

Heterogeneous Structure of *cis*-Isoprene Rubber and Oligodiene Diisocyanate Blends

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Synopsis

The structural peculiarities of *cis*-1,4-isoprene rubber, oligodiene diisocyanate, and derivative of phenol-formaldehyde resin blends have been studied by WAXS and SAXS methods and electron microscopy. It has been demonstrated that the addition of modifiers and further thermal treatment under conventional curing conditions change considerably the microheterogeneous structure and morphology and contribute to the improvement of the short-range order in the rubber matrix.

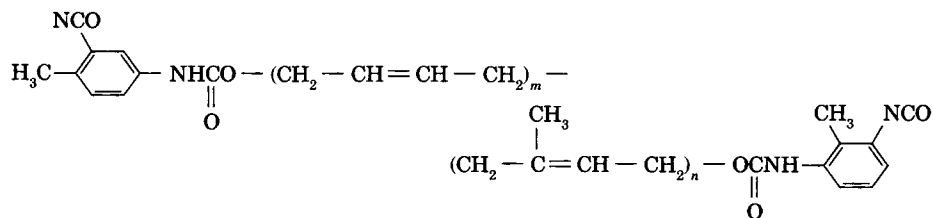
INTRODUCTION

One of the most promising ways of a further improvement of commercial properties of *cis*-isoprene-based rubbers is the addition of modifiers containing oligodienes with polyfunctional end groups. We have shown earlier¹ that the heat stability, heat aging resistance, and thermal oxidation resistance of vulcanizates can be increased by adding oligodiene diisocyanate together with other coagents. It is quite natural to associate such changes of physicochemical properties with the structural modification of blends.

To elucidate the modifying effect of reactive oligomers on the structure of the *cis*-isoprene rubber, these blends have been studied by WAXS and SAXS methods and electron microscopy.

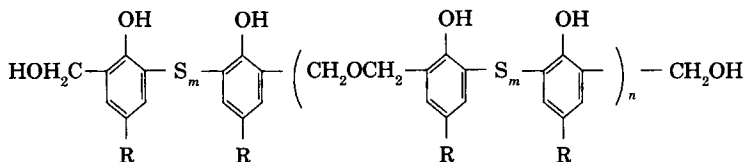
EXPERIMENTAL

Materials. (1) The *cis*-1,4-isoprene rubber (SKI-3) having $M_v = 0.35\text{--}1.3 \times 10^6$. (2) Oligodiene diisocyanate (ODI), obtained by the treatment of oligodiene diol by 2:1 molar excess of toluene diisocyanate (2,4/2,6-isomers mixture 65%/35%). $M_v = 3\text{--}4 \times 10^3$, and *cis/trans*/vinyl percentage is (>80%)/(10–15%)/(5%). Its structural formula is



where $m/n = 4/1$.

(3) The derivative of the phenol-formaldehyde resin PFR having $M_v = 6-8 \times 10^2$ with the structural formula



where $m, n = 1-6$ and R is the hydrocarbon radical, were used as initial components. Blends of the rubber SKI-3 with 5 wt % ODI and 1 wt % PFR were prepared by dissolving the mechanical mixture of components in a common solvent (benzene). Films 0.3 mm thick were casted from 0.04 g/mL solutions. The solvent was evaporated at room temperature in air for 48 h. The residual solvent was removed under vacuum for 6 h at 60°C. Both initial blends and blends thermally treated for 50 min at 143°C (in accordance with conventional curing conditions) were studied.

Methods. WAXS studies were performed with a DRON-2.0 Diffractometer. The scattering intensities were measured by a scintillation detector scanning in 0.2° steps over the range of angles of 3–35°. SAXS studies were performed with a Kratky diffractometer² and a total internal reflection monochromator in the primary beam.³ The scattering intensities were measured in 0.02° steps over the range of angles of 0.04–2.20°. Nickel-filtered copper anode radiation was used for all X-ray experiments. Optimal experimental conditions (cross section of the primary beam, detector slit width, exposure time) were chosen proceeding from the preset distortion values (2–5%) for true profiles.⁴

Experimental values of WAXS and SAXS intensities after the subtraction of background scattering were corrected for the absorption of CuK_α radiation and normalized to the equal intensity of the primary beam according to Ref. 5. The curves for diameter distribution of microregions of heterogeneity were calculated from SAXS data according to the algorithm presented in Ref. 6.

Electron microscopic studies on carbon replicas from fracture surfaces of the samples were performed with a JEM-100C microscope according to a procedure described in Ref. 7.

RESULTS AND DISCUSSION

WAXS curves of initial components are presented in Figure 1. The diffuseness of scattering patterns is indicative of the amorphous structure of these materials. The differences in the scattering profiles of the components are clearly seen from the figure. One intensive diffuse maximum at the scattering angles of 18.4° and 19.2° corresponds to the lateral spacing in the arrangement of macromolecular fragments in SKI-3 and ODI, respectively. The scattering curves for PFR are characterized by two intensive diffuse maxima at the scattering angles of 4.2° and 18.0°. These maxima are associated with the presence of benzene rings in the main chain of PFR. The

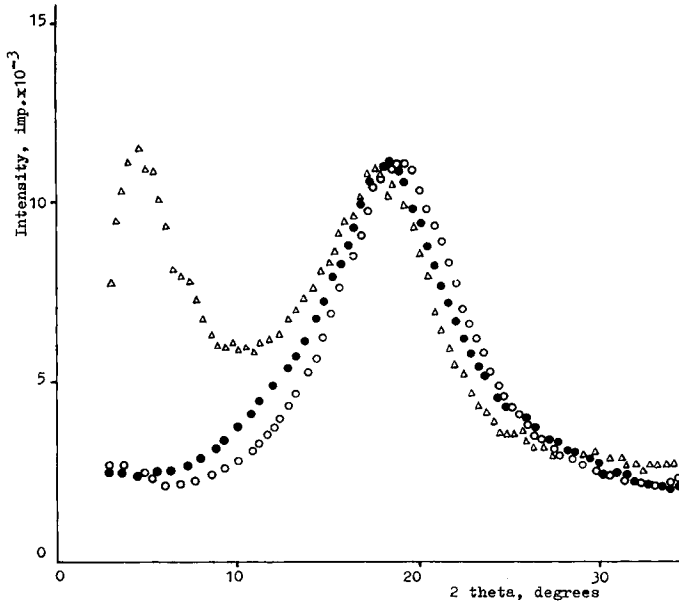


Fig. 1. WAXS curves of blend components: (●) *cis*-1,4-isoprene rubber SKI-3; (○) oligodiene diisocyanate ODI; (△) derivative of phenol-formaldehyde resin PFR.

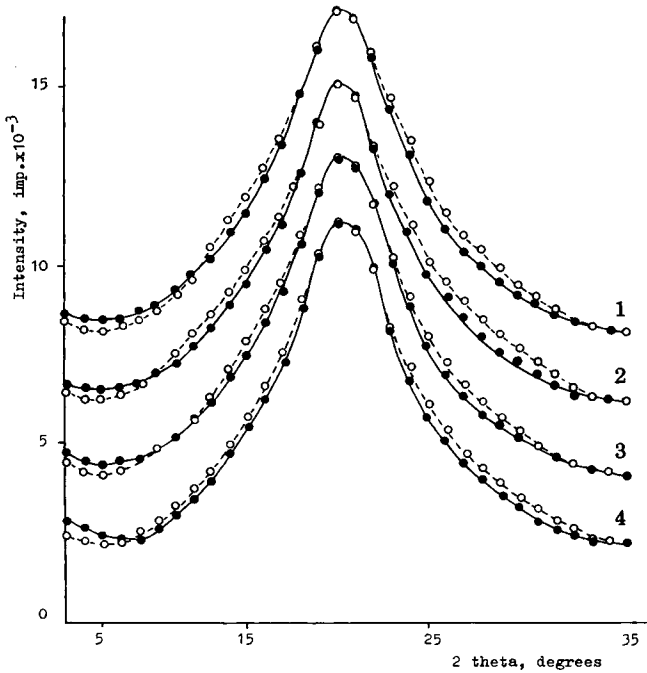


Fig. 2. WAXS curves of the blends under study before (1,3) and after the curing for 50 min at 143°C (2,4): (1,2) binary blend containing 5 wt % ODI and 95 wt % SKI-3; (3,4) three-component blend containing 1 wt % PFR, 5 wt % ODI, and 94 wt % SKI-3 [(●) experimental intensity values; (○) additive intensity values].

first one corresponds to the lateral spacing in the arrangement of macromolecular axes in the plane of benzene rings; the second one, to the spacing in the direction normal to these planes.

WAXS curves of the blends investigated before and after curing are presented in Figure 2. Here experimental intensity values are presented together with additive values calculated from the scattering curves for the initial components assuming that they preserve their structural peculiarities in the blend.⁴ From the comparison of experimental and additive scattering profiles one can see the decrease of the main diffuse maximum half-width observed both for initial and cured blends. The position of this maximum remains unchanged. From this fact one can draw a conclusion that during SKI-3 and ODI blending the perfection of lateral order of molecular fragments in the rubber matrix occurs. The addition of a third component PFR to the blend and further curing do not influence its short-range order.

SAXS curves for pure SKI-3 and its blends are given in Figure 3. Here rather high scattering intensity for the pure *cis*-isoprene rubber is observed in the range of angles near to the primary beam. Such scattering pattern indicative of considerable heterogeneity is not typical for the majority of flexible linear polymers.⁸ As we have demonstrated earlier,⁹ in the *cis*-isoprene rubber the microheterogeneous structure is observed; it is caused by the existence of microregions with a higher or lower degree of order. The diffuseness of SAXS curves presented in Figure 3 is indicative of the polydispersity of regions of heterogeneity and the absence of order in their arrangement.⁴

The comparison of SAXS intensities for pure SKI-3 and its blends demonstrates that the addition of modifiers does not affect considerably the microheterogeneous structure of the rubber matrix. Only a slight reduction of the intensities for the initial angles of scattering is observed. The latter

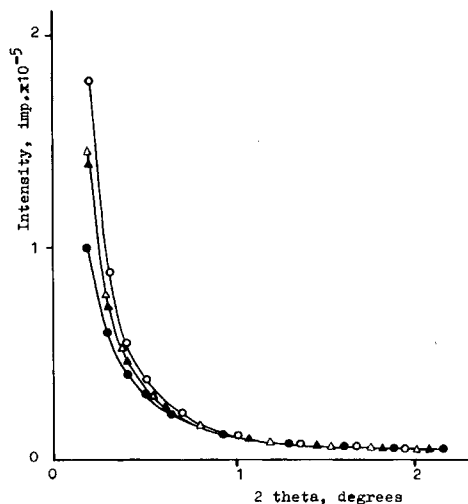


Fig. 3. SAXS curves for SKI-3 (○); cured binary blend (●); three-component blend before (△) and after curing (▲).

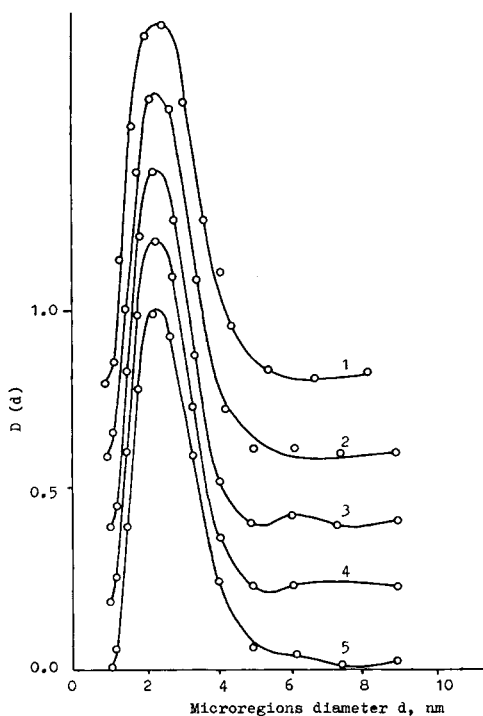


Fig. 4. Diameter distribution functions for microregions of heterogeneity: SKI-3; (1); binary blend before (2) and after curing (3); three-component blend before (4) and after curing (5).

can be associated with the redistribution of sizes of microregions of heterogeneity, viz., with the reduction of large microregion fraction.

As can be seen from Figure 4, where the diameter distribution functions for microregions of heterogeneity are presented, they are characterized by one intensive well-defined maximum and an extended weakly defined wing stretching up to diameter values of some scores of nanometers. The comparison of maximum positions shows that the most probable diameter of microregions of heterogeneity in pure SKI-3 is 2.5 nm, while at the addition of modifiers the values of the most probable diameter are reduced to 2.0 nm. After the curing of blends their microheterogeneous structure is mainly preserved. It should be noted that in all the blends under study the relative fraction of microregions having diameters greater than 5 nm is rather small.

Electron micrographs of replicas from the fracture surfaces of the samples under study were obtained in two different scales. At the first scale level weakly defined globular structures a few micrometers in diameter, randomly distributed in the matrix consisting of microregions of far smaller sizes are observed in the pure SKI-3 rubber [Fig. 5(a)]. The binary blend at this scale level reveals microregions of heterogeneity a few tenths of a micrometer in size, more densely packed as compared with pure SKI-3 [Fig. 5(b)]. The curing of this blend results in considerable change of its morphology, wormlike regions about 0.5 μm in diameter being formed [Fig. 5(c)].

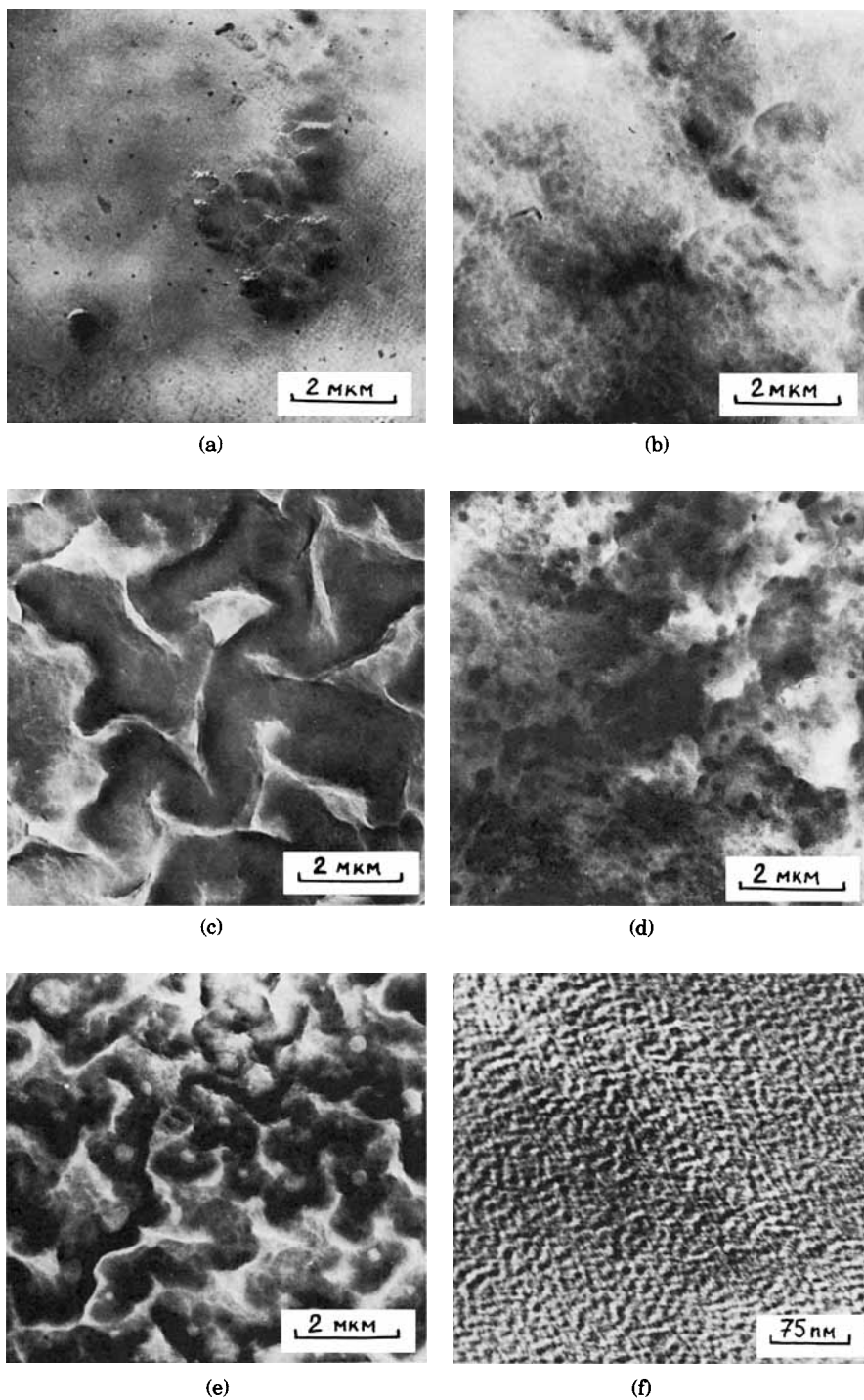


Fig. 5. Electron micrographs of carbon replicas from fracture surfaces of the samples: (a) SKI-3; (b) binary blend before curing; (c) binary blend after curing; (d) three-component blend before curing; (e) three-component blend after curing; (f) SKI-3 (greater magnification); (g) binary blend before curing; (h) binary blend after curing (greater magnification).

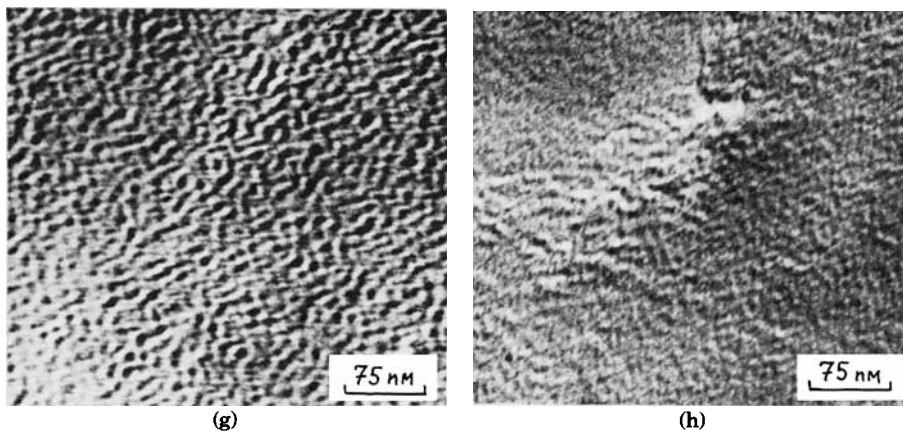


Fig. 5. (Continued from the previous page.)

The three-component blend is characterized by more developed heterogeneity as compared with the binary one. In particular, together with small well-defined microregions, larger, but not so well-defined ones can be observed [Fig. 5(d)]. The curing of such blend results in a structure similar to the structure of the cured binary blend, but the diameter of the corresponding microregions is about two times smaller [Fig. 5(e)].

Micrographs obtained at greater magnification give evidence of anisometric microregions some nanometers in size, i.e., having such sizes which can be measured by SAXS methods [Fig. 5(f)–(h)]. In the binary and three-component blends before the curing the sizes of these microregions are somewhat larger than in pure SKI-3. This fact can be associated with the changes in microstructure of the rubber matrix when modifiers are added. After the curing the sizes of microregions become smaller.

CONCLUSION

Thus, the modification of the *cis*-1,4-isoprene rubber with ODI and PFR contributes to the perfection of the short-range order of molecular fragments in the rubber matrix. The latter is accompanied with the reduction of average sizes of microregions of heterogeneity. The addition of modifiers changes considerably the morphology of blends at the scale level of some microns. The heterogeneity at this structural level becomes higher. The curing of blends results in the reduction of sizes of microregions of heterogeneity. It is to be supposed that the improvement of physicochemical properties of the *cis*-1,4-isoprene rubber observed in practice is associated with the changes mentioned of the polymer structure both at the level of molecular fragments and at the morphological level.

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