Physical Properties and Blend Miscibility of Hydrogenated Acrylonitrile-Butadiene Rubber

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ABSTRACT: An experimental study of the thermal transition behavior and blend miscibility of hydrogenated acrylonitrile-butadiene rubber (HNBR) is described. Glass transition temperatures were determined as a function of composition. It was found that copolymers in the 40–50% composition range crystallized as did low acrylonitrile copolymers. The tendency for the former was much greater. For the former, HNBRs are miscible with chlorinated polyethylene and chlorosulfonated polyethylene. They are immiscible with polychloroprene, ethylene acrylate copolymers and various hydrocarbon rubbers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1521–1529, 2000

Key words: thermal transition behavior; blend miscibility; hydrogenated acrylonitrile-butadiene rubber; glass transition; copolymers

INTRODUCTION

Butadiene-acrylonitrile copolymers (NBR) were first synthesized by Konrad and Tshunkur[1] in 1930 using free radical emulsion polymerization. They were introduced commercially in 1934 by the IG Farbenindustrie as Buna N and later as Perbunan. NBR has been widely used as an oil-resistant rubber since that time.[2]

NBR has always had problems with ultraviolet light and ozone attack. This led to researchers from Bayer AG[3–8] and subsequently Nippon Zeon[9–12] and Goodyear[13] to hydrogenate NBR to lower the double bond content. The new product, generally known as hydrogenated acrylonitrile-butadiene rubber or HNBR, is an oil-resistant rubber with superior aging. Surprisingly it is also reported[6,12–14] as a polymer that at high acrylonitrile levels undergoes stress-induced crystallization similar to natural rubber[15] and polychloroprene.[16]

With one exception,[14] all of the basic studies of the properties of HNBR have been published by the two companies Bayer AG and Nippon Zeon, which now manufacture the new polymer. There have been few studies of blends. In the present paper, we describe studies of the materials properties, including transitions and non-Newtonian viscosity. Comparisons are made to acrylonitrile-butadiene rubber. We also describe an investigation of blend miscibility for HNBR with other polymers.

EXPERIMENTAL

Materials

A wide range of commercial HNBRs produced by Nippon Zeon (and its USA subsidiary Zeon Chemical) and Bayer AG were used in this investigation. These materials are summarized in Table I. All in all seven Nippon Zeon (HNBR-1 to HNBR-7) and five Bayer AG (HNBR-8 to HNBR-12) were investigated. The HNBR-6 and HNBR-7 should be recognized as the modified polymers (probably terpolymers) described by S. Hayashi et al.[17]

Table I   HNBRs Included in this Study

Designation	Nominal Percent Acrylonitrile	Unsaturation	Source
HNBR-1	49.9	9	Zeon Chemical Zetpol 0020
HNBR-2	44.1	9	Zeon Chemical Zetpol 1020
HNBR-3	36.3	9	Zeon Chemical Zetpol 2020
HNBR-4	36.1	<1	Zeon Chemical Zetpol 2000L
HNBR-5	36.0	15	Zeon Chemical Zetpol 2030L
HNBR-6	25.1	10	Zeon Chemical Zetpol 3120
HNBR-7	16.37	10	Zeon Chemical Zetpol 4120
HNBR-8	42.0	4.5–6.5	Bayer Corp. Therban C4550
HNBR-9	37.5–39.5	Max 0.9	Bayer Corp. Therban 1907
HNBR-10	34.5–37.5	1.5–2.5	Bayer Corp. Therban B3850
HNBR-11	33.8	4.5–6.5	Bayer Corp. Therban 1767
HNBR-12	20	5.0	Bayer Corp. Therban XN535C

For comparison purposes, we also studied series of acrylonitrile-butadiene copolymers. These are summarized in Table II.

In our blend investigations, we studied a wide range of hydrogenated elastomers, polar ethylene copolymer elastomers, and chlorinated polymers. These are summarized in Tables III–V.

Characterization

Differential Scanning Calorimetry

In both our investigations of transitions and blend miscibility, we made use of differential scanning calorimetry. Studies were made using both a Perkin Elmer and a Dupont 9900 System

Table II   NBRs Included in this Study

Designation	Nominal Percent Acrylonitrile	Type	Source
NBR-1	51.4	Cold (5°C)	Zeon Chemical Nipol 100 × 132
NBR-2	44.4	Cold (5°C)	Zeon Chemical Nipol VT4580
NBR-3	36.1	Cold (5°C)	Zeon Chemical Nipol 3635
NBR-4	21.0	Hot (5°C)	Zeon Chemical Nipol 1014
NBR-5	18.5	Cold (5°C)	Zeon Chemical Nipol DN401LL

Table III Hydrocarbon Elastomers Involved in Blend Studies

Designation	Type	Source
EPDM-2	Ethylene propylene terpolymer	Copolymer Kalten 55
IR-1	*cis*-1,4 polyisoprene	Goodyear Natsyn 2200
SBR	33% Styrene butadiene copolymer	Bridgestone Firestone Duradene 753

Differential-Scanning Calorimetry (DSC). For DSC measurements of T_g, the following procedure was used. Samples were initially sealed and heated at 50°C/min. in order to remove any previous history. The samples were then quenched at the same rate to -100°C and then heated from -100 to 100°C at 20°C/min.

For studies of crystallization, annealing experiments were carried out in the DSC prior to scan at 20°C/min.

X-ray Diffraction Experiments

A General Electric X-ray apparatus employing CuK$_\alpha$ radiation was used to obtain X-ray diffraction film patterns. Generally, film sheets were initially compression molded at 100°C and cooled to room temperature. Small rectangular samples were cut from these sheets. In some cases, these film samples were then uniaxially stretched 600% at room temperature. The oriented samples were mounted in the X-ray units specimen holding device to help retain orientation induced structures.

Shear Viscosity Measurements

Shear viscosity measurements for the HNBRs and NBRs of Tables I and II were made at 100°C over the range of shear of 10^{-6} to 10^3 s^{-1}. At the highest shear rates (> 10 s^{-1}), the measurements were made in a capillary rheometer (Monsanto Processibility Tester). At intermediate shear rates (0.01–3 s^{-1}), measurements were made in a pressurized biconical rheometer. At the lowest shear rates, a sandwich rheometer was used to make measurements. Our measurements were made at 100°C.

Blend Miscibility

Blend miscibility experiments were carried out as follows. First, the blends were prepared using a batch type mixer (CW Brabender) with cam rotors. The fill factor for the mixing chamber was 0.70. The samples were mixed at 100°C for 12 min.

Various techniques were used to evaluate miscibility. These include (1) DSC investigations to determine glass transition temperatures, (2) the characterization of films formed by precipitation from solution by optical microscopy, and (3) scanning electron microscopy.

RESULTS

Transitions in HNBR and NBR Copolymers

We have made DSC investigations of HNBR of Table I and the NBR of Table II. Typical DSC

Table IV Chlorinated Polymers Investigated in Blend Studies

| Designation	Type	Chlorine Content	Source
CPE-1	Chlorinated polyethylene	42.1	Dupont-Dow Tyrin 4211 P
CPE-2	Chlorinated polyethylene	24.9	Dupont-Dow Tyrin 725
CPVC-1	Chlorinated polyvinyl chloride	76.4	BF Goodrich Temprite CPVC-674X705
CPVC-2	Chlorinated polyvinyl chloride	67.3	BF Goodrich Temprite CPVC-674X571
CSM-1	Chlorosulfonated polyethylene	42	Dupont Hypalon 48
CR-1	Polychloroprene		Bayer Corp. Baypren 121
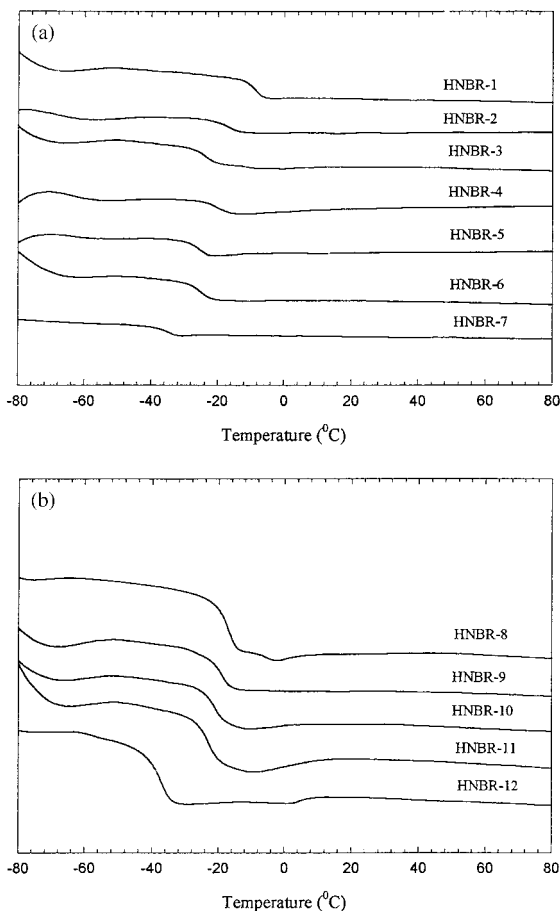
Figure 1 DSC scans for hydrogenated acrylonitrile-butadiene copolymer. (a) HNBR-1 to HNBR-7; (b) HNBR-8 to HNBR-12.

scans at 20°C/min for the HNBR are shown in Figure 1. Generally, only a T_g is observed, which increases with acrilonitrile content. The glass transition temperatures of HNBR are summarized in Table V. Similar measurements were made on the NBR. The results are summarized in Table VI.

Melting Transition

Our DSC analysis of various unstretched samples from −100 to 100°C revealed only the presence of glass transitions that were below 0°C.

We sought to anneal several of the HNBRs for different period of times. In one of our early studies, we annealed the HNBR-1 and HNBR-7 for 6 h at 10°C. No effect was found. We then studied annealing at 0°C of a wider range of polymers. For HNBR-1, HNBR-6, HNBR-7, and HNBR-8, significant development of crystallinity was now devel-

Table V DSC Behavior of HNBR

Designation	Acrylonitrile Content	T_g	Evidence of Crystallization
HNBR-1	49.9	−9.2	Yes
HNBR-2	44.1	−17.2	Yes
HNBR-3	36.3	−23.4	
HNBR-4	36.1	−20.0	
HNBR-5	36.0	−25.3	
HNBR-6	25.1	−25.7	
HNBR-7	16.37	−31.0	Yes
HNBR-8	42.0	−17.0	Yes
HNBR-9	37.5–39.5	−19.0	
HNBR-10	34.5–37.5	−21.0	
HNBR-11	33.8	−22.5	
HNBR-12	20.0	−37.8	

oped. DSC traces after various periods of annealing are shown in Figure 2.

X-Ray Diffraction Results

We found the occurrence of crystalline diffraction peaks in HNBR-1, HNBR-2, and HNBR-8. From Table I, HNBR-1, HNBR-2, and HNBR-8 have acrylonitrile contents between 49.9 and 42%.

The high acrylonitrile samples exhibited three diffraction peaks, especially when uniaxially stretched as shown in Figure 3. They exhibited equatorial peaks at 3.6 and 5.1 Å and a meridional peak at 7.5 Å. However, experiments carried out on low acrylonitrile HNBRs found no crystallization.

Non-Newtonian Shear Viscosity Measurements

Non-Newtonian shear viscosity measurements for HNBR-1 to HNBR-7 at 100°C are shown in Figure 4. At low shear rates, the shear viscosity tends to become independent of shear rate, i.e.,

Table VI Glass Transition Temperature of NBR

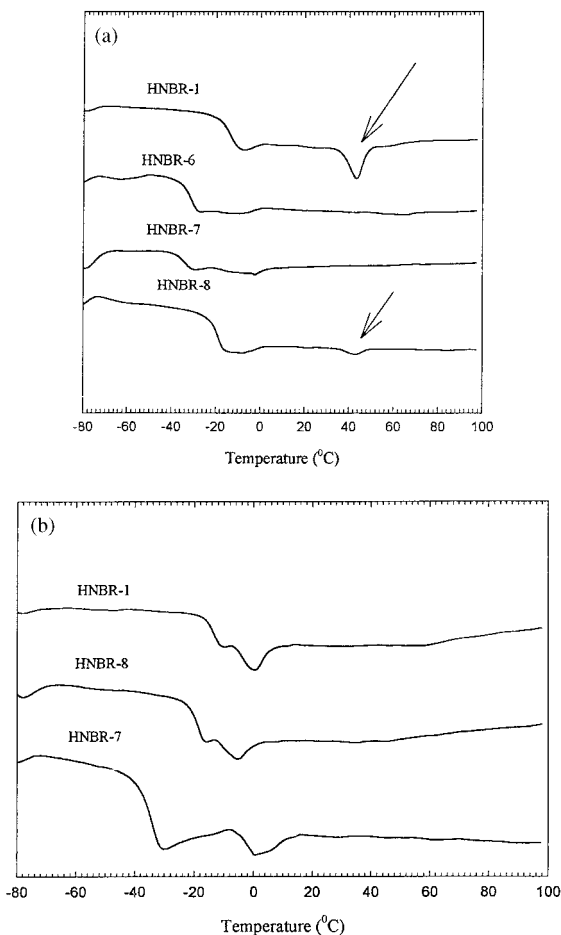| Designation	Acrylonitrile Content	T_g	Evidence of Crystallization
NBR-1	51.4	−3.10	No
NBR-2	47.3	−7.0	No
NBR-3	35.1	−19.6	No
NBR-4	19.4	−33.6	No
NBR-5	15.4	−44.5	No
BR[24]	0	−85	No

Figure 2 (a) DSC scans for HNBR-1 [49.9% acrylonitrile (ACN)], HNBR-6 (25.10% ACN), HNBR-7 (16.37% ACN), and HNBR-8 (42.0% ACN) annealed for one hour at 0°C. (b) DSC traces for HNBR-1 (49.9% ACN), HNBR-8 (42% ACN), and HNBR-7 (16.37% ACN) annealing for 3 months at 0°C.
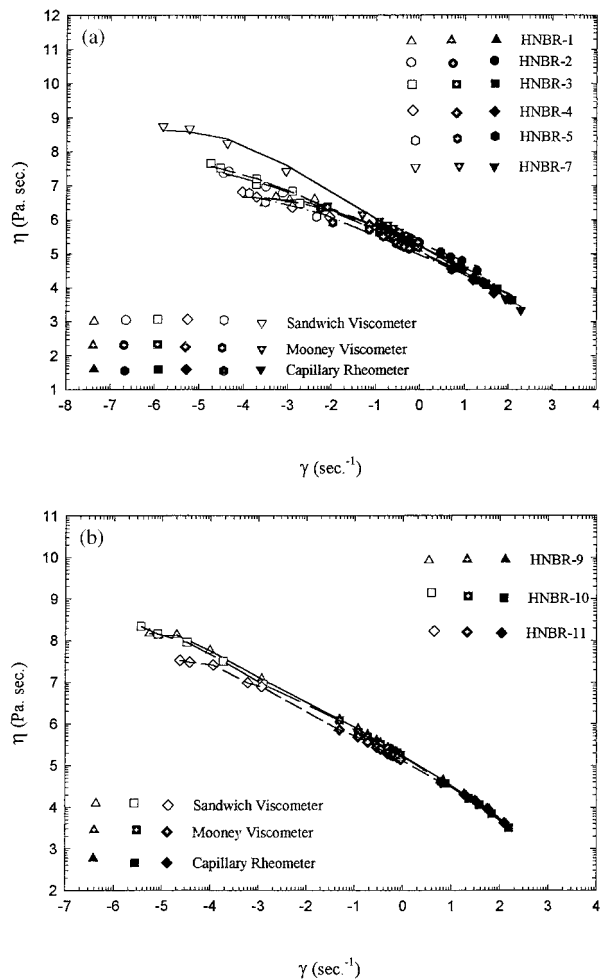

Figure 4 Non-Newtonian shear viscosity of HNBR as a function of shear rate at 100°C. (a) HNBR-1 HNBR-7; (b) HNBR-9 to HNBR-11.

Newtonian in character. This tendency is also seen in NBR, as shown in Figure 5. At higher shear rates the viscosity of both HNBR and NBR decrease. On a logarithmic plot, the shear viscosity at high shear rates decreases linearly, indicating power law behavior.

Blend Miscibility

DSC traces were made for various HNBR blend systems. Typical DSC traces of blends with different hydrocarbon elastomers are shown in Figure 6(a–c). It can be seen that EPDM-1, polyisoprene, and the 33% styrene SBR blends exhibit two glass transition temperatures. These T_g's are the same as for the pure components. This indicates a lack of miscibility, which is also supported by microscopy investigations.

Figure 3 Wide angle X-ray scattering (WAXS) film pattern of uniaxially stretched HNBR-1.
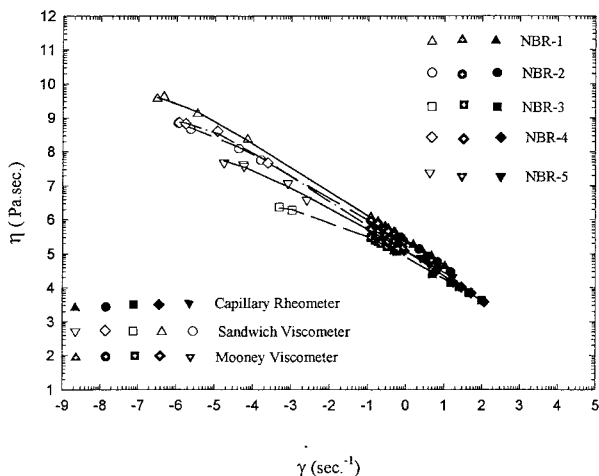
Figure 5   Non-Newtonian shear viscosity of NBR as a function of shear rate at 100°C.

DSC traces of blends with chlorinated polyethylene CPE-1 and chlorosulfonated polyethylene CSM-1 are shown in Figure 7(a–c). These indicate only a single T_g and miscibility of the two polymer components. Not all chlorinated polymers are miscible with HNBR, as can be seen in Figure 8. For the 24.9 chlorine CPE-2 blended with HNBR-7, there are two T_g's, which vary with HNBR content [Fig. 8(a)]. This indicates partial miscibility. Chlorinated polyvinyl chloride blends with HNBR also exhibit two T_g's, which also vary with composition [Fig. 8(b)]. Blends of HNBR with polychloroprene (CR) exhibit two composition-independent T_g's and no miscibility, as can be seen in Figure 8(c and d).

DISCUSSION AND INTERPRETATION

Glass Transition Temperatures

The composition dependence of the glass transition temperature of hydrogenated acrylonitrile rubber and acrylonitrile-butadiene copolymer is very similar at higher acrylonitrile contents ($\geq 35\%$), but at low acrylonitrile, they differ. The HNBR tends to have higher T_g's than NBR. The unexpected high T_g of copolymers of ethylene with other vinyl monomers has long been observed in the literature.[18] It has been reported for ethylene-copolymers of vinyl acetate, vinyl chloride, and different acrylates. Other earlier investigations[6,12,13] have remarked on this behavior in HNBR.
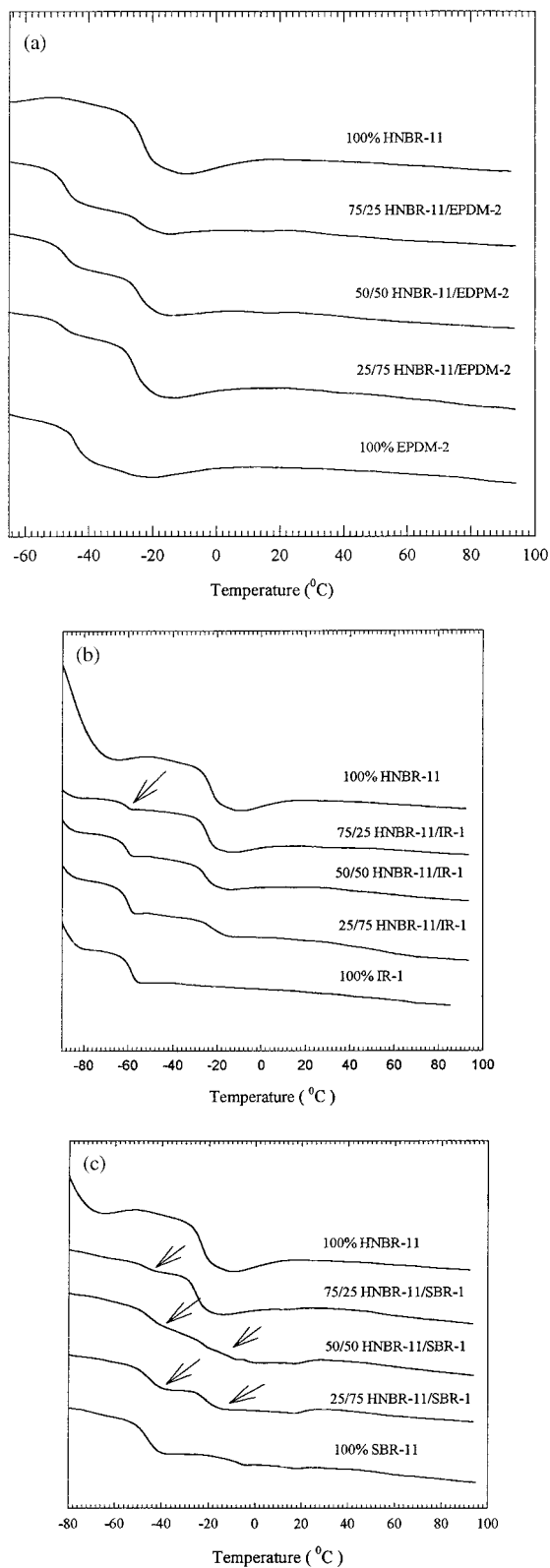
Figure 6   DSC scans for blends of HNBR with hydrocarbon elastomers. (a) EPDM-1; (b) IR-1; (c) SBR-1.
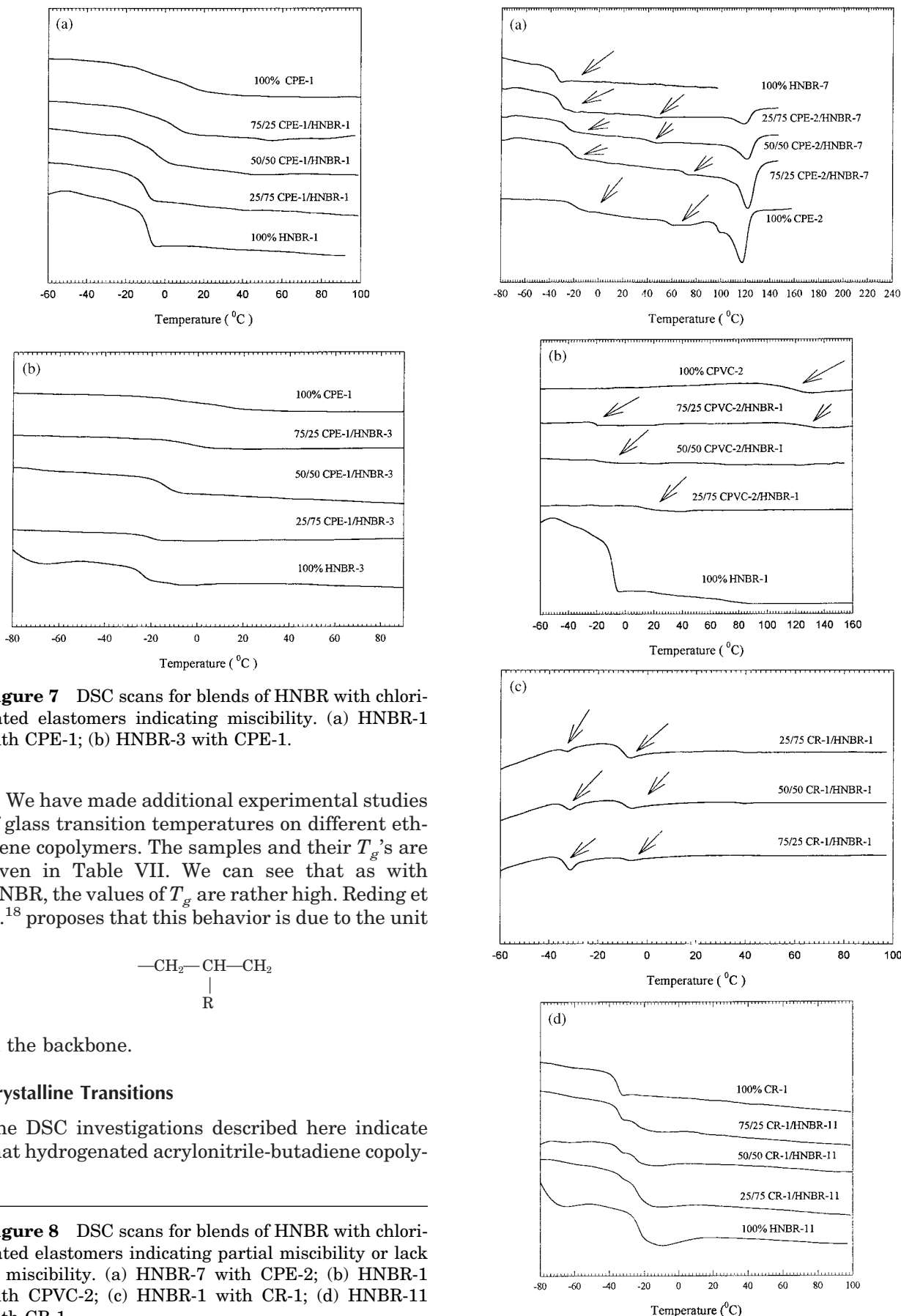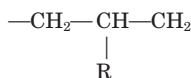
Figure 7 DSC scans for blends of HNBR with chlorinated elastomers indicating miscibility. (a) HNBR-1 with CPE-1; (b) HNBR-3 with CPE-1.

We have made additional experimental studies of glass transition temperatures on different ethylene copolymers. The samples and their T_g's are given in Table VII. We can see that as with HNBR, the values of T_g are rather high. Reding et al.[18] proposes that this behavior is due to the unit

$$-CH_2-CH-CH_2$$
$$|$$
$$R$$

in the backbone.

Crystalline Transitions

The DSC investigations described here indicate that hydrogenated acrylonitrile-butadiene copoly-
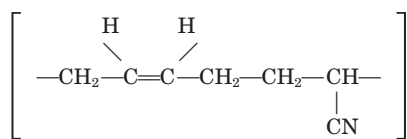
Figure 8 DSC scans for blends of HNBR with chlorinated elastomers indicating partial miscibility or lack of miscibility. (a) HNBR-7 with CPE-2; (b) HNBR-1 with CPVC-2; (c) HNBR-1 with CR-1; (d) HNBR-11 with CR-1.

Table VII   Glass Transition Temperature of Various Ethylene Copolymers

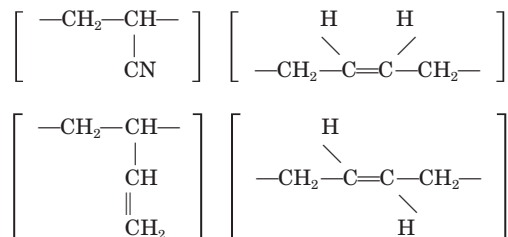| Designation	Type	Ethylene Mole %	T_g
EVM-1	Ethylene vinyl acetate	82.0	−28.98
EVM-2	Ethylene vinyl acetate	75.0	−24.96
EVM-3	Ethylene vinyl acetate	67.0	−23.51
EVM-4	Ethylene vinyl acetate	57.0	−11.91
EPDM-2	Ethylene–propylene–terpolymer	75.86	−47.54

mers exhibit melting transitions in two different composition ranges. First, striking melting transitions are observed in the range 40–50% acrylonitrile. Second, melting transitions are observed at low acrylonitrile contents. The latter transition was weaker in our studies. The observations of the DSC experiments are reinforced by the stretching experiments, which induced crystallization in only the high acrylonitrile samples.

The 7.5 Å meridional WAXS repeat distance observed is a striking result as this is the same value found by Furukawa and his co-workers.[19] For the crystallizable alternating copolymer of acrylonitrile and *trans*-1,4 polybutadiene, which has an effective structural unit,

$$\left[\begin{array}{c} \quad\ \overset{H}{\diagdown}\quad\overset{H}{\diagup} \\ -CH_2-C{=\!\!=}C-CH_2-CH_2-CH- \\ \hspace{5.5cm}| \\ \hspace{5.5cm}CN \end{array} \right]$$

Furukawa et al.[19] note that if one adds the bond length dimensions for this structural unit, one obtains 7.5 Å.

The structure of HNBR is different. It originates as a free radical copolymer of butadiene and acrylonitrile with structural units

$$\left[\begin{array}{c} -CH_2-CH- \\ | \\ CN \end{array} \right] \quad \left[\begin{array}{c} \overset{H}{\diagdown}\quad\overset{H}{\diagup} \\ -CH_2-C{=\!\!=}C-CH_2- \end{array} \right]$$

$$\left[\begin{array}{c} -CH_2-CH- \\ | \\ CH \\ \| \\ CH_2 \end{array} \right] \quad \left[\begin{array}{c} \overset{H}{\diagdown} \\ -CH_2-C{=\!\!=}C-CH_2- \\ \hspace{2.2cm}\diagdown \\ \hspace{2.4cm}H \end{array} \right]$$

The reactivity ratios of the copolymerization of butadiene and acrylonitrile at 5°C are

$$r_a = \frac{k_{AA}}{k_{AB}} = 0.02$$

$$r_B = \frac{k_{BB}}{k_{BA}} = 0.28$$

suggesting that at 50 mole percent acrylonitrile, a reasonably alternating copolymer is obtained and a high concentration of AB dyads is obtained. Hydrogenation of both *trans*-1,4 and *cis*-1,4 polybutadiene lead to BA dyads of tetramethylene and acrylonitrile, i.e.,

$$\left[\begin{array}{c} -CH_2-CH_2-CH_2-CH_2-CH_2-CH- \\ \hspace{5.5cm}| \\ \hspace{5.5cm}CN \end{array} \right]$$
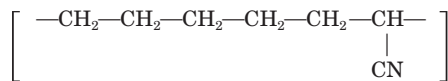
This unit would seem to be the repeat that caused the crystallization; adding bond lengths it leads to the 7.5 Å repeat the same as Furukawa et al.'s alternating copolymer.

Miscibility in Blends

In some rare occasions, miscibility in the absence of some specific interaction does occur. In general, blends are miscible due to strong interaction between functional groups leading to a negative enthalpy of mixing. In the case of HNBR and the hydrocarbons, i.e., polyisoprene, styrene-butadiene, and EPDM, the blends were immiscible due to polarity difference and dissimilar structure and absence of molecular interaction.

Miscibility was observed for the blend made of HNBR and polymers containing high level of chlorine, i.e., chlorinated polyethylene (42% chlorine), chlorosulfonated polyethylene (43% chlorine), and polyvinyl chloride.[20] At a lesser chlorine content, no miscibility was noted. Thus, polychloroprene was found immiscible with HNBR. Chlorinated polyethylene (25 wt % Cl) and chlorinated polyvinyl chloride (CPVC) (67 wt % Cl) demonstrated lesser levels of miscibility. Due to the origin of HNBR, the miscibility behavior noted could best be understood by looking at previous studies of chlorinated polymers and NBR. We note the studies of Huh et al.[20,21] and Cowie et al.[22,23] The miscibility is enhanced by the interaction of the CHCl group in chlorinated polymers and CHCN in HNBR or NBR. Low chlorine polymers do not have enough CHCl and high chlorine polymers

such as CPVC tend to have CCl_2 rather than CHCI. This reduces the miscibility window.

CONCLUSION

Our study indicates that the glass transition temperature behavior in HNBR was typical of ethylene copolymers. Furthermore, HNBR had tendency to crystallize in the unstretched and stretched state. The shear viscosity of HNBR was well behaved and crystallization tendency of this polymer was noted in rheological properties at 100°C. HNBR had a Newtonian-type viscosity at low shear rate and a non-Newtonian behavior at high shear rate. HNBR was miscible with chlorinated polymer such as chlorinated polyethylenes and chlorosulfonated polyethylene. Too low or too high chlorine levels reduced miscibility.

REFERENCES

1. Konrad, E.; Tschunkur, E. German Patent 658,172, April 20, 1931.
2. Hofmann, W. Rubber Chem Technol 1963, 37(2), 52.
3. Oppelt, D.; Schuster, H.; Thormer, J.; Braden, R. Belgium Patent 845,775, 1975.
4. Thörmer, J.; Marwede, G.; Buding, H. Kautsch Gummi Kunstst 1983, 36, 269.
5. Buding, H.; Konigshofen, H.; Szentivanyl, Z.; Thörmer, J. U.S. Patent 4,581,417, 1986.
6. Obrecht, W.; Buding, H.; Eisele, U.; Szentivanyi, Z.; Thormer, J. Angew Makromol Chem 1986, 145/146, 161.
7. Thörmer, J.; Hirza, J.; Sventivanyi, Z.; Obrecht, W.; Rhode, E. Rubber World 1989, 201(2), 25.
8. Eisele, U.; Szentivanyi, Z.; Obrecht, W. J Appl Polym Sci Appl Polym Symp 1992, 50, 185.
9. Kubo, Y.; Ohura, Y. U.S. Patent 4,337,329, 1982.
10. Kubo, Y.; Onishi, T.; Onura, K. U.S. Patent 4,384,081, 1983.
11. Kubo, Y.; Hashimoto, K.; Watanabe, N. Kautschuk Gummi Kunst 1987, 40, 118.
12. Sawada, H. Int Polym Sci Technol 1994, 21(2), T64.
13. Weinstein, A. H. Rubber Chem Technol 1984, 57, 203.
14. Braun, D.; Haufe, A.; Leiss, D.; Hellmann, G. P. Angew Makromol Chem 1992, 202/203, 143.
15. Treloar, L. R. G. Physics of Rubber Elasticity, 2nd Ed.; Oxford University Press: Oxford, 1958.
16. Carothers, W. H.; Williams, I.; Collins, A. M.; Kirby, J. E. J Am Chem Soc 1931, 53, 4203.
17. Hayashi, S.; Oyama, M.; Hasmimoto, K.; Nakagawa, T. Presented at 140th Meeting of the Rubber Division of the American Chemical Society, Detroit, MI, October 1991.
18. Reding, F. P.; Faucher, J. A.; Whitman, R. D. J Polym Sci 1962, 57, 483.
19. Furukawa, J.; Kobayashi, E.; Uratani, K.; Iseda, Y.; Umemura, J.; Takenaka, T. Polym J 1973, 4, 358.
20. Sotiropoulou, D.; Avramidou, E.; Kalfoglou, N. K. Polymer 1993, 34(11), 2297.
21. Huh, W.; Karasz, F. Macromolecules 1992, 25, 1057.
22. Huh, W.; Karasz, F. E. Polymeric Material Science and Engineering, Proceeding of the ASC Division of Polymeric Materials 1989, 60, 792.
23. Cowie, J. M. G.; Elexpuru, E.; Harris, J. H.; McEwen, I. J. Makromol Chem Rapid Commun 1989, 10, 691.