Hybrid binders in polymer composites. Peculiarities of structure and properties conditioned by micro-phase separation

Yu. S. Lipatov

Institute of Macromolecular Chemistry, Ukr. SSR Academy of
Sciences, 252160, Kiev, USSR

Abstract - To hybrid binders or matrices for polymer composite
materials the following types of multicomponent polymeric sys-
tems may be related: (1) mixtures of two or more linear poly-
mers, thermoplastic hybrid matrics; (2) mixtures of linear and
cross-linked polymers, so-called semi-interpenetrating polymer
networks; (3) interpenetrating polymer networks; (4) polyblock
network polymers; (5) segregated or interconnected networks.
Thermodynamic incompatibility of components arises in hybrid
binders during their curing or quenching which causes incom-
plete microphase separation in the system. Hybrid matrix
within which the segregation of microvolumes of constituent
components has occurred, owing to incomplete microphase separa-
tion, may be considered as a self-reinforced (filled) disperse-
-reinforced system, whereas the size, properties and distribu-
tion of the microregions of microphase separation (quasi-par-
ticles of filler) is determined by a phase diagram of a binary
or multicomponent system, conditions of system transition
through the binodal and spinodal and by the nucleation or spi-
nodal mechanisms of phase separation.

1. HYBRID BINDERS: DEFINITION

The necessity of improving fundamentally the physico-chemical and mechanical
properties of polymer composites demands a new approach to the development
of binders forming the matrix of the composite. Binders of the second genera-
tion should represent polymer composite materials. This work deals with the
first attempt to formulate the notion of hybrid binders and to substantiate
the attribution of one or the other polymer system to hybrid binders (ref. 1).
It is essential also to determine the general regularities of their structure
discriminating them from traditional binders (including multicomponent ones),
as it is well-known that the majority of thermoreactive binders are multicom-
ponent mixtures on the basis of reactive oligomers, chain extenders, cross-
linking agents, etc. The application of polymer-oligomer composition, repre-
senting one-phase solutions of a linear polymer in an oligomer, capable of
forming a three-dimensional network at curing (refs 2, 3), also relates to
this case, as well as interpenetrating polymer networks and other systems.
We relate systems of the following types to hybrid binders or matrices for
polymer composites on the basis of the principle discussed below: 1) Mixtures
of two or more linear polymers - thermoplastic hybrid matrices; 2) mixtures
of linear and network polymers, so-called semi-interpenetrating polymer net-
works; 3) interpenetrating polymer networks (refs 4, 5); 4) polyblock network
polymers; 5) segregated or interconnected networks (ref. 6), and other feasi-
ble systems characterized by a common distinctive feature.

Thermodynamic incompatibility of components arises in hybrid binders during
their curing or cross-linking reaction and the formation of network fragments,
which causes incomplete microphase separation of the system. Incompleteness
of the microphase separation process causes the development both of micro-
phase separation regions of variable composition in the hybrid matrix and
transition or interphase layers between the co-existing microregions. The
system with incomplete microphase separation is not in the state of thermo-
dynamic equilibrium (ref. 7). A segregated structure develops in the matrix
as a consequence of these processes with a complex of specific properties:
appearance of regions with different density, composition and mechanical pro-
perties, appearance of internal interphase boundaries, etc. Hence, we can
give the following definition: a hybrid polymer matrix, wherein segregation

of microvolumes of constituent components has occurred owing to incomplete microphase separation, may be considered as a self-reinforced (filled) or disperse-reinforced system, wherein the size, properties and distribution of the regions of microphase separation-quasiparticles of filler are determined by a phase diagram of a binary or multicomponent system, conditions of system transition through the binodal and spinodal, and by the mechanism of phase separation (nucleation or spinodal) (ref. 1).

Thus, hybrid matrices may really be considered by their structure as composite materials with specific mechanical behaviour and a significant role of the interphase layers on the properties of the matrix by analogy with filled polymers. Accordingly, it is necessary to introduce and consider two groups of interphase phenomena in the case of polymer composites on the basis of hybrid matrices: at the interface of co-existing phases in the hybrid matrix, and at the boundary between the dispersed or reinforcing filler and the components of the hybrid matrix.

An essential feature of structure formation in hybrid matrices is the fact that the microphase structure develops directly in the course of chemical cross-linking and the formation of a network structure. Both processes, i.e., microphase separation and cross-linking, occur simultaneously, although microphase separation starts in the majority of investigated cases long before the system reaches the gel-point, i.e. final chemical formation of the system does not occur under homogeneous but proceeds under heterogeneous conditions of a system partly separated into microphases of variable composition. It has been shown for a series of mixtures of oligoisoprene hydrazide and different epoxy resins, polyblock network polymers, semi-interpenetrating and interpenetrating polymer networks, rubber-oligomer composites, polyurethane urea on oligobutadiene, ion-bearing polyurethane ureylenes (refs 5, 7-14), etc., that the morphology and structural specific features of the developing systems and, consequently, their properties depend greatly on the rate of the chemical reaction, because the latter causes retardation of phase separation owing to an increase in viscosity, in the diffusion coefficient as well as in the cross-linking density of the system. The comprehensive experimental material enables us to draw the conclusion that the degree of segregation, characterizing quantitatively the degree of microphase separation, depends on some competing factors, i.e. on the rate of three-dimensional network formation and rate of interdiffusion of the components, specifying the development of microphase separation regions. As a result, microphase separation in these systems is far from being complete. Cross-linking establishes nonhomogeneity of the component distribution, determined by thermodynamic incompatibility, and hampers the process of phase separation and attaining the equilibrium. Correspondingly, microphase separation of thermoplastic hybrid matrices (material formation) occurs at a drop in temperature (for systems with UCST) and is determined by the rate of transition via the spinodal and binodal, i.e. by the conditions of freezing of thermodynamically non-equilibrium structures.

Thus, it is possible to consider that the theoretical basis for developing hybrid binders is the thermodynamic theory of compatibility of polymer-polymer systems and the theory of phase separation - the theory of nucleation and spinodal decomposition (refs 15, 16).

2. DEGREE OF COMPONENT SEGREGATION IN HYBRID BINDERS

The basic problem arising in the formation of hybrid matrices is determination of a relationship between the conditions of their formation and the microphase structure. The latter structure may be characterized by one fundamental parameter, viz., the degree of segregation, which may be determined experimentally by two independent methods. The small-angle X-ray scattering (SAXS) permits to determine the degree of segregation as

$$\alpha = \Delta\overline{\rho}^2/\Delta\overline{\rho}_C^2 = \Delta\rho^2/\phi(1-\phi)(\rho_1-\rho_2)^2$$

where $\Delta\overline{\rho}^2$ is the mean square electron density fluctuation calculated from the absolute values of the SAXS; $\Delta\overline{\rho}_C^2$ is the theoretical estimation of the mean square electron density fluctuation, made assuming microphase separation at the level of pure components; ϕ is the volume fraction of one component, and ρ_1 and ρ_2 are the electron densities (ref. 17) of the two components, respectively.

A more graphic scheme of the microphase separation process and determination of the degree of segregation may be presented as follows. It is based on an estimation of the coefficient of mechanical losses. As is known, its maximum is in the area of relaxation transitions and changes experimentally at glass temperature more than by an order of magnitude. It is known also that one of the criteria of component compatibility in a binary or multicomponent oligomer system is the presence of several glass temperatures.
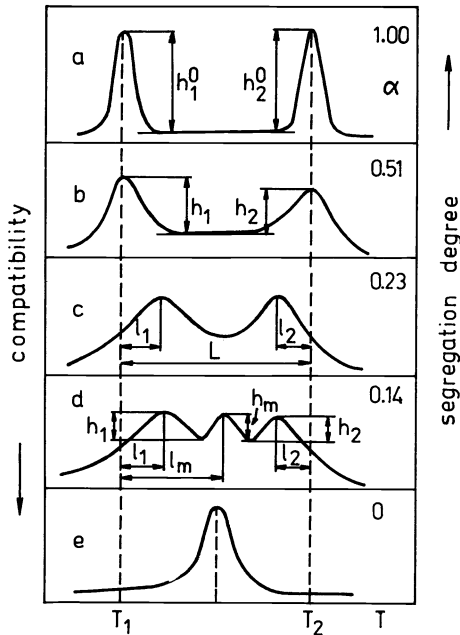

Fig. 1. Schematical represen-
tation of the temperature
dependences of mechanical
losses with a different
degree of component segre-
gation and compatibility

Let us consider schematically the temperature dependence of mechanical losses in a two-phase polymer system with a different degree of component segregation (compatibility) (ref. 18; Fig. 1). The diagram is idealized and can be described as follows. Case $\underline{a}$ corresponds to a mixture of two components where the phases are clearly separated and each one is characterized by its own glass temperature (by maximum losses). An increase in the component interaction and their mixing causes a decrease in the maximum of their absolute value and convergence of the maxima $\underline{b}$ and $\underline{c}$. The compatibility level obtained after a stable interphase region has been formed is characterized by a glass temperature T_m between T_1 and T_2. Eventually, an increase in the interaction gives rise to an extensive maximum which tends to converge on attaining compatibility on the molecular level, i.e. by the formation of a one-phase system. This type of dependence may be found in hundreds of works investigating viscoelastic properties of polymer composites. A reverse sequence of changes will be observed accordingly in the transition from the initial one-phase system to a two-phase one with incomplete microphase separation. An analytical characteristic of the degree of segregation may be obtained as follows. $\alpha = 1$ meets the case of complete separation, $\alpha = 0$ that of complete mixing. Numerous experimental data indicate that the absolute value of max $tg\delta$ is more sensitive to a structural change than the shift of $tg\delta$ across the temperature scale. The following may be written, then, for the case $\underline{b}$, considering only a decrease in the absolute value:

$$\alpha = (h_1 + h_2)/(h_1^0 + h_2^0)$$

where h_1^0, h_2^0 are the values of mechanical loss for pure components (case of complete phase separation), while h_1, h_2 are those for each component at a different degree of segregation.

These changes may be considered as those in the number of relaxator units (segments) participating in the cooperative process of glass formation at the given temperature. A decrease in h for phase 1 indicates that the number of

these units has decreased, owing to their interaction with the relaxator units of phase 2, and vice versa. The maxima may expand in this case, but the parameter h predominates.

Then we consider the convergence of max $tg\delta$ when the compatibility increases. To this end, we introduce the empirical parameter λ_T into the expression for α, considering the shift of max $tg\delta$ across the temperature scale for phases 1 and 2

$$\lambda_T = (l_1 h_1)/L + (l_2 h_2)/L$$

where l_1, l_2 are the shifts of the maximum across the temperature scale, and L is the interval between the glass temperatures of the pure components.

The appearance of a relaxation maximum in the interphase region is considered using another parameter

$$\lambda_m = (l_m h_m)/L$$

where l_m is the maximum shift of interphase layer across the temperature scale as related to phase 1. The following expression may be written in this case for α

$$\alpha = (h_1 + h_2)/(h_1^0 + h_2^0) - (\lambda_T + \lambda_m)$$

The minus signs of coefficients λ_T and λ_m are evident from physical consid- erations, because the shift of max $tg\delta$ and the development of an interphase layer is a result of decrease in the segregation degree. The final expression for calculating the degree of segregation is:

$$\alpha = (h_1 + h_2 - (l_1 h_1 + l_2 h_2 + l_m h_m)/L)/(h_1^0 + h_2^0).$$

Calculations using this correlation produce the following data for the dia- gram b) $\alpha = 0.5$; c) $\alpha = 0.23$; d) $\alpha = 0.14$. A comparison of α calculated thereby for real segregated oligodienes with a variable molecular mass of the diene block (from 3850 to 1100) has given values $\alpha = 0.41$ and 0.29 by X-ray data and $\alpha = 0.43$ and 0.34 by max $tg\delta$.

The phase separation follows the spinodal mechanism during the initial stages of the process, as has been indicated by our experimental data for a large number of systems related to hybrid binders (refs 7-14). It is necessary to note, at the same time, that the complexity of the processes, wherein phase separation is superimposed on the chemical reaction, makes it difficult in some cases to isolate purely spinodal or nucleation mechanisms of phase sepa- ration and one mechanism may be replaced by another at different stages of formation of a network structure up to the point where phase separation be- comes entirely impossible. As a result of these specific features hybrid binders are characterized by the presence of stable diffuse microregions of phase separation, i.e. the degree of segregation is far from unity in these systems.

These specific features of structure formation of hybrid binders are extreme- ly significant for the understanding of their mechanical properties.

3. SIMULATING PROPERTIES OF POLYMER COMPOSITES PRODUCED BY THE SPINODAL MECHANISM OF PHASE SEPARATION

Two extreme cases may be considered when simulating properties.

1. Phase separation occurs by the nucleation mechanism. The system may be considered in this (rarer) case, even under conditions of incomplete phase separation, by analogy with dispersed filled systems, wherein the particles of the isolated phase act as a polymer filler. The properties of these sys- tems may be calculated by known methods (ref. 19) to predict the properties of two-phase systems of the "matrix-inclusion" type.

2. Phase separation occurs by the spinodal decomposition mechanism. Interrelated mosaic structures develop in this case, characterized by phase continuity.The equations known for systems "matrix-inclusion" are not applied here, owing to the presence of two continuous phases.

An equation which satisfies the requirement of symmetry for two-phase systems containing two continuous phases may be written as follows in the general form (ref. 20):

$$P = P_A^n \phi_A + P_B^n \phi_B \; ,$$

where P is some property of the system, for example, the modulus of elasticity, ϕ_A, ϕ_B are the volume fractions of the components, n is the exponent, characterizing the type of the system structure and possibly the type of properties.
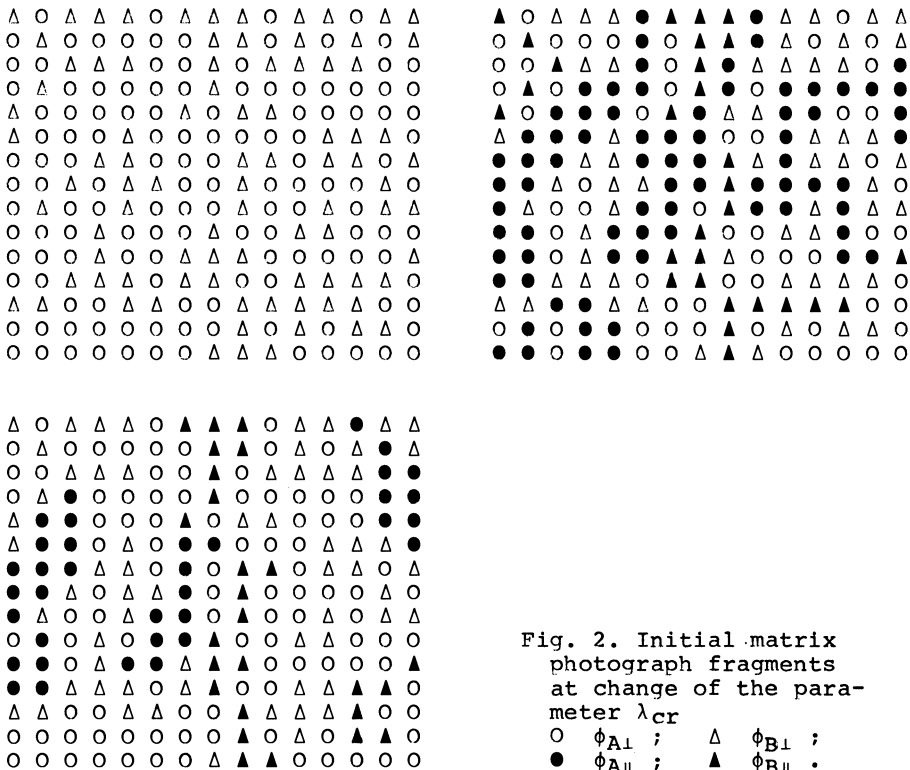
As has been said before, the moduli of elasticity of block copolymers and polymer mixtures (ref. 19) follow the logarithmic rule of mixing. It has been found for some mixtures (ref. 21) that n = 1/3 when we calculate the dielectric permittivity and n = 1/5 when we calculate the modulus of elasticity.

Our calculations of the effective properties of a two-phase polymer system are given below for the case of an interconnected continuous structure developing as a result of spinodal decomposition. The equation proposed by Nielsen (ref. 20) for systems with two continuous phases is used in the calculations:

$$P = P_A \phi_{A\parallel} + P_B \phi_{B\parallel} + P_A P_B (\phi_{A\perp}+\phi_{B\perp})/(P_A \phi_{B\perp} + P_B \phi_{A\perp}) \; ,$$

where $\phi_{A\parallel}$ and $\phi_{B\parallel}$ are the volume fractions of components A or B, which behave like a continuous medium; $\phi_{A\perp}$ and $\phi_{B\perp}$ - volume fraction of components which behave as a dispersed phase when subjected to the force (mechanical, electric, etc.). It is clear that

$$\phi_{A\parallel} + \phi_{A\perp} = \phi_A; \quad \phi_{B\parallel} + \phi_{B\perp} = \phi_B; \quad \phi_A + \phi_B = 1.$$

```
Δ O Δ Δ Δ O Δ Δ Δ O Δ Δ O Δ Δ      ▲ O Δ Δ Δ ● ▲ ▲ ▲ ● Δ Δ O Δ Δ
O Δ O O O O O Δ Δ O Δ O Δ O Δ      O ▲ O O O ● O ▲ ▲ ● Δ O Δ O Δ
O O Δ Δ Δ O O O Δ O Δ Δ Δ O O      O O Δ Δ Δ ● O ▲ ● Δ Δ Δ Δ O ●
O Δ O O O O O Δ O O O O O O O      O ▲ O ● ● ● O ▲ ● O ● ● ● ● ●
Δ O O O O O Δ O Δ Δ Δ O O O O      ▲ O ● ● ● O ▲ ● Δ Δ ● ● O O ●
Δ O O Δ O O O O O O Δ Δ Δ O O      Δ ● ● ● Δ ▲ ● ● ● O O ● Δ Δ ●
O O O Δ Δ O O O Δ Δ O Δ Δ O Δ      ● ● ● Δ Δ ● ● ● ▲ Δ Δ ▲ Δ O Δ
O O Δ O Δ Δ O O Δ O O O O Δ O      ● ● Δ O Δ Δ ● ● ▲ ● ● ● ● Δ O
O Δ O O Δ O O O Δ O O Δ O Δ Δ      ● Δ O O Δ ● ● O ▲ ● ● Δ ● Δ Δ
O O O Δ O O O O Δ O O Δ Δ O O O    ● ● O Δ ● ● ● ▲ O O Δ Δ ● O O
O O O Δ O O Δ Δ Δ O O O O O Δ      ● ● O Δ ● ● ▲ ▲ Δ O O O ● ● ▲
O O Δ Δ Δ O Δ Δ O O Δ Δ Δ Δ O      ● ● Δ Δ Δ O ▲ ▲ O O Δ Δ Δ Δ O
Δ Δ O O Δ Δ Δ O O Δ Δ Δ Δ Δ O O    Δ Δ ● ▲ Δ Δ O O ▲ ▲ ▲ ▲ ▲ O O
O O O O O O O O Δ O Δ O Δ Δ O      O ● O ● ● O O O Δ O Δ O Δ O Δ O
O O O O O O O Δ Δ Δ O O O O O      ● ● O ● ● O O Δ ▲ Δ O O O O O O
```

```
Δ O Δ Δ Δ O ▲ ▲ ▲ O Δ Δ ● Δ Δ
O Δ O O O O O ▲ ▲ O Δ O Δ O ▲ O
O O Δ Δ Δ O O Δ O Δ Δ Δ Δ ● ●
O Δ ● O O O O Δ O O O O O O Δ
Δ ● ● O O O Δ O Δ Δ O O O ● ●
Δ ● ● O Δ O ● ● O O O Δ Δ Δ ●
● ● ● Δ Δ O ● O ▲ ▲ O Δ Δ O Δ
● ● Δ O Δ Δ ● O ▲ O O O O Δ O
● Δ O O Δ ● ● O ▲ O O Δ O Δ Δ
O ● O Δ O ● ● ▲ O O Δ Δ O O O
● ● O Δ ● ● Δ ▲ ▲ O O O O O ▲
● ● ▲ Δ Δ Δ O Δ ▲ O O Δ Δ ▲ ▲ O
Δ Δ O O Δ Δ Δ O O ▲ Δ Δ Δ ▲ O O
O O O O O O O O O ▲ O Δ O ▲ ▲ O
O O O O O O O Δ ▲ ▲ O O O O O
```

Fig. 2. Initial matrix photograph fragments at change of the parameter λ_{cr}

O $\phi_{A\perp}$; Δ $\phi_{B\perp}$;
● $\phi_{A\parallel}$; ▲ $\phi_{B\parallel}$.

According to (ref. 2), the morphology of a system with two interconnected components is characterized by two parameters of phase connectivity:

$$C_A = \phi_{A\parallel} / \phi_{A\perp}; \quad C_B = \phi_{B\parallel} / \phi_{B\perp}.$$

We have constructed a matrix with dimensions 100x100 elements, which by means of unities and zeroes depicts a two-phase structure in a plane close to interconnected structures formed by the spinodal mechanism of phase separation.

In the case, chosen by us, $\phi_A = 0.3856$ and $\phi_B = 0.6144$. An algorithm has been developed with parameter λ_{cr} which makes possible to relate each of the 10000 matrix elements to the continuous or dispersed phase. λ_{cr} is a value altering the response (reaction) of the two-phase system under consideration to the action of force F. The interconnectivity of the components decreases with increasing λ_{cr}, which is indicated by a decrease in the parameters C_A and C_B.

However, it is possible to find out formal indications, whereby λ_{cr} may characterize different stages of phase separation. We shall deal with this formalism after discussing phenomenological aspects of the calculations.

The effective values of the property P has been calculated for different values of λ_{cr} and for several ratios of the properties of the components, $P_A:P_B = 100:1$, $10:1$, $5:1$. The ratios $P_A:P_B$ overlap the conceivable scatter of properties of the polymer phases in the actually existing composites.

An increase in λ_{cr} in all the cases without any exception causes a decrease in $\phi_{A\parallel}$ and $\phi_{B\parallel}$, and in the coefficient of connectivity of phases C_A and C_B. These changes considerably affect the effective values of the property P. The property P of a two-phase system decreases for all $P_A:P_B$ values with increasing λ_{cr} (or decreasing phase connectivity). After having normalized P versus P_{max} at $\lambda_{cr} = 5$, we developed the dependence of P/P_{max} on λ_{cr}. It has been found that this dependence is of nonlinear character and synonymously indicates that the effective property P of the composite decreases with increasing λ_{cr}. The influence of phase interconnectivity on P is more clearly displayed in Fig. 3, plotted as the P/P_{max} ordinate versus C_A. This dependence is linear, and the slope may characterize the influence of interconnectivity of the components on the general properties of the system P at various P_A/P_B values. The effect of interconnectivity is most essential at larger differences between the properties of the components.
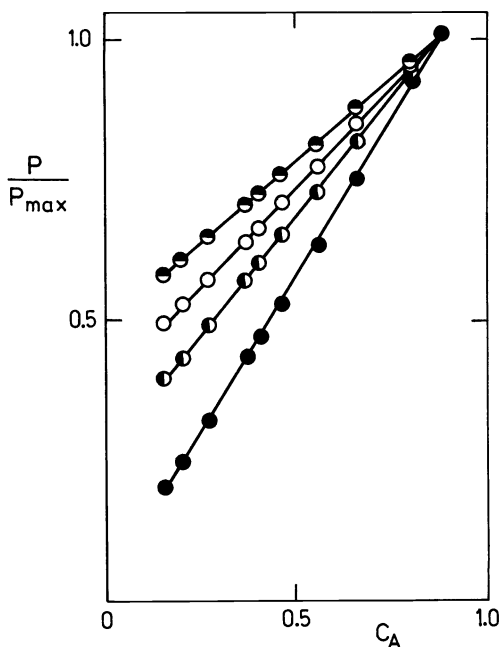

Fig. 3. Dependence of P/P_{max} on the phase connectivity coefficient C_A

P_A/P_B: ◕ 2; ○ 5; ◐ 10; ● 100.

Thus, the calculations make it possible to state that the interconnectivity of components, characteristic of the spinodal mechanism of phase separation, may influence considerably the final properties of the polymer composite.

Let us return to the formal indications according to which the phenomenological calculations may characterize different stages of phase separation. The calculations were made so that the values of $\phi_{A\parallel}$, $\phi_{A\perp}$, $\phi_{B\parallel}$, $\phi_{B\perp}$ for each value of λ_{cr} were computarized and the matrix was reproduced, referring each element to the continuous or dispersed phases by means of different subscripts.

Photographs of the initial matrix and its transformations at λ_{cr} = 10 and 30 are given in Fig. 2; they depict clearly the shift from an intensively interconnected structure of the initial matrix at λ_{cr} = 10 to structures with weak interconnectivity at λ_{cr} = 30. In the latter case the matrix elements related to ϕ_A and ϕ_B are more likely an ingredient inclusion in a continuous medium. It stands to reason that we have compared not only the three photographs in Fig. 2, but the photographs of the transformed matrix at all λ_{cr} as well. λ_{cr} seems to be a characteristic dimensionless parameter of morphology, enabling us to follow the process of phase separation in two-phase polymer systems.

The problem under consideration may be quantitatively described in terms of percolation theory. It may be supposed that the initial matrix represents the structure, where phase A and phase B are infinite clusters.

The introduction of the parameter λ_{cr} allows us to distinguish various parts in both clusters, i.e. parts reacting on force field as continuous media (participating in the deformation process) and parts reacting as a dispersed phase. Hence, when investigating the effect of percolation on the mechanical properties of polymer composites, one has to take into account both the existence of infinite clusters and their morphological peculiarities.

Polymer materials are currently developed with interpenetrating phases (IPN, semi-IPN, segregated networks, etc.) (refs 4-6). However, the influence of phase interconnectivity on the final properties of these materials has not been investigated in these studies. The establishment of such regularities enables us to disclose new ways of adjusting and improving many physico-mechanical properties of polymer composites. Despite the fact that the calculations were made without considering the actual dimensions of structural elements responsible for the interconnectivity of the components, it is clear that the formation of interconnected structures by the spinodal mechanism of decomposition (with the dimensions of the structural elements being several nm) will ensure maximum advantages for the final properties of the composites, in particular, for mechanical properties. The practical aspect of this problem consists in a controlled management of the phase separation process and fixation of the composite structure in certain stages of decomposition.

4. CONTRIBUTION OF INTERPHASE LAYERS TO THE PROPERTIES OF HYBRID BINDERS

The development of microheterogeneity regions, as well as periodic or modulated structures in hybrid matrices, points to the role played by interphase interaction and interphase layers influencing the properties of these systems. The latter may be investigated by X-ray diffraction. Several theoretical studies deal with phase separation and estimation of the thickness of the interphase region. According to theoretical and experimental estimates, the thickness of the transition layer ranges from several nm to some tens nm and their volume fraction in the matrix may reach 30-50 % (ref. 22). The increase in the segregation degree leads to the decrease in the thickness and fraction of the transition layers. The thickness of the transition layers in IPN (by X-ray data) reaches 4 nm and the volume fraction is 25 %. It should be noted that the thickness of the interphase layer (the distance between the microphase particles) in the case of spinodal decomposition is of the order of spinodal decomposition wavelength. According to the results published until now, the thickness of the interphase layer in polymer-polymer systems does not exceed 10 nm as given by structural data, though theoretically it should be of the order of the coil correlation radius, i.e. at least 2-3 times larger. At the same time, the thickness reaches several microns according to data of electron microscopy and IR spectroscopy. This is due to the fact that electron microscopy and IR spectroscopy estimate the morpho-

logy and conformation changes, while X-ray methods estimate the interphase layer associated with the density gradient. Even if the density of components at a considerable distance from the interface corresponds to that of components within the polymer volume, the conformations may still differ from those in the pure phase. The effect of thickness of interphase regions is negligible on the macroscopic level when compared to the dimensions of the body; this is not the case of small regions connected with microphase separation, the effect being of the same order as before: this requires to consider their contribution to the properties of a hybrid matrix. These layers ensure a gradient of property changes during the transition from microregions with an advantageous content of one component to those with an advantageous content of another component. The contribution of interphase layers increases with the growing thickness and with decreasing dimensions of phase separation microregions. A theoretical estimate of the influence of interphase layers on the viscoelastic characteristics of the hybrid matrix may be presented on the basis of simple phenomenological models of the Takayanagi type within the framework of notions suggested by us to consider the role of the interphase layer in filled polymers (ref. 23).

A theoretical analysis of the contribution of interphase layers to the properties of a composite material (refs 24, 25) makes it possible to derive an approximation based on simplified models of the composite, which gives the following result:

$$E_c = (1-\lambda) E_n + \lambda ((1-\phi)/E_n + \phi/E_1)^{-1} ,$$

where E_c is the modulus of composite, λ and ϕ are the parameters of model based on calculation, E_n is the modulus of polymer, E_1 is the value of modulus associated via model parameters with the modulus of elasticity of interphase layer.

This equation permits us to estimate the modulus of elasticity of the composite for different concentrations and properties of the interphase layers.

However, it should be noted that a quantitative estimation of the contribution of the interphase layers to the properties of the hybrid binders is still a matter of future investigation.

5. FILLING HYBRID BINDERS

The influence of a solid body (filler) surface on the processes of microphase separation in hybrid binders is of great interest, especially when we deal with processes applicable for polymer composite materials.

As noted above, the principal feature of hybrid binders is the occurrence of processes of microphase separation. From this standpoint, the structure of polymer composites based on hybrid binders will be determined, along with the factors discussed before, also by the influence of the interface with a solid phase on the processes of microphase separation in hybrid binders. Hence, it is possible to add one more specific feature of hybrid binders, i.e. as systems where changes occur during the microphase separation by the formation of a composite under the influence of the solid surface. Though the amount of experimental data in this respect is quite limited, it may be considered that the introduction of a filler might bring about two different effects on the processes of microphase separation (ref. 26). If one of the components of the binary system interacts advantageously with the surface, the change in the free energy at adsorption, $\Delta G_{21} < \Delta G_{31}$ (1 – filler, 2 and 3 – components of hybrid binder), contributes to an increase in the microphase separation rate, and the degree of segregation appears to be higher. If the energy of component interaction with the surface is similar, then the process of microphase separation will be retarded, owing to adsorption effects and adsorption decrease in molecular mobility near the phase boundary (refs 27, 28), and the system will be characterized by increased thermodynamic stability. It is also possible to demonstrate that a change is possible in the position of the curves of phase equilibrium - binodal and spinodal under certain conditions, owing to the influence of the solid body surface. The filler surface may be the nucleation "centre" in the case of the nucleation mechanism of phase separation, or as a result of absorption effects it may cause fluctuations in the concentration, contributing to the onset of spinodal decomposition, whereas its rate and other characteristics are determined by the level of interaction at the interphase boundary.

These effects have been investigated experimentally to a small extent only. However, the data for thermoplastic hybrid matrices - mixtures of linear polymers (polyethylene-polyurethane) and (polymethyl methacrylate-polybutyl methacrylate) illustrate a marked decrease in the parameter of thermodynamic interaction χ_{23} in the presence of a filler, which indicates an increase in the thermodynamic stability of the hybrid system in the presence of a filler. Presumably, this effect is associated with the experimental fact of a change in the fractional free volume of boundary layers of each component at the interface with the solid phase, and of respective change in the mixing conditions of two components in accordance with the Prigogine-Flory theory (refs 29, 30).

It is possible that the solid surface adsorbing simultaneously macromolecules of both components changes the conditions of their interaction in the boundary layer, i.e. the adsorption prevents the microphase separation and collapse of the macromolecule of each incompatible component (refs 31, 32) near the demixing point. The solid surface takes here the part of the "cross-linking agent", ensuring forced compatibility of the components. At the same time, the complex dependence of the parameter χ_{23} on the filler content indicates the contribution of selective adsorption increasing the thermodynamic stability.

Presumably, it is possible to point out one more reason according to which the introduction of fillers into a hybrid binder ought to bring about a more essential effect compared with common three-dimensional networks.It is quite evident that the hybrid network structure will be more defective due to a chain microheterogeneities formed in the network under conditions of phase separation. As a result, the number of elastic non-active chains may be increased. Adsorption of these non-active chains on the filler surface (called "anchor-attached chain") may increase the number of elastic active chains in the networks. It should be noted that this circumstance has never been considered in the theories of polymer network reinforcement, though it is undoubtedly significant for common systems and primarily, for rubber.

CONCLUSION

The structure of hybrid binders discussed above has a great effect on the physico-chemical and mechanical characteristics of the composite materials. The advantages of utilizing hybrid binders as compared with traditional ones are the following: 1) a cured system is a microfilled disperse-reinforced system; 2) it is sufficient to introduce even a small amount of one of the constituent components into hybrid binders to improve greatly the physico-mechanical properties in a certain region of composition; 3) as a rule, hybrid binders are characterized by considerably higher adhesion to the surfaces of the fillers than their constituent components. A theoretical basis of these notions is given in some studies (refs 27, 28, 33).

Thus, a conclusion may be drawn that hybrid binders have the following specific features: thermodynamic nonstable systems are developed as a result of microphase separation and remain mechanically stable for any period of time owing to kinetic factors. Hybrid binders arising by curing may be described adequately by applying the principles of non-equilibrium thermodynamics and the concept of dissipative structures (ref. 34). What has been discussed from the standpoint of the thermodynamics of equilibrium phase separation refers, in principle, to the process of structure formation and to the conditions of microphase separation determined by the nucleation or spinodal mechanism of separation.

Concepts of the structure of hybrid matrices with respect to the contribution of microphase separation processes to their properties and the appearance of extended interphase layers are at the initial stage of development today. However, a shift to a qualitatively new type of concepts of structure of the matrix, including the influence of a filler on phase equilibrium in the matrix, in our view, seems to be quite prospective. Discussion of these phenomena and associated processes of forming dissipative structures seems to us to be an indispensable stage of development of the theory of matrices for polymer composites. An essential advantage of hybrid binders is the basic possibility to change their structure (in thermoreactive systems) by adjusting the reaction conditions (temperature, initiator concentration) associated with those of phase separation; in the case of thermoplastics the change can be achieved by the rate of cooling, while for both types, by introducing specially selected fillers.

Certainly, we could deal here only with some problems associated with the development of hybrid binders, and have not dwelled on many other important questions, some of which we have reported in other papers.

All things are full of labour, man cannot utter it; the eye is not satisfied with seeing, nor the ear filled with hearing (Ecc. 1, 8).

REFERENCES

1. Yu.S. Lipatov, Mechanics of Composite Materials, No 5, 771 (1983).
2. A.A. Berlin, S.M. Mezhikovsky, J. Vses. Chim. Ob. "D.I. Mendeleyev", 21, 531 (1976).
3. A.A. Berlin, G.V. Korolev, T.Y. Kefeei, Yu.M. Sivergin, Acrylic Oligomers and Materials, Khimiya, Moscow (1983).
4. Yu.S. Lipatov, L.M. Sergeyeva, Interpenetrating Polymer Networks (in Russ.), Naukova Dumka, Kiev (1979).
5. L.H. Sperling, Interpenetrating Polymer Networks and Related Materials, Plenum Press, New York-London (1981).
6. Yu.S. Lipatov , V.F. Rosovitsky, Y.V. Maslak, J. Appl. Polymer Sci. 27, 4541 (1982).
7. Yu.S. Lipatov, V.V. Shilov, Komposiz. Polimern. Mater., No 11, 55 (1981).
8. Yu.S. Lipatov, V.V. Shilov, Yu.P. Gomza, V.S. Skorodzievsky, A.I. Ustinov, K.V. Tchuistov, Polymer 25, 459 (1984).
9. Yu.S. Lipatov , V.V. Shilov, Yu.P. Gomza, G. Kovernik, P. Kochetov, Angew. Makromol. Chem. 119, 173 (1983).
10. Yu.S. Lipatov, V.V. Shilov, Yu.P. Gomza, G. Kovernik, O.P. Grigoryeva, L.M. Sergeeva, Makromol. Chem. 185, 347 (1984).
11. V.V. Shilov, Yu.S. Lipatov , V.A. Bogdanovich, D.P. Kochetov, V.K. Gistchenko, Vysokomolek. Soed. A25, 921 (1983).
12. Yu.S. Lipatov, V.V. Shilov, Dokl. Akad. Nauk Ukr. SSR, B, No 6, 35 (1983).
13. Yu.S. Lipatov, O.P. Grigoryeva, Dokl. Akad. Nauk Ukr. SSR, B, No 11, 43 (1983).
14. V.V. Shilov, Yu.S. Lipatov, L.V. Karabanova, L.M. Sergeeva, J. Polym. Sci. Chem. 17, 3083 (1979).
15. Yu.S. Lipatov, V.V. Shilov, Uspekhi khimii 53, 1197 (1984).
16. K. Binder, H.L. Frisch, J. Chem. Phys. 81 (4), 2126 (1984).
17. Yu.S. Lipatov, V.V. Shilov, Y.P. Gomza, N.E. Kruglyak, X-Ray Methods of Studying Polymer Systems (in Russ.), Naukova Dumka, Kiev (1982).
18. Yu.S. Lipatov, V.F. Rosovitsky, Dokl. Akad. Nauk USSR 278, 1408 (1984).
19. L. Nielsen, Mechanical Properties of Polymer and Composites, Marcel Dekker New York (1974).
20. L. Nielsen, J. Appl. Polymer Sci. 21, 1579 (1977).
21. K. Ziegel, A Romanov, J. Appl. Polymer Sci. 17, 1119 (1973).
22. V.V. Shilov, V.V. Tsukruk, Yu.S. Lipatov, Vysokomol. Soed. A26, 1347 (1984).
23. Yu.S. Lipatov, N.I. Korzhuk, V.F. Babich, in: Molecular Characterization of Composite Interfaces, p. 237, Plenum Press, New York-London (1985).
24. Yu.S. Lipatov, V.F. Babich, Vysokomolek. Soed. B24, 548 (1982).
25. V.F. Babich, L.I. Perepelizyna, Yu.S. Lipatov, Komposiz. Polimern. Mater. Kiev, No 20, 14 (1984).
26. Yu.S. Lipatov, Colloid Chemistry of Polymers (in Russ.), Naukova Dumka, Kiev (1984).
27. Yu.S. Lipatov, Interphase Phenomena in Polymers (in Russ.), Naukova Dumka, Kiev (1980).
28. Yu.S. Lipatov, Physical Chemistry of Filled Polymers, British Library, RARPA, Shrewsbury (1979).
29. I. Prigogine, The Molecular Theory of Solutions, Interscience, New York (1959).
30. B. Eichinger, P.J. Flory, Trans. Farad. Soc. 64, 2035 (1968).
31. J.C. Joanny, F. Brochard, J. Phys. (France) 42, 1145 (1981).
32. R. Koningsveld, R.F.T. Stepto, Macromolecules 10, 1166 (1977).
33. Yu.S. Lipatov, Mechanics of Composite Materials No 3, 499 (1983).
34. P. Lyndenmeyer, Polymer J. 11, 677 (1979).