Influence of Molecular Parameters and Processing Conditions on Degradation of Hydrogenated Nitrile Butadiene Rubbers

R. A. Chaudhry, I. A. Hussein, M. B. Amin, B. F. Abu Sharkh

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

ABSTRACT: The thermomechanical modification of hydrogenated nitrile butadiene rubbers (HNBR) of different molecular parameters was investigated by rheological and light scattering techniques. The influences of acrylonitrile content, degrees of hydrogenation, and Mooney viscosity were examined. A melt blender with Banbury-type mixing blades was used to condition the rubber samples in the temperature range from 190 to 260°C. Light scattering was used to determine the effect of conditioning on MW and hydrodynamic radius of the rubber molecules. Dynamic viscosity (η') and storage modulus (G') were measured for the as-received and conditioned samples. Experimental results showed that degradation in these rubbers occurred through chain scission and crosslinking. Depending on the molecular parameter, it was found that one of these two mechanisms dominated the degradation process in most brands. Addition of adequate amounts of antioxidants (Irganox 1010 and Irgafos 168) was successful only in preventing degradation by crosslinking. Compared to thermal degradation, thermomechanical degradation was found to be much more severe and progressed at much higher rates. Rheology was found to be a very sensitive technique to structural parameters of the polymers and could be used to detect and identify the mechanism of degradation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1432–1441, 2005

Key words: degradation; HNBR; crosslinking; rheology, light scattering

INTRODUCTION

Rubber articles are formed using conventional techniques such as injection molding and extrusion. The conditions at which the material is processed in these techniques, such as elevated temperature, presence of oxygen, closed environment, and mechanical stresses, can cause chemical changes to occur.[1] Even a small extent of reaction can have immense effects on the physical properties of the polymer. These chemical changes can cause "self-vulcanization."[2] In elastomers, the process of vulcanization is mandatory before the material can be shaped into products.

Structural modifications during processing of rubbers is a complex phenomenon that involves multiple reactions occurring at the same time, with individual mechanisms, such as isomerization, cyclization, oxidation, crosslinking, and chain scission.[3] On the molecular level, two competing processes dominate degradation: molecular scission, which results in shorter chains; and crosslinking, which gives a more tightly networked structure.[4]

Nitrile elastomers, the materials investigated in our present study, are produced by emulsion polymerization of butadiene (BD) and acrylonitrile (ACN). Properties of the resulting elastomer are dependent on the acrylonitrile/butadiene ratio. A review of the structure of the elastomer indicates that its structure is very complex.[5] The butadiene copolymerizes into three different structures: *trans*, *cis*, and 1,2-. The *trans* configuration dominates (~ 78%) in a typical sample. The *cis* configuration (~ 12%) serves to break up substantial crystallinity because it enters in a statistical pattern. The 1,2- sites (~ 10%) are free vinyl groups that typically cause branching and gel formation. The ACN groups are inserted in a statistical pattern ranging from head–tail to head–head to tail–tail.[5]

In copolymers of such nature, different parts of the copolymer differ greatly in thermal stability. The double bond present in the diene part of the elastomer is generally more susceptible to thermal and oxidative degradation, and shows two stages of degradation.[3] Selective hydrogenation of this olefinic unsaturation in NBR imparts significant improvements in resistance to degradation and other properties.[6,7] The ACN content ultimately determines the resistive nature of a typical brand and usually an increase in ACN content results in an increase in oil, fuel, abrasion, and heat resistance as well as an increase in hardness and tensile strength.[7] Extensive studies regarding nitrile buta-

TABLE I
Characterization Data of Elastomers

Designation	% ACN	Specific gravity	% Hydrogenetion	Mooney viscosity	Brand name
Z-1	44	0.98	98	63–77	Zetpol-1000L
Z-2	17	0.98	95	60–100	Zetpol-4310
Z-3	44	0.98	91	71–85	Zetpol-1020
Z-4	36	0.95	96	120>	Zetpol-2010H
Z-5	50	1	91	58–72	Zetpol-0020
Z-6	36	0.95	85	50–65	Zetpol-2030L
Z-7	36	0.95	96	50–65	Zetpol-2010L

diene rubber (NBR) are available in the literature where stability of NBR and hydrogenated NBR (HNBR) has been investigated under different operating conditions and numerous techniques such as thermogravimetry, IR, DSC, FTIR, SEM, and rheology were used for this purpose.[8,3] However, most of the studies on degradation have focused on rubber/rubber and rubber/plastic blends.[9–14]

Studies on degradation of pure raw rubber have been limited to natural rubber. Very few studies raised the question of influence of molecular structure and processing conditions on degradation of raw, uncured NBR.[3,8] For example, Bhattacharjee et al. used TGA to investigate low- (75–150°C) and high-temperature (800°C) degradation of HNBRs and reported generation of ester (–COOR) and carbonyl groups (–C=O).[8] For highly saturated nitrile rubber, an increase in molecular weight (MW) was observed, whereas a decrease in MW was reported for NBR. The increase in MW of saturated nitrile rubbers was suggested to be caused by the conversion of the (–C≡N) group to (–C=NH).

The degradation of NBR occurs through attack of the double bond, whereas that of highly saturated HNBR is likely to occur through the (–C≡N) functionalities and free-radical decomposition.[8] Sarkar et al.[3] investigated the degradation of hydrogenated styrene–butadiene rubber (HSBR) using TGA analysis, DSC, IR, and NMR spectroscopy. HSBR was found to be more stable than SBR in nitrogen atmosphere. Garbarczyk et al.[4] characterized nitrile rubber by NMR spectroscopy and microimaging and reported that ageing proceeds mainly by additional crosslinking. Scission of the polymer chain does not appear to contribute to ageing.

Batch blenders are widely used in polymer research laboratories, yet not much consideration has been given to thermomechanical structural modification of polymers in these blenders. A survey of the existing literature reveals that only few articles raised the topic of degradation during processing of raw nitrile rubbers. It is interesting to note that melt blending was used to prepare samples for miscibility and other studies involving different elastomers.[15–22] However,

the possibility of thermomechanical degradation during the blending process was not examined in detail. Thermomechanical degradation renders inconclusive results with regard to polymer–polymer miscibility.[23] Similarly, for all such studies in which blends are prepared in these internal mixers, the possibility of polymer modification during melt blending should be examined and adequate amounts of antioxidant should be added.[23] In addition, practical applications of HNBRs in the oil and other industries involve subjecting these rubbers to both thermal and mechanical stresses.[5] Thus, studies of thermomechanical degradation of HNBRs are very important. Among many different techniques such as NMR, DSC, GPC, and HPLC, rheology was found to be one of the most sensitive techniques in detecting polymer degradation.[23] In addition, some studies used light scattering to investigate changes in molecular weight and size resulting from degradation of rubbers and rubber blends.[23–26]

In this study, rheology was used to study the influence of processing conditions on the thermomechanical degradation of pure HNBR elastomers. Light scattering (static and dynamic) was used to confirm the rheological findings and to validate the ability of rheology to detect structural changes. Also, the influence of structural parameters such as ACN content, degree of hydrogenation, and Mooney viscosity (M_w) on degradation were investigated.

EXPERIMENTAL

Materials

The HNBRs used in this study were obtained from Zeon Chemicals (Louisville, KY). The characterization data such as ACN content, specific gravity, Mooney viscosity, and degree of hydrogenation, as obtained from the manufacturer, are reported in Table I. For convenience, the HNBRs are designated as Z-1 to Z-7. The polymers were selected from a wide range of brands in such a way so that they could be paired to study the influence of the above molecular parameters one at a time. For example, Z-6 and Z-7 have the same
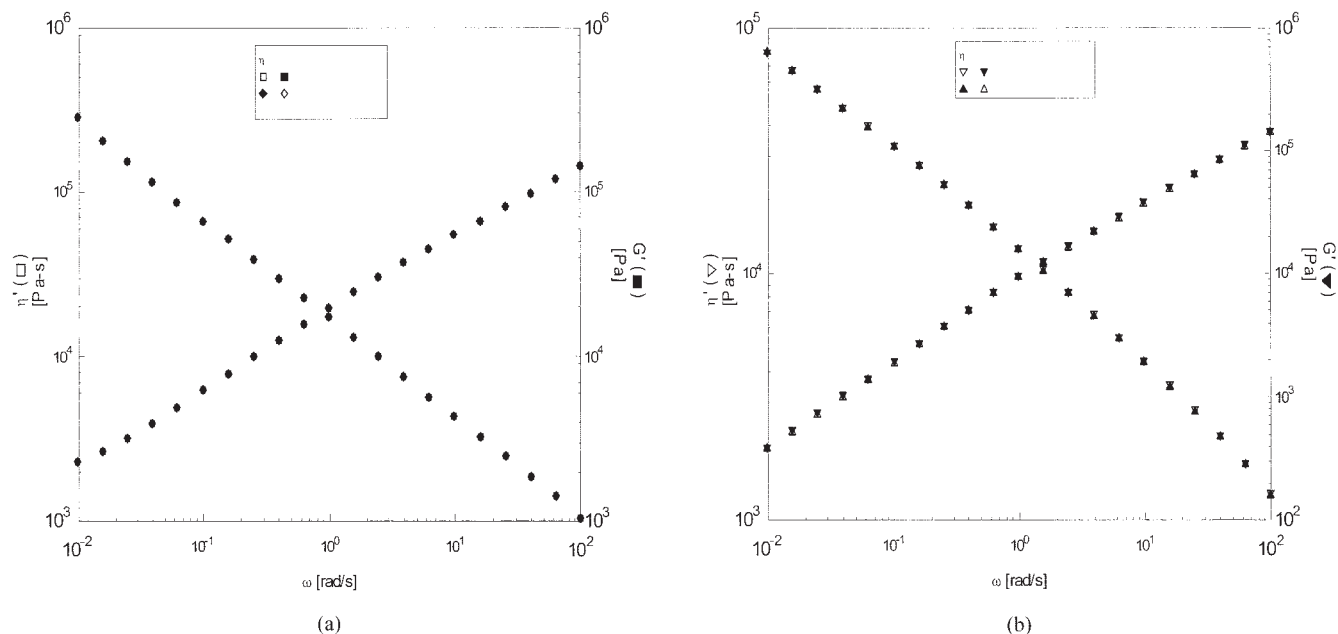
Figure 1   (a) Reproducibility test (sample Z-6); (b) effect of grinding mill on the degradation of Z-6.

or close values of ACN and density but vary in the degree of unsaturation. Thus, the comparison of Z-6 versus Z-7 will disclose the effect of the degree of hydrogenation on degradation. Similarly, comparison of Z-4 versus Z-7 could reveal the effect of Mooney viscosity (M_w). For comparison purposes an NBR was also studied.

A mixture of antioxidants (AO), consisting of a 50/50 blend of the primary AO Irganox 1010 {phenol B, tetrakis[methylene 3-(3′,5′-di-*tert*-butylphenol) propionate] methane, MW = 1178} and a secondary AO Irgafos 168 {P-1, tris[2,4-di-*tert*-butylphenol] phosphite, MW = 646} was used in this study. These AOs were supplied by Ciba Speciality Chemicals (Consett, UK).

Blending conditioning and sample preparation

All as-received rubbers were cut into small pieces and then ground in a Fritsch grinding mill (Fritsch GmbH, Idar-Oberstein, Germany). Then, the rubbers were conditioned in a Haake PolyDrive mix blender (Haake, Bersdorff, Germany) for 10 min at 50 rpm using Banbury-type internal mixing blades at different temperatures. The samples were then pressed in a Carver press to form the disks to be inserted between the ARES platens as described in a previous publication.[23] Tests for degradation of all samples during the conditioning process at different temperatures (190, 250, and 260°C) were performed and compared with the rheology of as-received samples, to determine the extent of degradation each rubber was undergoing.

Rheological measurements

All rheological tests of the conditioned and as-received samples were carried out using a parallel-plate geometry, with 25-mm-diameter platens. A gap of 1.5 mm and strain amplitude (γ^0) of 15% were used for all polymers. The 15% strain was selected after a strain sweep test. The frequency ω for sweep testing was used in the range ω = 0.01–100 rad/s. All measurements were conducted using nitrogen as a convective heating medium to avoid any possible oxidation during the sweep tests. In this study, degradation was assessed through the measurements of dynamic viscosity η' and the elastic modulus G'. Reproducibility tests were performed for sample Z-6 [see Fig. 1(a)]. The agreement of both viscous and elastic properties shows the excellent reproducibility of the rheological measurements.

To rule out the possibility of degradation occurring in the grinding process, a study of the as-received and the just-ground sample (unconditioned) was performed on a representative sample (Z-6). In Figure 1(b), viscoelastic properties of the as-received and ground Z-6 are shown. The excellent agreement between the two sets of data clearly indicates the absence of any measurable degradation during the grinding process.

Solution preparation for light scattering

Stock solutions were prepared by dissolving the rubber samples in pure 99.9% solvent-grade acetone (Fluka GmbH, Neu-Ulm, Germany). The solutions
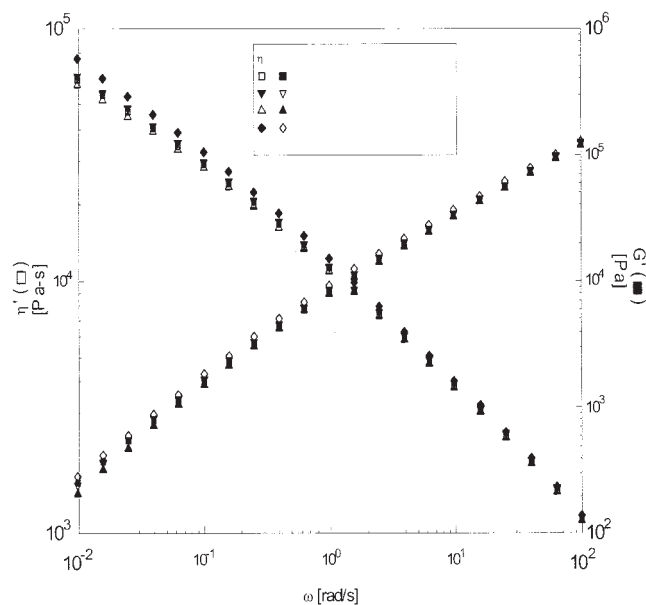
Figure 2 Degradation behavior of Z-1 conditioned at different temperatures ($T_{\text{test}} = 190°C$, $\gamma^0 = 15\%$).

were left overnight for proper dissolution. Stock solutions were further diluted to obtain proper dilutions (1.0×10^{-4}, 5.0×10^{-5}, and 2.5×10^{-5} g/mL) for the static light scattering (SLS) experiments. Samples were filtered twice to obtain dust-free solutions using 0.22-μm Millipore filters (Millipore, Milford, MA).

Static and dynamic light scattering

SLS measurements were made using a fully computerized DAWN-EOS laser light-scattering instrument (Wyatt Technologies, Santa Barbara, CA) with ASTRA software. The refractive index increment (dn/dc) was measured using an RFM-340 refractometer (Bellingham and Stanley, Kent, UK). The laser source for the light-scattering instrument was a He–Ne laser ($\lambda_0 = 690$ nm). For dynamic light scattering studies, a Wyatt QELS instrument was used in combination with the DAWN-EOS instrument. QELS batch software was used to determine the average value of the hydrodynamic radius using the Dynals algorithm.

RESULTS AND DISCUSSION

Extent of degradation

In this section, the degradation of pure samples Z-1 to Z-7 (see Table I) is discussed. Changes in η' and G' were monitored for samples treated under different conditions. Usually crosslinking leads to increases in both η' and G', whereas chain scission results in a decrease in both. In Figure 2, results of η' and G' for Z1 are given. Very little degradation was observed in this sample. There was almost no degradation up to a

temperature of 250°C, indicating the high stability of the sample. Elevating the temperature to 260°C leads to a slight increase in viscoelastic properties at low ω (sensitive to structural changes). The extraordinary stability of Z-1 (up to 250°C) can be attributed to the excellent proportion of ACN content and high level of saturation. ACN content usually varies between 15 and 50%, and this sample contains 44%, which is high enough to resist any thermal degradation.[6] In addition, it is known that the main susceptible part for degradation is the butadiene portion (which contains the double bond). High ACN means low percentage of butadiene and with 98% hydrogenation of butadiene, there is a little chance for heat to become absorbed at the double bond. The small increase in MW at 260°C might have been caused by crosslinking at the (–C≡N) group, which was suggested to be converted to (–C=NH).[8] Crosslinking can also occur as a result of oxidative addition reaction at the double bond of the diene part. However, the increase in molecular weight is very small and this sample can generally be considered highly stable. This result is expected for a sample with high ACN content and high degree of hydrogenation.

Results of η' and G' for Z-2, as a function of ω, are given in Figure 3. A marked decrease in viscosity was observed as a result of thermomechanical treatment. The dynamic viscosity decreased as the material was progressively conditioned at high temperatures. This decrease in viscosity is attributed to a decrease in MW (chain scission). The ACN content of this sample is very low compared to that of Z-1 (17%); thus, butadiene is abundant in the sample. However, most of the
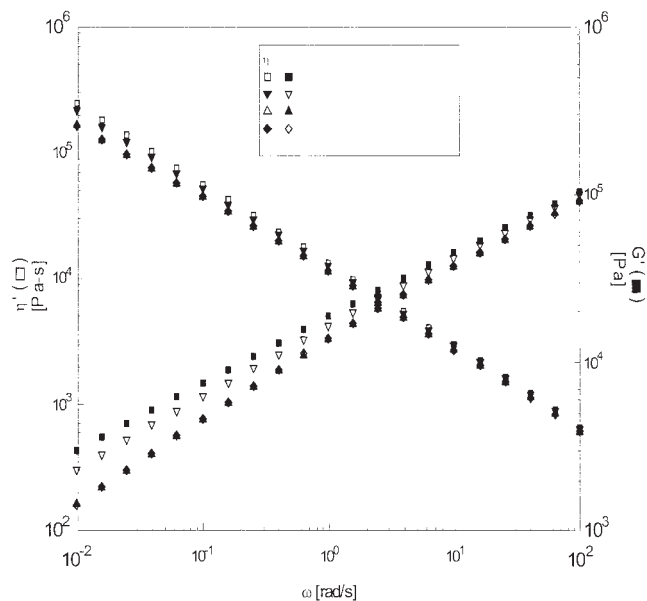

Figure 3 Values of η' and G' for Z-2 conditioned at different temperatures ($T_{\text{test}} = 190°C$, $\gamma^0 = 15\%$).

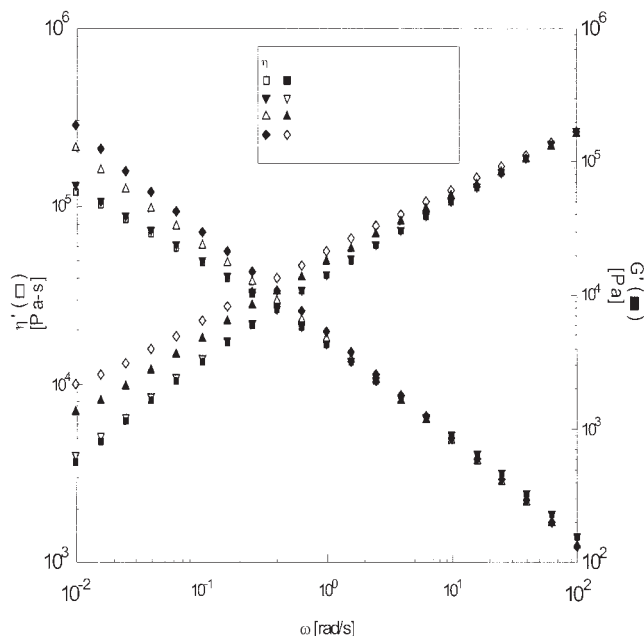**Figure 4** Thermomechanical degradation of Z-3 (T_{test} = 190°C, γ^0 = 15%).

unsaturation is removed because the percentage hydrogenation for Z-2 is 95% (see Table I). It is likely that the absence of double-bond sites in the butadiene part forces the thermomechanical degradation to proceed by chain scission and, in fact, a decrease in MW was observed.

Z-3 was examined under the same conditions to study the influence of the degree of hydrogenation on degradation. Z-3 has an ACN content and Mooney viscosity (M_w) that are almost the same as those of Z-1. However, the only major difference between the two HNBRs is the degree of hydrogenation. The degree of hydrogenation for Z-1 is 98%, whereas that for Z-3 is only 91%. As shown in Figure 4, conditioning of Z-3 at 190°C did not result in measurable degradation. However, increases in viscous and elastic components were observed for samples treated at 250 and 260°C, indicating an increase in molecular weight. Comparison of Z-1 and Z-3 suggests that the most probable mechanism of crosslinking is oxidative addition at the double bonds. An overall comparison of degradation results of the three rubbers (Z-1, Z-2, and Z-3) indicates that the stability of HNBR could be extended to higher temperatures by increasing the ACN content and the degree of hydrogenation.

In Figure 5, rheological results for Z-4 are shown. A very different behavior was observed for this sample compared to that of samples Z-1, Z-2, and Z-3. Here, decreases in both η' and G' were detected over the entire range of ω. This suggests major changes in the structure of Z-4 resulting from thermomechanical degradation. This decrease in viscoelastic properties is

observed at all test temperatures and is maximum at high temperatures. Here, chain scission is suggested as the dominant mechanism for degradation. As shown in Table I, Z-4 has relatively high ACN content (36%), high degree of hydrogenation (96%), and has the highest Mooney viscosity (M_w). The decrease in viscoelastic properties is a result of the high mechanical stresses developed during processing arising from the high viscosity of this brand of HNBR. This result indicates that mechanical stresses have a major contribution in overall degradation. This contribution increases with increasing MW (viscosity) of the brand.

In Figure 6, the trend of Z-5 degradation is almost similar to that of Z-3. Again, crosslinking is suggested as the mechanism of degradation. The structural parameters of the two HNBRs, and thus their degradation behavior, are very similar. The high ACN content is likely behind the stability at the low temperatures (190°C). However, crosslinking occurs at high temperatures.

The effect of the degree of hydrogenation on degradation of HNBR with high ACN content was examined by comparing the results for Z-6 and Z-7. The results are shown in Figure 7 and Figure 8, respectively. The two HNBRs have the same ACN content (36%) and Mooney viscosity (50–65). However, the degree of hydrogenation is 85% for Z-6 and 96% for Z-7. The results for Z-6 suggest polymer stability at 190°C, but extensive crosslinking is observed at 250 and 260°C. The large extent of crosslinking observed in the relatively unsaturated Z-6 is likely to occur at the butadiene double bonds by oxidative addition reactions, as previously suggested.
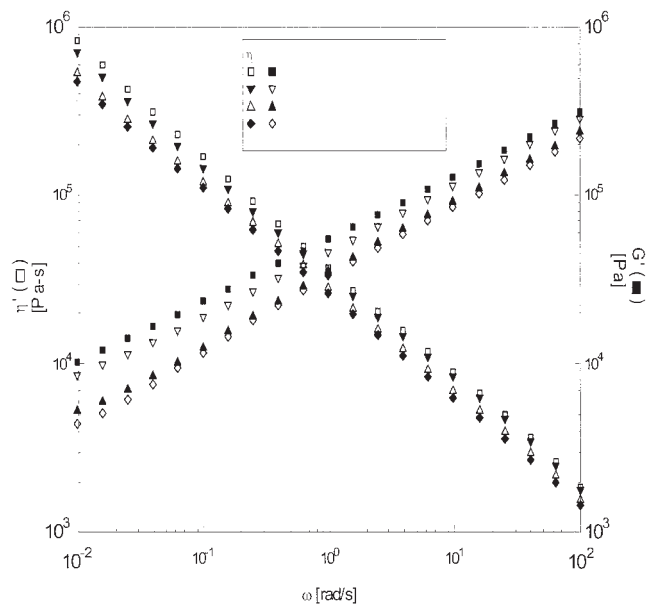

Figure 5 Thermomechanical degradation of Z-4 (T_{test} = 190°C, γ^0 = 15%).

Figure 6 Thermomechanical degradation of Z-5 (T_{test} = 190°C, γ^0 = 15%).

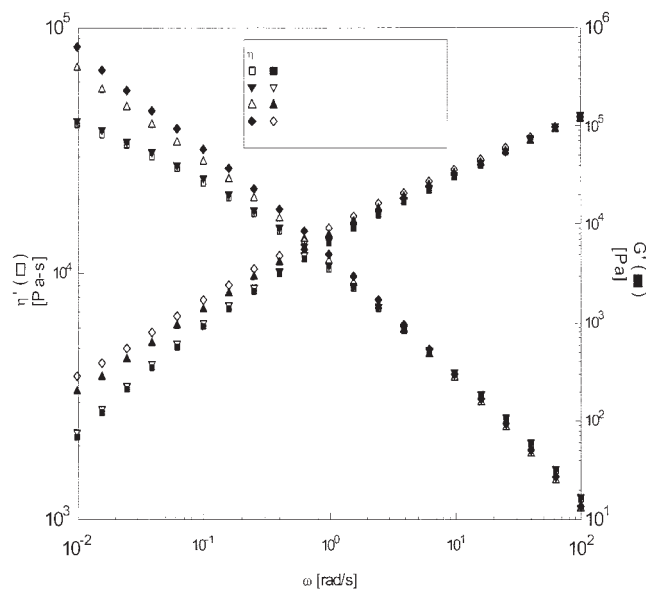**Figure 8** Thermomechanical degradation of Z-7 (T_{test} = 190°C, γ^0 = 15%).

As shown in Figure 8, Z-7 is very stable, with only minor decreases in η' and G' at elevated temperature. A comparison of Z-6 and Z-7 indicates that the chain-scission mechanism of degradation dominates at high saturation levels. On the other hand, crosslinking dominates at low saturation levels.

A comparison of Z-4 and Z-7, with the same ACN and level of hydrogenation and different Mooney viscosities, reveals the effect of MW. The extensive chain scission that was observed in the high-MW HNBR, Z-4, is absent in Z-7. This result again indicates that
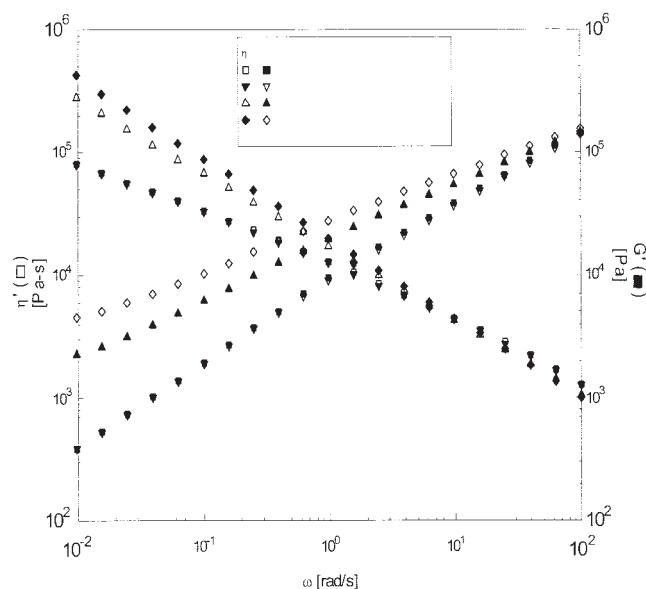
mechanical stresses have a major effect on degradation of these rubbers during processing.

Furthermore, quantitative measures were used to assess the degradation of the HNBRs under investigation. Enhancement of the dynamic viscosity η' of the conditioned HNBR over that of the as-received (AR) one was calculated. The same definition is applied to the ratio of G'. This ratio is calculated at the same ω for all HNBRs (ω = 0.025 rad/s). Results for the enhancement factors ($\eta_{\text{cond}}/\eta_{\text{AR}}$, $G_{\text{cond}}/G_{\text{AR}}$) as a function of temperature are given in Figure 9(a) and (b), respectively. As expected, G' was found to be more sensitive than η'. The trends of the two curves are similar. The relatively unsaturated resin, Z-6, showed the highest degree of degradation and its high temperature sensitivity is obvious. Enhancement factors that are <1 (chain scission) were obtained for Z-2 and Z-4 at all temperatures. Also, a factor of about 1 was obtained for Z-1 and Z-7 at 190°C; however, minor degradation is observed at higher temperatures. For Z-3 and Z-5, degradation was detected at 250 and 260°C.

Light scattering

The molecular weight and hydrodynamic radius results, obtained by static and dynamic light scattering of a selected group of samples, are depicted in Table II. The thermomechanically degraded samples at different temperatures (190 and 250°C) showed variations in M_w in accordance with the predictions made by rheology. A typical Zimm plot is shown in Figure 10. The mol wt of Z-3 showed an increase from 3×10^5 to 6.31×10^5 with increasing processing temperature, from 190 to 250°C. This result corresponds with the

Figure 7 Thermomechanical degradation of Z-6 (T_{test} = 190°C, γ^0 = 15%).
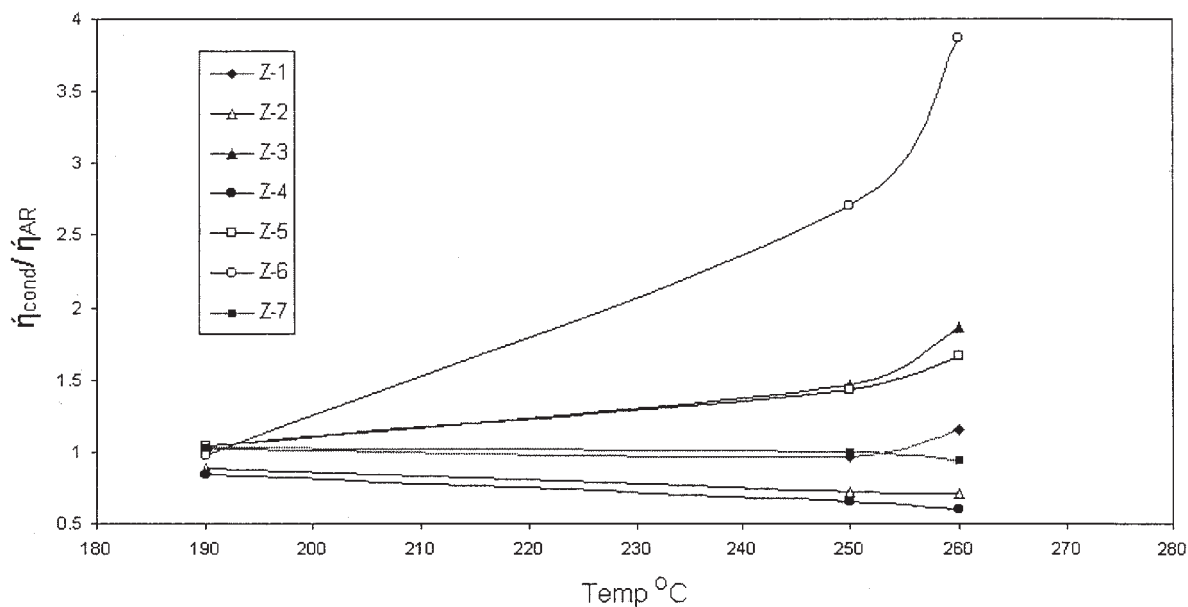
(a)

(b)

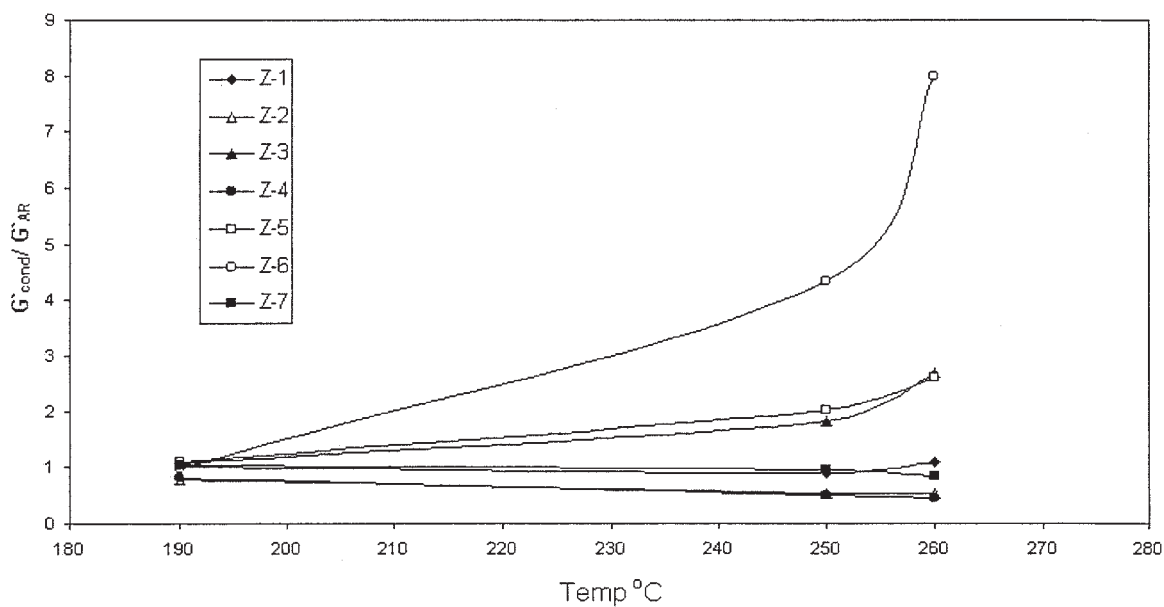**Figure 9** (a) Enhancement of viscosity of HNBRs at different temperatures; (b) enhancement of elastic modulus of HNBRs at different temperatures.

rheology results that indicated an increase in molecular weight caused by crosslinking. The hydrodynamic radius of Z-3 determined by dynamic light scattering showed a similar trend. Z-4 was found to have the highest molecular weight (4.5×10^6 g/mol) among the three elastomers shown in Table II. This result is expected because of its high Mooney viscosity (>120). Unlike Z-3, Z-4 showed a decrease in molecular weight and hydrodynamic radius upon increasing the processing temperature from 190 to

250°C. Again, these results correspond with the rheology results that indicated a decrease in molecular weight caused by chain session at the higher processing temperature. The relatively unsaturated Z-6 that showed maximum increase in molecular weight attributed to crosslinking in rheological results showed a greater than threefold increase in molecular weight (from 1.93×10^5 to 6.2×10^5). The values of molecular weights were found to be close to those reported for nitrile rubbers in the litera-

TABLE II
Static and Dynamic Light Scattering Results for Z-3, Z-4, and Z-7

Sample	Conditioned at 190°C		Conditioned at 250°C	
	$M_w \times 10^{-5}$ (g/mol)	Hydrodynamic radius, R_h (nm)	$M_w \times 10^{-5}$ (g/mol)	Hydrodynamic radius, R_h (nm)
Z-3	3.0 ± 0.2	98 ± 8	6.3 ± 0.7	120 ± 11
Z-4	45.0 ± 0.9	163 ± 12	17.7 ± 0.2	125 ± 9
Z-6	1.90 ± 0.07	82 ± 9	6.214 ± 0.5	130 ± 12

ture.[24] The hydrodynamic radius (R_h) was found to vary in accordance with the variations in MW.

Thermal versus thermomechanical degradation

To differentiate between thermal and thermomechanical degradation effects, two HNBRs were selected for further investigation (Z-2 and Z-6). Z-6 was selected because it shows a high level of thermomechanical degradation by crosslinking, whereas Z-2 shows an intermediate level of degradation by chain scission. Thermomechanically conditioned samples were compared with thermally conditioned samples. Thermal treatment of polymers was conducted by placing the samples in an oven at 250°C for 10 min (same conditioning time and temperature as those in the Haake blender). A temperature of 250°C was chosen for the comparison because most samples showed marked degradation at this temperature. Results of η' and G' for oven-heated and thermomechanically conditioned Z-6 and Z-2 are shown in Figure 11(a) and (b),

respectively. In Figure 11(a), some thermal degradation was detected in Z-6; however, thermomechanical degradation was much more severe. This suggests that it is the combined effect of heat and stress that leads to degradation in these blenders. Thermal effects alone contributed about 25% of the overall degradation of Z-6 (measured as enhancement to viscosity). Marked thermal degradation in Z-2 was detected by G' only [see Fig. 11(b)].

The comparison of thermal and mechanical effects on degradation indicates that degradation is caused by the direct thermal effects (heating) in addition to viscous heating and mechanical stretching (arising from stresses). In most of the cases of conditioning, the melt temperature of the material was not more than 4–5°C degrees above the set temperature. Mechanical effects were thus a major contributor to degradation. In addition, mechanical mixing causes the oxygen to access more of the bulk of the rubber, thus accelerating all forms of oxidative degradation.
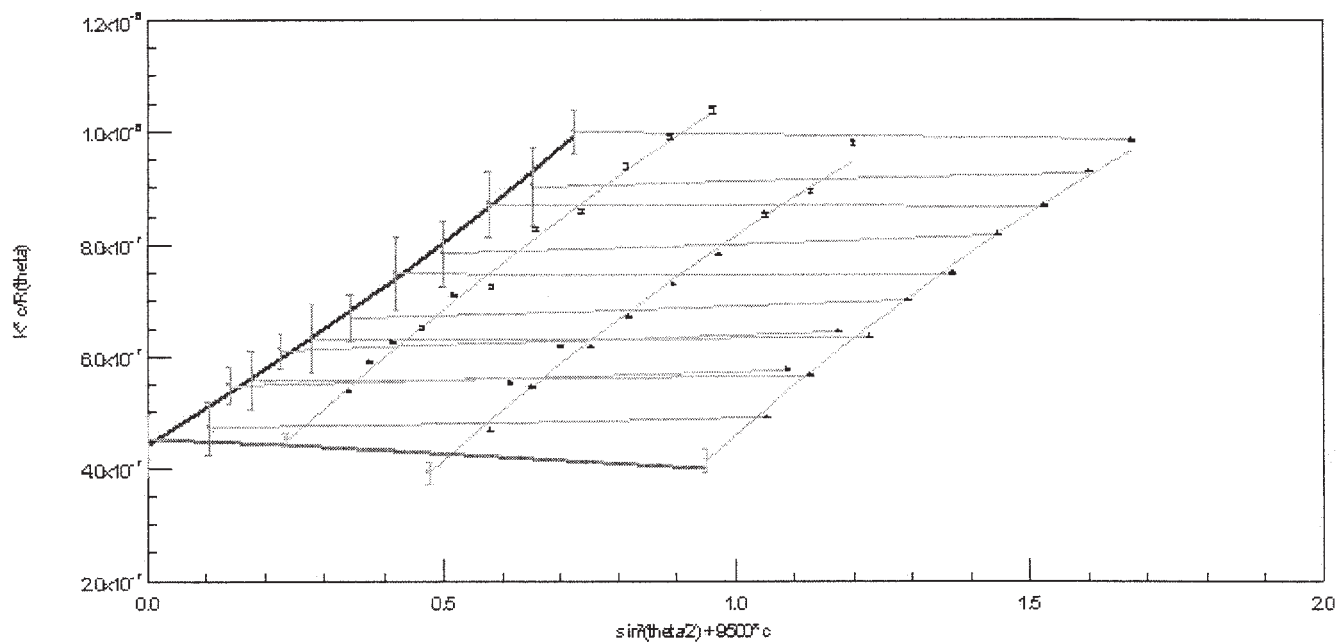

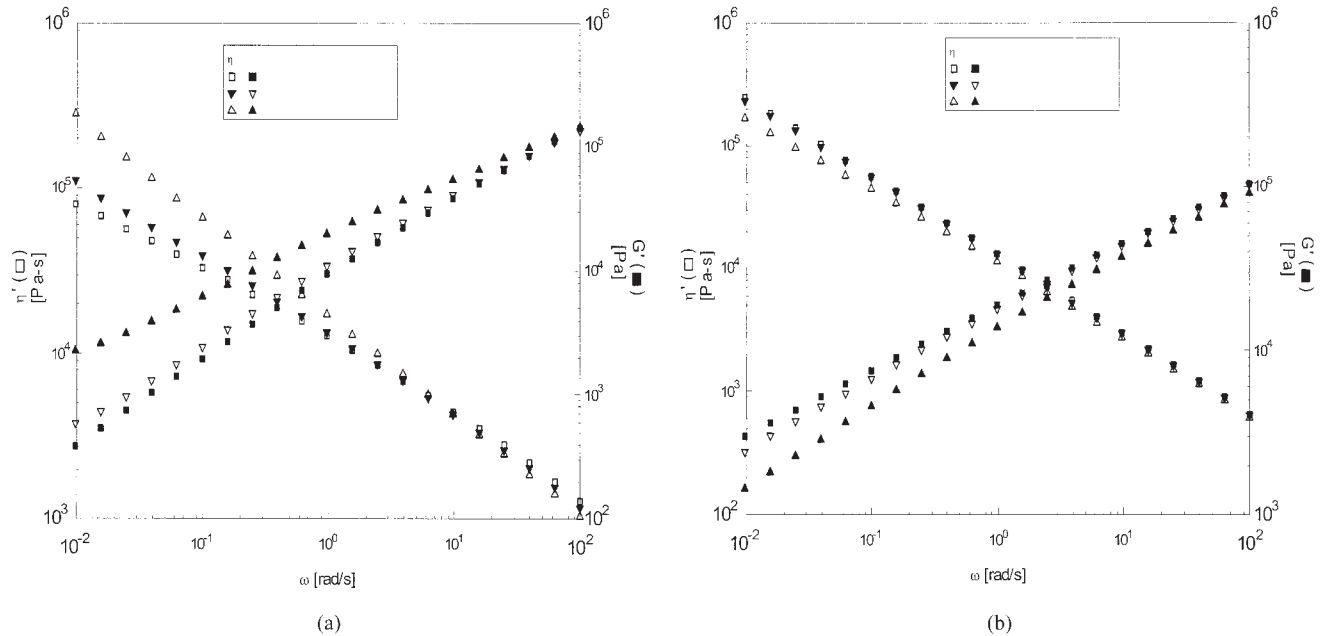**Figure 10** Typical Zimm plot of static light scattering.

Figure 11   (a) Thermal versus thermomechanical degradation of Z-6; (b) thermal versus thermomechanical degradation of Z-2.

Effect of AO on degradation

The same two samples, Z-2 and Z-6, which showed marked decrease and increase in MW resulting from degradation, were used in another study. Here, the effect of addition of AO on the degradation was examined. Different amounts of AO were added to Z-2 and Z-6 during conditioning. The AO is a 50/50 blend

of a primary AO (Irganox 1010) and a secondary AO (Irgafos 168). This blend of AO is usually used for polyolefins and it is effective against free-radical degradation. Figure 12(a) and (b) show the results of viscoelastic properties for Z-6 and Z-2, respectively. The samples were conditioned in the presence of different amounts of AO. For Z-6, where crosslinking dominates, the addition of different amounts of AO
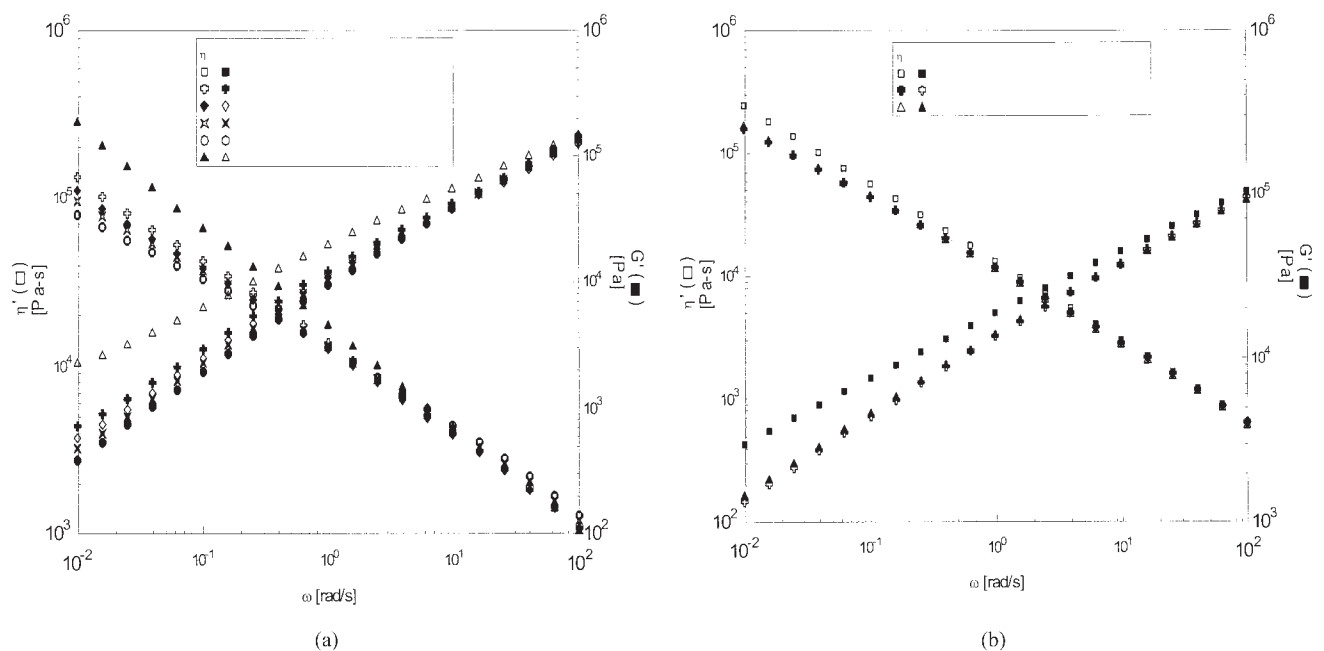

Figure 12   (a) Influence of AO on thermomechanical degradation of Z-6; (b) influence of AO on thermomechanical degradation of Z-2.

was found to be effective in reducing crosslinking. The doses of added AO were 1000, 2000, 4000, and 5000 ppm. As shown in Figure 11(a), the AO succeeded in reducing both viscous and elastic properties of degraded Z-6. Increasing the amounts of AO from 1000 to 5000 ppm shifted the trend toward the as-received Z-6 (control sample). At 250°C 5000 ppm of AO was needed to fully save Z-6 from degradation. This amount reduced both η' and G' to values of the as-received resin, which suggests that the AO is effective against crosslinking caused by oxidative degradation of double bonds.

On the other hand, Z-2 was conditioned in the presence of 1000 ppm of AO. It was shown earlier that the dominating mechanism in Z-2 degradation was chain scission. The results of the rheological analysis for Z-2 are given in Figure 12(b). Unlike Z-6, degradation of Z-2 did not slow down with the addition of 1000 ppm of AO. Further addition of AO was also unsuccessful in preventing the degradation to any extent. Thus, it is likely that the AOs used are not effective against alkyl radicals. Other types of additives will be examined in a future study. Also, other methods such as FTIR and SEM will be used to investigate the thermomechanical degradation of these HNBRs. It is worth noting that previous thermogravimetric studies reported onset degradation temperatures for HNBRs that are much higher than those reported in this study.[8]

CONCLUSIONS

In this study, different brands of HNBR rubbers were studied for thermomechanical degradation. It was found that thermomechanical treatment does affect these rubbers in the temperature range used in this study (i.e., 190 to 260°C) and molecular parameters have an effect on the selection of dominating degradation mechanism. From all of the above cases, it is clear that degradation is a combination of chain scission and crosslinking. In addition, it was found that a high degree of ACN content and high saturation result in increasing stability. Comparison of Z-1 and Z-3 or Z-6 and Z-7 showed that the stability of HNBRs is strongly influenced by the degree of hydrogenation. Low degrees of hydrogenation result in a high extent of degradation. Relatively unsaturated HNBRs were found to degrade by crosslinking. For highly saturated HNBRs with relatively high ACN content, the MW plays an important role. In this case, high MW leads to degradation through chain scission. In addition, high ACN content shifts the thermomechanical degradation to higher temperatures as a result of the high activation energy of the C≡N group. However, the net degradation level and mechanism also depend on the level of unsaturation. In the case of low ACN and high degree of hydrogenation, degradation proceeds by chain scission (decrease in MW). Light scattering confirmed the ability of rheology to detect degradation of HNBR.

References

1. Moss, S.; Zweifel, H. Polym Degrad Stab 1989, 25, 217.
2. Anthony, P.; De, S. K. Rubber Chem Technol 1997, 74, 376.
3. Sarkar, M.; Mukunda, P.; Prajna, P.; Bhowmick, A. Rubber Chem Technol 1997, 70, 856.
4. Garbarczyk, M.; Kuhn, W.; Kilnowski, J.; Jurga, S. Polymer 2002, 43, 3169.
5. Hertz, D.; Bussem H.; Ray, T. In: Nitrile Rubber—Past, Present & Future, Proceedings of the Rubber Division, American Chemical Society, October 11–14, 1994.
6. Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. In: Handbook of Engineering Polymeric Materials; Cheremisinoff, N. P., Ed.; Marcel Dekker: New York, 1997; p 555.
7. Morton, M. Rubber Technology, 3rd ed.; Van Nostrand Reinhold: New York, 1987.
8. Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. Polym Degrad Stab 1991, 31, 71.
9. Saha, S. Eur Polym Mater 2001, 37, 2513.
10. Setua, D. K.; Soman, C.; Bhowmick A. K.; Mathur, G. N. Polym Eng Sci 2002, 42, 10.
11. Chaung, C.; Han, C. J Appl Polym Sci 1984, 29, 2205.
12. Ioan, C.; Aberle, T.; Burchard, W. Macromolecules 2001, 34, 326.
13. Zhu, S. H.; Chan, C. M. Polym Eng Sci 1999, 39, 1998.
14. Clarke, J.; Clarke, B.; Freakley, P. K. Rubber Chem Technol 2000, 74, 1.
15. Chung, O.; Coran, A. Y. Rubber Chem Technol 1987, 70, 781.
16. Sirisinha, C.; Limcharoen, S.; Thunyarittikorn, J. J Appl Polym Sci 2001, 85, 1232.
17. Severe, G.; White, J. J Appl Polym Sci 2000, 78, 1521.
18. Ahn, S. J.; Lee, K. H.; Kim, B. K.; Jeong, H. M. J Appl Polym Sci 2000, 78, 1861.
19. Sirisinha, C.; Limcharoen, S. B.; Thunyarittikorn, J. J Appl Polym Sci 2003, 87, 83.
20. Saha, S. Eur Polym Mater 2001, 37, 399.
21. Schaal, S.; Coran, A.Y. Rubber Chem Technol 1999, 73, 225.
22. Schaal, S.; Coran, A. Y. Rubber Chem Technol 1999, 73, 240.
23. Hussein, I. A.; Ho, K.; Goyal, S.; Karbashewski, E.; Williams, M. Polym Degrad Stab 2000, 68, 381.
24. Yasuda, O.; Ougizawa, T.; Inoue, T.; Miyasaka, K. J Polym Sci Polym Lett 1983, 21, 813.
25. Boisserie, C.; Marchessault, R. H. J Polym Sci Part B: Polym Phys 1977, 15, 1211.
26. Chaudhry, R. A. MS Thesis. King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia, 2003.