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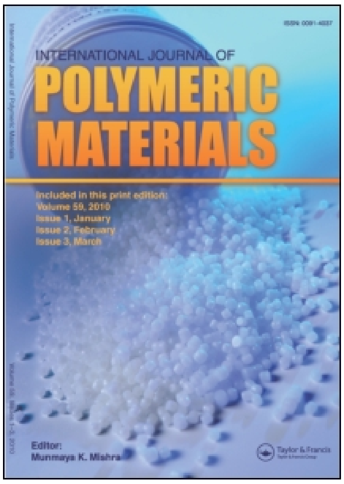

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Stabilization of Phase Structure of Elastomer Blends

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Factors controlling the stabilization of phase structure of elastomer blends are reviewed. The effects of the most important ones are discussed. The roles of; component content, conditions of mixing and vulcanization, nature of crosslinking agents, formation of chemical bonds at interphases, and degree of crosslinking in each phase are presented.

KEY WORDS Elastomer blends, phase structure, stabilization, phase structure control.

RESULTS AND DISCUSSION

Among the main features controlling the structure of cross-linked elastomer blends are the nature of elastomers blended, mode of action of crosslinking agents (including the time of induction period of network formation), formation of chemical bonds between elastomer phases. In the case of incompatible elastomers, structures with phase separation are formed with discrete or continuous phases of one component in the matrix of another one. Two continuous phases can form interpenetrating network structures.

In the case of elastomer blends, the phase structure is usually changed during blend preparation, both before and after its vulcanization. That is why the processing methods have a great influence on structure and properties of vulcanizates from elastomer blends.[1]

The blend of cis-polyisoprene (PI) and chlorobuthyl rubber (ChBR) was one of most suitable systems for the study. We used two crosslinking systems: 1) with high rate and without a noticeable induction period (thiuram with sulfur) and 2) with relatively high rate in the main period but with long induction period (sulfenamide, dithiodimorpholine with sulfur). The blends were prepared on the laboratory mill and vulcanized in the press at 140–150°C under pressure of 20 mPa. The phase structure depends on viscosity ratio of elastomers[2] and their chemical structure. The similarity of the latter (solubility parameters) for the elastomers blended leads to intense dispersing action because of high interaction in the inter-

TABLE I

The influence of the crosslinking system on structure of elastomer blends and their vulcanizates

Blends and its composition	Average diameter of dispersed phase particles (μ) Unvulcanized blend	Vulcanized with sulphenamide	Vulcanized with thiuram
PI/ChBr, 7:3	0.48	1.19	0.82
PChP/ChBR, 7:3	0.70	IPN's*	1.18

*Interpenetrating network structure.

phase layer. This is true for discussed elastomers (16.44 for PI and 15.42 for ChBR in (J/sm^3)$^{1/2}$). Coarser dispersions were noted in blends of polychloroprene (PChR) and ChBR for which these corresponding values are 25.32 and 15.42. The particles of dispersed phase in unvulcanized blends are distributed more homogeneously than in their covulcanizates (Table I).[3]

The main tendency of phase structure change in process of its formation and vulcanization is enlarging of dispersed phase particles. This effect depends mainly on the duration of induction period, i.e. on the time when blend is in a viscous-fluid state.

The growth of ChBR particles is observed for sulphenamide system with long induction period (to 15–20 min). The sizes of dispersed phase in the blend of PChP/ChBR (7:3) grow to such extent that particles after coalescence form the continuous structure.[3]

Dependence of tensile strength of PI/ChBR blends vulcanizates on the blend composition shows maximum for 7:3 content. This maximum coincides with the minimum of the average value of Gibbs energy[4] for the same composition, possibly reflecting the achievement of "critical conditions" for polymer-polymer emulsion formation.[1] The value of the tensile strength maximum depends on the type of crosslinking system used—its value is greater for sulfenamide group as compared with the thiuram one.[4] This difference in vulcanizate structures was confirmed by the investigation of paramagnetic probe mobility in vulcanizates (Figure 1).

The overall picture of vulcanizate structure of PI/ChBR blend has been investigated by estimating the stress relaxation rates of vulcanizates in presence of ozone (Table II).

Thus, phase structure of elastomer blends is changed during blending and vulcanization. Mechanical action at processing leads to coalescence of dispersed phase particles because of microrheological factors at molding; phase morphology of blends depends on duration of induction period of crosslinking, i.e. type of crosslinking systems. The improvement of vulcanizate properties may be achieved by two main factors; i) formation of microheterogeneous systems and ii) use of crosslinking systems which covulcanize the elastomers at the interface boundary.

The phase structure of covulcanizates can be estimated by the change of specific volume at stretching if the elastomer-matrix crystallizes at high elongation. Crystallization is observed when specific volume value sharply decreases. Figure 2 shows the relationship between specific volume change and elongation of covulcanizates

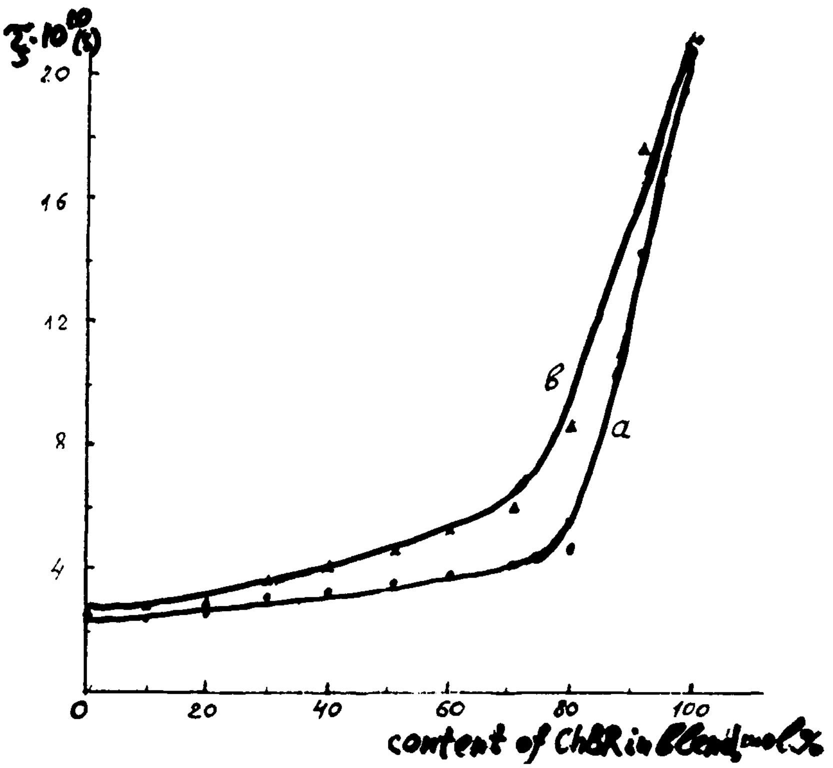

FIGURE 1 The mobility of paramagnetic probe (2,2′,6,6′-tetramethylnitroxil radical) in vulcanizates of PI/ChBR blends with thiuram (a) and sulfenamide (b) in crosslinking systems.

TABLE II

Comparative data on stress-relaxation rate of vulcanizates PI/ChBR blends in ozone medium (ozone concentration in air $5 \cdot 10^{-5}$ mole/l, initial strain—80%, temperature −70°C)

ChBR content in the blend with PI (vol.%)	Relative rate of stress-relaxation	Type of vulcanizate structure
up to 30	low	discrete phase of ChBR
60–80	high	two interpenetrating networks
more than 80	low	discrete phase of PI

of PI-NBR blends. As can be seen, the content of nitrile group in NBR has great influence on such properties of covulcanizates. Note that with an increase of nitrile groups content, i.e. the polarity and uncompatibility of phase in matrix of non-polar elastomer, the interphase interaction in covulcanized blend decreases. If both components of elastomer blend have the ability to crystallize at stretching and can be covulcanized, the difference in their polarity does not prevent the crystallization of covulcanizates. In blends of PI with PChP specific volume decreases on strain induced crystallization. Mode of action of crosslinking agents, and particularly the existance of an induction period and macromolecular modification before cross-

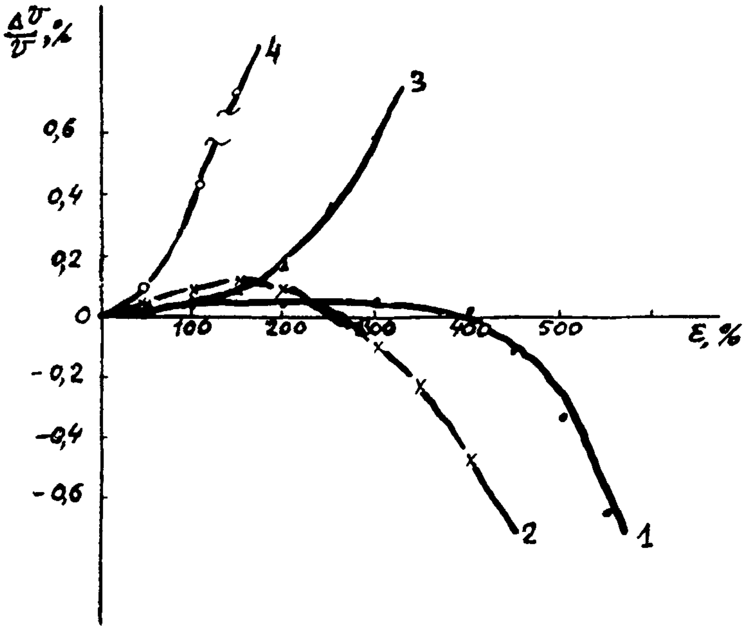

FIGURE 2 Change of specific volume at elongation of vulcanizates of PI (1) and its blends with 20 vol.% of NBR with 18 (2), 26 (3) and 40 (4) mol.% of nitrile groups.

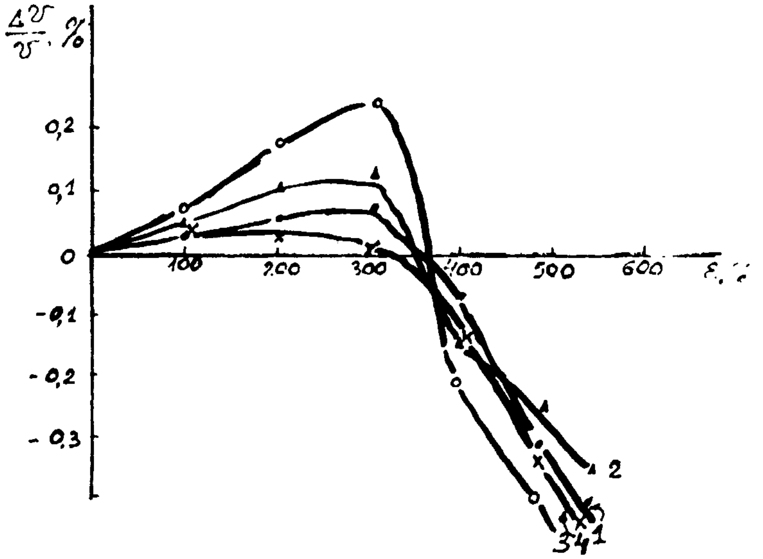

FIGURE 3 Change of specific volume at elongation of vulcanizates of PChP (1) and its blends with 10 (2) and 20 (3) vol.% of ChBR with thiurame and 20 vol.% (4) with sulfenamide as crosslinking systems.

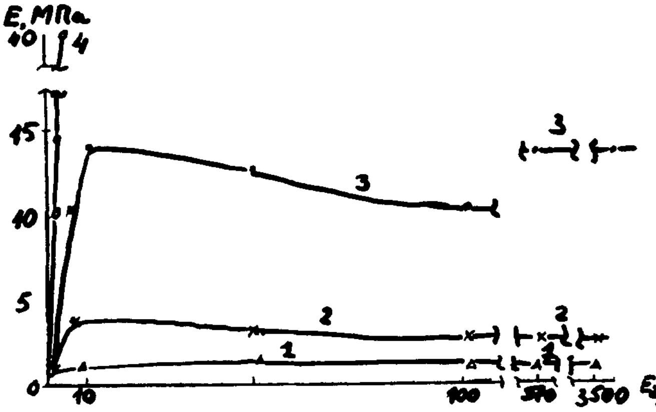

FIGURE 4 Dependence of modulus (E) of blend vulcanizates of NBR with ChBR on phase-moduli ratio (E_2/E_1) and composition of blends in mol.% of NBR to ChBR: 1—8/92; 2—25/75; 3—34/66; 4—44/56.

linking, greatly influence the crosslinks formation between phase particles (ChBR) and matrix (PChP). The use of thiurame and diphenylguanidine (without induction period) and dithiodimorpholine and sulfenamide (with prolonged induction period and macromolecular modification) is the example of such phenomenon (Figure 3). With the first crosslinking system chemical bonds are not formed between phase (ChBR) and matrix (PChP). With the second crosslinking system, however, such bonds are formed and therefore, the specific volume increases are not observed.

One of the important features of covulcanized elastomer blends structures is the evaluation of network density in phases and its role in the properties of covulcanizate. For this purpose the NMR-method is very informative.[5] We used it for estimation of network structures in blend of PI with PB and with ChBR. The crosslinking systems have different induction period for each of elastomers and for their binary blends as well. The rates of crosslinking in the main period of reaction, overall crosslinks density, degree of macromolecular chemical modification before network formation were also different. In a blend of PI-PB the phase of PB was more cross-linked than PI one because of migration of crosslinking agents into PB-phase. At PB content of less than 30 vol.% the increasing of network density in PB-phase is the greatest. With regard to PI, if its content in the blend is less than 30 vol.%, the network density equals that of most PI. At PI content of more than 50 vol.%, the network density in its phase sharply decreases. This effect depends on the time of induction period of crosslinking for each of the elastomers. If the network structure in PI is formed earlier than in PB, the decrease of network density in PI is less. If network is formed without induction period the dependence of network density on elastomer content is insignificant.

In blends of PI-ChBR network density of PI-phase monotonically increases with decreasing PI content in a blend. This reflects the migration of crosslinking agents into PI phase. All these phenomena correlate with changes of tensile strength of such covulcanizates.

Differences in network density of elastomer phases in covulcanized blends mean that such composite has phases with different moduli.[7] The effect of this difference was evaluated on blends of ChBR and NBR (40 mol. % of acryl-nitrile component).[8] The phase of ChBR was selectively crosslinked by zink oxyde, that of NBR—by a large amount of sulfur (35 w.p.). Depending on the time of vulcanization the degree of crosslinking of NBR increased up to levels in hard rubber (ebonite), but that of ChBR did not change significantly. The ratio of dispersed phase modulus (NBR) to matrix modality (ChBR) was changed from 3 to 3500. Large influence of this ratio on the mechanical properties of blend vulcanizates is noted when the level of phase modulus/matrix modulus is ratio 15–20 (Figure 4). That means that below this value, particles of phase are deformed together with matrix, but when this value is about 20, the particles have as hard filler in matrix. Segregation of selectively crosslinked phase at stretching increases in the same range as the phase moduli ratio. This was confirmed by the investigation of specific volume change. The greatest increase of resistance to crack growth was noted with phase/matrix modulus ratio about 3 and dispersed phase content (NBR) in matrix (ChBR) about 25–30 vol. %. Covulcanization of dispersed phase particles with matrix has the positive influence on tensile strength provided the amount of the dispersed phase does not exceed 30 vol. %. In blends with greater amount of NBR in ChBR the phase segregation increases rapidly. That means that covulcanization of phase particles with matrix improve the strength and elongation value of composite only when the system contains discrete particles of a phase in the matrix of another elastomer. This effect depends on values of moduli ratio and has the limit when this value is about 20.

This short review of problems of phase structure stabilization in blends of different elastomers shows that there are some principal features which govern structures of such blends. These include the nature of elastomers, the content of components, conditions of mixing and vulcanization, mode of action of crosslinking agents, formation of chemical bonds at interphase layers, degree of crosslinking of dispersed phase and matrix, and dispersed phase/matrix modulus ratio. All these factors must be considered and accomplished in the preparation of vulcanized blends tailored for specific applications.

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