

Thermodynamic and Structural Properties of Acrylonitrile–Butadiene Rubber / Polyethylene Blends

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Synopsis

Thermodynamics of interaction, adhesive properties, and the structure of acrylonitrile–butadiene rubber/low density polyethylene blends have been investigated. Enthalpy and entropy components of interaction parameters supporting an incompatibility of studied systems and a possibility of highly organized structure formation on the phase interface were determined by inversion gas chromatography. The formation of highly organized structures on the interface is made possible by a local diffusion of polybutadiene fragments into polyethylene phase. That is why acrylonitrile microblocks are oriented. By this manner adhesion between rubber and polyethylene phases is enforced and simultaneously a number of morphological changes take place.

INTRODUCTION

Polyethylene is widely used in the rubber industry as a rubber modifier, e.g., to reinforce semiproducts or to improve dielectrical properties of rubber goods. The presence of noncrosslinked polyethylene in the crosslinked rubber causes, however, an increase of the permanent set values of vulcanizates based on isoprene, butadiene, and methylstyrene–butadiene rubbers. Blends of polyethylene with acrylonitrile–butadiene rubber are an exception. That is why it would be important to find their structure and the adhesion between both the components. For the thermodynamics affinity has an decisive influence on the structure of polymer blends, the thermodynamics of an interaction between polyethylene and acrylonitrile–butadiene rubber has been investigated. Interaction parameters were determined by inversion gas chromatography applied to polymers first by Guillet.¹⁻³

EXPERIMENTAL

Materials

Polyethylene. Low density polyethylene with a density of 893 kg m^{-3} , a flow temperature of 112°C , and a melt index of $2 \text{ g (10 min)}^{-1}$ is sold in the USSR.

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Acrylonitrile-Butadiene Rubbers Sold in the USSR.

Type	Acrylonitrile content	Mooney viscosity ML(1 + 4) at 100°C
SKN-18	18%	60
SKN-26	26%	70
SKN-40	40%	80

Isoprene Rubber. SKI-3 is a Ziegler type of *cis*-1,4-polyisoprene with *cis*-1,4 addition content of 96% and Mooney viscosity of 70 ML(1 + 4) at 100°C sold in the USSR.

Methylstyrene-Butadiene Rubber. SKMS-30 with methylstyrene content of 30% and Mooney viscosity of 60 ML(1 + 4) at 100°C is sold in the USSR.

Preparation of Blends and Vulcanizates

Polymer blends were mixed on a laboratory mill at 120°C. The mix formulation was rubber (100 parts), stearic acid (1.0 phr), zinc oxide (5.0 phr), N 330 carbon black (30 phr), sulfur (1.0 phr for isoprene rubber, 1.5 phr for acrylonitrile-butadiene rubber, and 2.0 phr for methylstyrene-butadiene rubber), 2-mercaptobenzothiazole (1.0 phr for acrylonitrile-butadiene rubber and 2.0 phr for isoprene and methylstyrene-butadiene rubbers), polyethylene, variable.

Polymer blends were cured 45 min at 143°C in an electrically heated laboratory press. Before testing, vulcanizates were left to mature 10 days at a temperature from 20 to 25°C.

Determination of Interaction Parameters

Interaction parameters χ_{23}^+ between polyethylene and rubber were determined by inversion gas chromatography on a Cvet-102 apparatus. *N*-octane was used as a sorbate. The experimental procedure used as well as the calculation of interaction parameters has been completely described in our recent publications.^{4,5}

According to the temperature dependence of the χ_{23}^+ parameter enthalpy $\chi_{23(H)}^+$ and $\chi_{23(S)}^+$ were determined:

$$\chi_{23(H)}^+ = -T \frac{\partial \chi_{23}^+}{\partial T}$$

$$\chi_{23(S)}^+ = \chi_{23}^+ - \chi_{23(H)}^+$$

Determination of Acrylonitrile-Butadiene Rubber Orientation on the Phase Interface

An orientation of acrylonitrile-butadiene rubber (NBR) chains on the phase interface was determined by chromatography.⁶ NBR was spread on a polyethylene powder (particle size of 200 μm) from toluene solution as a stationary phase. From the tenable volume of methanol Gibbs energy ΔG_a , enthalpy ΔH_a , and entropy ΔS_a , were calculated.⁷

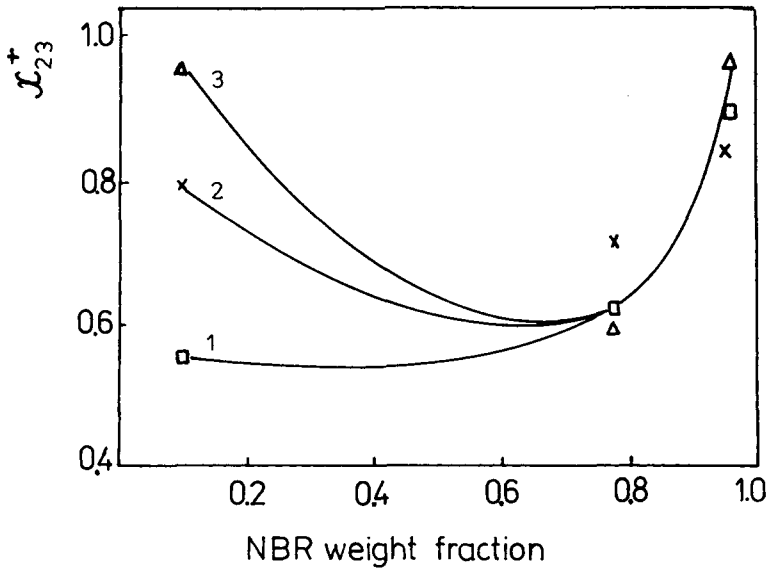


Fig. 1. Influence of temperature [(1) 115°C; (2) 125°C; (3) 135°C] on the concentration dependence of χ_{23}^+ parameter for NBR (SKN-18)/PE system.

Determination of a Degree of Polyethylene Crystallinity

A degree of polyethylene (PE) crystallinity was determined by inversion gas chromatography on the base of the temperature dependence of the *n*-octane specific retention volume on PE or PE/NBR blend packing.⁸ Two step measuring by the EMV-100 L electron microscope was carried out with a carbon-chrome feed at a magnification of 17,000.

Determination of NBR / PE Adhesion

NBR/PE adhesion was measured as a force needed to the mechanical destruction of an NBR/PE joint⁹ and expressed as a resistance *R*, in N m^{-1} . Test pieces with a joint were stressed at a room temperature on a Instron type tensile testing machine (2001-R-05, USSR made). The tensile rate was 60 mm min^{-1} .

RESULTS AND DISCUSSION

Thermodynamics of NBR / PE Interaction

Figure 1 shows a concentration dependence of χ_{23}^+ parameter for SKN-18/PE interaction. Positive values of χ_{23}^+ indicate an incompatibility of both the components over the entire concentration range.

For SKN-26/PE blends at 0.73/0.23 weight ratio, the value of χ_{23}^+ is also positive, about 0.2.

At a weight ratio SKN-18/PE greater than 0.5, the χ_{23}^+ value is practically independent of temperatures, i.e., the $\chi_{23(H)}^+$ value is close to zero, but at a weight ratio SKN-18/PE smaller than 0.5, the temperature dependence is significant and the $\chi_{23(H)}^+$ value is greater than zero. At the weight ratio

TABLE I
Values of $\chi_{23(S)}^+$ Parameter for NBR/PE Systems

Polymer blend	Weight ratio	Temperature of mixing (°C)		
		115	125	135
SKN-18/PE	0.90/0.10	0.88	0.83	0.98
SKN-18/PE	0.74/0.26	0.62	0.72	0.58
SKN-18/PE	0.10/0.90	9.70	10.09	10.49
SKN-26/PE	0.73/0.27	0.22	0.16	0.23

SKN-18/PE = 0.1/0.9, $\chi_{23(H)}^+ = -9.52$. So a strong temperature dependence of the χ_{23}^+ parameter was found first, as far we know in an incompatible system, though it was registered more times in compatible systems.¹⁰⁻¹²

Enthalpy of mixing is interconnected with a change of internal energy and volume during a mix formation ($h_x = \Delta u + p\Delta v$). A negative value of the enthalpy parameter $\chi_{23(H)}^+$ is an evidence either of the strong interaction among miscellaneous molecules in a mix or of reinforcing of a system. For there is only a little probability of a component interaction, it is more probable to propose reinforcing of a system during mixing of components that is also in accordance with the $\chi_{23(S)}^+$ parameter values shown in Table I.

The values of the $\chi_{23(S)}^+$ parameter confirm negative noncombinatory loading of mixing entropy [$\Delta S = f(-X_S)$]. That means the structure in an NBR/PE system may be more regular than that in the components. A higher regularity of the structure in incompatible systems may be an effect of a residual association of macromolecules in the blend, i.e., a consequence of a degree of regularity increases in short distances. Such a possibility in a incompatible system of polystyrene homologues has been shown.¹³

By this manner it is possible to conclude from thermodynamic data a self-association ability of the components in incompatible NBR/PE systems

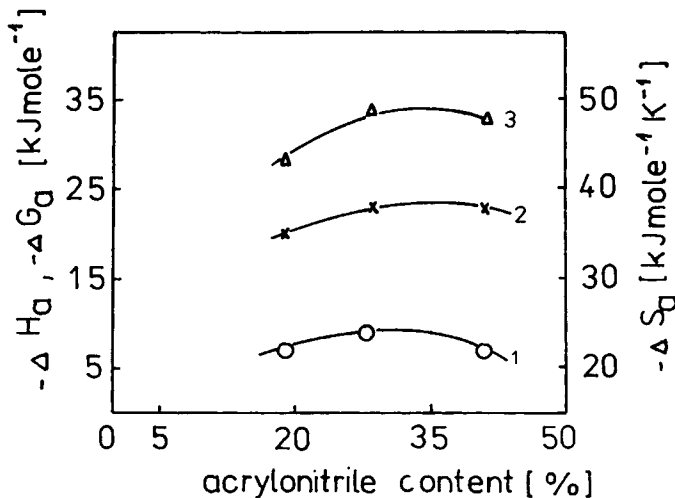


Fig. 2. Dependence of ΔG_α (1), ΔH_α (2), and ΔS_α (3) on the content of nitrile groups in NBR at the adsorption of methanol.

and a formation of highly organized structures on the phase interface. In order to demonstrate an oriented surface layer of NBR on PE particles, the adsorption of methanol on thin layers of NBR has been investigated. Figure 2 shows ΔG_a , ΔH_a , and ΔS_a values for methanol plotted against the acrylonitrile groups content in rubber. It can be seen that all the dependences show a maximum which may be an effect of two different factors:

1. By increasing the polar groups content in the rubber, the absorption of methanol must increase too.

2. By decreasing a degree of polar groups organization in rubber layers, the absorption of methanol must decrease. A proposition that the degree of polar groups organization decreases with the increase in polar group content is in accordance with the simultaneous decreases of $\chi_{23(S)}^+$ parameter negative values.

According to Voyuckii and Vakula,⁹ an interface layer is formed on the basis of a penetration of elastomer segments into similar segments of a substrate. Such segments may be microblocks of polybutadiene in the main chain of NBR, but also pendent branches formed by 1,2-addition; according to Dogadkin et al.,¹⁴ their content in SKN rubbers is about 10%. It is possible to propose that acrylonitrile microblocks would be displaced from the PE phase and would form on its surface a layer oriented by some order. If an ability of polybutadiene microblocks to the local diffusion is decreased with increasing acrylonitrile content in rubber,⁹ the ratio of highly organized structures in rubber layer which is in a contact with PE is decreased too.

Adhesion of NBR to PE at Doubling

Figure 3 shows that the adhesion of rubbers to PE is very low at a doubling temperature of 20°C. Increasing the doubling temperature, the adhesion

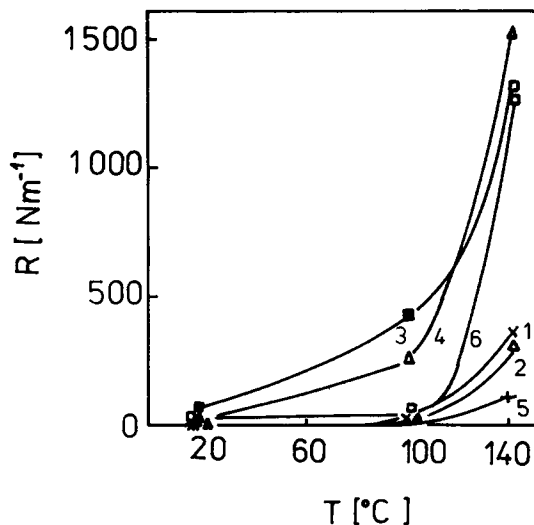


Fig. 3. Influence of doubling temperature on the adhesion of PE to the rubbers: (1) BR (SKD); (2) IR (SKI-3); (3) NBR (SKN-18); (4) NBR (SKN-26); (5) NBR (SKN-40); (6) MSBR (SKMS-30).

TABLE II
Values of Angle of Melted PE Drop on a Rubber Surface

Type of rubber	Angle of contact at wetting (°)
IR (SKI-3)	108
MSBR (SKMS-30)	105
NBR (SKN-18)	83
NBR (SKN-26)	79

resistance values increase, particularly when the doubling temperature is higher than that of melting of PE.

The mechanical strength of adhesion bonds is influenced besides other factors by an interface contact area which is determined especially by wettability. It was evaluated as an angle of melted PE drop on a rubber sheet.¹⁵ Table II shows the results. From these it is clear that angle values for nitrile rubbers are smaller than those for isoprene and methylstyrene-butadiene rubbers. As can be seen, a great wettability of NBR surface by PE and the presence of an oriented layer of acrylonitrile microblocks on NBR/PE interface cause relatively strong adhesion of PE to SKN-18 and also to SKN-26. This explains results presented in Figure 3.

Structure of NBR / PE Blends

The overmolecular structure of rubber/polyethylene blends is formed under the effects of the following factors:

(a) During mixing of polymers, interdiffusion of macromolecules or their fragments determined by thermodynamic compatibility of components takes

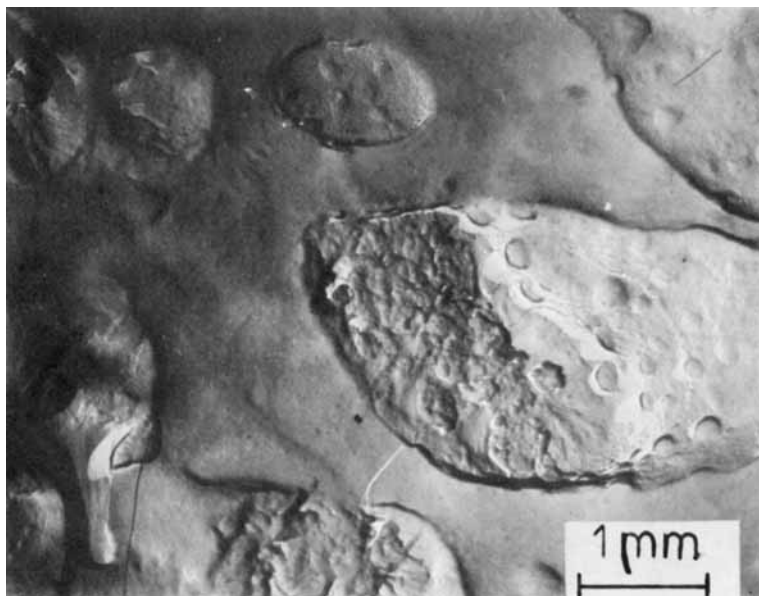


Fig. 4. Photomicrograph of unfilled NBR/PE blend vulcanizate (SKN-18/PE = 0.83/0.17).

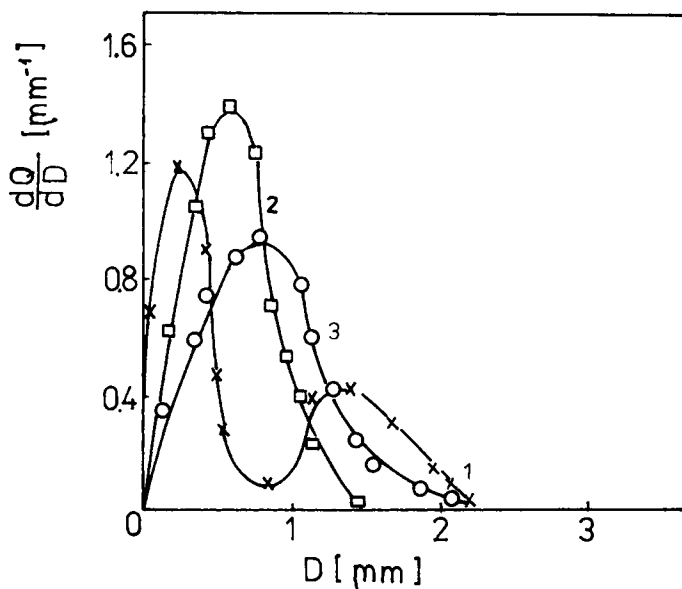


Fig. 5. Character of PE particle size distribution when PE is mixed with the rubbers: (1) NBR (SKN-18); (2) IR (SKI-3); (3) MSBR (SKMS-30); rubber/PE = 0.83/0.17.

place; in a thermodynamically incompatible system interdiffusion takes place only on the phase interface.

(b) For surface tension values for polymers in the contact zone which are similar, it is probable that a self-emulsification takes place.¹⁶

(c) During cooling (transfer from mixing and cure temperatures to room one) a process of component separation combined with crystallization of PE takes place.

From these points of view it will be useful to discuss results obtained by electron microscopy. Figure 4 shows that overmolecular structure of SKN-18/PE blend is characterized by higher organization in the rubber phase contacting PE one. Unlike blends of nonpolar rubbers (e.g., isoprene or methylstyrene-butadiene rubbers) with PE, where PE particle distribution has a monomodal character, blends of SKN-18 with PE are characterized by bimodal form of PE particle distribution (Fig. 5). Formation of large particles of PE results from the distribution of components at mixing of incompatible polymers. Small particles are formed probably in the area of the segmental solubility of polybutadiene microblocks on NBR (SKN-18). An arising emulsification layer is stabilized by the orientation of the rubber acrylonitrile groups on the PE surface.

Temperature dependences of the *n*-octane specific retention volume on PE and SKN-18/PE blend packing (Fig. 6) as well as decreases in melting temperatures prove the diminution of PE crystals. As is evident, by increasing the rubber content in a polymer blend, the melting temperatures of PE is decreased. The fact that the melting temperature of a crystalline component is decreased in a blend with an incompatible amorphous polymer is very interesting, for it has been mentioned only several times.^{10,17} It can be elucidated¹⁸ on the basis of morphological changes influenced by the presence of the amorphous polymer component which may cause defects in the crystal

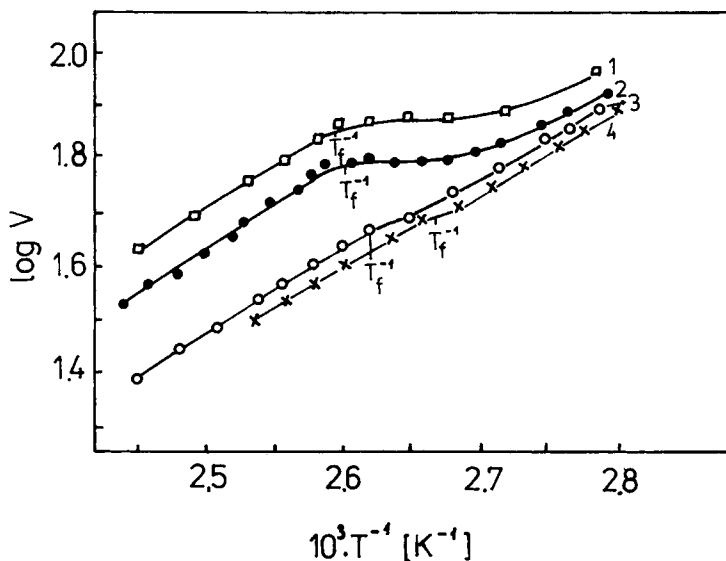


Fig. 6. Temperature dependence of *n*-octane specific constant volume for PE (1) and for PE/NBR (SKN-18) blends of components weight ratio 0.9/0.1 (2), 0.27/0.73 (3), and 0.1/0.9 (4).

lattice and a diminution of a crystal size. The presence of the amorphous component influences also kinetics of PE crystallization. Its degree is decreased from 63% to 3%.

CONCLUSION

An orientation of acrylonitrile microblobs on particles of PE caused by a local diffusion of polybutadiene fragments reinforces the phase interface in NBR/PE blends and simultaneously causes morphological changes in PE.

Interaction of the incompatible components in a rubber/PE blend determinates its special structure characterized by relatively high values of mechanical properties. Thus for instance the addition of 30% PE into a rubber mixture leads to the increase in tensile strength of a vulcanizate by a factor of 1.9 in the case of SKN-18, but only by a factor of 1.3 in the case of much less polar (and less incompatible for this reason) methylstyrene-butadiene rubber (SKMS-30). In both cases, however, the tensile permanent set is significantly decreased.

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Received November 21, 1986

Accepted February 13, 1987