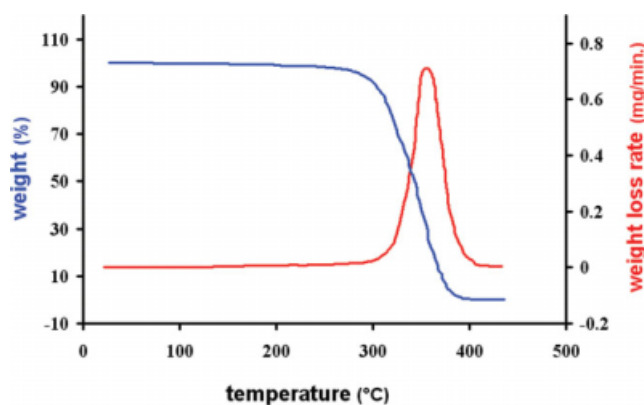


Figure 6 TGA and DTG curves of crosslinked PS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal properties

TGA and DTG curves of vulcanized carbon-black-reinforced NR are presented in Figure 5. NR starts to degrade at 300°C, and a residue of 23% remains at 490°C. In the case of NR, below 250°C, there is no degradation. In the temperature range of 290–400°C, about 60% of the material is degraded. During this stage, weight loss and volatilization of the degradation products take place rapidly. Beyond 400°C, the weight loss is about 12–13%. In the DTG curve, the major peak is at 368°C (maximum of the weight-loss rate).

PS degradation occurs in a single step (Fig. 6). The TGA curve shows that PS is stable up to 250°C, and after that, degradation occurs rapidly. The degradation starts at about 276°C, and at 385°C, almost 96% of degradation is complete. Above 430°C, no residue remains. The major peak in the DTG curve is at 360°C. This corresponds to chain scission, which provides monomer along with some amount of dimer, trimer, tetramer, and pentamer.

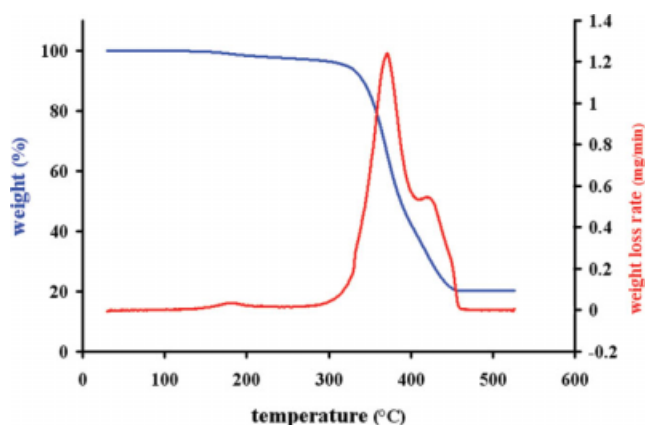


Figure 7 TGA and DTG curves of sample CN₉₄. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

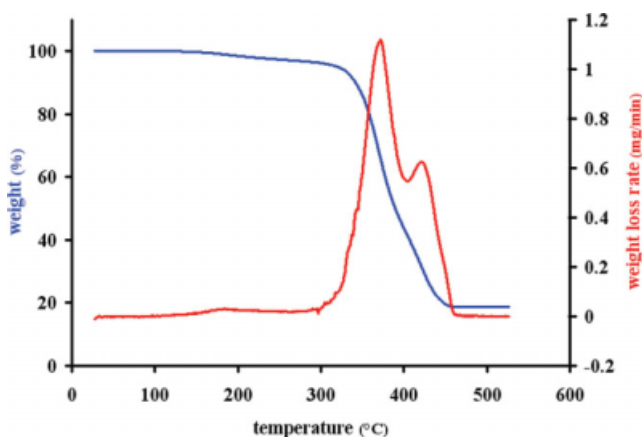


Figure 8 TGA and DTG curves of sample CN₈₁. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

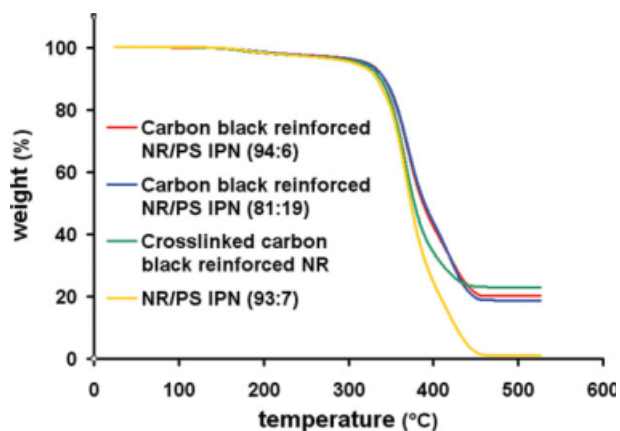


Figure 10 TGA curves showing the composition effect on the thermal stability of the samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The chemical structure of NR and PS consists of $-C-C-$ linkages alone. During the vulcanization of NR with DCP and polymerization and crosslinking of PS, the formed crosslinks are also $-C-C-$ linkages. The $-C-C-$ bond length is 1.54 Å, and the bond energy is 20.3 kJ/mol.¹⁴ Therefore, the differences in the degradation behavior of different IPNs are more dependent on the crosslinking level, component ratio, and initiating system rather than the nature of the linkages present. The presence of interfacial crosslinks between the NR and PS phases also cannot be ruled out.

In the case of IPNs in the temperature range of 200–300°C, there is no appreciable weight loss (Figs. 7–9). Therefore, the IPNs are more resistant to thermal degradation than the component homopolymers. In carbon-black-filled IPNs at 300°C, 1.5–4% weight loss can be observed, and at 400°C, the

weight loss increases dramatically. When we consider the effect of the component ratio on the thermal degradation, we can observe that in sample CN₉₄, the weight loss is 58% at 400°C, and for sample CN₈₁, the weight loss is 56%. This shows that as the PS content increases, the thermal stability is enhanced. The TGA and DTG curves of samples CN₉₄, CN₈₁, and N₉₃ are presented in Figures 7–9, respectively. The weight loss of sample N₉₃ is 75% at 400°C. In the case of filled IPNs, the weight loss in the temperature range of 300–400°C is lower than that of an unfilled IPN (Fig. 10). At 400°C and higher, the weight loss is rapid. In the DTG curves of IPNs, two peaks can be observed corresponding to NR and PS degradation. Generally, in the case of full IPNs, the compact network formed by the interpenetration and physical entanglement of two phases makes bond rupture difficult.¹⁴

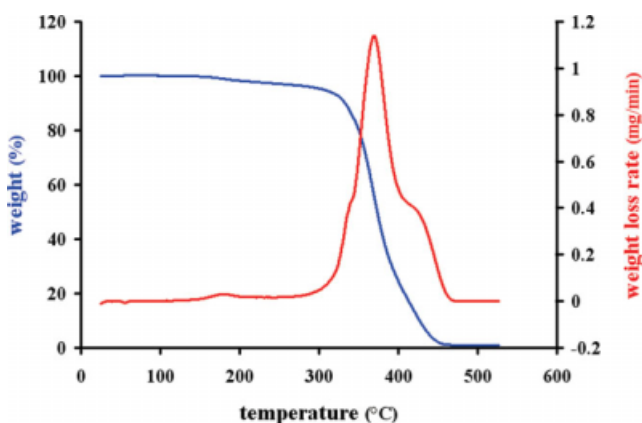


Figure 9 TGA and DTG curves of sample N₉₃. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

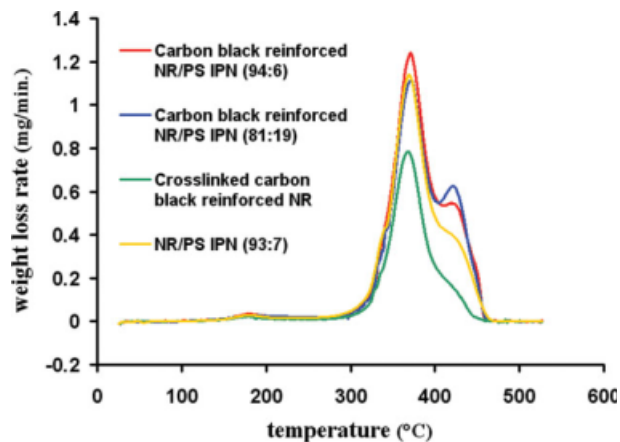


Figure 11 DTG curves showing the composition effect on the thermal stability of the samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As can be seen from Figure 10, filled IPNs have more thermal stability than unfilled IPNs. Among the filled IPNs, sample CN₈₁ has a lower maximum weight-loss rate. This is clear in Figure 11. This may be due to the greater thermal stability of PS versus NR.

CONCLUSIONS

Gel content measurements of carbon-black-reinforced NR/PS full IPNs have revealed that the gel content is higher than 98% in all cases, showing the occurrence of crosslinking in both phases. In the carbon-black-filled IPNs, the tensile strength increases as the PS content increases from 5 to 12%, and with greater PS content, the strength drops. In the unfilled IPNs, the trend of the tensile strength increasing with increasing PS content continues at least to 16% PS. The tensile strength increases because of the interlocking of NR and PS networks. In fact, increasing phase mixing is the reason for this enhancement of the tensile properties. The tensile strength decreases because of the phase separation of NR and PS, which depends on the composition. The elongation at break decreases with increasing plastic content because of the plastic nature and lower elongation of PS in comparison with NR.

According to the DMTA studies, when an IPN possesses a broad peak in the spectrum of the temperature dependence of $\tan \delta$, it exhibits reinforced mechanical properties. The presence of two discrete $\tan \delta$ peaks indicates phase separation of NR and PS; in this case, the mechanical properties are weak or drop. Generally, when a broad glass-transition region is observed, enhanced mechanical properties are indicated. In fact, there is a direct relation between the dynamic properties and static properties, so mechanical properties such as tensile properties can be predicted by an analysis of the dynamic

properties. It seems that the presence of carbon black in the NR/PS IPNs decreases the miscibility of NR and PS, and the resulting phase separation occurs with less PS content.

An investigation of the thermal behavior of the samples by TGA has shown that as the PS content increases, the thermal stability of IPNs increases. This is indicative of the enhanced thermal stability of the IPNs versus the homopolymers. IPNs with greater PS content have a lower maximum weight-loss rate. Carbon-black-filled IPNs have more thermal stability than unfilled IPNs.

The authors are grateful to the Institute for Colorants, Paint, and Coatings for performing TGA. The authors thank Mohamad Reza Pourhoseini at the Rubber Testing Laboratory of the Malek Ashtar University of Technology for his help with this research.

References

1. Akay, M.; Rollins, S. N. *Polymer* 1993, 34, 1865.
2. Alcantara, R. M.; Rodrigues, A. P. *Polymer* 1999, 40, 1651.
3. Vancaeyzeele, C.; Fichet, O. *Polymer* 2006, 47, 2046.
4. Klempner, D.; Berkowski, L.; Frisch, K. L. *Polym Mater Sci Eng* 1985, 52.
5. Das, B.; Sinha, S. *Eur Polym J* 1993, 29.
6. Mathew, A. P.; Radusch, H. J.; Thomas, S. *Eur Polym J* 2001, 37.
7. Mathew, A. P.; Sabu, T. *Mater Lett* 2001, 50.
8. Dean, K. M.; Cook, W. D.; Lin, M. Y. *Eur Polym J* 2006, 42, 2872.
9. Hourston, D. J.; Schafer, F. U. *J Appl Polym Sci* 1996, 62, 2025.
10. Hourston, D. J.; Song, M.; Schafer, F. U. *Polymer* 1999, 40, 4769.
11. Trakulsujaritchok, T.; Hourston, D. J. *Eur Polym J* 2006, 42, 2968.
12. Paul, D. R.; Sperling, L. H. *Multicomponent Polymer Materials; Advances in Chemistry Series 211; American Chemical Society: Washington, DC, 1986.*
13. Sperling, L. H. *Sound and Vibration Damping with Polymers; American Chemical Society: Washington, DC, 1981.*
14. Mathew, A. P.; Thomas, S. *Polym Degrad Stab* 2001, 72, 423.