

Property-composition dependence of hydrogenated poly(butadiene-*co*-acrylonitrile)/poly(vinyl chloride) blends

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The compatibility of hydrogenated poly(butadiene-*co*-acrylonitrile) (HNBR) with poly(vinyl chloride) (PVC) was investigated in the complete composition range. Dynamic mechanical spectroscopy, d.s.c. and phase-contrast microscopy indicated that the blends are miscible at the segmental level. Depending on composition, a wide spectrum of tensile properties may be obtained. The maximum energy for tensile failure was observed at about 40 wt% rubber content. T_g and the blend modulus dependence on composition supports the view that moderate interactions are present leading to synergism. The overall blend properties suggest that the system does not have microheterogeneities observed for the non-hydrogenated copolymer NBR/PVC blends at a comparable acrylonitrile content.

(Keywords: hydrogenated nitrile rubber; miscible PVC blends; miscibility prediction; properties of HNBR/PVC blends)

INTRODUCTION

Thermoplastic modification through blending provides considerable stimulus for technological research and innovation¹. Lately, commodity plastics recycling has provided an additional challenge since it confronts plastics technology with the task of utilizing mixtures of discarded plastics that are difficult to separate².

Among thermoplastics, poly(vinyl chloride) (PVC) modification presents a variety of options. Its polar nature allows preparation of compatible blends with other 'complementary dissimilar' polymers, thus obtaining a continuous range of properties³. On the other hand the addition of a suitable immiscible partner leads to impact modification and further property diversification⁴. Among the compatible blends, those based on PVC and poly(butadiene-*co*-acrylonitrile) (NBR) were the first commercially utilized miscible polyblends⁵ and their properties have been reviewed⁶. At moderate (20–40 wt%) PVC levels these blends show increased u.v. and ozone resistance while at higher PVC levels NBR acts as a polymeric plasticizer. A recent development in the area of nitrile rubbers has been the introduction of hydrogenated NBR obtained by the controlled hydrogenation of the butadiene comonomer^{7,8}. The hydrogenated NBR (HNBR) has the additional advantages of heat, chemical, increased ozone resistance and good low-temperature flexibility due to the polyethylene portion in the copolymer backbone⁹.

This report covers the compatibility of HNBR/PVC in the complete composition range. The techniques used

were phase-contrast microscopy, dynamic mechanical analysis (d.m.a.), d.s.c. and tensile testing. It was of interest to assess whether this system differs, and to what extent, from the NBR/PVC blend.

EXPERIMENTAL

HNBR was donated by Bayer-Polysar International S.A. It had a 38 wt% AN content, a residual unsaturation of ca. 0.5 mol% and a small percentage of pendant ethyl groups originating from the hydrogenation of the 1,2 vinyl groups in the butadiene comonomer. M_n was 52 000 g mol⁻¹ and the polydispersity index $I = 3.35$. PVC was obtained from EKO Chemicals Co and had a $M_n = 35 000$ g mol⁻¹ and $I = 2.53$. Blends were prepared by dissolving the components in a warm common solvent (butanone-2), solvent evaporation and drying to constant weight at 50°C in a vacuum oven. A PVC stabilizer (dibutyltin dilaurate 2% calculated on PVC) was added to the blend solution. Films were prepared by compression moulding between Teflon sheets at ca. 170°C and 15 MPa for 0.5 min and quenching at 0°C.

Thin films prepared by melt pressing on the microscope slide were examined under a phase-contrast microscope with oil (refractive index $n_D^{23} = 1.516$) immersion in bright field. D.s.c. measurements were carried out using a 910 calorimeter system coupled with a 990 programmer-recorder. Calibration was made with an indium standard. Sample weight was 15 mg and the first heating cycle to 180°C was followed by quenching to -80°C to determine T_g . Dynamic viscoelastic data, loss tangent $\tan \delta$ and complex modulus $|E^*|$ were obtained at 110 Hz using the direct reading viscoelastometer (Rheovibron,

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model DDV II-C Toyo-Baldwin). Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester (model T5001) and film strips measuring $6.0 \times 1.20 \times 0.05 \text{ cm}^3$. Crosshead speed was 25 cm min^{-1} .

RESULTS

Phase-contrast micrographs did not show any features other than those present in the homopolymer films. This is taken as an indication that no gross phase separation is present in the blends; see *Figure 1*.

Mechanical and thermal properties

The thermomechanical spectra for the blends studied are summarized in *Figures 2* and *3* in terms of the storage and loss modulus, E' and E'' , respectively. D.s.c. results are given in the final section. In *Figure 3* the existence of a single primary blend relaxation, shifting regularly with composition, is an indication that the system is miscible at the level of dispersion that d.m.a. can detect (ca. 100 \AA)¹⁰. Judging from the small width of the relaxations it is also concluded that no heterogeneities are present in all compositions. In the pure components the β -PVC relaxation¹¹ at ca. -20°C and the broad transition below T_g for HNBR¹² may be attributed to pendant groups. The temperature dependence of E' is typical of a miscible system: see *Figure 2*. It is of interest to note the high storage modulus values in the PVC-rich

blends at temperatures above ca. 40°C , where synergism is observed: compositions 95/5 and 90/10.

Figure 4 and its inset give the average stress-strain curves obtained by computer averaging data from all specimens at a given composition. The 40/60 blend with distinct yielding displays the characteristics of a tough material and marks the transition from rubbery to stiffer materials. Noteworthy for these last compositions is their high tensile modulus even with moderate amounts of HNBR. The results on ultimate tensile properties are summarized in *Figure 5*, where significant strength and rigidity is retained up to 30 wt% rubber. Tensile data were further analysed using the area under the force-elongation curve to obtain the composition dependence of tensile rupture energy given in *Figure 6*. Maximum energy is obtained at ca. 40 wt% rubber content. It is of interest to note that a maximum in the impact strength was observed¹³ at similar rubber contents in compatible NBR/PVC blends.

DISCUSSION AND CONCLUSIONS

Both the d.m.a. and microscopy results support the view that the blend studied is miscible. No peak broadening at intermediate compositions¹⁴ was observed, in contrast to NBR/PVC blends where miscibility was established by d.m.a. but electron microscopy and n.m.r. revealed microheterogeneities^{15,16}. In *Figure 7* the T_{gb} dependence on composition is linear or, excluding the terminal points, a small positive curvature may be detected. The results

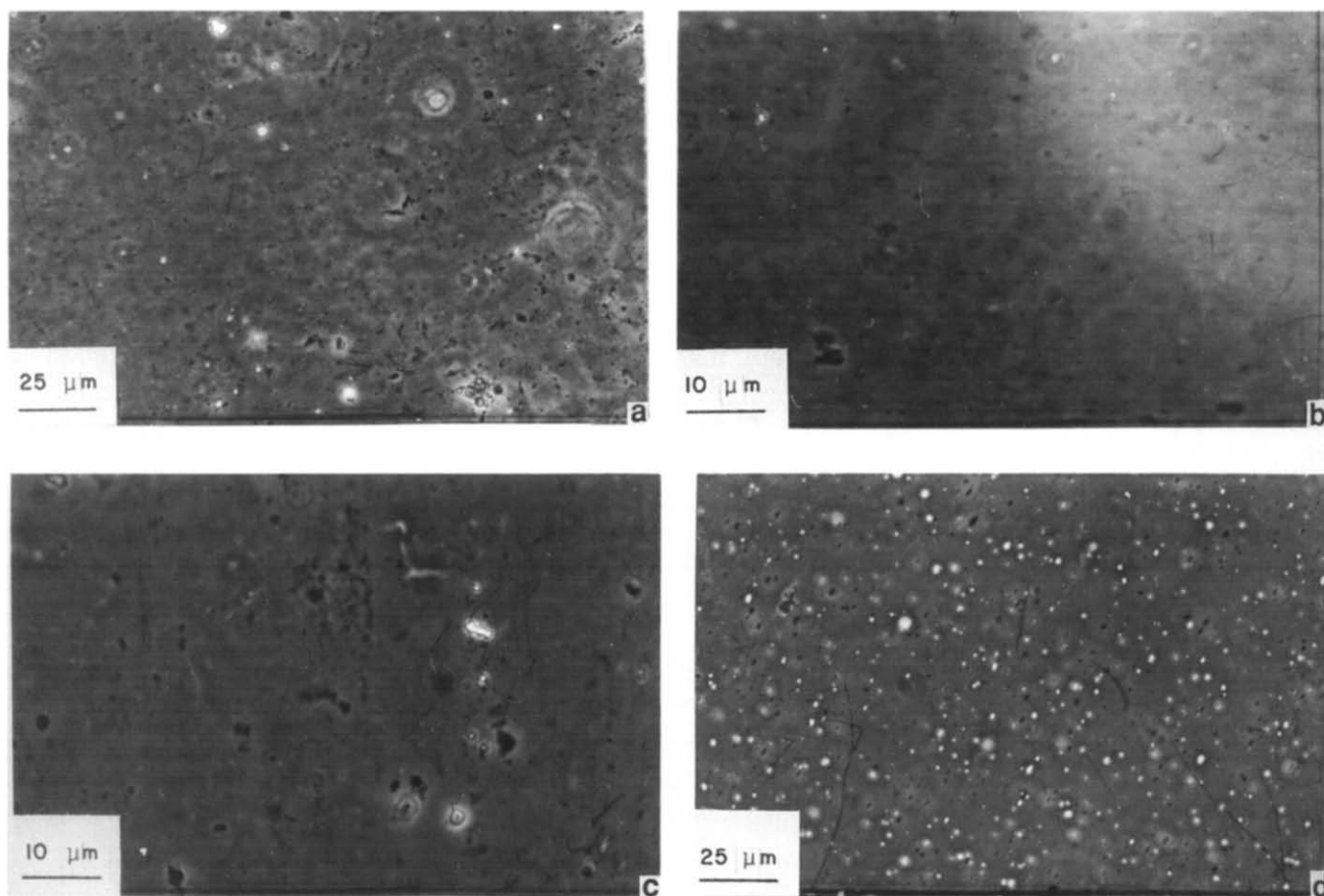


Figure 1 Phase-contrast micrographs of HNBR/PVC blends: (a) 100/0; (b) 80/20; (c) 60/40; (d) 0/100

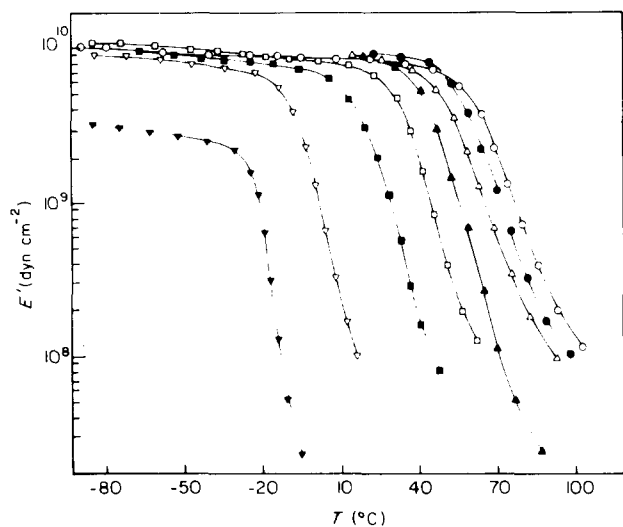


Figure 2 Temperature dependence of the storage modulus of HNBR/PVC blends: (○) 0/100; (●) 5/95; (△) 10/90; (▲) 20/80; (□) 35/65; (■) 50/50; (▽) 75/25; (▼) 100/0

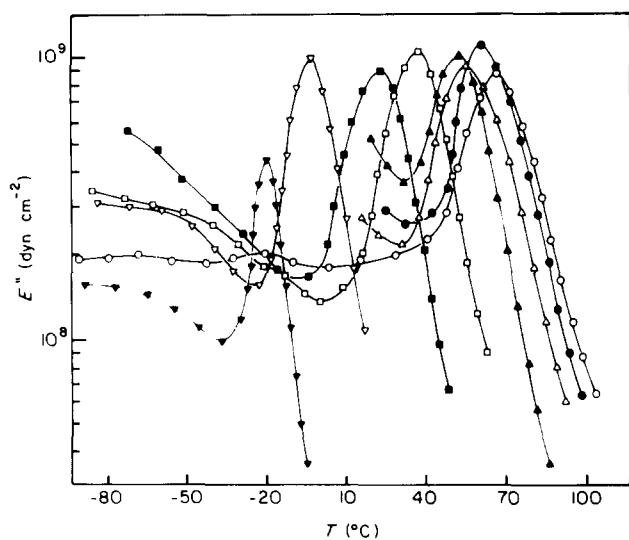


Figure 3 Temperature dependence of the loss modulus of HNBR/PVC blends: (○) 0/100; (●) 5/95; (△) 10/90; (▲) 20/80; (□) 35/65; (■) 50/50; (▽) 75/25; (▼) 100/0

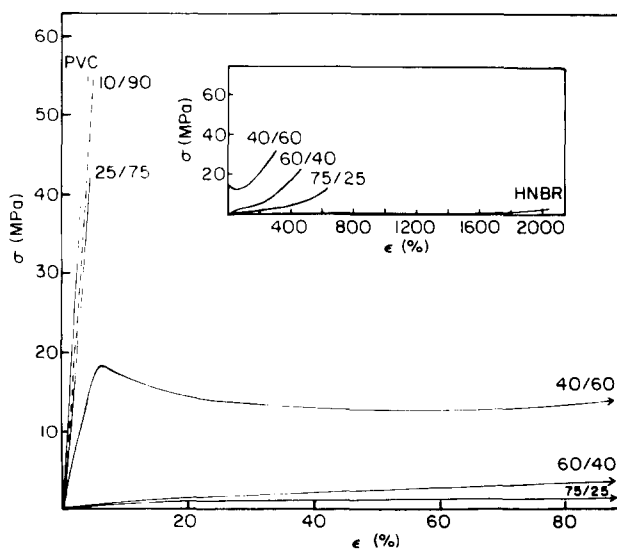


Figure 4 Stress-strain properties, σ vs. ϵ %, of HNBR/PVC blends at the indicated compositions. Note a change of coordinates in the inset

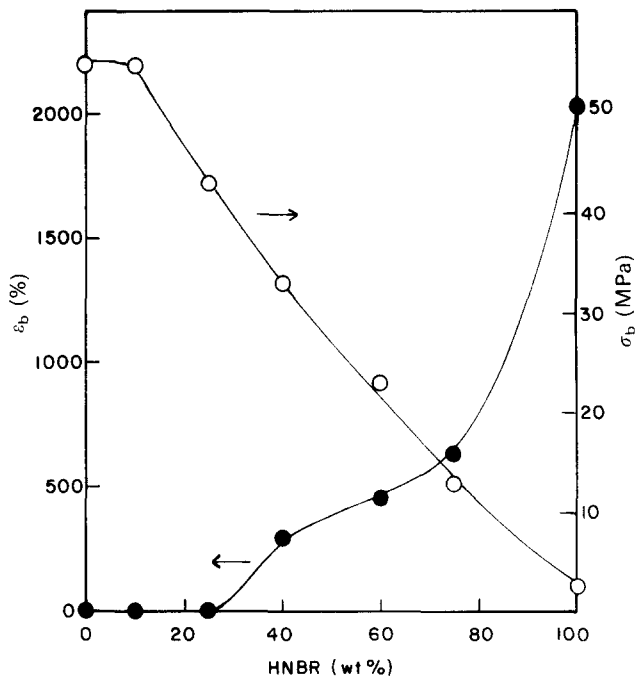


Figure 5 Ultimate stress σ_b and strain ϵ_b of blends vs. wt% of HNBR in blends

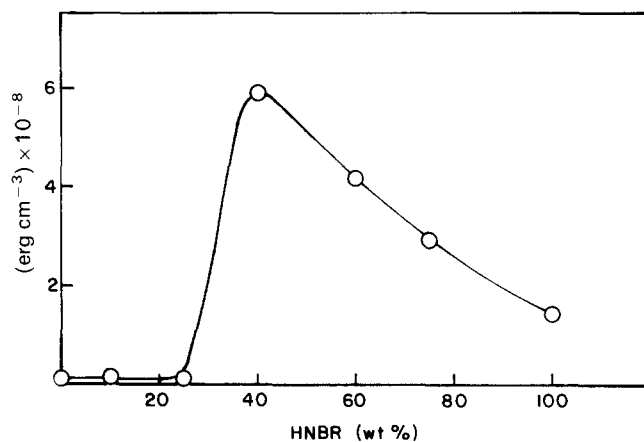


Figure 6 Energy to tensile failure of blends vs. wt% of HNBR in blends

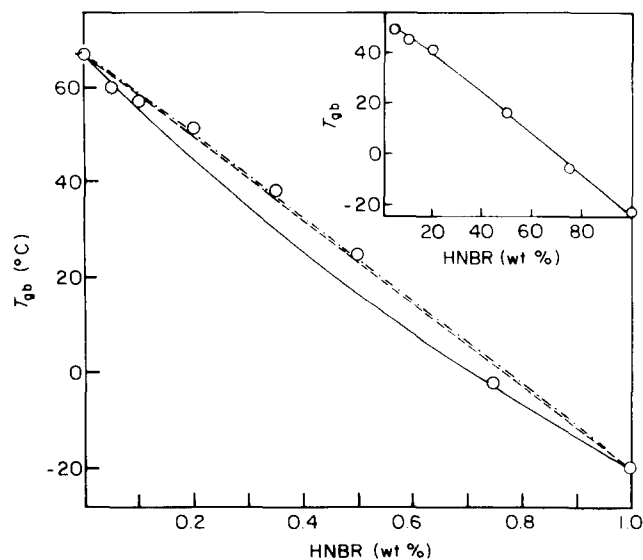


Figure 7 Comparison of experimental and calculated T_g values of blends: (○) experimental values; (—) Fox equation, (---) Gordon-Taylor equation, (---) Kwei equation, using parameters given in text. Inset: d.s.c. data of T_g

were analysed using the equations proposed by

$$\text{Fox}^{17}, \quad \frac{1}{T_{gb}} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \quad (1)$$

$$\text{Gordon-Taylor}^{18}, \quad T_{gb} = T_{gA} + k \frac{W_B}{W_A} (T_{gB} - T_{gA}) \quad (2)$$

$$\text{and Kwei}^{19}, \quad T_{gb} = \frac{W_A T_{gA} + k W_B T_{gB} + q W_A W_B}{W_A + k W_B} \quad (3)$$

In the above equations, T_{gb} is the T_g of the blend, W_i and T_{gi} are the weight fraction of component i and its T_g , respectively, and k is the ratio between the volume expansion coefficient difference in the viscoelastic and glassy state of the homopolymers. The parameter q , according to Kwei¹⁹, gives a measure of the overall specific interactions in the blend. The Fox equation¹⁷ is not satisfactory. The best fit for equations (2) and (3) was obtained with $k=1$ and $q=1$. The above analysis indicates moderately strong interactions. It is well documented²⁰ that strong and/or specific interactions lead to a positive deviation from the straight line. D.s.c. data included in the inset show similar trends; however, T_{gb} values are systematically lower due to a frequency effect.

Miscibility and synergism^{21,22} are also supported by the blend storage modulus, E'_b , variation with composition at constant temperature, as displayed in Figure 8, where it is seen that E'_b is higher and that at some compositions it coincides with the value predicted by the parallel coupling of pure components providing for maximum reinforcement. In this work, synergism is used in a more general context, meaning an enhanced level of (storage) modulus caused by segment-segment

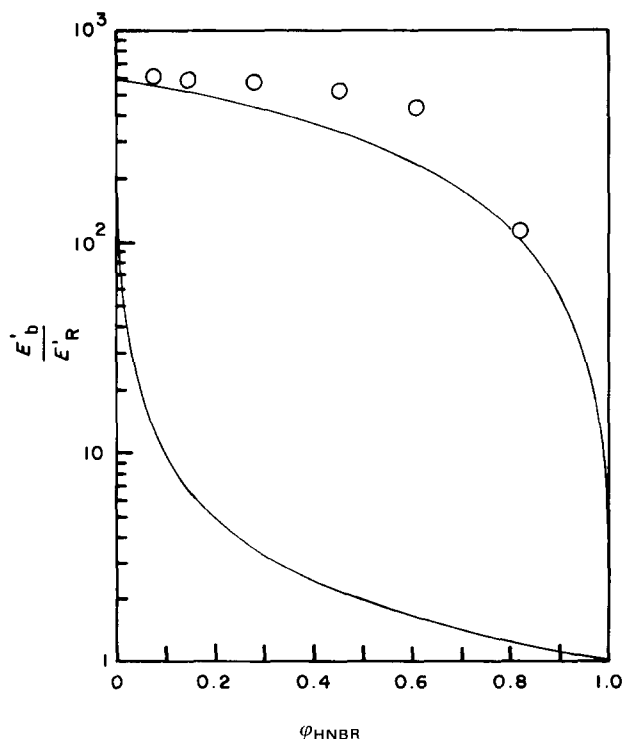


Figure 8 Dynamic storage modulus prediction at 0°C using parallel (upper curve) and series (lower curve) phase connectivity. E'_b and E'_R , storage modulus of blend and rubber, respectively, and ϕ is the volume fraction

interactions. In other miscible blends one observes values intermediate between the limiting values predicted by these simple mechanics models. Although these and other more sophisticated versions have been proposed for heterogeneous blends and composites, Takayanagi and coworkers extended them to include molecularly dispersed systems¹⁴. Modulus variation with composition at constant temperature is significantly different from PVC/NBR compatible blends where microheterogeneities were detected²³. In the work of Jordan and coworkers²³ the transition from the glassy to soft component modulus was evident (matrix inversion) when Kerner's and Nielsen's models were used to analyse data. The fact that our data cannot be fitted to the simple mechanics model is an indication that the blends are homogeneous. As to the origin of the molecular interactions leading to miscibility, it may be traced to the presence of a proton donor (PVC) and a proton acceptor (CN group) present in this system²⁴. Another possibility would be dipole-dipole interactions proposed by Huh and Karasz to explain miscibility in CPVC/NBR blends²⁵. A solubility parameter scheme proposed by Coleman and coworkers²⁶ and applied to the NBR/PVC blend could also predict the range of AN contents required to obtain miscibility. Relevant published work by Zakrzewski²⁷ indicates that the AN content to obtain miscibility at all blend compositions lies within 23–45 wt%. These findings were essentially confirmed by Huh and Karasz²⁵.

The scheme in essence is based on matching the solubility parameters of the two components by varying the AN content in the copolymer. The results of such a calculation for the present system are summarized in Figure 9. In Figure 9a the solubility parameter of HNBR is plotted as a function of the $-\text{CH}_2-\text{CH}(\text{CN})-$ content. The extreme values refer to polyethylene and polyacrylonitrile. Relevant molecular data were obtained from ref. 26. From this plot it is seen that the solubility parameters of the two components coincide at 38.5 wt% AN where the horizontal line at $\delta_{\text{PVC}} = 9.9 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ intersects the curve giving δ_{HNBR} . Assuming that the interaction parameter χ may be expressed by²⁸

$$\chi = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (4)$$

one obtains at this composition $\chi = 0$.

Hence, also taking into account that the components are complementary dissimilar the system should be miscible. In Figure 9b a composition range of the copolymer may be predicted to obtain miscibility, by combining equation (4) with the critical value of the interaction parameter χ_c given by²⁸

$$\chi_c = \frac{1}{2} (N_A^{-1/2} + N_B^{-1/2})^2 \quad (5)$$

where N_i is equal to the degree of polymerization of component i in terms of the molar volume of the smallest repeat unit, $V_r = 42.4 \text{ cm}^3 \text{ mol}^{-1}$. For the present system $\chi_c = 2.26 \times 10^{-3}$. Therefore, as seen in Figure 9b, for those copolymer compositions where $\chi < \chi_c$ one obtains a miscibility window defined by the intersection of the horizontal line at $\chi_c = 2.26 \times 10^{-3}$ and the parabolic curve calculated using equation (4). From this figure and the above condition for miscibility it is predicted that an AN content of 35–42 wt% in the copolymer is required for miscibility. The range of AN content is predicted to be more narrow than obtained by the experiment²⁷. This range however is determined by the

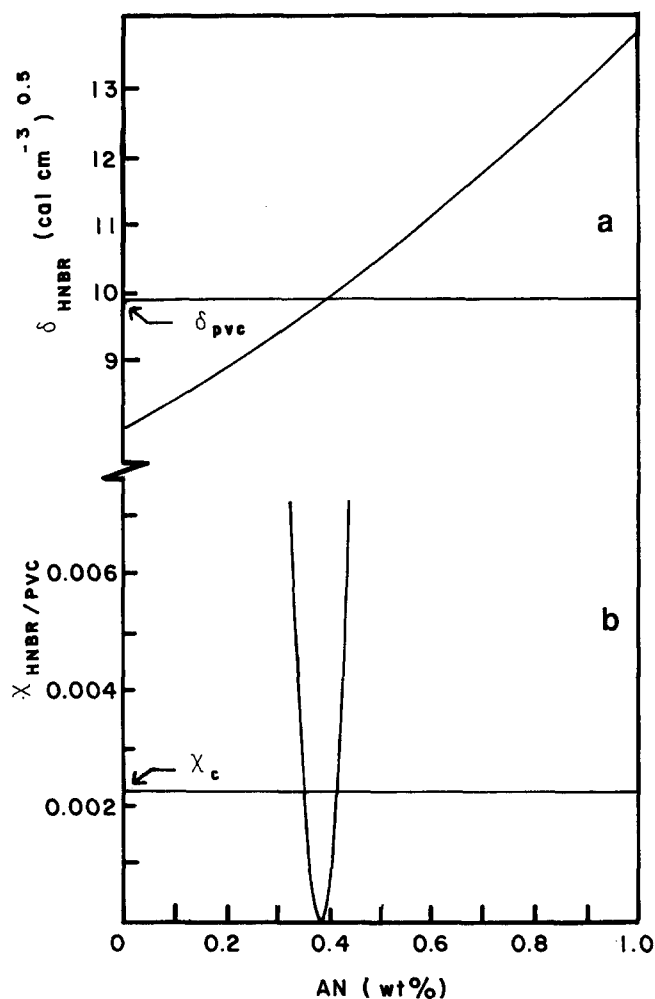


Figure 9 Miscibility prediction of blends: (a) a plot of calculated solubility parameter for HNBR as a function of AN content. (b) Calculated values of χ for HNBR/PVC blends

χ_c used. In ref. 26, evidence is presented that, in blends where moderate interactions are present, it is justified to use a higher χ_c value (0.02). This considerably widens the miscibility window, thus substantiating this predictive scheme. Copolymer-copolymer miscibility theory predicts²⁵ a wider miscibility window at $\chi_c = 0.002$. The results, however, using the two schemes cannot be simply compared since different constants and different assumptions have been used. Characteristically, the former scheme ignores 'repulsion' effects. One should also bear in mind that in the work of Huh and Karasz²⁵ the constants used were obtained by the analysis of experimental data.

To conclude, the HNBR/PVC blend is miscible and there is no evidence for the existence of microheterogeneities detected in the closely related NBR/PVC compatible blends. Moderately strong intermolecular interactions were observed affecting viscoelastic relaxations and tensile properties. As to the reason for improved

miscibility, one of the referees suggested that solvents may have been responsible for this differentiation. A definitive clue could be drawn if samples prepared by melt mixing were available for comparison and/or films cast using different solvents (' $\Delta\chi$ effect') were also studied. This could be the object for a future report. It is tentatively suggested that since hydrogenation does not greatly alter the polarity of NBR, the reason for the improved miscibility of HNBR vs. NBR may be traced to the more extended *trans*-1,4 chain conformation obtained by hydrogenation. This may interact more effectively with the PVC component.

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REFERENCES

- 1 Utracki, L. A. *Int. Polym. Process.* 1987, **2**, 3
- 2 Rowatt, R. J. *Polym. Mat. Sci. Eng.* 1990, **63**, 614
- 3 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1979, p. 339
- 4 Rudolph, H. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 57
- 5 Emmett, R. A. *Ind. Eng. Chem.* 1944, **36**, 730
- 6 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1979, p. 322
- 7 Rempel, G. and Azizian, H. Polysar Ltd. US Patents 4464515 and 4503196
- 8 Nippon Zeon Co. Ltd., Ger. Offen 2913992
- 9 Hayashi, S., Sakakida, H., Oyama, M. and Nakagawa, T. *Rubber Chem. Technol.* 1991, **64**, 534
- 10 MacKnight, W. J., Karasz, F. E. and Fried, J. R. 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 1, Ch. 5
- 11 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967, p. 426
- 12 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967, p. 328
- 13 Matsuo, M., Ueda, A. and Kondo, Y. *Polym. Eng. Sci.* 1970, **10**, 253
- 14 Takayanagi, M., Harima, H. and Iwata, Y. *Memoirs Fac. Eng. Kyushu Univ.* 1963, **23**, 57
- 15 Matsuo, M., Nozaki, C. and Jyo, Y. *Polym. Eng. Sci.* 1969, **9**, 197
- 16 Fukumori, K., Sato, N. and Kurauchi, T. *Rubber Chem. Technol.* 1991, **64**, 522
- 17 Fox, T. G. *Bull. Am. Phys. Soc.* 1965, **1**, 123
- 18 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493
- 19 Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* 1984, **22**, 307
- 20 Pugh, C. and Percec, V. *Macromolecules* 1986, **19**, 65
- 21 Kalfoglou, N. K. *J. Polym. Sci., Polym. Phys. Ed.* 1982, **20**, 1259
- 22 Kallitsis, J. K. and Kalfoglou, N. K. *Angew. Makromol. Chem.* 1987, **148**, 103
- 23 Jordan, E. F. Jr., Artymyshyn, B. and Riser, G. R. *J. Appl. Polym. Sci.* 1976, **20**, 2757
- 24 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New York, 1979, p. 206
- 25 Huh, W. and Karasz, F. E. *Polym. Mat. Sci. Eng.* 1989, **60**, 792
- 26 Coleman, M. M., Serman, C. J., Bhagwagar, D. E. and Painter, P. C. *Polymer* 1990, **31**, 1187
- 27 Zakrzewski, G. A. *Polymer* 1973, **14**, 347
- 28 Krause, S., 'Polymer Blends' (Eds. D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 1, Ch. 2