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The influence of the nature of the chemical reaction on the structure and properties of blends in the reactive blending of polymers

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Abstract. Polymer blends, the preparation of which is accompanied by various chemical reactions and the formation of specific intermolecular bonds between the components, are analysed. The factors influencing the phase structure of the materials obtained are identified and their relative contributions to its formation are estimated. The influence of the blend composition, nature, and concentration of the functional groups and of the temperature regimes in the blending process is examined. A systematic treatment of the results of experimental and theoretical studies of the method of utilisation of functional groups — direct interaction of the reaction groups in the blended polymers or the introduction of low- and high-molecular reagents capable of interacting with the macromolecules of the blend components — is proposed. It is noted that quantitative data on the variation of the thermodynamic affinity of the blend components and on the rates of mass transfer controlling the formation of the phase structure are limited. Certain theoretical models of the structure of reactive polymer blends, which explain their mechanical properties, are discussed. The priority aspects of studies on the processes involved in the reactive blending of polymers are noted. The bibliography includes 212 references.

I. Introduction

The use of polymeric materials in industry has been expanding and the requirements which they must meet have become more stringent. Special interest has been shown in multicomponent blends and alloys. The creation of such polymer systems entails the potential possibility of combining the attractive qualities of each component of the polymer blend in a single material.[1–5] Much attention has been devoted in recent years to the processes involved in the preparation of polymeric materials by blending components in which chemical reactions take place. Such blending is called reactive.[3]

The increased attention to reactive blending processes has been induced by the fact that only a few polymers are fully thermodynamically compatible and produce blends which are homogeneous at the molecular level.[6] The majority of polymers exhibit limited compatibility and their blends possess a heterogeneous morphology. Practice has shown that, precisely as a consequence of the multiphase nature of multicomponent polymer systems, the materials based on them frequently possess unique performance characteristics, for example an increased resistance to impact loads and optimum stress-strain properties. The chemical nature of the disperse phase and of the dispersion medium as well as the parameters of the phase structure, namely the volume phase ratio, the size and size distribution of the particles of the disperse phase, the degree of dispersion and the coherence of the disperse phase, and interfacial adhesion, are of primary importance in the generation of useful properties.[7–9] The blend composition and viscoelastic properties of individual components and the conditions in the blending process determine the parameters of the phase structure and the resistance of the blends to coalescence.[10,11]

It follows from the fundamental relations describing the thermodynamic equilibrium in disperse systems[12] that the most effective factor which makes it possible to regulate the parameters of the phase structure is the thermodynamic affinity of the components. A low thermodynamic affinity leads to a high interfacial tension and hinders the dispersion of the components on mixing in the melt. In its turn, this leads to a low interfacial adhesion in the solid state and is responsible for the premature mechanical fracture of the material.[8,9] Within the framework of traditional approaches (specific selection of the chemical nature of the components, the composition of the blends, and the processing temperature, as well as the introduction of low-molecular or polymeric additives), the compatibilisation problems — the improvement of thermodynamic compatibility and the regulation of the parameters of the phase structure and of its influence on the physicomechanical characteristics of polymer blend — have been investigated fairly completely.[13–27]

Since the end of the 1980s, reactive blending, in which physical and/or chemical interactions between the molecules of unlike blend components may occur together with blending processes (in the melt or in solution), has attracted increasing attention. The occurrence of exothermic (as a rule) processes, specific intermolecular or chemical interactions — is accompanied by a decrease in the entropy component and an appreciable decrease in the enthalpy component of the free energy. As a result of the decrease in the free energy of mixing (dispersion), the possibilities for the regulation of the phase structure parameters of multicomponent polymeric materials are expanded.

An increase in the thermodynamic affinity of two polymers may be achieved if interchain exchange reactions (mainly transesterification) take place during the blending process or certain

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specific intermolecular interactions occur,[28,29] such as connecting as a result of the formation of hydrogen bonds,[30] ion–dipole and dipole–dipole interactions,[31] acid–base and ion–ion interactions,[32] the formation of π–π complexes,[33] and the formation of molecular charge-transfer complexes.[34,35] In a number of instances, the decrease in the free energy of mixing (dispersion) is achieved as a result of the increase in its entropy component due to intramolecular repulsion effects.[36,37]

The reviews of theoretical and experimental studies on compatibilisation,[38–40] reactive extrusion,[41] and reactive blending of polymers,[6,42,43] attempts were made to interpret and classify the processes involved in the reactive blending of polymers. The number of experimental studies in the field of the reactive blending of polymers has been increasing, which necessitates a further systematic treatment and classification of the studies in this field.

A classification of multiphase reactive polymer blends with allowance for the differences in the way that reactive blending is carried out is proposed in the present review.

Group A. Reactive polymer blends capable of forming strong physical or chemical bonds between macromolecules under the conditions of thermal and mechanical influences and on specific catalysis. Polymer blends, one of which has been subjected to a preliminary chemical modification in order to introduce functional groups capable of reacting with the macromolecules of the other polymer under the blending conditions, may be assigned to the same group.

Group B. Reactive blends obtained as a result of the introduction of a third high-molecular component capable of reacting with at least one of the main components of the polymer blend to form compatibilising copolymers.

Group C. Reactive blends formed following the introduction of low-molecular components promoting intermolecular and/or intramolecular cross-linking (dynamic vulcanisation) of the phases.

A wide class of blends, formed on blending a linear or network polymer with a monomer or oligomer and subsequent chemical solidification (polymerisation, polycondensation), can also be assigned to reactive polymer systems. These are the so called partial (or complete) interpenetrating polymer networks in which the stages involving the blending of the components and their chemical reaction are as a rule separated. Such attention has been devoted in the literature[44–47] to the study of the structures and properties of various types of interpenetrating polymer networks and we shall therefore not consider them here.

Table 1. Reactive blending of polymers in solution (group A blends).

Polymer 1	Polymer 2	Brief process characteristics	Ref.
PBT	POR	Transesterification	52
	PAr	"	53
PC	PBT	"	54
	PET	"	55
	PETG	"	56
	s-PMMA	"	57
PS	PTCB	Interpolymer Friedel–Crafts reaction	58
PVC	PU	Formation of hydrogen bonds	59
PVP	E–VA	Ditto	60
PVP, POR	PAMA	See [a]	65
POR	Various polyesters	Formation of hydrogen bonds	61
	ENR	Ditto	62
PVC	PCL	Specific intermolecular interactions of unknown nature	63
	Various polyesters	Ditto	64
PC	PPMA	"	66
PVME	SBS	"	67
PA6	PPO	"	68

Note. The following designations have been adopted for the polymers; PBT = poly(butylene terephthalate); POR = phenoxy-resin (bisphenol A polyhydroxyether); PAr = polyarylate (copolyester of bisphenol A and terephthalic and isophthalic acids in proportions of 2 : 1 : 1); PC = polycarbonate; PET = poly(ethylene terephthalate); PETG = copolyester of cyclohexane-1,4-dimethanol, ethylene glycol, and terephthalic acid (1 : 2 : 3) ; s-PMMA = syndiotactic poly(methyl methacrylate); PS = polystyrene; PTCB = poly-1,1,2-trichlorobuta-1,3-diene; PVC = poly(vinyl chloride); PU = polyurethane; PVP = poly-4-vinylphenol; E–VA = ethylene–vinyl acetate copolymer; PAMA = poly(alkyl methacrylates); ENR = epoxidised natural rubber; PCL = poly-ε-caprolactone; PPMA = poly(phenyl methacrylate); PVME = poly(vinyl methyl ether); SBS = styrene–butadiene–styrene copolymer; PA6 = polyamide 6; PPO = poly(propylene oxide).

[a] According to Chong and Goh,[65] the nature of the intermolecular interaction has not been established in this case.

II. The influence of interchain exchange and of specific interactions in binary polymer blends (group A)

Reactive blending processes may be carried out in solution, in the melt, and in the solid phase. In the solid phase, such processes occur as a result of an external mechanical action, leading to nonelastic deformations and plastic flow. The results of studies on the mechanisms and rates of solid-phase chemical reactions at a high pressure in combination with shear deformation have been examined in detail in a number of communications[48–51] and are outside the scope of the present review.

Examples of the preparation of group A reactive polymer blends in solution are presented in Table 1. The initial polymers are usually blended in a common solvent and the blends are then precipitated and treated in a specific temperature–time regime. Under such conditions, the most typical interchain exchange reaction for polyesters is transesterification, *i.e.* transesterification of high-molecular polyesters, leading to the formation of the corresponding block copolymers. Hydrolytic chain degradation and chain polycondensation processes occur under these conditions.[56] According to Fourier-transform infrared spectroscopic (FTIR) data, the transesterification in certain polymer blends at high temperatures may be accompanied also by thermal degradation with recombination of macromolecular free radicals, which leads to the formation of graft copolymers.[57] The formation of an interpolymer microgel in a study of the Friedel–Crafts reaction occurring under mild conditions in a blend of two virtually incompatible polymers has been established.[58] According to a number of investigators,[52–58] the compatibilisation of polymer blends is due to the formation of copolymers or interpolymers.

The compatibilisation of polymer blends is also promoted by the formation of hydrogen bonds between the blend components[59–62] (Table 1). Signs of intermolecular association and of the formation of molecular complexes as a result of strong hydrogen bonding have been observed by high-resolution ^{13}C NMR and differential scanning calorimetry in model blends of low-molecular poly(ethylene oxide) and resorcinol, which have two eutectic points on the phase diagram.[69] The compatibilisation of blends of diethyl maleate-modified ethylene–propylene rubber with polystyrene and with poly(vinyl chloride),[70] of polyamide 6 with the Mn salt of sulfonated polystyrene[71] and alkaline (Li and Na) ionomers of sulfonated polystyrene,[72] and also of the styrene–4-vinylpyridine block copolymer with the Zn salt of a carboxylated ethylene–methacrylate copolymer[73] is due to the formation of polymeric complexes. Examples of the compatibilisation of polymer blends as a result of specific interactions[63–68] can also be found in Table 1. The dependence of the intensity of

the intermolecular interactions on the blend composition has been demonstrated.[74]

For ecological reasons, reactive blending has been carried out recently with increasing frequency in polymer melts (in the absence of a solvent). Batch mixers and continuous screw extruders are used as the reactors. Studies on a series of model reactions in solution and in homogeneous melts have shown [75] that the mechanisms and kinetics of the reactions are virtually analogous in both homogeneous media, provided that diffusion is not the limiting factor. However, as a rule, reactive blending processes are carried out in heterogeneous melts. Interchain block or graft copolymers may then be formed in different proportions (*via* new covalent or ionic bonds). Such *in situ* compatibilisers have molecular segments chemically identical with the segments in the corresponding unreacted homopolymers. The compatibiliser segments are distributed predominantly at the interface, which entails a decrease in interfacial tension and adhesion is strengthened.[6]

The heterogeneous nature of the reactive polymer system predetermines the characteristic features of the kinetics of the chemical reaction. It has been shown in relation to the transesterification reaction in the ethylene–methyl acrylate copolymer/monohydroxylated polystyrene system [75, 76] that the degree of conversion decreases appreciably with increase in the molecular mass of the monohydroxylated polystyrene. The graft copolymer formed at the interfaces promotes an increase in interfacial adhesion and the stabilisation of the morphology. However, its accumulation at the interface greatly reduces the overall reactivity of the system. The intensity of mechanical mixing becomes a very important factor for the given reaction, since it influences the depth of diffusion and the formation of new interfaces. A marked effect due to the introduction of small amounts of the solvent is also observed: the addition of 1 mass %–2 mass % of 1,2,4-trichlorobenzene or *n*-hexane to the melt of the ethylene–methyl acrylate copolymer/monohydroxylated polystyrene blend greatly increases the overall degree of conversion. According to the authors,[75, 76] this effect can be accounted for by the increase in compatibility, the improvement in interfacial mixing, and the mutual diffusion in the presence of a solvent. Unfortunately, the relationship between the reaction kinetics and the phase structure of the blend as well as the operating characteristics of the material obtained had not been established in the above investigations. On the whole, information about the diffusional mobility, mutual solubility of the components, the area of interfacial contact, the concentration profiles of the reactants in the interfacial region, as well as the nature of their time variation is needed for the interpretation of kinetic data in heterogeneous reactive polymer systems.[75, 76]

The conclusions reached in the above studies [75, 76] agree well with the results of the investigation of transesterification in polyester blends,[77] for which the influence of the compatibility of the initial components, blending conditions (temperature, duration, and intensity of blending), the ratio of the viscosities of the components, and the presence of catalysts [78, 79] or inhibitors [80] in the system on the rate of transesterification has been established. It has also been shown [81] that, in the course of the transreaction , the viscosity of the melt changes; the viscosity increases until both components of the reactive blend have fully reacted.

Transesterification is most often employed in the preparation of group A reactive blends in the melt. An improvement of the compatibility of the components in the melt has been achieved in blends of polycarbonate with poly(butylene terephthalate),[82–85] poly(ethylene terephthalate),[78, 79, 86] polyarylate (the copolyester of bisphenol A and terephthalic and isophthalic acids in proportions of 2 : 1 : 1),[87, 88] the copolyester based on cyclohexane-1,4-dimethanol and terephthalic and isophthalic acids (Kodar A150),[89] a thermotropic polyester consisting of the copolymer of 4,4′-dihydroxybiphenyl and terephthalic and isophthalic acids (Ultrax KB4002),[90] and polyamide 6.[91, 92] The transesterification reaction is known to proceed at an appreciable rate at temperatures above 200 °C.[77] Below this temperature, the rate of reaction falls and at higher temperatures the Kolbe rearrangement involving the carbonate groups and the pyrolysis of the ester groups makes a significant contribution.[93] In a number of instances, the cross-linking and degradation reactions have also been observed, for example in polyacrylamide — chloroprene rubber [94] and polyacrylic acid — epoxidised natural rubber [95] blends.

Under the conditions of intense shear blending of incompatible polymers, interchain reactions were noted, as a result of which various copolymers compatibilising the system appeared. Maxwell and Jasso [96] observed the formation of a three-dimensional network of 'intertwined' homopolymeric stands on blending poly(methyl methacrylate) with polyethylene in an elastic-melt extruder. Under analogous conditions in the blending of polypropylene with high-density polyethylene in the melt, a block copolymer (formed as a result of the cross reactions of the macroradicals), responsible for the improvement of the compatibility of the system components, appears in the blend melt together with the homopolymers.[97]

The series of studies by Santra and coworkers,[98–101] indicating unlimited mutual solubility in the melt comprising polydimethylsiloxane rubber modified by the inclusion of vinyl groups and the ethylene–methyl acrylate copolymer,is by no means unique. The unlimited mutual solubility is due to the chemical reaction between the vinyl groups at the silicon atoms in the polydimethylsiloxane chains of the rubber with the α-methine groups of the methyl acrylate fragment of the copolymer.[98, 99] According to the results of dynamic mechanical analysis, for all blend compositions there is a positive deviation of the single glass-transition temperature from the values calculated by Fox's equation.[98] Synergistic effects have also been observed for the given system in the study of mechanical characteristics,[99] thermal stability,[100] and rheological properties.[101]

The improvement of compatibility in reactive blending in the melt may be achieved also as a result of specific interactions, for example the formation of hydrogen bonds between the functional groups of the blend components, as in the poly(ethylene terephthalate)/poly(ether imide) (Ultem 1000),[102, 103] poly(ethylene terephthalate)/polyurethane, and poly(butylene terephthalate)/polyurethane [104] systems.

The possibilities for compatibilisation and the range of polymeric objects used in reactive blending processes are greatly expanded if one or both components are subjected to a preliminary chemical modification. The aim of the chemical modification in this instance is the introduction into the macromolecules of functional groups capable of reacting under the blending conditions with formation of graft copolymers compatibilising the system. Table 2 presents the blending processes in which one of the components is subjected to preliminary chemical modification. An example of blends with preliminary chemical modification of both components is that of blends comprising 3-mercaptopropyltrimethylsilano-grafted poly(vinyl chlorides) and chlorinated polyethylene in which compatibilisation as a result of the mutual cross-linking of the components was observed.[131] The results of rheological studies, FTIR, and dynamic mechanical analysis of a blend of polypropylene modified by maleic anhydride with the Zn salt of the sulfonated ethylene–propylene–diene monomer have also demonstrated an improved mutual solubility compared with the unmodified polypropylene/ethylene–propylene–diene monomer blends as a consequence of the compatibilisation of the system *in situ*.[132]

In order to create nucleophilic or base-functionalised polymers for reactive blending with various electrophilic polymers, graft copolymers of olefins, in particular linear low-density polyethylene, with a tertiary amine — 2-methylaminoethyl methacrylate (DMAEMA) [133] — or a secondary amine — *tert*-butylaminoethyl methacrylate (TBAEMA) [134] — have been successfully synthesised. Model studies have demonstrated [135] that secondary amino-groups can form both ionic and covalent bonds, whereas only ionic bonds or polar interactions with polymers

Table 2. Reactive blending processes in the melt with participation of chemically modified polymers (group A blends).

Polymer 1	Polymer 2 (modified)	Brief process characteristics	Ref.	Polymer 1	Polymer 2 (modified)	Brief process characteristics	Ref.
PA6	PP–g–MAn	Compatibilisation *in situ* by the graft copolymer formed as a result of the reaction of the anhydride (carboxy-group) and an amine	105–107	S–MAn	LLDPE–g–TBAEMA	Formation of a graft copolymer *in situ* as a result of reactions leading to the formation of both ionic and covalent bonds	125
	PP–g–AA	Ditto	107		EPR–g–pA	Formation of graft copolymer *in situ* as a result of the reaction of the anhydride and the amine	126
	EPR–g–MAn	"	108–110				
	EPR–g–AnSA	"	111				
	EPDM–g–MAn	"	112				
	E–MAA	"	113				
	E–AEs–MAn	"	114	MMA–MAA	LLDPE–g–TBAEMA	Formation of graft copolymer *in situ* as a result of reactions leading to the formation of both ionic and covalent bonds	127
	S–EP–S–g–MAn	"	115				
	PS–g–MAn	"	116				
	PE–g–MAn	"	117				
	POLDPE	"	118				
PA66	PP–g–MAn	"	119				
	S–EP–S–g–MAn	"	115				
PBT	PP–g–GMA	"	120, 121	PBT	E–AEs–GMA	Ditto	114
E–AA	OPS	Formation of graft copolymer *in situ* (emulsifying effect)	122	EPDM	PAr–g–BCB	Cyclisation reaction [a]	128
				E–MA	HPS	Transesterification	129
				HDPE	ZSSEPTR	Improvement of compatibility as a result of specific intermolecular interactions	130
PVC	LLDPE–g–MAn	Miscibility based on specific intermolecular interactions	123				
S–MAn	LLDPE–g–DMAEMA	Improvement of compatibility as a result of the formation of ionic bonds (polar interactions)	124				

Note. The following designations have been for the polymers: PP–g–MAn = polypropylene modified by maleic anhydride; PP–g–AA = polypropylene modified by acrylic acid; EPR–g–MAn = ethylene–propylene rubber modified by maleic anhydride; EPR–g–AnSA = ethylene–propylene rubber modified by the anhydride of succinic acid; EPDM–g–MAn = ethylene–propylene–diene monomer modified by maleic anhydride; E–MAA = ethylene–methacrylic acid copolymer; E–AEs–MAn = ethylene–acrylic ester–maleic anhydride terpolymer; S–EP–S–g–MAn = styrene–(ethylene-propylene)-styrene triblock copolymer modified by maleic anhydride; PS–g–MAn = polystyrene modified by maleic anhydride; PE–g–MAn = polyethylene modified by maleic anhydride; POLDPE = photooxidised low-density polyethylene; PA66 = polyamide 66; PP–g–GMA = polypropylene modified by glycidyl methacrylate; E–AA = ethylene–acrylic acid copolymer; OPS = oxazoline-modified polystyrene; LLDPE–g–MAn = linear low-density polyethylene modified by maleic anhydride; S–MAn = styrene–maleic anhydride copolymer; LLDPE–g–DMAEMA = linear low-density polyethylene modified by dimethylaminoethyl methacrylate; LLDPE–g–TBAEMA = linear low-density polyethylene modified by *tert*-butylaminoethyl methacrylate; EPR–g–pA = ethylene–propylene rubber modified by a primary amine; MMA–MAA = methyl methacrylate–methacrylic acid copolymer; E–AEs–GMA = ethylene–acrylic ester–glycidyl methacrylate terpolymer; EPDM = ethylene–propylene–diene monomer; PAr–g–BCB = polyarylate based on bisphenol A and terephthalic and isophthalic acids (2 : 1 : 1) modified by 1,2-dihydro-4-chloroformylbenzocyclobutene; E–MA = ethylene–methyl acrylate copolymer; HPS = monohydroxylated polystyrene; HDPE = high-density polyethylene; ZSEPDM = Zn salt of sulfonated ethylene–propylene–diene monomer.

[a] Thermally reversible cyclisation reaction between the unsaturated side bonds of EPDM and the *o*-quinondimethane end groups of PAr–g–BCB.

containing carboxy- or maleic anhydride groups are characteristic of tertiary amino-groups. The reactive blending of linear low-density polyethylene, chemically modified by DMAEMA, with the styrene–maleic anhydride copolymer in the melt ensures an improved compatibility of the components. This conclusion was reached on the basis of electron microscope data and was accounted for by the strong specific polar interactions between the acid anhydride and the basic amino-groups. However, the improvement of the mechanical properties of these reactive blends proved to be slight.[124, 125] It was also established that the secondary amino-group in TBAEMA is more reactive in relation to the carboxy- or anhydride groups than the primary or tertiary amino-groups. A decrease in the size of the particles of the disperse phase, accompanied by an increase in the tensile strength σ_b, the relative tensile elongation at break ε_b, and the breaking energy on impact by 20%–50% compared with the nonreactive linear low-density polyethylene/styrene–maleic anhydride blends was observed under these conditions in systems comprising linear low-density polyethylene modified chemically by TBAEMA and the styrene–maleic. anhydride copolymer.[125]

A more significant increase in the stress-strain characteristics has been observed in the reactive blends of linear low-density polyethylene modified chemically by TBAEMA with the methyl methacrylate–methacrylic acid copolymer (by 500%–800%) compared with the nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends.[127] Three macromolecular reactions take place in blends of linear low-density polyethylene modified chemically by TBAEMA and the methyl methacrylate–methacrylic acid copolymer: the formation of the amide, the formation of the

carboxylate anion, and the formation of the imide ring as a result of the interactions of two neighbouring carboxy- and carboxylate groups of the copolymer with the amino-group of the linear low-density polyethylene modified chemically by TBAEMA with elimination of isobutene and an alcohol.[127, 135, 136] The last reaction leads to the formation of a graft copolymer, which increases interfacial adhesion and hence greatly improves the stress-strain characteristics of the reactive blends.

As can be seen from the relation presented in Fig. 1, the values of U_t for the reactive blends containing more than 50 mass % of the linear low-density polyethylene modified chemically by TBAEMA exceeded the additive values ('positive' effect [137]). For plastics with improved (as a result of the inclusion of rubber particles in the brittle polymer matrix) impact strength, such effects have been frequently observed.[1, 7, 10] Among the polymer blends consisting of a ductile (plastic) matrix and a brittle disperse phase, only very few exhibit 'positive' effects [for example, the polycarbonate/poly(methyl methacrylate) and polycarbonate/styrene–acrylonitrile copolymer systems].[137] Within the framework of the 'cold drawing' concept,[138] the absorption of impact energy in these systems can be explained by the plastic deformation of the brittle disperse phase. The reason for such deformation is the high compressive stress arising on bulk-phase deformation of a two-phase system by the tensile stress in the equatorial planes of spheres dispersed in a matrix and caused by the difference between the Young's moduli and the Poisson coefficients of the disperse spherical phase and the matrix. According to Liu *et al.*,[127] the 'positive' effect in the compatibilised linear low-density polyethylene chemically modified by the TBAEMA/methyl methacrylate–methacrylic acid copolymer blend can be explained by a brittle-to-ductile transition in the disperse phase. According to electron microscope data, such blends are characterised by a more finely disperse and inhomogeneous morphology than nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate)–methacrylic acid copolymer blends. The particles of the methyl methacrylate–methacrylic acid copolymer are anchored to a matrix comprising the linear low-density polyethylene modified chemically by TBAEMA with the aid of fibril-like elements, which appear as a result of the drawing of such polyethylene during impact fracture and indicate very strong adhesion between the phases.

The strong interfacial adhesion in the systems obtained by reactive blending has been confirmed by the results of the analysis of the concentration dependence of the elastic modulus E within

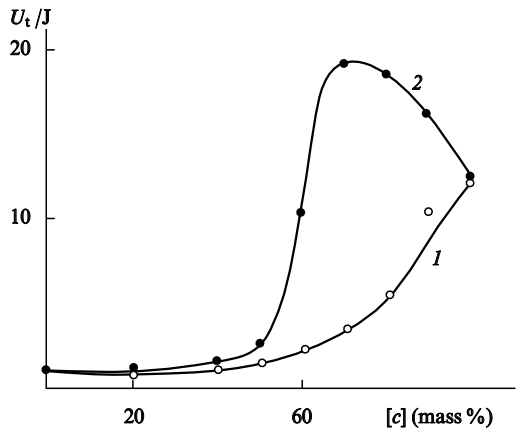


Figure 1. The influence of blend composition on the total absorbed impact energy U_t for nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends (*1*) and reactive linear low-density polyethylene chemically modified by TBAEMA/methyl methacrylate–methacrylic acid copolymer blends (*2*);[127] [*c*] — content of the linear polyethylene modified chemically by TBAEMA.

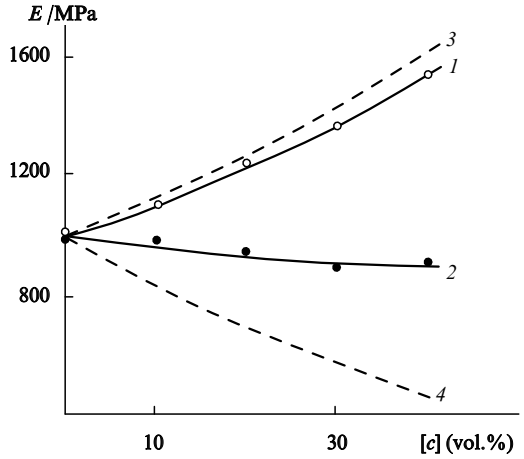


Figure 2. Experimental (*1*, *2*) and theoretical (*3*, *4*) dependences of Young's modulus on the volume fraction of the poly(methyl methacrylate) disperse phase for nonreactive linear low-density polyethylene chemically modified by TBAEMA/poly(methyl methacrylate) blends (*2*, *4*) and reactive linear low-density polyethylene chemically modified by TBAEMA/methyl methacrylate–methacrylic acid copolymer blends (*1*, *3*);[127] [*c*] — content of the methyl methacrylate–methacrylic acid copolymer [or poly(methyl methacrylate)].

the framework of Takayanagi's adhesion theory.[139] As can be seen from Fig. 2, the experimental data for the linear low-density polyethylene modified chemically by TBAEMA/methyl methacrylate–methacrylic acid copolymer reactive blends (curve *1*) virtually coincide with data calculated in accordance with the 'perfect adhesion' model (curve *3*). For the nonreactive linear low-density polyethylene modified chemically by TBAEMA/poly(methyl methacrylate) blends, the experimental Young's moduli (curve *2*) lie appreciably below the 'ideal adhesion' line but appreciably above the 'loose inclusions' line (curve *4*). According to Liu *et al.*,[127] the transfer of stress between the phases in the given nonreactive system takes place by virtue of a mechanical interfacial contact arising on cooling the mixture, because the matrix comprising linear low-density polyethylene modified chemically by TBAEMA crystallises after the solidification of the poly(methyl methacrylate) phase inclusions and may compress them.

Cross reactions of various types always occur in the blending of polymers in melts: chain transfer by the radical degradation products and subsequent recombination of the macroradicals, chain transfer with rupture as a result of molecular and ionic reactions, and cohydrolysis and transesterification reactions. Deliberate employment of these reactions may exert a favourable influence on the morphology and properties of polymer systems.

III. Reactive blending in multicomponent polymer systems with participation of high-molecular compatibilisers (group B)

The introduction of a third high-molecular component may serve as one of the methods for the compatibilisation of blends of two incompatible polymers. Polymeric compatibilisers, consisting of reactive copolymers or chemically modified polymers of type X–Z (where Z is a long-chain reactive segment or functional group attached to the main chain), may compatibilise the polymer pair X and Y subject to the condition that Z is capable of reacting chemically with the polymer Y. Table 3 presents certain examples of systems of this kind investigated in recent years (the studies published up to 1990 have been examined in another review [6]). The chemical nature and structure of the component X and of the unreactive segment of the polymeric compatibiliser frequently differ, but the latter is nevertheless capable of specific interactions

Table 3. Processes involving compatibilisation by means of reactive copolymers or chemically modified polymers introduced separately (group B blends).

Compatibilising blend	Polymeric compatibiliser	Ref.
PA6/ABS	Various S–AN and S–MAn	140
PA6/PS	PS–g–TAn or S–MAn	141
PA6/PS	S–MAA Na-ionomer	142
PA6/S–AN	S–MAn	143
PA6/S–AN	MAn- or oxazoline-grafted styrene copolymers	144
PA6/HNBR [a]	Chemically modified nitrile rubbers in the presence of cross-linking agent	145
PA6/PP (or HDPE)	E–MAA–ICA	146
PA6/PP	PP–g–MAn	105, 147
PA6/PP	PP–g–AA	148
PA6/PP	Peroxide emulsifiers	149
PA6 (or PA6,6)/PP	(1) PP/E blend (2) PP–g–MAn	150–152
PA6,6/PP	PP–g–MAn	153
LCP/PP	(1) PP/E blend (2) PP–g–MAn	151, 152 154
LCP(PDMPO/PS)	S–GMA	155
SEPTR/PP	E–MAA Na- and Zn-ionomers	156
NR/HDPE [a]	Liquid NR	157
PDMPO/IPE	S–VP	158
PS/LDPE	PS–g–O-CPE	159
PMMA/S–AN	S–ECA	160

Note. The following designations have been adopted for the polymers: ABS = ternary acrylonitrile–butadiene–styrene copolymer; S–AN = styrene–acrylonitrile copolymer; PS–g–TAn = polystyrene modified by trimellitic anhydride; S–MAA = styrene–methacrylic acid copolymer; HNBR = hydrogenated nitrile rubber; PP = polypropylene; E–MAA–ICA = ethylene (80 mol. %)–methacrylic acid–isobutyl acrylate terpolymer (Surlyn 9020); E = reactive ethylene-based terpolymer (Lotader AX-8660); LCP = liquid-crystal polymer based on 6-hydroxy-2-naphthoic acid (70 mol. %) and *p*-hydroxybenzoic acid (30 mol. %) (Vectra A950); PDMPO = poly(2,6-dimethyl-1,4-phenylene) oxide; S–GMA = styrene–glycidyl methacrylate copolymer; NR = natural rubber; IPE = ionomeric polyethylene [Zn-neutralised ethylene–methacrylic acid copolymer (Surlyn 9730)]; S–VP = styrene-4-vinylpyridine block copolymer; LDPE = low-density polyethylene; PS–g–O-CPE = polystyrene (modified by oxazoline)-carboxylated polyethylene graft copolymer; PMMA = poly(methyl methacrylate); S–ECA = styrene–ethyl 2-cyanoacrylate copolymer.

[a] In this cases cross-linking reactions take place together with the interfacial reactions during the blending process.

leading to an increase in the thermodynamic affinity of the components. It is noteworthy that a considerable proportion of ternary polymer systems (Table 3) may be obtained from binary blends (Table 2) by 'dilution' with an unmodified basic polymer (for example, polyamide/polyolefin modified by maleic anhydride/polyolefin).

In the majority of reactive blends of this category, a polyamide (polyamide 6 or polyamide 66) is used as a component which may react with compatibilisers containing the anhydride or carboxy-functional groups [105, 140–153] with formation of amide or imide bonds. Other examples of this kind are the inclusion of either the reactive oxazoline group [159, 161] or the epoxide group. The latter may be present in epoxidised rubber [162] or in the terpolymer based on poly-ε-caprolactone. A different approach to the improvement of compatibility has been described [156, 158, 163] — as a result of ionic interactions of interchain Na or Zn salts. This method affords rubber-modified blends with an improved impact strength.[163]

The principle of the interaction of reactive groups of diverse polymers capable of forming statistical or block copolymers, acting as compatibilisers in blends, has been used in the blending in a melt of polyamide 6 with various styrene and acrylonitrile copolymers. The compatibilising effect is manifested by styrene–acrylonitrile copolymers containing functional groups of the type of maleic anhydride or oxazoline. In order to regulate the dimensions of the disperse phase of the styrene–acrylonitrile copolymer, an attempt has been made to optimise the composition of the reactive system as regards the type and concentration of the functional groups, the content of the reactive compatibiliser, and its compatibility with the styrene–acrylonitrile copolymer.[140, 144]

The same principle has been used to improve the compatibility of blends of polyamide 6 and polypropylene by the introduction of acrylic acid-modified polypropylene as the reactive compatibiliser.[148] Together with the strong hydrogen-bonding interactions in such ternary blends, the terminal amino-groups of the polyamide are capable of reacting with the acid groups of the modifier. The influence of the blending conditions in the extruder (temperature, rate, the moment of rotation during blending, the presence of a vacuum, *etc*.) on the strength properties and morphology of the blends has been described. The formation of a graft copolymer on introduction of a polymeric compatibiliser has been demonstrated by IR spectroscopy.

Even a small amount of the compatibiliser may alter significantly the structure of the polymer blend. It has been shown [147] that maleic anhydride-modified polypropylene,introduced at a concentration up to 1.5 mass %, can fully alter the kinetics of the crystallisation and the crystalline structure of the polypropylene/polyamide 6 blend. The crystallisation of polyamide 6 is almost fully suppressed at its usual crystallisation temperature and virtually complete so called retarded (or concerted) crystallisation of polyamide 6 and polypropylene takes place. This effect had been observed earlier in noncompatibilised blend systems such as polyamide 6/poly(vinylidene fluoride), poly(butylene terephthalate)/poly(vinylidene fluoride), and polyethylene/polyoxymethylene [164] and also in compatibilised blends.[150] It has been suggested that this effect is a consequence of the dilution of the polyamide phase by the polypropylene–polyamide 6 graft copolymer.[147]

Blends of poly(2,6-dimethyl-1,4-phenylene) oxide with Surlyn 9730 ionomeric polyethylene, which is a Zn-neutralised statistical ethylene–methacrylic acid copolymer, constitute an example of compatibilisation as a result of specific interaction in ternary polymer/polymer/polymeric compatibiliser systems.[158] The styrene–4-vinylpyridine block copolymer with a ratio of the styrene and vinylpyridine blocks of 59/41 was used as the compatibiliser. According to differential scanning calorimetric data, the styrene and vinylpyridine blocks of this copolymer interact with the poly(2,6-dimethyl-1,4-phenylene) oxide and ionomeric polyethylene phases respectively. According to the results of FTIR studies, the specific interaction between the vinylpyridine blocks of the compatibiliser and the ionic groups of the ionomeric polyethylene is of the ion–dipole type. The results of mechanical tests (Fig. 3) have shown that the introduction of the styrene–4-vinylpyridine block copolymer increases the values of E and σ_b over the entire range of compositions. The values of ε_b vary in parallel with increase in the content of the compatibiliser in blends enriched in poly(2,6-dimethyl-1,4-phenylene) oxide and the variation is antiparallel in blends enriched in the ionomeric polyethylene. According to Jo *et al*.,[158] these results are a consequence of the increase in the degree of dispersion of the polymeric filler and the adhesion between the poly(2,6-dimethyl-1,4-phenylene) oxide and ionomeric polyethylene phases. The fractograms, obtained by scanning electron microscopy, of the blend specimens after tensile tests confirm the improvement of the interfacial adhesion in the presence of the block copolymer: in the absence of the styrene–4-vinylpyridine block copolymer, the spherical particles of the disperse phase [poly(2,6-dimethyl-1,4-phenylene) oxide] separate from the matrix owing to the weak transfer of stresses and deformations, while in the presence of the styrene–4-vinylpyr-

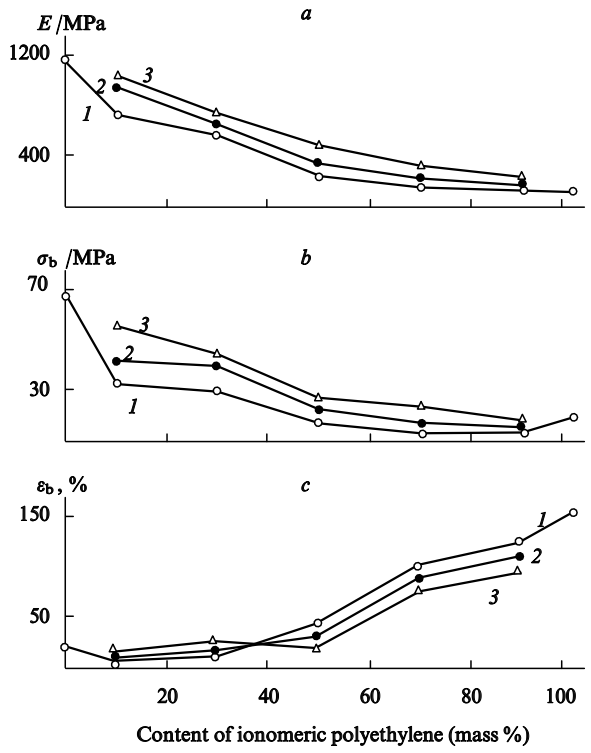


Figure 3. The influence of the introduction of the styrene–4-vinylpyridine block copolymer on the elastic modulus E (*a*), the tensile strength σ_b (*b*), and the relative elongation at break ε_b (*c*) for poly(2,6-dimethyl-1,4-phenylene) oxide/ionomeric polyethylenes of different composition blends.[158] Content of the styrene–4-vinylpyridine block copolymer (mass %): (*1*) 0; (*2*) 5; (*3*) 10.

idine block copolymer the disperse phase is deformed and elongated, as a result of which it is anchored more strongly to the matrix. The specific interaction between 4-vinylpyridine and the transition metal cation has been used also for the compatibilisation of blends comprising rubbers and amorphous polymers, for example the sulfonated polystyrene/ethyl acrylate–4-vinylpyridine copolymer,[165] the sulfonated ethylene–propylene–diene monomer/styrene–4-vinylpyridine block copolymer,[166] and the Cu-neutralised carboxylated polybutadiene/styrene–4-vinylpyridine block copolymer [167] blends.

IV. Reactive blending with participation of low-molecular compounds. Dynamic vulcanisation (group C)

A promising approach to the compatibilisation of polymer blends is the introduction of reactive low-molecular compounds which tend to form covalent bonds with one or both blend components and promote the formation reactions of statistical, block, or graft copolymers, linear or branched (compatibilisation mechanism I), cross-linked in one of the coexisting phases (compatibilisation mechanism II), or cross-linked in both polymer phases (compatibilisation mechanism III). Small amounts (0.1 mass %–3.0 mass %) of added low-molecular compounds are usually employed. This constitutes their main economic advantage over polymeric compatibilisers, which, apart from the expense and complexity of their synthesis, are as a rule effective at higher concentrations.

Examples of the formation of group C reactive blends are presented in Table 4. The compatibilisation mechanism I involves the formation of compatibilising copolymers under the influence of catalytic and noncatalytic interchain reactions. Toluene-*p*-sulfonic acid or phosphites catalyse transamidation reactions in a melt comprising blends containing various polyamides and polyesters.[168, 169] Free-radical reactions, initiated by peroxides and/or shear, also lead to the formation of compatibilising copolymers as a result of the recombination of the macroradicals formed, in the presence of an additional reagent — the interchain connecting agent (ICA), for example reagents such as bismaleimide.[170, 171] In blends comprising poly(butylene terephthalate) and a fumaric acid-modified ethylene–propylene–diene copolymer, polyamide oligomers can act as ICA as a consequence of reactions with carboxy-groups.[172] It is noteworthy that Table 4 does not include examples of compatibilising systems containing fillers and reinforcing agents (mica, graphite, talc, calcium carbo-

Table 4. Compatibilisation of polymer blends with participation of reactive low-molecular compounds (group C blends).

CM [a]	Compatibilised blend	Low-molecular compound	Ref.
I	PET/PA6,6	Toluene-*p*-sulfonic acid	168, 169
	PA6/PA6,6	Triphenyl phosphite	169
	LLDPE/S–VBA	Peroxide + coreagent	170
	PVC/PP	Bismaleimide	171
	PBTP/EPDM–g–FA	Oligomers	172
	S–MAn/BBR	Dimethylaminoethanol	173
II	PP/PE	Peroxides	174–177
	PVC/PE	Benzoyl peroxide + + TAIC	178
	PVC/E–VA	Benzoyl peroxide + + TAIC	179
	PP (or PA6)/nitrile rubber	Di(hydroxymethyl)phenolic derivatives	180
	PP/E–VA (or E–MA)	Dibutyl tin oxide	181
	ER/PC	Dicarboxylic acid anhydride	182, 183
	ER/PEI [b]	Di(aminophenyl)sulfone	184
	PI/PAmA [b]	Pyridine + acetic anhydride	185
	PS/SBR	Dicumenyl peroxide	186
	PS/EPDM	Lewis acids	187
	PP/EPDM	Peroxide or sulfur cross-linking agents	188–193
	PP/SEPR	Peroxides	194
	PP/PEVP/SEPTR	Dicumenyl peroxide	195, 196
	PP/BANR	Bismaleimide and peroxide	197
	PA/BANR	Peroxide or sulfur cross-linking agents	198
	PCL/HNK	*p*,*p*′-Dibenzoylquinone dioxime	199
III	VDF–HFP/nitrile rubber (or ECHR)	Triazinedithiol complex	200
	NR/LDPE	Peroxide and coreagents	201
	PP (or PP–g–AA)/PBD (or BNR, SEPR, NR, SBR)	Ditto	202

Note. The following designations have been adopted for the polymers: LLDPE = linear low-density polyethylene; S–VBA = styrene–vinylbenzaldehyde copolymer; EPDM–g–FA = ethylene–propylene–diene monomer modified by fumaric acid; BBR = brominated butyl rubber; TAIC = triallyl isocyanurate; ER = epoxide resin; PEI = poly(ether imide) (Ultem 1000); PI = polyimide; PAmA = poly(amic acid); SBR = styrene–butadiene rubber; EPR = ethylene–propylene rubber; BANR = butadiene–acrylonitrile rubber; VDF–HFP = vinylidene fluoride–hexafluoropropylene copolymer; ECHR = epichlorohydrin rubber; PBD = *cis*-polybuta-1,4-diene; BNR = butadiene–nitrile rubber.
[a] Compatibilisation mechanisms (CM): I — formation of copolymers; II — formation of copolymers and cross-linking of one phase; III — formation of copolymers and cross-linking of both phases of the blend.
[b] Blending of polymers in solution.

nate, cellulose, glass fibre, *etc*.). Such systems have been examined in Xanthos' review.[203] Standard organofunctional silanes or titanate and zirconate compounds developed later are widely used as ICA in these systems. In the polypropylene/$CaCO_3$ systems, sulfonyl azides, having the general formula $N_3SO_2-R'-COOH$ and containing the azide and carboxy-groups, are reactive in relation to both polypropylene and $CaCO_3$.[204]

It has been shown [173] that dimethylaminoethanol forms bonds between brominated butyl rubber and the styrene–maleic anhydride copolymer. Reactive organofunctional titanates compatibilise various polymer systems (for example, polyoxymethylene/polyacrylate [205]) via catalytic exchange reactions and also via their involvement in other reactions, depending on the type of polymer and the structure of the titanate.

The compatibilisation mechanism II (Table 4) operates in the presence in the blend of a component capable of being cross-linked on treatment with various reagents. It is usually believed [6, 203] that compatibilising copolymers are then formed simultaneously *in situ*. With the exception of plastic/plastic blends, such as polypropylene/polyethylene,[174–177] poly(vinyl chloride)/polyethylene,[178] epoxide resin/polycarbonate,[182, 183] epoxide resin/poly(ether imide) (Ultem 1000),[184] and polyimide/poly(amic acid),[185] all the examples of the compatibilisation mechanism II refer to blends of the plastic/rubber type. These blends are obtained with the aid of the so called 'dynamic vulcanisation', *i.e*. the process involving the cross-linking of only the rubber component on blending in the melt.[179–181, 186–199]

The intercured (intercross-linked) rubber/rubber [200] and rubber/plastic [201, 202] blends (Table 4) can serve as examples of the compatibilisation mechanism III. It is believed that the phase segregation in these systems is suppressed by the formation of chemical bonds in the interfacial layer. It has been postulated that such morphology occurs in various blends compatibilised by cross-linking, such as styrene–butadiene rubber/butyl rubber, natural rubber/butyl rubber, *etc*.[1, 206] which include components undergoing cross-linking at approximately the same rate. The required properties may be obtained also by reducing the overall rate of cross-linking, which favours interdiffusion and mutual overlapping of the phases.[201] In the field of study of rubber blends, efforts have been mainly concentrated on the development of common cross-linking agents (such as the triazinedithiol complex [200]) with comparable rates of vulcanisation and similar solubilities in the blend components.

Among all the variants of the reactive blending of polymers examined, dynamic vulcanisation (DV) has been most fully investigated. The thermoplastic elastomers (TPE) formed on dynamic vulcanisation are rubber materials, which can be processed in the melt like the usual thermoplastic materials but at the operating temperature possess properties analogous to those of a vulcanised elastomer.[207] In recent years, there has been a steady growth of interest in these materials, which compete successfully with traditional thermocured rubbers in the market for industrial cured rubber products.[11, 181] The main task is to use of the DV method to create a multicomponent system with particles of the vulcanised elastomer included in a plastic matrix which can be processed in the melt. The rubber components should be vulcanised during its blending with the thermoplastic polymer.

The first compositions of this kind were obtained in the 1960s–1970s.[208, 209] A series of rules governing the appearance of the set of useful properties of materials of the TPE type have now been discovered. The study of dynamically cross-linked compositions based on a large series of rubbers and thermoplastics [180, 196, 210] has demonstrated that thermoplastic vulcanisates, in which the surface energies (critical wetting surface tensions) of the plastic and elastomer are similar, the molecular length between the entanglements in the initial elastomer is small, and the plastic has a degree of crystallinity of the order of 15%–30%, possess the most effective stress-strain properties. In relation to the polypropylene/ethylene–propylene–diene monomer system, obtained by the DV method in the presence of a sulfur-containing cross-linking system, it has been shown that the stress-strain behaviour of TPE depends on the particle size of the dispersed rubber, the composition of the blend (Fig. 4), and the density of the cross-links in the elastomer phase (Fig. 5).[210] It was found that a small number of cross-links [5×10^{-5} mol (ml of elastomer)$^{-1}$] is needed for a significant improvement of the elastic recovery after drawing. The tensile strength σ_b of the given TPE increases monotonically with increase in the number of cross-links of the elastomer phase, but the compositions remain processable as thermoplastics even for high cross-linking densities, only small changes in the hardness of the compositions being observed following a significant alteration of the degree of vulcanisation.[210] For the TPE based on polypropylene and the ethylene–propylene–diene monomer (Santoprene 201-73), it has been shown [190] that the elastic recovery is greater, the lower the value of Young's modulus and the higher the yield stress of the matrix polymer (polypropylene).

The dynamic vulcanisation of a component of ethylene–propylene rubber alters radically the structure and properties of the

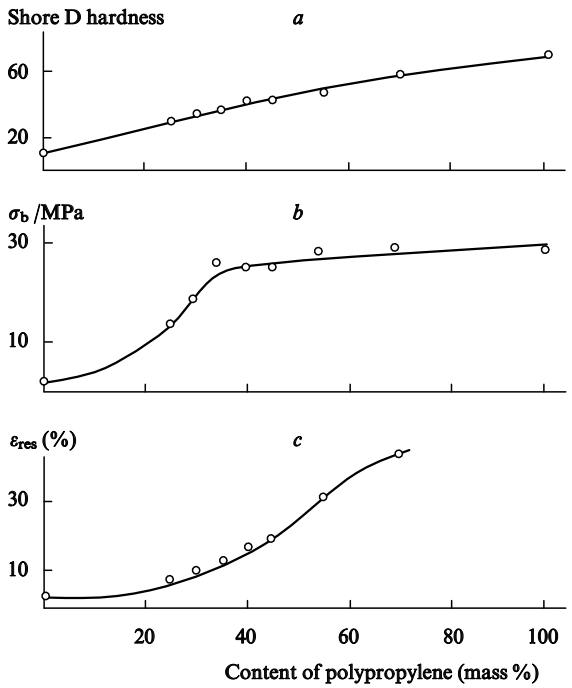


Figure 4. Dependence of the hardness (*a*), tensile strength (*b*), and residual deformation (*c*) on blend composition for dynamically vulcanised TPE based on polypropylene and the ethylene–propylene–diene monomer.[210]

TPE based on polypropylene and ethylene–propylene rubber.[194, 211] The blend containing noncross-linked ethylene–propylene rubber is characterised by the presence of polypropylene domains randomly distributed in the rubber matrix. Dynamic vulcanisation leads to phase inversion, as a result of which the plastic phase (polypropylene) becomes continuous. After crystallisation, its structure resembles a cobweb surrounding the particles of the cross-linked ethylene–propylene rubber. The melting behaviour of the polypropylene phase in nonvulcanised polypropylene/ethylene–propylene rubber blends is independent of the overall blend composition and the molecular mass of the ethylene–propylene rubber. In the presence of the cross-linked rubber component, an appreciable decrease in the effective (observed) melting point of the polypropylene in the blend is observed. The supermolecular structure of the polypropylene phase has been described within the framework of the 'leaf-spring' model, according to which the individual lamellae in the stacks (piles) are linked

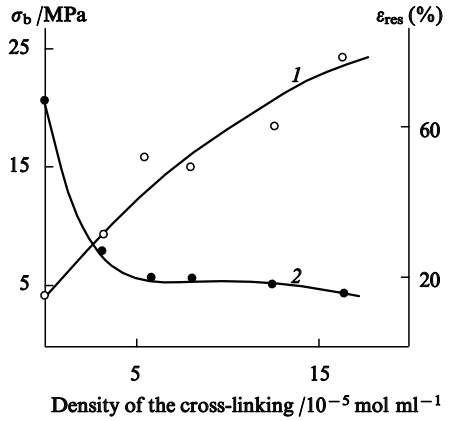


Figure 5. The influence of the density of the cross-linking of the elastomer phase on the tensile strength σ_b (*1*) and the residual elongation on extension ε_{res} (*2*) for dynamically vulcanised TPE based on the polypropylene/ethylene – propylene – diene monomer blend (40/60).[210]

solely to their upper and lower neighbours in the network of nodes, whilst the regions between lamellae remain unconnected. By virtue of this unusual geometry, this polypropylene with stacked lamellae can undergo almost complete elastic recovery even after appreciable deformation.[194]

The formation of covalent bonds between the thermoplastic and rubber phases in the course of the DV process is a decisive factor in the establishment of the stress-strain properties of the TPE. It is seen from the drawing diagram for blends of different polypropylenes and rubbers (Fig. 6) that the values of σ_b for the vulcanised materials are significantly higher than for the non-cross-linked systems (curves *1*). Cross-linking systems ensuring the covulcanisation of the polymeric components are preferable for the improvement of the stress-strain characteristics (curves *3*). The effectiveness of covulcanisation increases if polypropylene has been subjected to a preliminary chemical modification, for example with acrylic acid (curves *3* and *4* in Fig. 6*b*). The improving of adhesion between the phases as a result of the formation of covalent bonds reduces the glass transition temperature of the amorphous regions of the polypropylene.[202]

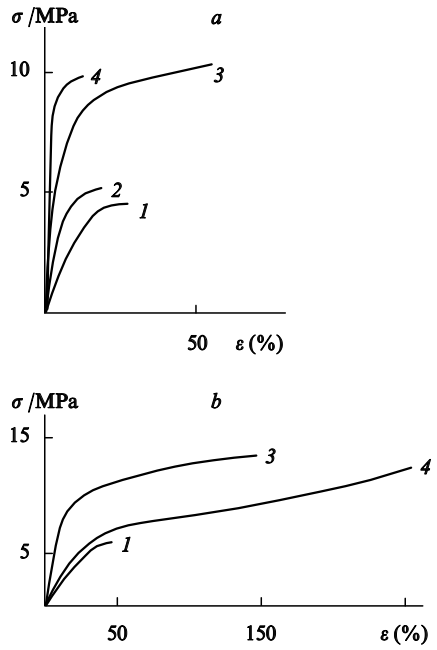


Figure 6. The drawing diagrams for TPE based on polypropylene/brominated butyl rubber (40/60) (*a*) and polypropylene modified by acrylic acid/butadiene – nitrile rubber containing terminal amino – groups (40/60) (*b*) blends. TPE: nonvulcanised (*1*) and vulcanised in the presence of tetramethylthiuram disulfide/sulfur (*2*), bismaleimide/dicumenyl peroxide (*3*), and phenolic resin (*4*) systems.[202]

Thus, by regulating the nature of the polymer chain of the compatibiliser and the reactivity of the functional groups, it is possible to alter specifically the structure and interaction energy in the interfacial layer. The increase in the cohesion energy in one of the phases as a result of specific cross-linking makes it possible to regulate effectively the degree of dispersion and the physicomechanical properties of the filler polymer.

V. Conclusion

The development of polymer blends and alloys based on reactive or compatibilised *in situ* polymeric components is one of the fields of study of high-molecular compounds undergoing the most vigorous dynamic development. According to data from various sources, in 1993 the market in compatibilisers and ICA (without modifying agents) was estimated as 10 000 – 20 000 tonnes annually. It is expected[40] that by the year 2000 this amount will have increased to 80 000 annually.

The technology for the reactive blending of polymers not only opens the way to new possibilities for the employment of polymeric products already available but also permits the creation of blends the preparation of which has been economically unfavourable. The extensive possibilities of synthetic organic chemistry can be used, in principle, for the preparation by the reactive blending method of diverse high-molecular substances and polymer blends based on a relatively small number of available polymers.[38, 39, 212]

The store of experimental data accumulated hitherto makes it possible to characterise the past stage in the study of reactive blending processes as empirical. A multiplicity of types of chemical reactions and specific interactions in polymer solutions and melts, acting on the thermodynamic compatibility of components of reactive systems and on the parameters of their phase structure, have been tested and the influence of the blend composition, concentration of functional groups, and the temperature-time blending regimes has been discovered. At the same time, in the vast majority of cases, the relations obtained must be assessed as qualitative. The fundamental conclusion that the thermodynamic affinity of the components improves on reactive blending is usually based on indirect data, such as the decrease in the particle size of the disperse phase and, more rarely, the mutual approach of the glass-transition temperatures of the coexisting polymeric phases. There has been virtually no monitoring of the degree of conversion of the reactive groups, which is of fundamental importance for the establishment of correlations between the component ratio, the concentration and nature of the reactive groups in the initial blends, and the blending regime (temperature, duration, rate, and intensity of mixing), on the one hand, and the parameters of the morphology and phase structure and the physicomechanical characteristics of the material after the completion of the reactive blending process, on the other.

The construction of a theoretical model which would permit a quantitative prediction of a property of polymeric materials of this kind appears extremely problematical at the present time owing to the deficiency of systematic studies embracing simultaneously the chemical (the nature and kinetics of the reactions) and physicochemical (diffusion, crystallisation, and phase segregation) aspects of the formation of the structure and the establishment of properties. The kinetic theory of macromolecular reactions in multicomponent heterogeneous solutions and melts of polymer blends in a flow (for example in the extruder or continuous operation mixer), taking into account three-dimensional diffusion and the variation of the phase state of the system during the reaction, is of particular interest. Variation of the ratio of the rates of the chemical reaction, responsible for the variation of the

composition of the reaction system, and of mutual diffusion, which controls the redistribution of the components in the bulk of the coexisting phases and in the interfacial region, opens a path to the regulation of the parameters of the phase structure (including interfacial adhesion) and ultimately of the set of technological and performance characteristics of the polymeric materials obtained by reactive blending.

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