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Modification of polymers by polymeric additives

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ABSTRACT. The conditions for the thermodynamic compatibility of polymers and methods for its enhancement are examined. The study of the influence of various factors on the concentration-temperature limits of compatibility, dispersion stabilisation processes, and methods for the improvement of adhesion between phases in mixtures of thermodynamically incompatible polymers is described. Questions concerning the improvement of the physicomechanical characteristics of polymer dispersions are considered.

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I. Introduction

The acceleration of scientific and technical progress requires the creation of new materials with the needed set of properties. Composite materials incorporating polymers containing a wide variety of fillers, mixtures and blends of two or more polymers, etc. have been acquiring an increasing role in the solution of this problem at the present time.

Since the preparation of new polymeric materials with the required properties can no longer be wholly based on the synthesis of new high-molecular-weight compounds, the era of problems concerning the modification of polymers already produced by industry and the preparation of materials with the required properties on their basis has now dawned. One of the most readily available and economically favourable modification procedures involves the preparation of mixtures and blends of two or more polymers, interpenetrating networks, etc. The properties of such systems are determined by their structure, whose formation is associated with the thermodynamic compatibility or incompatibility of the components and mechanism of phase separation under the conditions of the preparation of the composition and its conversion into finished articles. The practical experience gained in the preparation and use of finished articles made from such materials has shown that, in order to obtain the desired properties, thermodynamic compatibility of the components is needed in some cases, whilst in others it is in fact undesirable. For example, the view has been expressed[1] that, in terms of their mechanical properties, two-phase mixtures are superior to single-phase mixtures and that the subdivision of systems into thermodynamically compatible or incompatible has no great practical value. On the other hand, analysis of literature data has led Paul and Barlow[2] to the conclusion that materials obtained from compatible systems have on the whole better properties. A truly homogeneous product can be obtained from thermodynamically compatible polymers. In the case of compatible systems, a synergism is observed in a series of important physicomechanical properties such as moduli and strength, the transparency of the materials is ensured, and there are other advantages.[3–8] The compatibility of polymers guarantees also the operational reliability of the articles made from them, especially under the conditions of variable loads and in different temperature regimes. Much attention has therefore been devoted in recent years, particularly abroad, to the search for thermodynamically compatible pairs and significant progress on these lines has been achieved: about 300 thermodynamically compatible polymer pairs have now been discovered.[8–12]

In those cases where for the attainment of the required properties mixtures of thermodynamically incompatible polymers are used (impact-resistant plastics, certain adhesives), it is essential to stabilise the dispersion because, owing to the weak adhesion between the phases in such cases, difficulties arise in the attainment of the required degree of dispersion of the mixture components during their processing and their stability is impaired both during preparation and during use.[3] In many instances the weak adhesion between the phases impairs the mechanical properties.[3,13–16] Much attention has therefore been devoted nowadays to problems of the stabilisation of mixtures of this kind, the improvement of adhesion between the phases, etc.

This review surveys the literature data on the compatibility of polymers and on its dependence on various factors. Questions concerning the stabilisation of dispersions and the regulation of the properties of materials made from mixtures of thermodynamically incompatible polymers are also considered.

II. The compatibility of polymers and methods for its regulation

A large number of both original publications and reviews and monographs have been devoted to problems of the compatibility of polymers and the search for thermodynamially compatible polymer systems.[2,8,12,17,18] The study of the thermodynamic compatibility of polymers has led to the conclusion that in the vast majority of cases it is determined by specific interactions, which ensure the exothermicity of the mixing process, i. e. lead to a negative enthalpy of mixing.[3,10,18–22] It has been demonstrated for the first time by Tager and co-workers[23,24] that the entropy of mixing of thermodynamically compatible polymers is also negative. On this basis, the requirement that $\Delta S < 0$ has been put forward as one of the conditions for the compatibility of polymers.[25] Since the enthalpy

and entropy of mixing of compatible systems are negative, these systems should separate into layers on heating, i.e. should be characterised by the presence of a lower consolute temperature (LCT). Indeed the majority of the thermodynamically compatible polymer pairs found hitherto do have a LCT.[9-11] Upper consolute temperatures (UCT) are characteristic mainly of oligomer–oligomer and oligomer–polymer mixtures, mixtures of polymers with plasticisers, and mixtures of certain homopolymers with copolymers.[11,26-30]

In order to account for the exothermicity of the mixing process, the concept of the "mutually complementary difference" was put forward,[17] whose essential feature is that the macromolecules of the mixed polymers should contain groups complementing one another and capable of forming hydrogen bonds with one another or electron donor–electron acceptor complexes. This concept actually constitutes the basis of the study of polymer solutions.[31] A somewhat different approach has been used[32] to describe processes involving the mixing of homopolymers with variable-composition copolymers (binary interactions model). We shall consider these approaches in relation to specific examples.

1. The formation of ion pairs

Polystyrene is known to be incompatible with polyacrylate and polyisobutylene.[33] Nevertheless, polystyrene modified by a sulphonic acid or 4-vinylpyridine is compatible with the above polymers provided that polyacrylate, for example, is modified by 4-vinylpyridine, while polyisobutylene is modified by a sulphonic acid.[34] Such mixtures are compatible over the entire range of compositions, provided that the number of modifying groups in each polymer exceeds 5%.[34] The compatibility is caused by the formation of ion pairs as a result of the protonation of the pyridine ring by the sulphonic acid group. The Coulombic interaction between the ions is sufficient to ensure compatibility. Similarly the formation of stable intermolecular pyridine–carboxylate bonds (ion pairs) ensures the compatibility of oppositely charged polyelectrolytes such as the butadiene–methacrylic acid copolymer and the butadiene–2-methyl-5-vinylpyridinium iodide copolymer.[35,36] The formation of ion pairs leads to the compatibility of the lithium salts of the styrene–methyl methacrylate copolymer with poly(ethylene oxide) and poly(propylene oxide) [37-39] and also of the lithium salts of the ethyl acrylate–acrylic acid copolymer with polyethyleneimine.[40] It has been shown[38] that an increase in the radius of the cation (the replacement of Li by K or Na) in the salts of the styrene–methyl methacrylate copolymer containing 10.4 mol% of acrylate reduces the phase separation temperature of its mixtures with poly(ethylene oxide) and poly(propylene oxide) (systems with a LCT).

2. Other specific interactions

Polyolefins with high molecular weights are as a rule incompatible with other polymers.[33] However, chlorination of polyethylene, for example, makes it compatible with poly(vinyl chloride),[41-43] poly(methyl methacrylate) (when polyethylene contains between 27 and 50% of chlorine),[44-46] polycaprolactone (when polyethylene contains more than 25% of chlorine),[47] and poly(neopentyl glycol adipate) (when polyethylene contains between 42 and 48% of chlorine).[48] The compatibility of chlorinated polyethylene for example, with poly(methyl methacrylate) has been explained by the negative enthalpy of mixing, which can be caused by the formation of hydrogen bonds between the α-hydrogen atoms of polyethylene and the C=O groups of poly(methyl methacrylate) or by dipole–dipole interactions of the type C=O...Cl–C.[44] In particular, the compatibility of chlorinated polypropylene with polyesters has been explained[49] by dipole–dipole interactions of the type C=O...Cl–C, because the chlorinated polypropylene used in the above study did not have sufficient α-hydrogen atoms for the formation of hydrogen bonds with the C=O groups of the polyesters.

The method involving the Fourier transformation of IR spectra has been widely used in recent years to detect the occurrence of specific interactions (for example, hydrogen bonding).[50-62] It has been shown for mixtures of poly-4-vinylphenol with ethylene–vinyl acetate copolymers[52] that this method makes it possible to estimate even quantitatively the strength and number of intermolecular bonds and their temperature dependence. Measurements of the absorption band intensities in the region of 1738 and 1708 cm^{-1} (the frequencies of the free and hydrogen-bonded C=O groups) have been used[52] to estimate the fraction of carbonyl groups participating in the formation of hydrogen bonds and the heats of formation of the complex. The calculations were performed for two specimens: one of them was obtained from solution and dried at room temperature, while the other was first heated to 463 K. The spectra of the first specimen were obtained on heating and those of the second on cooling. In the former case, the free carbonyls participated in the formation of hydrogen bonds. If the intensities (areas) of the absorption bands near 1738 and 1708 cm^{-1} of the dried film obtained from the solution are designated by I_1 and I_2 respectively and those of the bands of the heated film are designated by I_1' and I_2', then

$$a_2(I_1 - I_1') = a_1(I_2' - I_2),$$

whence

$$a_1/a_2 = (I_1 - I_1')/(I_2' - I_2),$$

where a_1 and a_2 are the absorption coefficients for 1738 and 1708 cm^{-1} bands respectively. Having determined the ratio a_1/a_2, it is possible to calculate the fraction of carbonyl groups involved in the formation of hydrogen bonds.

In order to calculate the intermolecular interaction forces, the 1 : 1 complex is represented as a mixture of poly-4-vinylphenol with the ethylene–vinyl acetate copolymer at molar concentrations designated by [–OH] and [–C=O] respectively. The concentration of carbonyl groups involved in the formation of hydrogen bonds is designated by x. We then have in a simplified form

$$\text{—OH} + \text{—C=O} \overset{K}{\rightleftarrows} \text{—OH...O=C—},$$
$$K = x/([\text{—OH}] - x)([\text{—C=O}] - x),$$
$$\ln K = (-\Delta H/RT) + C,$$

where K is the equilibrium constant and ΔH the enthalpy of formation of the complex.

The dependence of $\ln K$ on $1/T$ is illustrated in Fig. 1, which shows that, below the glass point of the system (T_g = 360 K), the dependence of $\ln K$ on $1/T$ becomes non-linear, which may be associated with the non-equilibrium nature of the system. The values of ΔH and C were determined from the initial section of the $\ln K = f(1/T)$ relation and were found to be 21.4 kJ mol^{-1} and −6.55 respectively. Using these values as a basis, Moskala et al.[52] calculated the fraction of carbonyl groups participating in the formation of hydrogen bonds and found that at temperatures below T_g it exceeds the experimental value (curves *2* and *5* in Fig. 2). This is evidence that below T_g the system is indeed in a state of non-equilibrium possibly because of the low mobility of the

macromolecules under these conditions. With increase in the vinyl acetate content in the system, the consolute temperature increases, i.e. hydrogen bonding becomes possible at a higher temperature (Fig. 2). It has also been suggested that the LCT be estimated approximately from the temperature variation of the shift of the stretching vibration frequency of the C=O groups.[53] For example, it has been shown by this method[53] that the LCT should be observed in the temperature range 363–383 K for mixtures of chlorinated poly(vinyl chloride) with the ethylene–vinyl acetate copolymer and in the range 383–403 K for mixtures of poly(vinyl chloride) with the ethylene–vinyl acetate copolymer.

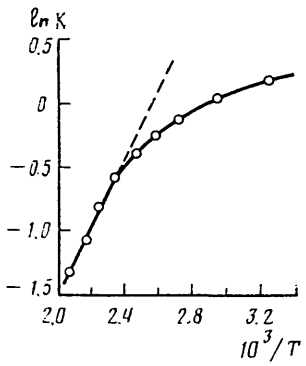


Figure 1. Dependence of $\ln K$ on $1/T$ for an 8 : 8 mixture of poly-4-vinylphenol with the ethylene–vinyl acetate copolymer (45% of vinyl acetate).[52]

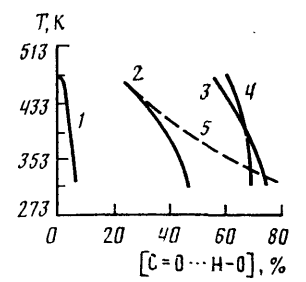


Figure 2. Temperature dependence of the fraction of C=O groups participating in the formation of hydrogen bonds for mixtures of poly-4-vinylphenol with 8 : 2 ethylene–vinyl acetate copolymers for different contents of vinyl acetate in the copolymer:[52] *1*–*4*, experimental data; *5*, calculation. Content of vinyl acetate in the copolymer (%): *1*, 25; *2* and *5*, 45; *3*, 70; *4*, 100.

A shift of the absorption bands of the hydroxy-group (3100–3700 cm^{-1}) has been observed in mixtures of poly(methyl vinyl ether) with polycaprolactone [57] and of poly(methyl vinyl ether) with the polyhydroxylated ether of bisphenol A with increase in the content of the second component.[58] The occurrence of specific interactions has been observed by this method also in mixtures of polycarbonate with poly(hexamethylene adipate),[59] of polycaprolactone with poly(vinylidene fluoride)–vinyl chloride and vinylidene chloride–acrylonitrile homopolymers and copolymers,[59,60] of poly(vinyl chloride) with poly-ε-caprolactone,[51] of poly(vinyl chloride) with poly-α-methyl-α-n-propyl-β-propiolactone and poly-β-valerolactone,[50] of poly(vinyl chloride) with ethylene–dimethacrylamide ethylene dimethacrylate–ethyl acetate–CO, ethylene dimethacrylate–vinyl acetate–CO, and ethylene dimethacrylate–ethylhexyl acrylate–CO copolymers,[62] of poly(vinyl chloride) with ethylene–vinyl acetate copolymers,[53] of poly(vinylidene fluoride) with poly(methyl methacrylate),[52] and also of the styrene–allyl alcohol copolymer with poly(vinyl acetate), polycarbonate, and poly(methyl methacrylate) with different degrees of stereoregularity.[61] In mixtures of the styrene–allyl alcohol copolymer with polycarbonate, the maximum degree of compatibility was attained when the content of OH groups in the copolymer was approximately 9%, while in its mixtures with polycaprolactone the dependence of the thermodynamic interaction parameter on the content of the OH groups passed through a minimum whose position corresponded to an approximately 3% content of these groups in the copolymer.[61,63] The formation of hydrogen bonds is the cause of the compatibility of polyhexafluoromethylvinylcarbinol and its copolymers with styrene (for styrene contents from 0.1 to 12%), poly(methyl methacrylate), poly(ethyl methacrylate), and poly(butyl methacrylate), polycaprolactone, and poly(methyl vinyl ether),[55] and also with poly-2,6-dimethyl-1,4-phenyleneoxybisphenol A carbonate.[56] In these systems, the hydrogen of the hexafluorocarbinol group forms a hydrogen bond with the carbonyl, ether, and carbonate groups of the polymeric admixtures. Under these conditions, an increase in the content of the OH groups in the copolymer raises the phase separation temperature (systems with a LCT).

Numerous studies have been devoted to the compatibility of poly(vinyl chloride) with other polymers.[64–84] A characteristic feature of these mixtures is that hydrogen and electron donor–electron acceptor bonds can be formed in them.[18,85,86] Poly(vinyl chloride) is compatible with poly(alkyl acrylates) when the number of carbon atoms in the alkyl group is less than 4 and with poly(alkyl methacrylates) if the number of carbon groups is less than 6. Thus it follows that poly(vinyl chloride) should mix with poly(methyl methacrylate). In practice, contradictory results have been obtained for this system. Thus the presence of a LCT has been observed,[67] while in other studies[83,84] a HCT has been noted! These contradictions have been explained[67] by the non-equilibrium nature of the system. The results of the study[87] in which the compatibility of poly(vinyl chloride) with poly(alkyl acrylates) and poly(alkyl methacrylates) was investigated are of interest from this point of view. It was observed that the curve relating the Flory–Huggins thermodynamic interaction parameter χ_{12} to the length of the alkyl group in poly(alkyl methacrylates) and poly(alkyl acrylates) passes through a minimum, i.e. there is a minimum concentration of ester groups at which these polymers mix with poly(vinyl chloride). An attempt was made to explain this finding by the relative contributions of the specific and dispersion interactions.[87] For this purpose, the heats of mixing were measured for the oligomers modelling the polymethacrylates and polyacrylates (M = 1000 to 3000) with chlorinated paraffin (M = 437, chlorine content 53.1%), modelling poly(vinyl chloride). The heats (enthalpies) of mixing, measured calorimetrically, proved to be negative in all cases, with the exception of the mixture with oligomethacrylate. The contributions to the heat of mixing by dispersion interactions, calculated on the

basis of the theory of solubility parameters, and by specific interactions (the difference between the overall and calculated heats of mixing) were estimated and it was noted that, in order to ensure compatibility, it is essential that the specific interactions should overlap the dispersion interactions. The heats of mixing of model compounds were clearly correlated with the compatibilities of the corresponding high-molecular-weight components. However, a reliable correlation was not observed between the heats of mixing and the thermodynamic interaction parameters χ_{12}, which can apparently be due to the contribution of the non-combinatorial entropy of mixing to the parameter χ_{12}.[18]

In connection with the use in a number of studies of model low-molecular-weight analogues, mention should be made of the method, proposed by Ebert et al.,[88] for the determination of the heats of mixing of compatible polymers by measuring the heats of the phase separation process. Differential scanning calorimetry (DSC) is used for such measurements. The sign of the DSC peak depends on the sign of the heat of mixing: an endothermic heat of phase separation corresponds to an exothermic heat of mixing and conversely. The size of the DSC peak, which is proportional to the integral heat of phase separation, corresponds approximately to the overall heat of mixing. The method has been tested in relation to a mixture of poly(ethyl acrylate) with poly(vinylidene fluoride). The heats of mixing found by this method agree with the corresponding values for oligomeric mixtures of the same type obtained calorimetrically.

The thermodynamic compatibility of chlorinated poly(vinyl chloride) (chloride content 67.2%) with polycaprolactone, poly(hexamethylene sebacate), poly-α-methyl-α-n-propyl-β-propiolactone, polyvalerolactone, poly(ethylene adipate), poly(ethylene succinate), and poly-β-propiolactone has been explained by specific interactions.[65,69] It has been shown in relation to a mixture of poly-ε-caprolactone with α-deuteriated poly(vinyl chloride) and solutions of polycaprolactone in carbon tetrachloride, tetrahydrofuran (THF), and chloroform and of methyl acetate (as a model analogue of ester groups) in pure water and in solution in carbon tetrachloride, that $-CH\ldots OOC-$ interactions between the $-CH(D)$ groups of poly(vinyl chloride) and the $-COO$ groups of polycaprolactone take place in systems of the poly(vinyl chloride)–polycaprolactone type.[54] The compatibility of the vinylidene chloride–acrylonitrile (20%), vinylidene chloride–vinyl acetate (20%), and vinylidene chloride–vinyl chloride (12%) copolymers with polycaprolactone, poly(hexamethylene sebacate), poly-α-methyl-α-n-propyl-β-propiolactone, and poly(ethylene adipate) is determined by the interaction of the C=O and C–Cl dipoles.[89] The altered thermodynamic interaction parameter is then a function of mixture composition. It is of interest that polylactones are incompatible with poly(vinyl fluoride) and poly(vinylidene fluoride).[79] It has been suggested[79] that this is associated with the significant difference between the electronegativities, atomic radii, and molar attractions of the chlorine and fluorine atoms (fluorine is more negative than chlorine, as a result of which it forms stronger chemical bonds with other atoms[90]). The compatibility of polylactones with poly(vinyl bromide) is greater than with poly(vinyl chlorides). On the other hand, poly(vinylidene fluoride) is compatible with many poly(alkyl methacrylates) and poly(alkyl acrylates) [98] containing short alkyl groups.

The compatibility of chlorinated polymers [poly(vinyl chloride), chlorinated poly(vinyl chloride), chlorinated polyethylene] with poly(ethylene terephthalate), poly(butylene terephthalate), and poly(hexamethylene terephthalate) and also of polyesters of the type of polycaprolactones, poly(2,2,-dimethyl-1,3-propylene adipate), poly(1,4-cyclohexanedimethylene succinate), and poly(2,2-dimethyl-1,3-propylene succinate) with chlorinated polymers has also been explained by the interaction of chlorine atoms with C=O groups.[93–96] Compatibility is achieved for a high chlorine content and for a definite concentration of C=O groups in the polymers.[97] The region corresponding to the compatibility of the hydroxyethyl ether of bisphenol A with aliphatic polyesters,[96] of chlorinated poly(vinyl chloride) with polyesters,[69] of poly(2,6-dimethyl-1,4-phenylene oxide) with aliphatic polyesters, etc.[98] is determined by the CH_3/COO ratio. Consequently it might have been expected that the introduction of C=O groups into the corresponding polymer or copolymer should have ensured its compatibility, for example, with chlorinated polymers, which has in fact been confirmed experimentally.[62,99,100] It has been suggested that in all the examples quoted the compatibility is determined by the formation of hydrogen bonds between the α-hydrogen atoms of poly(vinyl chloride) and the C=O groups of the added polymers or copolymers.

Interesting results have been obtained in the study of the influence of the position of the substituent on the compatibility of poly(2,6-dimethyl-1,4-phenylene oxide) with halogen-substituted styrene copolymers.[101–103] The above polymer is known to be compatible with polystyrene,[33] but is not compatible with poly-*o*-chlorostyrene, poly-*p*-chlorostyrene, or poly-*o*-fluorostyrene.[101,102] Poly(phenylene oxide) is compatible with styrene–halogenostyrene copolymers only for certain contents of halogenostyrene.[105] Thus poly(phenylene oxide) is compatible with *o*-chlorostyrene–*p*-chlorostyrene copolymers for a *p*-chlorostyrene content in the copolymer from 23 to 65%. It is also compatible with *o*-fluorostyrene–*o*-chlorostyrene copolymers for a *o*-chlorostyrene content between 15 and 36% and with *o*-fluorostyrene–*p*-chlorostyrene copolymers for a *p*-chlorostyrene content from 5 to 80%.[102] However, poly(phenylene oxide) is incompatible with the *p*-chlorostyrene–*p*-fluorostyrene copolymer of any composition.[102,103] The authors believe that in the examples quoted the compatibility is determined by repulsion effects, while incompatibility is determined by the specific interaction between different covalently linked comonomers.[103] The halogen content in the styrene–halogenostyrene copolymer for which poly(phenylene oxide) is compatible with the copolymer depends under these conditions on the type of halogen and increases in the following sequence: *o*-Br < *p*-F < *p*-Br < *o*-Cl < *o*-F.

It is noteworthy that in mixtures of homopolymers with copolymers the transition from compatibility to incompatibility occurs much more abruptly after a slight change in the composition of the copolymer.[96,104–106] A general characteristic feature of such mixtures is the presence of the so called "compatibility windows" which are observed also when the corresponding homopolymers are incompatible. For example, neither polystyrene nor polyacrylonitrile are compatible with poly(methyl methacrylate) and poly(ethyl methacrylate). However, the styrene–acrylonitrile copolymer is compatible with them.[107,108] The ethylene–vinyl acetate and butadiene–acrolynitrile copolymers are compatible with poly(vinyl chloride), but the corresponding homopolymers are incompatible with the latter.[73]

Clearly, such behaviour of systems of this kind cannot be accounted for by purely specific intermolecular interactions. In order to describe the thermodynamic behaviour of such systems, a binary interaction model has been proposed,[32] which includes intramolecular and intermolecular interactions. In this model, a mixture of a copolymer with a homopolymer is regarded as a ternary system incorporating as components the comonomers 1 and 2 of the

copolymer with volume fractions φ'_1 and φ'_2 respectively and the homopolymer 3, whose composition differs from those of the comonomers. Account is taken of three types of interactions: 1 with 2, 1 with 3, and 2 with 3. The parameter B_{ij} is used as the characteristic of the interactions. It is related to the usually employed Flory–Huggins thermodynamic interaction parameter χ_{ij} by the expression

$$\frac{B_{ij}}{RT} = \frac{\chi_{ij}}{V_i} = \frac{\chi_{ji}}{V_j} = \bar{\chi}_{ij},$$

where V_i and V_j are the molar volumes of the units of components i and j. For the effective interaction parameter, one can write

$$B = B_{13}\varphi'_1 + B_{23}\varphi'_2 - B_{12}\varphi'_1\varphi'_2, \qquad (1)$$

where B_{12} is the parameter of the interaction between the copolymer components 1 and 2 and B_{13} and B_{23} are the parameters of the interaction of the comonomers (1 and 2) of the copolymer with the monomeric units of the homopolymer (component 3). The first two terms of Eqn. (1) characterise the additional interaction of the polymer 3 with the comonomers 1 and 2, while the third term characterises the interaction between the comonomers 1 and 2 in the copolymer. It is seen from Eqn. (1) that, if $B_{12} > 0$, then the comonomers 1 and 2 are "unlike"[18] and the repulsion forces between them lead to values of B smaller than the additive values. On the other hand, if $B_{12} < 0$, then the values of B are greater than the additive values. Fig. 3 illustrates schematically the possible situation arising for different values of the parameters B_{ij}. The case presented in Fig. 3*b*, where all the B_{ij} are positive, is of interest. In this case the polymer 3 is not miscible with either comonomer 1 or 2. However, if the parameter B_{12} is fairly large, namely

$$B_{12} > (\sqrt{B_{13}} + \sqrt{B_{23}})^2,$$

a range of copolymer compositions φ'_1 arises in which $B < 0$ and this copolymer is compatible with the polymer 3. This apparently in fact accounts for the existence of the "compatibility windows" in many systems: the addition of the polymer 3 to the copolymer "dilutes" the unfavourable interactions between the comonomers 1 and 2 of the copolymer, creating "pure" exothermic conditions even when the binary interactions of the monomer 1 with the monomer 2 are endothermic, i.e. there are no specific interactions between the components.

Fig. 3 also illustrates other possible variants, which may lead to either the compatibility or the incompatibility of the components. For example, Fig. 3*c* illustrates the case where all the binary parameters are negative, i.e. any pair of the three mixture components is compatible. However, the model predicts that, for certain copolymer compositions, the latter will be incompatible with the homopolymer 3. Fig. 3*a* presents the standard situation in which the comonomer 2 of the copolymer mixed exothermically with the homopolymer 3, while the comonomer 1 is immiscible with the homopolymer 3. With increase in the fraction of the comonomer 1 in the copolymer, conditions for endothermic mixing are attained, the point corresponding to the transition from the exothermic to endothermic mixing then depending on the sign and magnitude of the parameter B_{12}.

The proposed model has been used[32] to describe the thermodynamic behaviour of mixtures of copolymers of different composition with other copolymers and homopolymers. For example, mixtures of the hydroxyethyl ether of bisphenol A with a series of polycarbonates, including also their low-molecular-analogues (the CH_x and CO groups), which were regarded as "comonomers", have been investigated.[32] Fig. 4 presents the dependence of the effective interaction parameter B, determined by various methods (calorimetry, melting point depression, sorption), for these mixtures on the volume fraction of the CH_x groups. By combining the parameters B_{ij}, it is possible to obtain with the aid of Eqn. (1) a curve which describes most effectively the experimental data. The continuous curve in Fig. 4 was obtained for $B_{12} = 1050$, $B_{13} = 350$, and $B_{23} = 700$ J cm^{-3}. It is striking that all three interaction parameters proved to be positive, i.e. in this case there are no specific interactions. When a number of other systems were considered, a satisfactory correlation was also found between the predictions of the model and experimental data.[109,110] For example, the model describes satisfactorily the results of the study of the compatibility of chlorinated poly(vinyl chloride) with ethylene–vinyl acetate copolymers[109] and of poly(tetramethylbisphenol A carbonate) with styrene–methyl methacrylate copolymers.[110] Apparently this model can be used to describe the thermodynamic behaviour of mixtures of three polymers and the interaction parameters can be determined using model oligomers.[111]

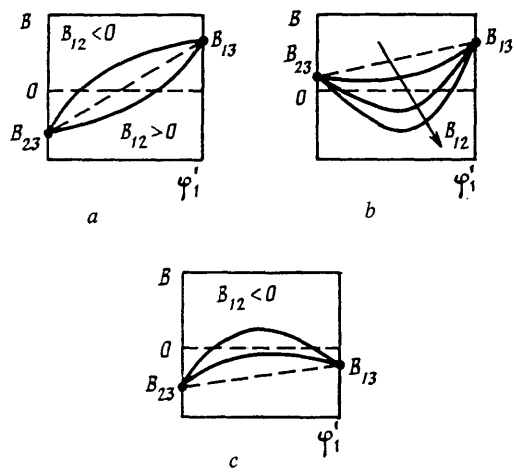


Figure 3. Schemes illustrating the concentration dependence of the effective interaction parameter B in mixtures of a homopolymer with variable-composition copolymers for different ratios of the binary interaction parameters:[32] *a*, B_{12} and $B_{23} < 0$ while $B_{13} > 0$ (upper curve) or B_{12} and $B_{13} > 0$ while $B_{23} < 0$ (lower curve); *b*, all three binary parameters (B_{12}, B_{13}, and B_{23}) are positive; *c*, all three binary parameters (B_{12}, B_{13}, and B_{23}) are negative. The curves in Fig. 3*b* are displaced downwards with increase in the parameter B_{12} and those in Fig. 3*c* are displaced upwards with increase in the parameter B_{12} in absolute magnitude [see Eqn. (1)].

3. The influence of other factors on the compatibility of polymers

(a) The introduction of a third component into a mixture of two polymers. If a third component (a polymer or copolymer), compatible with each of the polymers being mixed, is introduced into a mixture of two incompatible polymers, then such a ternary mixture becomes compatible.[112–116] Thus, when poly(vinylidene fluoride),

which is compatible with poly(methyl methacrylate) and poly(ethyl methacrylate) but the latter are incompatible with one another, is introduced into their mixture, the resulting ternary mixture proves to be compatible.[112] The mixture of poly(vinyl chloride) with the SKN-40 copolymer is compatible, while its mixture with the vinylidene chloride–vinyl chloride copolymer is incompatible.[115] On the other hand, the ternary mixture is compatible. However, the replacement of SNK-40 by SKN-30 makes all three pairs incompatible. Nevertheless, the ternary system is compatible.

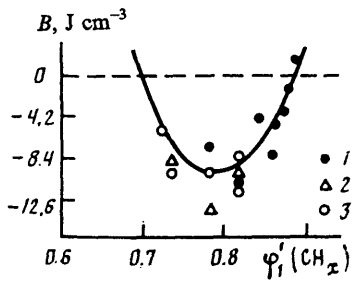


Figure 4. Interaction parameters for mixtures of aliphatic polyesters and their low-molecular-weight analogues with the polyhydroxylated ester of bisphenol A obtained by the calorimetric (*1*), melting point depression (*2*), and sorption (*3*) methods.[32]

Mixtures of polycarbonate with styrene–acrylonitrile copolymers containing 13 or 25% of acrylonitrile in the copolymer are incompatible.[116] However, the addition of even 1% of a polyester of the type of poly(1,4-butylene adipate), poly(1,4-cyclohexane-dimethylene succinate) or poly-ε-caprolactone is sufficient to obtain a single-phase mixture with polycarbonate : copolymer ratios of 1 : 1 or 1 : 3. The region of compatibility in the ternary mixture then increases with increase in the acrylonitrile content in the copolymer from 13 to 25%. The introduction of butadiene and styrene copolymers respectively into a mixture of polybutadiene and polystyrene oligomers lowers the phase separation temperature (system with a UCT).[114]

(b) Deuteriation of one of the mixture components. The temperature and concentration ranges corresponding to the miscibility of two copolymers can be altered by deuteriating one of the components. For example, non-ideal mixing is observed in mixtures of deuteriated and non-deuteriated polystyrenes.[117] Deuteriation of polystyrene increases the phase separation temperature of its mixtures with poly(vinyl methyl ether) (a system with a LCT).[118,119] The replacement of hydrogen by iodine in polystyrene makes the polystyrene–iodine-containing polystyrene system incompatible.[120] The UCT is increased similarly in the polystyrene–polybutadiene system on deuteriation of polybutadiene.[118] The change in compatibility in such systems has been explained by the change in the chain conformation on deuteriation.[118,119]

(c) The influence of the stereoregularity of one of the components. The stereoregularity of one of the mixture components has a significant influence on compatibility.[61,121,122] Thus, according to the results of Fourier transform IR spectroscopic analysis, maximum intermolecular interaction is observed in a mixture of the styrene–allyl alcohol copolymer with syndiotactic poly(methyl methacrylate), while in the mixture with the isotactic homopolymer the interaction is a minimum.[61] Isotactic poly(methyl methacrylate) is incompatible with poly(vinyl chloride) over the entire range of compositions, whereas with the syndiotactic homopolymer it forms a compatible system when the latter contains up to 60% of the syndiotactic polymer. For higher contents of syndiotactic poly(methyl methacrylate) (>60%), the system separates into two phases, one of which contains the pure syndiotactic poly(methyl methacrylate) while the other is a 60 : 40 mixture of syndiotactic poly(methyl methacrylate) and poly(vinyl chloride).[78] The influence of the stereoregularity of poly(methyl methacrylate) and its compatibility with poly(vinylidene fluoride) can be inferred from the Flory–Huggins thermodynamic interaction parameter χ_{12}, which is −0.13, −0.10, and −0.06 for mixtures with isotactic, atactic, and syndiotactic poly(methyl methacrylates) respectively.[122]

(d) The influence of the solvent. In many cases mixtures of polymers are obtained from their solutions in a common solvent.[33] It has been demonstrated experimentally and theoretically[17,123,124] that the compatibility of polymers in a common solvent depends on the difference between the parameters of the thermodynamic interaction of the solvent with each polymeric component (the so called "$\Delta\chi$ effect"[123]). Hence errors may arise in the assessment of the compatibility of two polymers isolated from a common solvent. For example, polystyrene is compatible with poly(vinyl methyl ether),[11] but in solvents with different affinities for the two polymers "closed regions" of incompatibility may be observed.[124] The films obtained from such solutions may contain microheterogeneous regions because during the evaporation of the solvent the system passes through a region of incompatibility and the structure formed in this composition range is retained, since the viscosity of the mixture increases significantly under these conditions.[125]

Thus the compatibility or incompatibility of polymers in solution does not alone guarantee their compatibility or incompatibility after the removal of the solvent. A mixture of poly(bisphenol A carbonate) with poly(methyl methacrylate), which many workers have regarded as incompatible,[11,126] may serve as a typical example. It has been shown[127] that in a number of instances the mixture separates into two phases: for example, if it has been obtained from solution in methylene chloride and THF by evaporating the solvent or by precipitating the polymers from the solution with methanol and also if it has been prepared from the melt. On the other hand, the system obtained by precipitating the same polymers from the same solvents with heptane is compatible over the entire range of compositions and it has a LCT. This must be borne in mind in considering systems in which both a LCT and a UCT are observed.

The influence of the difference between the affinities of the solvent for each polymer can exceed the influence of the interaction between the polymers on their compatibility in solution. For example, in a study of mixtures of poly(ethylene oxide) with the styrene–methacrylic acid copolymer,[128] it was observed that the compatibility of these polymers in benzene increases with increasing content of methacrylic acid in the copolymer (up to 8 mol%) as a consequence of weak specific interactions beween the polymers. The same effect is observed in THF but it is weaker, while in chloroform the polymers are incompatible.

The study of the influence of the affinity of plasticising agents on the compatibility of polychloroprene and butadiene-styrene rubbers[129] showed that the compatibility of the rubbers is impaired

in the presence of plasticisers which are good solvents for both rubbers (dibutyl sebacate and MP-604 oil), while after the introduction of a poor solvent (stabiloil-18) it hardly changes. The reduction of the compatibility of rubbers after the introduction of a good solvent has been explained[129] by the shielding of the functional groups of the rubbers as a result of the solvation of their macromolecules by the plasticisers. On the other hand, it has been shown[111] that, after the introduction into a mixture of two thermodynamically compatible polymers of a third polymer, which forms mixtures with each of the remaining polymers having similar consolute temperatures, the compatibility of the latter polymers increases. A significant decrease in compatibility occurs when the consolute temperatures for mixtures of the added third polymer with each of the blended polymers differ significantly. We may note that this system can be described satisfactorily within the framework of the binary interactions model.[32]

Apart from the factors enumerated, the consolute temperature is influenced significantly also by applied pressure.[130-135] Thus it has been observed for mixtures of poly(ethyl acrylate) with poly(vinylidene fluoride)[130] that, when the content of the latter in the mixture is up to 30%, the turbidity point for the system initially decreases with increase in pressure, then passes through a minimum, and finally increases. With increase in the content of poly(vinylidene fluoride) in the mixture (in excess of 40%), the turbidity point monotonically increases with increasing pressure (system with a LCT). In mixtures of poly(2,6-dimethyl-1,4-phenylene oxide) with styrene–*p*-fluorostyrene copolymers, the LCT increased with increasing pressure over the entire range of the latter.[131] In mixtures having a UCT (mixtures of oligostyrenes with oligobutenes and oligopropylenes),[132] an increase in pressure results in an increase in the UCT.

Whereas the parabolic dependence of the consolute temperature on pressure predicted by the theory for polymer solutions[17] has been confirmed experimentally,[133] for mixtures of polymers the available experimental data are insufficient to reach general conclusions. It is only known that the application of an electric field increases the LCT.[136]

III. The stabilisation of dispersions and regulation of the properties of materials based on mixtures of thermodynamically incompatible polymers

Typical examples of the modification of one polymer by the addition of another are provided by the preparation of rubber-reinforced glass plastics,[137,138] epoxide resins,[139] rubbers reinforced by thermoplastics and thermoreactive resins, etc.[140] All these systems are multiphase. Important factors determining the properties of such systems are the degree of dispersion of the additive in the matrix of the other polymer, adhesion at the interface, and the structure and properties of the interfacial layer.[3,141] The adhesion between the phases is especially important, because, for example, under the conditions of poor adhesion, the mechanical stresses in one phase are not transmitted effectively to the second phase, as a result of which the mechanical properties of the system may be impaired.[3] Consequently, with the exception of certain special cases,[142] a good adhesion between the phases is essential in multiphase mixtures. For this purpose, one introduces the so called "compatibility inducers", which may be block or graft copolymers having blocks with the same chemical composition as the blended polymers,[3,143] as well as other polymers improving the compatibility of the initial components.[144] The mutual binding of the phases can also be improved by creating interphase cross-links[145-148] and by generating interpenetrating networks.[149]

In this review we shall consider mainly the results of the latest studies on dispersion stabilisation processes and methods for the regulation of properties of systems obtained from thermodynamically incompatible polymers.

1. Introduction of compatibility inducing additives

One of the ways of solving the problem of the stability of mixtures of incompatible polymers involves the wide scale employment of block and graft copolymers,[3,143] constituting compatibility inducing additives, especially in the preparation of impact-resistant compositions.[3] It has been shown in a number of studies[150-153] that the introduction of a graft copolymer such as hydrogenated butadiene–styrene into a mixture consisting of low density polyethylene and polystyrene increases the tensile strength but the elongation at rupture remains small. On the other hand, when 9% of a diblock copolymer with an equivalent composition is introduced into the mixture, then the tensile strength, elongation at rupture, and Young's modulus all increase and other system characteristics are also improved. With increase in the molecular weight of the copolymer, these characteristics are improved and even synergism of the properties is observed. A similar effect has been noted also after the introduction of such a copolymer into a mixture of high density polyethylene with polystyrene.

Comparative studies of the morphology and mechanical properties of polyethylene–polystyrene mixtures have shown that the introduction into them of a styrene–butadiene block copolymer whose blocks are separated by a styrene–butadiene statistical copolymer [for example of the type PS–$(PS/PBD)_{stat}$–PBD] induces a greater effect than introduction of the simple diblock copolymer.[153] The authors believe[153] that the unique effect of this copolymer is caused by its partial compatibility with polystyrene and polyethylene at the interface, i.e. it behaves as a stabilising agent for the homopolymers and promotes the creation of a "stepwise" modulus responsible for the improvement of the mechanical properties. Furthermore, after the introduction of such a block copolymer there is a significant increase in the dispersion of this system and synergism of the properties is manifested in the range of compositions where the mixture is enriched in the polymer matrix. When the mixture contains up to 80% of polystyrene, a system with a structure of the "network in network" type is produced. The introduction of the α-methylstyrene–methyl methacrylate block copolymer into a mixture of poly(vinylidene fluoride with poly-α-methylstyrene also leads to a decrease in the size of the dispersed particles and to an increase in tensile stress and Young's modulus.[151] The ethylene–propene copolymer, introduced into a mixture of polyethylene with polypropylene, also has an emulsifying effect.[154-157] The introduction of a copolymer increases the affinity between the components, which is manifested by a more effective homogenisation of the mixtures.[154] As a result, the mixtures are deformed more uniformly and are characterised by greater elongations with rupture. In the given instance, the macromolecules of the copolymer, dispersed in amorphous regions of polyethylene and polypropylene, ensure high degrees of interpenetration of the components.[154] Polyethylene and polypropylene are partially compatible in the melt,[155,156] but the introduction of the copolymer stabilises the two-phase structure of the melt.

An emulsifying effect has been observed also after the introduction of the α-methylstyrene–graft methyl methacrylate copolymer into a mixture of poly(vinylidene fluoride) with poly-α-methylstyrene.[157] In particular, the size of the particles diminished significantly in this system, a maximum appeared on the relation between the tensile strength and composition for a 70% content of poly(vinyl fluoride), and additivity of Young's moduli was observed. On the other hand, in the absence of the copolymer, the tensile strength and Young's moduli were described by curves with a minimum.

Other examples of the use of block or graft copolymers as compatibility inducing additives may be found in a review.[3] The choice of the appropriate copolymer should be based, according to Paul and Newman,[3] on the following requirements: (1) it must reduce the interfacial energy, (2) it must promote a finer dispersion of the components during the mixing process, (3) it must stabilise the mixture and prevent the separation of the components, and (4) it must improve the adhesion between the phases. The desired effects can be attained when the appropriate copolymer is located on the interface between two phases.[3]

The compatibility inducing agent may be also a third polymeric component introduced into a mixture of two thermodynamically incompatible polymers.[158–161] For example, in order to improve the properties of mixtures of low density polyethylene with other polymers [polystyrene poly(vinyl chloride), polypropylene], additives such as the ethylene–propene copolymer, natural rubber, polybutadiene, the acrylonitrile–butadiene–styrene ternary copolymer (ABS resin), copolymers of the butadiene–styrene type with a 72% content of butadiene, chlorinated polyethylene containing 42 and 20% of chlorine, and polyurethane containing ethylene adipate blocks.[161] It has been shown that the introduction of a third component into 1 : 1 mixtures improves the mechanical properties and that the increase in impact resistance is accompanied by an increase in elongation at rupture. Particularly high impact resistances and elongations at rupture have been observed after the introduction of the butadiene–styrene rubber into a mixture of polystyrene with polyethylene. The improvement of the properties of such systems can be accounted for by the formation of an elastomeric layer at the interface and by the dispersing capacity of the modifying additives. The improvement of the interfacial interaction and hence the improvement of the physicomechanical properties of mixtures of various rubbers (strength, ozone and weather resistance, resistance to thermal ageing, reduction of the embrittlement temperature, and reduction of the density of vulcanising agents) is promoted by the introduction of chlorinated polymers into such rubbers.[143] The modifying effect of additives of this kind is mainly determined by their polarity. Thus the modification of a mixture of thermoplastic polyurethane with poly(vinyl chloride) by a more polar rubber leads to the formation of compositions with high strength parameters.[162] The interaction between the components of a heterogeneous mixture of two polymers intensifies also after the introduction of surfactants of different classes,[163] for example, after the introduction of ionogenic surfactants into mixtures of poly(vinyl chloride) with natural rubbers. The introduction of a surfactant into a mixture of an epoxide resin and silicone rubber ensures the appearance of a region of compatibility in oligomer–natural rubber systems.[164] The factor determining the properties of mixtures of poly(vinyl chloride) with chlorinated polyethylene is the compatibility of the added oligomer (high-molecular-weight oligobutadienes and oligobutadienes with OH and CN groups) with each mixture component.[159] In certain cases, the additives introduced increased the rate of "dissolution" of, for example, rubbers in one another at the same temperature of the treatment of the mixture, which is important for the preparation of layered (doubled) compositions (the introduction of peroxides into a mixture of polybutadiene with butadiene–styrene rubber[165]).

2. The role of interphase cross-links

One of the effective ways of stabilising mixtures of incompatible polymers is interphase cross-linking.[145–148] Thus cross-linking has been used to increase the stability of mixtures of polyethylene with poly(vinyl chloride).[145] The cross-linking of poly(vinyl chloride) was achieved by introducing 6-diallylamino-1,3,5-triazine-2,4-dithiol (DAATD) and polyethylene was cross-linked by introducing a mixture of DAATD with peroxides of different types. It has been shown that the more intense the adhesion interaction between the components, the better the mechanical properties of the system (strength and elongation at rupture). Nakamura et al.[145] attribute this effect to the formation of chemical bonds between poly(vinyl chloride) and polyethylene phases during the mixing process and after pressing. The introduction of the same cross-linking agent (DAATD) into a mixture of fluororubbers based on vinylidene fluoride or hexafluoropropene with epichlorohydrine and polyisoprene led to the formation of vulcanised rubbers with a high degree of cross-linking and good adhesion and mechanism properties. In a pure form, these rubbers are incompatible, but the introduction of the additive leads to a high degree of covulcanisation of individual rubbers at the interface.[146] Heating of the system or the addition of tetraalkylammonium bromide together with DAATD facilitates significantly the formation of cross-linked at the interface.

The modification of polystyrene by peroxide, dithiocarbamate, or perthiocarbamate groups ensures its mixing with natural rubber, the ethylene–propylene copolymer, butadienenitrile rubber, polypropylene, and polybutadiene.[147] The vulcanised mixtures of modified polystyrene with, for example, polybutadiene behave under dynamic conditions similarly to three-block copolymers. Polystyrene modified by groups which react with the double bonds of the elastomer reinforces the elastomer matrix.[147,148]

3. Specific interfacial interactions

Specific interactions at the interface also promote the stability of two-phase polymer mixtures.[166–170] For example, mixtures of poly(urethane-urea) with poly(vinyl chloride) are incompatible, but the formation of hydrogen bonds between the α-hydrogen atoms of poly(urethane-urea) and the chlorine atoms of poly(vinyl chloride) ensures effective interfacial adhesion.[166] The impact strength of the system passes through a maximum for a 7.5–15% content of poly(urethane-urea).

The adhesion between phases increases when electron donor–electron acceptor bonds are formed at the interface.[167,168] Such bonds are formed in mixtures of electron-donating and electro-accepting polycarbonates, polyterephthalates, or polyisophthalates obtained from 2-(*p*-dimethylaminobenzyl)propane-1,3-diol (donor) and 2-(3,5-dinitrobenzyl)propane-1,3-diol (acceptor)[168] and also from poly[*N*-(2-hydroxyethyl)carbazolyl methacrylate] (donor) and poly(methacryloyloxy-β-hydroxyethyl-3,5-dinitrobenzoate) (acceptor).[169] In the latter case the intermolecular complex formation increases the modulus of the mixture in the region of low-frequency dynamic loads and high temperatures by three orders of magnitude compared with the pure components. It is believed[169] that intermolecular complex formation leads to the formation of thermoreversible networks with an unusual topology which results in

the expansion of the frequency range of the elastic response of the mixtures. The presence of a maximum in the dependence of the decomposition energy on the composition of mixture of the sodium and zinc salts of an ethylene ionomer with rubbers (acrylonitrile or carboxylated acrylonitrile rubbers) has also been explained by the ionic interaction of polar phases.[170] A tenfold increase in the impact resistance of powdered mixtures of poly(phenylene oxide) (50 parts), the zinc salt of sulphonated (1.4 mol% of sulphur), polystyrene (9 parts), sulphonated (0.6 or 1.4 mol% of sulphur) polystyrene (9 parts), the ethylene–propylene copolymer (9 parts), and zinc stearate (9 parts) in the presence of triphenyl phosphate (14 parts) is also caused by the interaction at the interface.[167] (The mixtures were obtained by dry blending with subsequent extrusion at 453–523 K.)

4. The addition of small amounts of one polymer to another

Numerous studies devoted to the influence of the addition of small amounts of one polymer to another on the physicomechanical and physicochemical properties of the systems, especially on their viscosity, have been published in recent years.[171–181] Viscosity is an important technological parameter and the characteristic features of its variation with composition have been examined in particularly great detail. Attention has been concentrated on the elucidation of the mechanism of the influence of additives on the viscosity.[172,181] A series of anomalies in the concentration dependence of the viscosities of melts of mixtures of polymers (over a narrow range of concentrations, predominantly for a low content of one of the components) have been discovered.[181] As a rule, at low concentrations of the additives a sharp decrease in viscosity is observed. For example, the viscosity of the incomptible thermoplastic polyamide–liquid crystal copolyester system based on 6-hydroxy-2-naphthoic and *p*-hydroxybenzoic acids diminishes sharply in the presence of small amounts of a copolymer in the mixture.[174] The addition of vinyl chloride–vinyl acetate or vinyl chloride–propylene copolymers reduces the viscosity of poly(vinyl chloride) and facilitates its treatment.[175] The greatest effect is then exhibited by copolymers with a low molecular weight. The addition of 10% of butadiene-styrene rubber to the butadiene–styrene–butadiene copolymer diminishes the viscosity of the latter almost by a factor of 2,[176] which has been explained by the localisation of the added rubber with short chains at the interface and the consequent facilitation of the flow of the copolymer. The similar introduction of small amounts of the styrene–maleic anhydride (14% of the anhydride) copolymer reduces significantly the fluidity of poly(bisphenol A polycarbonate).[177]

It is possible to quote very many similar examples.[182–186] In our view, among the existing explanations of the observed anomalies, that according to which their appearance is associated with the transition of the system from the single-phase state to the two-phase state and conversely can be regarded as the most acceptable.[180,181] This was first demonstrated in a study where the concentration dependence of the viscosity was compared with the Flory–Huggins prameter χ_{12} of the thermodynamic interaction between the mixture components in melts at identical temperatures. Satisfactorily parallel concentration variations of the viscosity and the parameter χ_{12} were observed. In particular, for positive values of χ_{12} (thermodynamically incompatible system), the viscosity proved to be less than the additive value, while for negative values (compatible system) it proved to be higher than the additive value. It was concluded that a sharp fall of the viscosity of melts of polymer mixtures at low concentrations of the added polymer occurs when the system passes from the single-phase to the two-phase state.[179] The form of the phase diagram apparently make it possible to predict the concentration and temperature dependences of the viscosities of melts of polymer mixtures. Hitherto, such comparison of the concentration variation of the viscosity with the phase diagram has been achieved in only one study.[179]

Extremum changes have been observed also in a number of other physicochemical and physicomechanical characteristics of systems at low concentrations of the added polymer.[187–200] Thus the improvement of high density polyethylene after the introduction into the latter of small amounts of thermoelastoplastics has been explained by the latter being distributed in the non-ordered regions of the polyethylene with retention of the primary crystalline state.[191]

It has been suggested that the increase in strength on extension of polypropylene containing small amounts of a thermoelastoplastic (up to 1%) occurs as a result of the surface interaction of the polystyrene units with the structural formations in polypropylene, which leads to the joint orientation of polypropylene and the thermoelastoplastic.[193] The authors[191] concluded that the micro-additives play the role of a filler of the structural defects, facilitating the plastic deformation and ensuring the formation of a finer and uniform structure. The reason why the strength properties of the systems are impaired on further increase in the amount of the additives are still not understood.

The high tensile strength (above the additive value) of low density polyethylene with added ethylene–propylene copolymer has been explained[195] by the partial compatibility of the copolymer with polyethylene in the melt: on cooling the mixture of polyethylene with the crystalline copolymer (with a degree of crystallinity from 1 to 20%), a cross-linked matrix is formed as a result of the joint crystallisation. The synergism of the properties of mixtures of high density polyethylene with the ethylene–propylene copolymer and also of isotactic polypropylene with the same copolymer has been explained by partial compatibility.[196] The strength properties are improved with increase in the compatibility of the modifying additive and the polymers. This is achieved, for example, by increasing the content of the component A in a copolymer of the A–B type when it is mixed with the corresponding type A homopolymer. The necessity for the partial compatibility of the components in order to achieve a high impact strength was also noted in a study of mixtures of poly(bisphenol A carbonate) with the styrene–acrylonitrile copolymer and the same copolymer grafted on polybutadiene.[197] The change in the position of the mechanical losses peak and of the complex shear modulus for a styrene block copolymer modified by resins has also been explained by the compatibility of the modifying additive with the polymer matrix.[198]

It is known that an excess volume of mixing obtained for compatible systems, i.e. $\Delta V = V_{mix} - \Sigma\varphi_i V_i < 0$. This reduces the number of external degrees of freedom[18] and hence lowers the mobility of the chains and increases the packing density. Partial compatibility ensures the mutual binding of the phases, i.e. interfacial adhesion as a result of which the physicomechanical characteristics of systems of this kind are improved.[3]

IV. Conclusion

The examples examined in the review indicate convincingly that polymers differing in chemical structrure and involving opposite principles, which complement one another, are most effectively miscible[10] (the concept of "the mutually complementing difference"

already mentioned[17]). Since in such cases the enthalpy of mixing is negative, systems of this kind should be characterised by a LCT. Indeed, according to Krause,[9] among the known thermodynamically compatible polymer pairs, 75% have a LCT. Consequently, in order to ensure thermodynamic compatibility it is essential to select components such that their functional groups are capable of strong interaction or one or both components must be modified in such a way that the "mutually complementing differences" are ensured.

In devising compositions which need not satisfy the requirement of thermodynamic compatibility, it is necessary to solve the problem of the stabilisation of the dispersion by introducing "compatibility inducing additives", by organising interphase cross-links, or by ensuring partial compatibility of the components both in the preparation of the composition and in its conversion into finished articles. In other words, it is essential to ensure a satisfactory interfacial adhesion at least in those cases where the system must have a high strength.

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