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Molecular polymer – polymer compositions. Synthetic aspects

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Contents

I.	Introduction	1
II.	Modern approaches to the description of the properties of polymer – polymer compositions	2
III.	*In situ* preparation of polymer – polymer compositions in the catalytic polymerisation of olefins	4
IV.	Synthesis of polar ingredients in the presence of polyolefins	9
V.	On some synthetic methods for preparation of polyolefin – polyolefin compositions	10
VI.	Improvement of compatibility of polymeric components by introduction of compatibilisers	13
VII.	Polyolefin-based polymer blends prepared by reactive blending	16
VIII.	*In situ* preparation of diblock chemical hybrids	18
IX.	Preparation of conducting composites using the principle 'compatibilisation *via* polymerisation'	20
X.	Formation mechanism and the structure of *in situ* prepared polymer – polymer compositions	22
XI.	Fields of application of *in situ* prepared polymer – polymer compositions	25
XII.	Conclusion	26

Abstract. The main ways of improving the compatibility of polymer – polymer compositions containing polyolefins as one component are considered. Considerable attention is given to the preparation of polyolefins in the presence of an ingredient bound to the catalyst in the catalytic (including consecutive) polymerisation of olefins. The so-called reactor blends and the synthesis and structure of diblock and conducting composites are described. The important role of compatibilisation of polymers of different nature with the use of a third component is pointed out. The formation mechanism of molecular compositions, the structure and properties of the intermediate layer and the main fields of application of synthetic polyolefin – polymer compositions are discussed. The bibliography includes 335 references.

I. Introduction

In recent decades, the assortment of composite materials produced from industrially important polymer blends or alloys has much expanded. Blending of two or more thermoplastics, an intricate physicochemical process which proceeds under the action of mechanical forces and high temperatures, is an efficient method for the preparation of novel materials with desired properties. Most pairs of polymers are incompatible; however, targeted modification of their morphology allows preparation of polymer blends with reasonable operating characteristics.

Molecular design of multicomponent polymeric systems is a rather complicated problem. That is why communications concerning various physicochemical, structural and other aspects of this problem have been reported only recently.[1–13] One of the reasons preventing direct blending of polyolefins (PO) with engineering plastics is the non-polar character of the PO. In this connection design of multicomponent thermoplastic composite materials requires that considerable attention be given to the structural and chemical modification of ingredients (compounds). To achieve compatibility means to minimise the interfacial stress and to improve the interfacial adhesion. This allows the preparation of materials with good deformation – strength characteristics, high impact viscosity, thermal stability, are readily reprocessed, *etc*., without essential modification of their structure. In particular, improvement of the operating characteristics (*e.g*., mechanical strength, crack resistance, light stability, colorability and printing sensitivity, reduction of electrifiablness and sweating, *etc*.) of PO and, first of all, low-density polyethylene (LDPE) and polypropylene (PP) requires that they be modified with various additives including those of high-molecular-mass. Modification of the PO components of polymer – polymer compositions (PPC) is performed in both the formation (copolymerisation) stage by post-modification (graft polymerisation, modification of the surface, *etc*.) and immediately during the preparation of PPC (the so-called reactor blends or *in situ* preparation of PPC). Such modified PO act as compatibilisers (interfacial agents) and improve the compatibility of ingredients.

Yet another reason for increased interest in PPC is the fact that these types of polymer blends are often formed as processing waste and cheap, degraded polymeric products can be reused.[14–16] For both economic and environmental safety reasons, the volume of utilised polymer blends and thermoplastic alloys has been substantially increased since the early 1980s. Currently, requirements imposed on the environmental safety of processing and consumption of polymeric products are continuously increasing. This gives an impetus to researchers to place the problems of recycling of such materials as PO (60% of the total volume of polymeric waste), polystyrene (PS), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PETP), poly(tetrafluoroethylene) (PTFE), polyurethane (PU), polyamide (PA), rubber, cross-linked polyethers, cellulose-containing and multilayered materials as a focus of their efforts. After development of efficient methods for separation, reprocessing and/or modification, these materials would be a cheap and important source of polymeric raw materials, since the countries with well-developed economies produce 20 vol.%, or 8 mass %,

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of nearly 200 million tons of solid household waste per year. However, different compositions of such complex raw materials are responsible for the formation of some incompatible ingredients in the recycling. This causes a deterioration in the physical properties of the end products and the materials become brittle. Moreover, some environmentally hazardous components of polymer blends favour the destruction of other blend components (in particular, PVC causes destruction of PETP and other polymers). Recycling and, especially, sorting expenditures aimed at separating raw materials into individual, compatible types of polymers lead to a substantial increase in the cost : property ratio compared to that for the processes based on the use of primary polymer blends. Different types of plastics, *e.g.*, thermoplastics, thermosetting plastics, multilayered blend-based composite materials, *etc.*, require a different approach.

A pair of polymers is considered compatible if its components have similar polarities, have similar functional groups or can interact under blending conditions to form donor–acceptor, hydrogen and other types of bonds, as well as if they are structurally similar and have similar solubilities. However, meeting these conditions is sometimes insufficient, so the number of compatible polymers is small. This especially concerns such nonpolar polymers as PO. For instance, LDPE and high-density polyethylene (HDPE) are poorly compatible; co-crystallisation of linear low-density polyethylene (LLDPE) and LDPE results in the formation of separate crystal aggregates on the micrometre level;[17] and PE and PP are immiscible on the molecular level. Moreover, even such a pair as isotactic and syndiotactic PP is also incompatible on the molecular level.

Therefore, when analysing polymer compatibility, one should take into account not only thermodynamic, but also chemical aspects, namely, the interaction between macromolecules. There are two approaches to the design of compatible polymer–polymer systems.[4] These are (i) linking of macromolecules by chemical bonds (the synthesis of block copolymers, interpenetrating polymer networks, cross-linking of blend components) and (ii) modification of the chemical structure of polymers to obtain negative free energy of mixing (if polymer macromolecules contain functional groups that can strongly interact, some of the components are either modified, thus changing the chemical structure of the monomer units, or copolymerised). Thermodynamic incompatibility of polymer blend components prevents the formation of a common crystal lattice (*i.e.*, no mixed crystals are formed). Nevertheless, an intermediate, interfacial layer between the ingredients of a PPC can exist in this case due to the formation of common supramolecular structures, specific packing of the polymer chains and the absence of well-defined interfaces between the elements of supramolecular order even for crystalline polymers. This to a great extent determines the strength and nature of adhesive forces in the system, which strongly affects the surface area of true interface (phase contact), microrheological processes and contact reactions at the interface. Specific features of the adhesive interactions also depend on the preparation conditions of PPC: *e.g.*, mechanical mixing of components leads to the formation of intermediate layers only as a result of physical interparticle interaction.

A way to design novel materials with improved properties involves the preparation of microheterogeneous compositions with controllable structural inhomogeneity. This class of materials comprises compositions containing PO as one of the ingredients. The results of economic and environmental analysis [16] of the 'life cycle' of polymers, which includes their synthesis, processing and modification, usage, waste separation, recycling, re-use and final utilisation of waste allowed one to rank (i) PO first among the widely used plastics and (ii) PP first among all PO. This choice is also determined by the variety of PO-based polymer blends, alloys and composites (including the *in situ* prepared compositions).

This review concerns main approaches to the PO-containing PPC. Particular emphasis is placed on the synthetic aspects of the problem. Often, though not always, the use of such systems allows compatibility of components on the molecular level. The definition of such compositions as 'molecular compositions' (see the title of this review) should be considered to some extent conventionally since the preparation of PPC involves blending of components not only on the molecular level, but also on the level of microphase aggregates consisting of a large number of like macromolecules. In addition, sometimes it is impossible to clearly distinguish between different procedures for the preparation of PPC because many of them can be formed following different mechanisms. This also makes formal classification of PPC difficult.

II. Modern approaches to the description of the properties of polymer–polymer compositions

To gain an insight into specific features of PPC-containing systems, we have to briefly outline the methods for analysis of their thermodynamic and physicomechanical properties.

It does not always happen that the use of simple physical polymer mixtures consisting of components with complementary properties leads to desired results. The reason is thermodynamic incompatibility of most polymer pairs, which is largely because of a small entropy of mixing. Therefore, all polymer compositions to some extent undergo separation into different phases that are characterised by weak adhesion, which deteriorates the properties of the compositions. Usually, 'compatibility' of polymers refers to their mutual solubility. In the case of polymer blends, the term 'miscibility' is most often used. A necessary, but not sufficient, condition for thermodynamic compatibility of polymers is negative free energy of mixing, G_m:

$$\Delta G_m = \Delta H_m - T\Delta S_m .$$

Due to the high molecular mass of polymers, the entropy of mixing of two macromolecules, ΔS_m, changes only slightly. Hence, compatibility of a pair of polymers requires that the enthalpy of mixing, ΔH_m, be negative, zero or very slightly positive. In addition, specific interactions between miscible polymers must occur (see above).

Methods for studying and improving the thermodynamic compatibility of polymers have been reviewed by Tager and Blinov.[18] According to their concept, the best miscibility is characteristic of those polymers whose molecules contain functional groups with opposite functionalities, capable of forming hydrogen, donor–acceptor, ionic, π-bonds and other types of bonds, rather than of structurally (or compositionally) similar polymers. The following simple equation for calculating the free energy of mixing of polymers was proposed by Tager:[19]

$$-\Delta g_x = \Delta G_{III} - (\omega_I \Delta G_I + \omega_{II} \Delta G_{II}),$$

where Δg_x is the mean free energy of mixing of polymers with each other per gramme of the blend; ΔG_I, ΔG_{II} and ΔG_{III} are the Gibbs energies of mixing of polymers I, II and their blend dissolved in the same solvent, respectively; and ω_I and ω_{II} are the mass fractions of polymers I and II in the PPC. Compatibility of polymers is strongly affected by not only the molecular nature and molecular masses of the components, but also their molecular mass distribution.[20] However, often, 'compatibility' of polymers means the achievement of good mechanical properties rather than compatibility on the thermodynamic level. Keeping this in mind, it should be noted that practically even compatible polymers can appear to be immiscible due to problems arising during the preparation of PPC.

There are three main methods for polymer blending. They include mechanical mixing, film casting from common (the same) solvent and *in situ* blending, *i.e.*, polymerisation of a monomer in the presence of the other (most often, preliminarily swollen) polymer. Each of these methods has specific advantages and drawbacks. For instance, the simplest method, mechanical mixing, cannot always be realised due to limited thermal stability of a

particular ingredient in specified temperature and homogenisation time ranges. Other polymers, being compatible at room temperature, can be incompatible at higher temperatures. Sometimes, casting from common (the same) solvent is precluded by solubility problems and by immiscibility of particular polymers in the presence of specific solvents. Often, the only way of overcoming these obstacles is to use *in situ* polymerisation. However, this is also not a universal procedure since during the polymerisation one monomer can become a solvent for the other polymer and this can induce phase separation of the components. For instance, polymerisation of vinyl chloride in the presence of chlorinated PE can result in monophase or two-phase products depending on the initial reagent ratio.[21] Nevertheless, *in situ* polymerisation is considered as a potentially promising industrial method for the preparation of polymer blends. Numerous PPC prepared in this manner have been patented. This method allows the preparation of thermodynamically stable PPC; however, they can become unstable on heating, which means that such PPC have lower critical solution temperatures (LCST) and, hence, should be prepared at temperatures below LCST.

Considerable attention has been given to the problems of design of PPC from ingredients with complementary properties. Unfortunately, no general equations for the description of the dependence of a particular property of a PPC on its chemical composition have been proposed so far. For instance, the problem of calculations of the modulus of elasticity, E_{PPC}, for a polymer blend from the known moduli of elasticity of particular components or phases is still to be solved.[22,23] The moduli of two-phase blends are often estimated using the Coran – Patel approach[24] based on the assumption that the magnitudes of the moduli of elasticity of a two-phase polymer blend (Young's modulus or shear modulus) must lie between the effective upper (E_u) and low (E_l) moduli calculated from the models of parallel and series linking of the components. The moduli E_u and E_l are calculated as follows:

$$E_u = \varphi_1 E_1 + \varphi_2 E_2,$$

$$E_l = \left(\frac{\varphi_1}{E_1} + \frac{\varphi_2}{E_2}\right)^{-1},$$

where E_1 and E_2 are the moduli of elasticity of the starting components 1 and 2 and φ_1 and φ_2 are their volume fractions ($\varphi_1 + \varphi_2 = 1$). The modulus of the two-phase blend, E, can be written in the form

$$E = fE_u + (1-f)E_l,$$

where $0 < f < 1$. The maximum and minimum value of the modulus of elasticity corresponds to $f = 1$ and $f = 0$, respectively.

Considering PPC as specific filled systems, one can use an approach known as the mean field approximation for spherulites in the matrix:[25]

$$\frac{E_c}{E_m} = \frac{(1-\varphi)E'_m + (v^* + \varphi)E_r}{(1+v^*\varphi)E'_m + v^*(1-\varphi)E_r},$$

where E_c, E_m, E_r are the moduli of the composite, matrix and an elastic inclusion with the volume fraction φ, E'_m is the real part of the elastic modulus of the matrix, $v^* = 2(4-\nu_m)/(7-5\nu_m)$ and ν_m is the Poisson coefficient of the matrix. This expression imposes no limitations on both the volume fractions of ingredients and the ratio of the modulus of elasticity of the matrix to that of the inclusion. If the moduli of elasticity of the matrix (E_m) and inclusion are substantially different, it is appropriate to use the simplified Guth relationship which takes into account the pair interaction between rigid particles:[26]

$$E_{PPC} = E_m(1 + 2.5\varphi + 14.1\varphi^2).$$

At $\varphi < 0.4$, the results of calculations using this formula coincide with experimental data.

There are many equations derived based on different models of matrix compositions (*e.g.*, the Smallwood and Takayanagi equations, *etc.*); however, they are rarely used. All of them use the volume fraction of a component, φ, as the only structural parameter, though the experimental data show that the physicomechanical properties of PPC are also affected by salient features of their morphology. For instance, the properties of ultrahigh-molecular-mass PE (UMMPE) depend not only on the volume fraction of crystallites, but also the ratio of the fractions of crystallites with compacted and aligned chains and on the type of mutual arrangement of these crystallites.[27]

Therefore, PPC should be described using such molecular models that take into account additional morphological parameters. For instance, if a model implies an interaction between components 1 and 2,[28] we get

$$E_{PPC} = E_1 + E_2(1-\varphi_1) + \Delta E.$$

The sign preceding ΔE points to the presence (a 'plus' sign) or the absence (a 'minus' sign) of an interaction. For instance, the modulus of elasticity of a PP – HDPE composition can be larger than those of the individual components at a particular component ratio and at rapid cooling of melt. In other words, the addition of the first ingredient improves the properties of the second (this is also called positive synergism of the polymeric constituents).

Recently, the elastic properties of partially crystalline material were studied theoretically based on the scaling concept and very good agreement with experimental data was achieved (see, *e.g.*, Ref. 29).

If the glass transition temperature, T_g, of the first component of a PPC approaches that of the second ingredient of the PPC, these polymers are partially compatible.[30] The degree of compatibility, D, is defined as the ratio of the difference between the T_g values of the blend components to the difference between the T_g values of pure polymers:[31]

$$D = \frac{T_{g1}^b - T_{g2}^b}{T_{g1}^p - T_{g2}^p}, \quad 0 < D < 1,$$

where T_g^b and T_g^p is the glass transition temperature of the blend component and of the pure polymer, respectively. The glass transition temperature of the PPC of compatible polymers is intermediate between the T_g values of the blend components and is determined using the Fox equation (the so-called blend rule)[32]

$$\frac{1}{T_g} = \frac{\varphi_1}{T_{g1}} + \frac{\varphi_2}{T_{g2}}.$$

Large deviations from the Fox equation are often considered as an indication of strong interpolymer interaction.[33]

According to the Hoffmann equation,[34] the melting temperature of a non-isothermally crystallised PPC (T_m) increases linearly as the crystallisation temperature of the ingredients (T_c) increases

$$T_m = \frac{1}{\delta}T_c + \left(1 - \frac{1}{\delta}\right)T_m^\circ,$$

where δ is the crystallite morphological factor and T_m° is the equilibrium melting temperature. For instance, a PPC consisting of poly(but-1-ene) (PB) and hydrogenated oligo(cyclopentadiene) (HOCP) has a $1/\delta$ value of ~ 0.34, while the ternary PP – PB – HOCP blend (50 : 30 : 20)† is characterised by T_m° = 456 K.[35]

Szabo *et al.*[36] showed that the interpolymer interaction between such blend components as poly(isobutylene) (PIB) and linear LDPE obtained by copolymerisation of ethylene with

† Hereafter, the concentrations of blend components are given in per cent by mass.

α-olefins (LLDPE) can be estimated using the modified Flory–Huggins equation [37]

$$\frac{1}{\varphi_1}\left(\frac{1}{T_m}-\frac{1}{T_m^\circ}\right)=-\frac{RV_2}{\Delta H_2 V_1}\chi_{12}(1-\varphi_2)^2,$$

where φ_1 and φ_2 are the volume fractions of the polymers 1 and 2, V_1 and V_2 are the molar volumes of repeating units of the polymers 1 and 2, respectively, ΔH_2 is the enthalpy of melting of PE, and χ_{12} is the Flory–Huggins interaction parameter. The ΔH_2 is 4.1 kJ mol^{-1} and the parameter χ_{12} is -0.022 at 393 K. This proves that even relatively weak dispersion forces can make two polymers compatible.

Interesting information for estimation of the interaction between the PPC components can be obtained from the results of measurements of the surface (γ) and interfacial tension.

$$\gamma = \gamma_d + \gamma_p,$$

where γ_d and γ_p are the components of the surface tension of the polymer, which are due to the dispersion and dipole interaction, respectively. These characteristics of intermolecular interaction are immediately related to the cohesive energy of the system under study. The surface tension and its components depend on the nature of PPC ingredients and decrease upon their modification (Table 1).[38] In addition, the higher the temperature the smaller the γ values (Table 2). The surface tension at the interface between two immiscible polymers in a PPC (γ_{12}) can be calculated using the following equation:[40]

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_{d1}\gamma_{d2}}{\gamma_{d1}+\gamma_{d2}} - \frac{4\gamma_{p1}\gamma_{p2}}{\gamma_{p1}+\gamma_{p2}},$$

where subscripts 1 and 2 correspond to the first and second components, respectively.

Table 1. Surface tension and its components (dyn cm^{-1}) for PP and PA-6.[38]

Polymer	γ_d	γ_p	γ
PP	28.3	12.5	40.8
PA-6	32.1	20.9	53.0
PP [a]	26.3	9.5	35.8
PA-6 [a]	30.1	10.7	40.8

[a] Modified by grafting maleic anhydride (MA, 1%).

Table 2. Surface tension γ (dyn cm^{-1}) for some polymers at different temperatures.[39]

T/K	LDPE	HDPE	PVA [a]	PMMA
293	35.3	35.3	36.5	41.1
413	27.3	28.8	28.6	32.0
453	24.6	26.5	25.9	28.9

[a] PVA stands for poly(vinyl acetate).

Next, we present the surface tension (γ_{12}) values at the interface between the first polymer and the second polymer in the PPC at 423 K.[41]

First polymer	LDPE	HDPE	PE	LDPE
Second polymer	PVA	PVA	PVA (25%)	PP
γ_{12}/dyn cm^{-1}	9.8	11.0	1.3	1.3

The surface tension at the interface can also be approximated using the Wendt–Owens equation [42]

$$\gamma = (\gamma_1^{1/2} - \gamma_2^{1/2})^2.$$

Thus, there are some modern methods that often allow a quite reasonable description of the properties of real PPC. However, many aspects of this problem remain unclear as yet.

III. *In situ* preparation of polymer–polymer compositions in the catalytic polymerisation of olefins

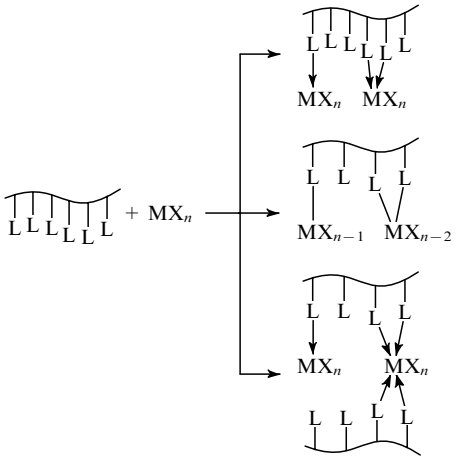
The method for the preparation of molecular PPC (hereafter, we will denote them 'the *in situ* prepared PPC') in the catalytic polymerisation or copolymerisation of α-olefins (ethylene, propylene, butene), diene monomers (butadiene, isoprene) and monomers of the acetylene type (acetylene, phenylacetylene, 3-bromopropyne, *etc.*) on metal complex catalysts involves the following stages.[43] First, this is a chemical or physical immobilisation of the catalyst components on the 'polar' ingredient of the PPC to be prepared. Usually, the catalyst components represent macromolecular metal complexes based on PMMA, PVC, PTFE, poly(vinylidene chloride) (PVDC), polyformaldehyde (PFA), PVA, poly(vinyl alcohol) (PVAlc), poly(4-vinylpyridine) (P4VP), cellulose and other polymers. The second stage consists of a liquid-phase or gas-phase polymerisation or copolymerisation of corresponding monomer resulting in the desired PPC.

In the text below we consider the main approaches to the synthesis of catalyst components (of the Ziegler–Natta type), some features of the polymerisations catalysed by these, in essence, polymer-immobilised [44] catalysts and, finally, selected experimental data on the structure of particular systems.

1. Synthesis of catalyst components

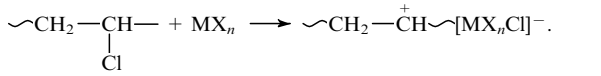
Polymers containing functional groups (L) are macroligands that can bind the components of catalytic systems, *viz.*, a transition metal compound MX_n [$TiCl_4$, VCl_4, $VOCl_3$, VCl_3, $TiCl_3$, $Ti(OBu)_4$, $CoCl_2$, $MoCl_5$, *etc.*], an organometallic (organoaluminium, organolithium, organomagnesium, organozinc) compound, *etc.*

A general scheme of metal complex immobilisation taking into account the formation of chemical bonds can be represented as follows:

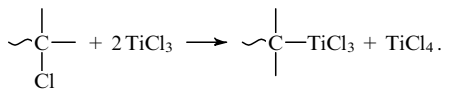


The penetration depth of the active catalyst into the near-surface layer of the component of a PPC can vary depending on the reaction conditions. This can be accompanied by both monodentate and polydentate coordination of MX_n by the intramolecular or intermolecular mechanism.[44] The optimum immobilisation procedures can involve either the use of a suspension of the PPC component or gas-phase coordination of the complexes. Many transition metal halides are relatively strong Lewis acids capable of forming ionic complexes. It is this type of

bonding that is used for the coordination of MX_n to PVC, PVDC, PTFE and poly-α-bromostyrene.



Yet another approach, applicable to crystalline compounds MX_n (*e.g.*, $TiCl_3$, VCl_3), is based on the formation of carboxylic acid salts. For instance, $TiCl_3$ is coordinated by chlorinated polymers (PVC, chlorinated PP, natural rubber) by the following mechanism:[45]

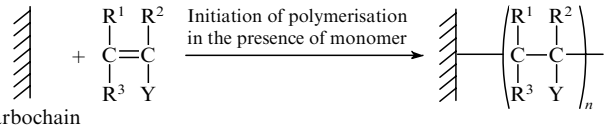


Joint grinding of $TiCl_3$ and PVC leads to complete disappearance of the crystalline phase. Nearly complete oxidation of Ti^{3+} into Ti^{4+} is evidence for essential transformations in the $TiCl_3$ – PVC system.

Special methods for immobilisation of compounds MCl_3 (with retention of their submicrostructure) on polymers have been developed. The most efficient procedure involves solid-phase mechanochemical synthesis in the presence of polymeric constituents of PPC (most often, PO). Experimentally, this is achieved by activation of the reacting components in the vibrating, ball or differential agate mills (usually, in an inert atmosphere).[46, 47]

The surface of polymers is also modified using cationic polymerisation,[48] which results in macromolecular analogues of stable carbonium salts.

To immobilise metal complexes on the surface of PO (the grafted layer is 10 to 30 Å thick), the surface of the polymer is functionalised by performing graft polymerisation of polar monomers.[46] In particular, the surface of PE, PP or ethylene/propylene copolymer can be modified by grafting, *e.g.*, acrylic acid, 4-vinylpyridine, acrylonitrile, allyl alcohol, vinylpyrrolidone, *etc.*



R^1 = H, Me; R^2 = H, Me, C_6H_5; Y = OH, NHR, CH_2NH_2, SR, CH_2OH, CH_2SR^2, CO_2H, OCOMe; R^3 = H, Me, C_2H_5, $CH_2CH{=}CH_2$, C_6H_5.

In the text below we will show that graft polymerisation products can also be used individually as the third components (compatibilisers) to improve the compatibility of components of binary PPC.

Table 3 lists some characteristics of catalyst components MX_n that are used for the *in situ* preparation of PPC.

Polymer – polymer compositions can also be prepared *in situ* by anionic-coordination or ionic polymerisation using an alternative approach which involves immobilisation of organometallic compound on the polar component. In this connection, it is of interest to consider the modification of the surface of PETP or PA-66 *via* 1,2-polyaddition of compounds LiR to carbonyl groups.[49] Organomagnesium compounds are immobilised on graft-functionalised polymers.[50] Addition reactions of AlR_3 or AlR_2H to the multiple bonds of polymers, resulting in the formation of reactive organometallic centres have been reported. In particular, addition products of dialkylaluminium hydrides to random styrene (25%)/butadiene copolymers have been studied in detail.[51, 52]

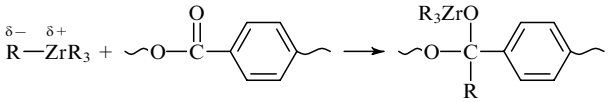
Table 3. Characteristics of catalyst components used for *in situ* preparation of PPC.[46]

Polymer	Component MX_n	Immobilisation conditions of MX_n on the polymer surface			Immobilised metal content /mg g^{-1}
		solvent	T /°C	time /h	
PVC	VCl_4	CCl_4	20 – 40	2.0	0.8
	$TiCl_4$	heptane	50 – 70	2.0	1.1
PVDC	VCl_4	CCl_4	30 – 35	2.0	1.5
PMMA	VCl_4	CCl_4	20 – 25	1.5	0.5
	$TiCl_4$	heptane	60	2.0	0.8
PFA	VCl_4	CCl_4	20 – 25	1.5	1.0
Cellulose	VCl_4	CCl_4	20 – 25	1.5	1.2
PTFE	VCl_4	CCl_4	20 – 25	1.5	0.6
HDPE	VCl_3	see [a]	20 – 40	0.5	10.0
	$TiCl_3$	"	20 – 40	1.0	10.0
PP	VCl_3	"	20 – 40	1.0	10.0
	$TiCl_3$	"	20 – 40	1.0	10.0
PE – g-P4VP	$TiCl_3$	"	20 – 40	0.5	10.0
	VCl_3	"	20 – 40	0.5	10.0
PE – g-PAA [b]	$Ti(OBu)_4$	heptane	60	1.0	0.5
PE – g-PAAc [c]	$Ti(OBu)_4$	"	60	1.0	1.0
	$Ni(acac)_2$	toluene	40	1.0	8.0
	VCl_4	CCl_4	25	1.0	7.5
PE – g-PVP [d]	$CoCl_2$	methanol	40	1.0	8.0
	VCl_4	CCl_4	25	1.0	6.0

[a] Immobilisation is performed by grinding a mixture of components in a ball mill in the absence of solvent. [b] PAA stands for poly(allyl alcohol). [c] PAAc stands for poly(acrylic acid). [d] PVP stands for polyvinylpyrrolidone.

Organoaluminium compounds can undergo insertion into the multiple bonds of functional groups of the polymeric constituents of PPC.[44] Most likely, immobilisation of alumoxanes proceeds by the same mechanism. Both components of the metal complex system can be immobilised on the same polymer.

The coordination mechanism of polymers to transition metal compounds (one-component catalysts of olefin polymerisation) is much simpler. In particular, immobilisation of ZrR_4 (R — benzyl, π-allyl) and Cr(π-allyl)$_3$ on the surface of polymer fibres proceeds *via* 1,2-polyaddition to the carbonyl groups of PETP or the reaction with amido groups of PA-66.[49]



Probably, organometallic zirconocene derivatives known as the most efficient catalysts of olefin polymerisation, are immobilised on polymers following the same mechanism.

Currently, a new method for immobilisation of two different reactive centres on the same polymeric constituent of PPC has been developed. It allows bifunctional catalysis, *i.e.*, simultaneous polymerisation of monomers of different chemical nature or conversion of one monomer into products of different structure. This method will be considered below.

2. *In situ* preparation of polymer – polymer compositions: general kinetic rules

The composition of PPC prepared *in situ* in the presence of catalyst components can be controlled by varying the polymerisation conditions and, first of all, duration of polymerisation and the amount of monomer consumed.

The rate of ethylene polymerisation (a PE-based, *in situ* prepared PPC) is to a great extent dependent on the nature of the polar component and the type of its bonding to the catalyst

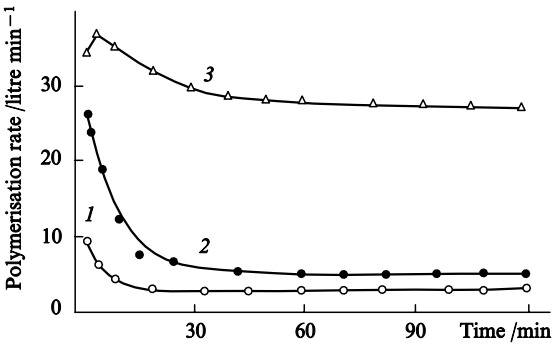


Figure 1. Catalytic activity of $VCl_4 \cdot L - AlBu^i_2Cl$ systems in the polymerisation of ethylene for different types of immobilisation.
Ligand (L): (*1*) vinyl acetate; (*2*) PVA; (*3*) PVAlc.

components. Generally, immobilisation of MX_n or AlR_xCl_{3-x} by covalent bonds is considered optimum. The component playing the role of macroligand stabilises the process,[53] which manifests itself as a steady-state polymerisation (except for the initial stage). It should be noted that polymerisation at 313 K in the presence of the traditionally used system $VCl_4 - AlR_2Cl$ is essentially a non-steady-state process. Here, the maximum activity is achieved immediately after blending the components; however, the rate of ethylene polymerisation reduces by a factor of 45 after 30 min.[54] In contrast to this, catalytic activity of the systems based on macrocomplexes reduces by 3 to 8 times after the same time interval. Systems in which VCl_4 is covalently bound to, *e.g.*, PVAlc, exhibit higher catalytic activity compared to macrocomplexes with PVA (Fig. 1). Catalyst components formed in the reactions of $TiCl_4$ or VCl_4 with PVC or PVDC also demonstrate a stabilising effect.

Kinetic studies revealed [55] that the rate constants for the chain propagation and chain termination (by monomer or organoaluminium compound) stages and the activation energies for the PE chain propagation in the presence of both the macrocomplex-based systems under consideration and traditionally used Ziegler–Natta catalysts have similar values. However, the formation of the reactive centres proceeds by different mechanisms, which is responsible for the stabilising effect of the polymeric catalysts.

The molecular mass of PE formed depends on the nature of the catalyst component and on the polymerisation conditions. Standard procedures for controlling the molecular mass of PE include addition of hydrogen. The *in situ* prepared PPC are isolated and treated using the same procedures as those used in the low-pressure polymerisation of olefins. This type of PPC can also be prepared under conditions of the gas-phase polymerisation of ethylene (in this case, the catalyst component is dispersed in the suspension layer).[56] Using components with specific molecular shape also allows preparation of granulated PPC.

Binary polyolefin compositions (*e.g.*, PE–PP) can be synthesised using the catalyst components obtained by co-grinding of PO and MCl_3 (*e.g.*, the size of $TiCl_3$ submicrocrystals co-ground with PE is $\sim$1 nm).[57] The stereosequence of PP formed on such catalysts is determined by conventional factors. This method also allows the *in situ* preparation of such PPC as PE–PB, PE–polycyclohexene, PE–PS, *etc.* The PE–polybutadiene (PBd) and PE–polyisoprene (PI) compositions are prepared by polymerisation of the diene monomer on the PE–g-P4VP$\cdot CoCl_2 - AlEt_2Cl$ system.[57] In these catalysts each Co atom produces the polydiene chain, the molecular mass of PI lies between 370 000 and 1 300 000 and the content of 1,4-*cis*-PI exceeds 80%.

In situ preparation of conducting compositions PE–polyacetylene (PAc) involves immobilisation of the catalytic system $Ti(OBu)_4 - AlR_3$ on the surface of modified PE films followed by gas-phase or liquid-phase polymerisation of acetylene [58] and results in the formation of *trans*-PAc similarly to the process in homogeneous systems.

Thus, the use of catalyst components allows the preparation of PPC based on polyolefins and various polymers in the anionic-coordination polymerisation. Let us consider the structure of particular PPC in more detail.

3. HDPE–PMMA Compositions

Main characteristics of the properties of the *in situ* prepared polymer–polymer compositions HDPE–PMMA and polymer blends of HDPE and PMMA (with similar molecular mass characteristics) are listed in Table 4.

Table 4. Density (ρ), yield stress (σ), elongation at break (ε) and glass transition temperature of polymer–polymer compositions HDPE–PMMA.[60]

Parameter	Starting components [a]	PMMA content in composition [b] /volume fraction			
		0.04	0.07	0.14	0.29
ρ /kg m^{-3}	1.190 0.948	0.959 0.962	0.968 0.965	0.983 0.965	1.019 1.017
σ /MPa	5000 2500	3200 2700	3155 1200	3500 1150	–
ε (%)	2–3 370	250 80	210 70	180 45	–
T_g /K	225 221	217 203	221 –	221 221	221 221

[a] The data for PMMA are listed in the numerator and the data for HDPE are given in the denominator. [b] The data for molecular (*in situ* prepared) compositions are presented in the numerator and the data for polymer blends are listed in the denominator.

An increase in the volume fraction of PMMA (φ) in the synthetic PPC is accompanied by a decrease in the relative elongation at break (ε) and an increase in the yield stress (σ). Compared to the *in situ* prepared PPC of similar chemical composition, polymer blends are characterised by smaller ε and σ values (by 3 to 4 times for ε and 1.5 to 2 times for σ). The glass transition temperatures of the components are virtually independent of the procedure for the preparation of PPC, which suggests low thermodynamic compatibility. Both components of such PPC are linear polymers whose chemical composition and structure can be studied by selective extraction. This method is often used for analysing polymer blends and, in particular, interpenetrating polymer networks (IPN).[59] Polymer blends prepared without the formation of a complex with VCl_4 in the ethylene polymerisation using the $VCl_4 - AlEt_2Cl$ system exhibit a ready and complete separation into the starting components. In the case of *in situ* prepared PPC the content of non-extractable PMMA ($\varphi = 0.007 - 0.14$) varies between 4.4 mass % and 6.7 mass %.[60] Most likely, this is evidence that a fraction of PMMA molecules is chemically grafted onto PE. This assumption is confirmed by the results of various physicochemical studies. For instance, new bands with maxima at 1740 and 1300 cm^{-1}, corresponding to stretching vibrations of carbonyl and ester groups, appear in the IR spectra of non-extractable products along with the main absorption bands typical of the PE backbone.

The assumption that the integrated intensity of X-ray diffraction reflections is proportional to the content of the crystalline component in a polymer blend consisting of amorphous and crystalline phases holds for any blend including polymer blends based on crystalline PE and amorphous PMMA. Hence it follows that if the structure of the PE constituent of a PPC is independent of the chemical composition of the PPC, the height of the most intense peak of PE, corresponding to the (110) reflection, can serve

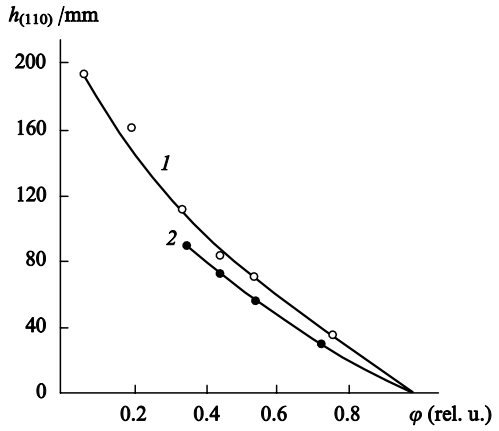


Figure 2. Empirical correlation between the height of the (110) peak of HDPE and the chemical composition of polymer blends of HDPE and PMMA (*1*) and molecular polymer – polymer compositions HDPE – PMMA (*2*).[60]

as a quantitative characteristic of the chemical composition of the PPC. For mechanically mixed polymer blends, this correlation corresponds to curve *1* in Fig. 2, whereas for *in situ* prepared PPC the plot is shifted to the left. This looks like an apparent reduction of the volume fraction of PE and does not correspond to the true chemical composition of the *in situ* prepared PPC determined independently (from the density, material balance of polymerisation, *etc*.). This contradiction can be readily eliminated assuming that some structural domains of PE formed do not contribute to the (110) peak intensity.

Indeed, in contrast to polymer blends, the X-ray diffraction patterns of the *in situ* prepared PPC display a clearly seen peak labelled by an arrow in Fig. 3. This peak corresponds to a new

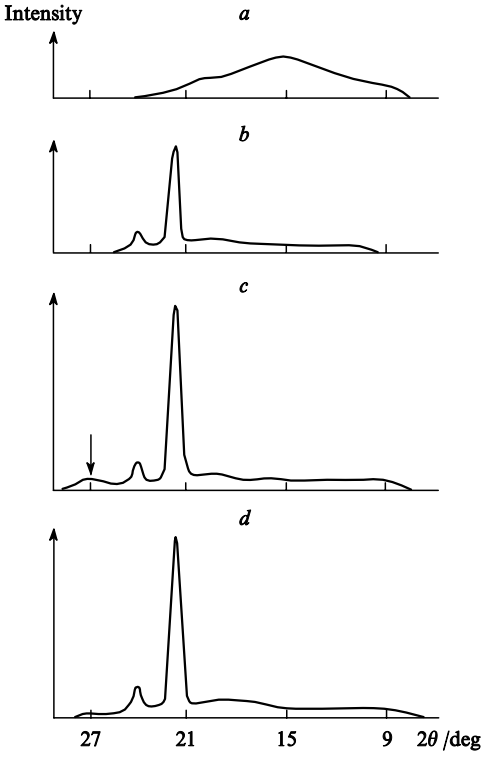


Figure 3. X-Ray diffraction patterns of PMMA (*a*), HDPE (*b*), *in situ* prepared composition HDPE – PMMA (*c*) and a blend of HDPE and PMMA (*d*) ($\varphi = 0.19$).[65]

interplanar distance (~3 Å) in the structure of PPC and is indicative of the interaction between PE and PMMA on the molecular level and of a local distortion of the phase boundaries. The latter is due to the fact that chain propagation (the growth) of the PE macromolecules is accompanied not only by crystallisation, but also by interpenetration of the first component into the bulk of the second component (due to diffusion of macromolecules or their segments). As the distance from the surface of PMMA increases, this interaction, which determines the thickness of the intermediate layer, weakens. If the intermediate layer is sufficiently thick, it can form an individual phase. In addition, a salient feature of this system is the propagation of the PE chains accompanied by mixing of the components, which also improves their compatibility and the physicomechanical properties of *in situ* prepared PPC (the so-called operating compatibility) compared to the properties of conventional polymer blends (see Table 4). This type of PPC, prepared by copolymerisation of propylene and CO on phosphinepalladium complexes resulting in a propylene – CO alternating copolymer and followed by blending with PMMA, is thought to be miscible.[61] Experiments [62] on multicomponent PPC containing LDPE and small amounts of hydrophilic polymers [PVA or poly(vinyl acetal), 2% to 6%] showed that, as a rule, in the presence of surfactants the macromolecular coils of the additives undergo insertion into the LDPE domains in both the amorphous phase and intermediate layer.

4. HDPE – PVC Compositions

PVC-Based materials exhibit some valuable properties. At the same time, they are characterised by low thermal stability and thermal plasticity in processing and by low impact toughness at negative temperatures. Sometimes, these drawbacks can be eliminated by modifying PVC with thermoplastic polymers or copolymers, and the resulting PPC combine the advantages of the starting components. This is also favoured by miscibility of PVC and a broad spectrum of polymers containing appropriate functional groups. Such composite materials can be used for the preparation of, *e.g*., polymer films for enclosing greenhouses.[63]

As applied to the HDPE – PVC systems, this method for *in situ* preparation of PPC involves immobilisation of VCl_4, $VOCl_3$ or $TiCl_4$ on the surface of PVC latex or suspension PVC ($M_n = 5.5 \times 10^4$, the specific surface area is 6 $m^2\ g^{-1}$ and the particle diameter lies between 50 and 100 μm) *via* the formation of a macromolecular carbonium salt following the above-mentioned mechanism.[49, 64–66] Similarly to the case of the HDPE – PMMA systems, the chemical composition of PPC is controlled by varying the consumption of ethylene for polymerisation. Using selective extraction with boiling THF in a Soxhlet apparatus for 24 h, the fraction of graft PVC was estimated (Table 5). The larger the volume fraction of PE in synthetic PPC, the larger the amount of non-extractable PVC due to an increase in the number of polymer

Table 5. Percentage of PVC grafted onto PE in the suspension polymerisation of ethylene using the $PVC \cdot VCl_4 - AlEt_2Cl$ system.

PVC content in composition		Percentage of grafted PVC [a] (mass %)
mass %	volume fraction	
17	0.12	3.3
25	0.19	3.0
32	0.25	2.3
46	0.38	2.4
60	0.52	1.8
80	0.76	1.0
56 [b]	0.25	5.6

[a] The content of PVC that could not be extracted with boiling THF in a Soxhlet apparatus for 24 h. [b] The polymer – polymer composition prepared by gas-phase polymerisation of ethylene.

chains or their segments that enter the reaction. The IR spectra of such graft polymers exhibit new bands at 615, 640, 833, 968 and 1260 cm^{-1} corresponding to PVC in addition to the absorption bands of PE. We will consider possible mechanisms of grafting in the next sections of the review.

Similarly to the HDPE–PMMA compositions, it was found that some of the structural domains of PE in the HDPE–PVC systems are X-ray silent. The plot of the empirical dependence of the height of the (110) peak on the chemical composition of the HDPE–PVC system is shifted to the left relative to the plot of analogous dependence for mechanically mixed polymer blends. The proportion of structural domains that do not contribute to the intensity of the (110) peak of PE is ~20% (estimated from the decrease in φ value taking into account the non-extractable fraction of PVC and also from the results of optical measurements). This value is in reasonable agreement with the decrease in the proportion of the 'X-ray responsive' PE. Unlike polymer blends, a salient feature of the structure of *in situ* prepared PPC is the appearance of a new interplanar distance (~4 Å). Therefore, grafting of the PE chains or their segments onto PVC macromolecules occurs in the loose, intermediate near-surface layer.

The mechanics of two-component systems treats this type of PPC as compositions with a framework or interpenetrating structure and adhesive interaction between the components over a wide range of component ratios. According to the cubic model which ignores any polymer–polymer interactions,[67] the yield stress of PE (σ_0) and PPC (σ) must be related by a simple formula:

$$\frac{\sigma}{\sigma_0} = 1 - \varphi^{2/3}.$$

Indeed, the experimental and theoretical data for polymer blends are in reasonable agreement (Fig. 4 *a*), which points to the absence of interactions between the HDPE matrix and PVC particles. No agreement between experiment and theory is observed for the *in situ* prepared PPC. This serves as additional evidence of the polymer–polymer interactions which favour a 60% (on the average) increase in the yield stress, σ, of such compositions. Polymer compositions containing a heat-treated component (*e.g.*, crystalline HDPE) become sensitive to the sample preparation conditions. In particular, the points corresponding to the samples prepared at low and high melt cooling rates are grouped near different theoretical curves (see Fig. 4 *b*).

Table 6 lists the numerical values of the main physicomechanical characteristics of different polymer–polymer compositions HDPE–PVC. As can be seen, the *in situ* prepared PPC are characterised by greater ultimate strength at elongation, relative elongation and tear resistance. The impact toughness of the film samples obtained was estimated from the impact cold resistance to a standard load (a 0.5 kg ball) fallen from a height of 0.5 m.[68] Polymer blends of analogous chemical composition exhibit poorer physicomechanical characteristics in the whole range of HDPE/PVC ratios.

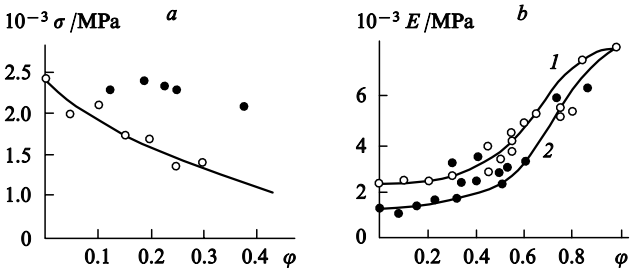


Figure 4. Theoretical (solid curves) and experimental dependences of the yield stress (*a*) and Young's modulus (*b*) for polymer blends of HDPE and PVC (open circles) and corresponding *in situ* prepared PPC HDPE–PVC (solid circles) on the volume fraction of PVC.[65]
Stress rate 0.03 s^{-1}; the cooling rate is 1 (*1*) and 20–30 K min^{-1} (*2*).

Yet another important feature of the *in situ* prepared polymer–polymer compositions HDPE–PVC, *viz.*, their ability to undergo high-frequency welding, should be pointed out. This is apparently due to the improved compatibility of the components and higher homogeneity of the PPC. As the PVC content increases from 23 mass % to 55 mass %, the duration of the welding process is reduced from 70 down to 18 s; however, the impact toughness of the PPC reduces at high PVC content. If the content of PVC is lower than 20%, high-frequency welding of molecular composites becomes impossible. Polymer blends do not undergo high-frequency welding in the whole range of component ratios, which is evidence of high inhomogeneity of their structure.

Comparison of strain–stress diagrams of conventional polymer blends and synthetic PPC showed that the latter behave as ductile materials and are not subject to brittle fracture both at room temperature and at 203 K. This allows the use of the *in situ* prepared PPC at low temperatures. The optimum content of PVC in such compositions is nearly 45 mass %.

It should be noted that the formation of a grafted layer from the polymer formed was also observed during the cationic polymerisation of styrene or isobutylene in a suspension of PVC with immobilised Et_2AlCl (in a heptane–1,2-dichloroethane

Table 6. Numerical values of physicomechanical characteristics of polymer–polymer compositions HDPE–PVC.[66]

Property	Starting components		PVC content in the *in situ* prepared PPC (mass %)					PVC content in mechanical mixtures (mass %)				
	HDPE	PVC	17	23	30	44	55	17	23	30	44.5	55
Ultimate strength at elongation /MPa	30.1	42.0	24	23.8	21.3	20.4	16.8	24.2	14.4	5.0	–	–
Relative elongation (%)	40	23	80	30	20	62.5	13	8.5	5	–	–	–
Rigidity /N	0.7	1.0	0.7	0.6	0.7	0.7	0.7	0.6	0.75	0.7	0.75	0.6
Tear resistance /kN m^{-1}	52	30	19	30	17	25	31	3.0	3.5	3.5	–	–
Impact cold resistance /°C	–	0	−80	−80	−80	−80	−60	see [a]	see [a]	see [a]	see [a]	see [a]
High-frequency welding [b]												
time /s	–	9	see [c]	70	56	30	18	see [d]	see [d]	see [d]	see [d]	see [d]
weld strength (%)	–	28		98	98	65	55					
weld cold resistance /°C	–	0		−70	−70	−70	−30					

[a] Room-temperature cracking. [b] High-frequency currents. [c] No welding. [d] No welding; surface combustion occurs.

mixture at 253 K).[48] Depending on the polymerisation conditions, the degree of heterophase grafting varied from 2 vol.% to 13 vol.% for PS and from 7 vol.% to 15 vol.% for PIB (with n-pentane as selective extracting agent). In the latter case, the 250 μm PVC particles were coated with a separable PIB layer 50 μm thick. Probably, flaking of the grafted layer from PVC is due to large differences in the surface energy (immiscibility) and mechanical properties of PIB and PVC. The concentration of chlorine in the exterior of the grafted layer is much lower than in the interior and sharply decreases as the thickness of the grafted layer increases.

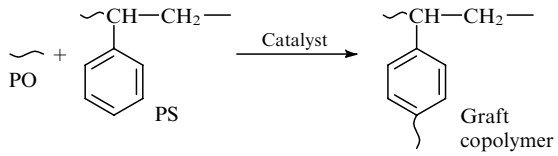
Thus, synthetic methods make it possible to prepare PPC with improved physicomechanical and operating characteristics. Simple blending of the corresponding components does not allow improvement of these characteristics.

IV. Synthesis of polar ingredients in the presence of polyolefins

An alternative approach to the *in situ* preparation of PPC implies the synthesis of the second (hereafter, 'polar') component in the presence of a PO. In the reaction bulk, the PO has little effect on either the radical and ionic polymerisation or on the polycondensation of the component precursors.

Polyolefins can be modified by mechanochemical treatment with the monomer in the presence of Lewis acids.[69] For instance, the preparation of a layered material based on PE fibre (glass fibre) involves stacking of aligned fibres that were preliminarily soaked with methyl methacrylate (MMA) in a sheet die followed by bulk polymerisation of MMA at room temperature [70, 71] with the amine – peroxide system as initiator.[72] The polymerisation is conducted until thickening of the material; shrinkage control is achieved by adding excess monomer. The final preparation stage of the composition involves heating to 328 K (this temperature corresponds to complete conversion of MMA).

Compatibility of particular pairs of polymers (*e.g.*, PO and PS) can be improved by performing *in situ* cationic polymerisation of styrene in the presence of corresponding polyolefins with Lewis acids (*e.g.*, $AlCl_3$) as catalysts.[73] The reaction mechanism is similar to the benzene ring alkylation according to Friedel – Crafts.



The degree of grafting depends on the nature of the Lewis acid and reaches a maximum value (15.7%) for $AlCl_3$.

The procedure for preparation of polymer – polymer blends based on crystalline polymers (HDPE, PP, PA-12) after their deformation *via* delocalised crazing by drawing in liquid monomers (styrene, MMA, *etc.*) involves drawing a polymer film (*e.g.*, PP) in MMA containing the necessary amount of both initiator and cross-linking agent.[74–76] As the desired degree of drawing is achieved, *in situ* polymerisation of the monomer in the PP matrix is carried out. Deformation is accompanied by continuous filling of the newly formed, porous polymer structure with the polymerised blend. Generally, delocalised crazing allows substantial enhancement of the swelling of the polymer (swelling of PP or PE in conventional monomers is at most 10 vol.% – 15 vol.%, since the low-molecular-mass component can penetrate only the amorphous domains of the polymer structure while crystallites remain intact). From the standpoint of the preparation procedure such PPC can be classified as IPN. Experiments with the HDPE – PMMA system showed that complete separation of the blend components by successive selective extraction with chloroform at 333 K for 6 h (to dissolve PMMA) and with n-decane at 393 K for 2 h (to remove HDPE) is also impossible, while the homopolymers are completely dissolved under these conditions. The content of the insoluble (non-extractable) product is 25 mass % – 30 mass %. This is due to either or both chemical grafting of the polymer chains and their interpenetration on the molecular level.

Thus, despite thermodynamic incompatibility of their components, the *in situ* prepared polymer – polymer compositions are to some extent compatible and the degree of compatibility is higher than in the case of simple mixing of polymer melts. Nevertheless, such PPC represent two-phase systems, which is confirmed by the data of calorimetric studies, according to which the glass transition temperatures of the components remain unchanged.

It is of considerable interest to consider the formation of the PU phase in PE in more detail. Thermoplastic PU is widely used in blends with other polymers including PO.[77] For instance, the formation of *in situ* compositions containing 85% PE and 15% PU from diisocyanates (diphenylmethane-4,4′-diisocyanate or dicyclohexylmethane-4,4′-diisocyanate) and diols (polyetherdiol or 1,4-butanediol) in PE melts (413 K) in the presence of catalyst was reported.[78] During the process the molecular mass of the dispersed phase changes in nearly the same manner as in the case of bulk polymerisation of virgin PU under analogous conditions (Fig. 5). Since the solubility of the isocyanate monomer in PE melts is rather high, while the solubility of the diol is low, the stoichiometry ratio between them violates, which imposes some limitations on the degree of polymerisation by *in situ* blending.‡ A number of procedures which facilitate the formation and favour strengthening of the interfacial layers was developed. As a rule this is achieved by introducing various additives (compatibilisers) which improve adhesive interactions between the starting components and the *in situ* formed phases.

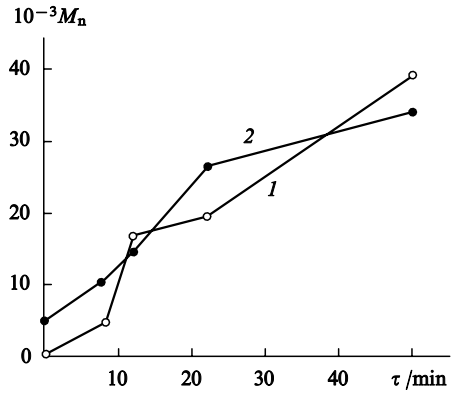


Figure 5. Formation kinetics of PU (curing at 413 K) in the dispersed phase (*1*) and in the bulk (*2*) under comparable conditions.[78]

For instance, consecutive anionic polymerisation of styrene and 4-vinylpyridine in the presence of BuLi at 195 K resulted in block copolymers which induce phase separation.[80] Block copolymers of styrene and 2-vinylpyridine were synthesised using consecutive polymerisation of the monomers with potassium cumene as initiator.[81] Atactic ethylene/propylene diblock copolymers were prepared by hydrogenation of poly(butadiene-b-2-methyl-1,3-pentadiene), polybutadiene and poly(2-methyl-1,3-pentadiene).[82, 83] The preparation of a partially deuterated ethylene/propylene diblock copolymer based on perdeuterated butadiene used as co-monomer was also reported.

‡ Semi-interpenetrating polymer networks based on cross-linked PU and linear poly(butyl methacrylate) are prepared by introducing the latter component in the monomeric form followed by performing radical polymerisation simultaneously with cross-linking.[79]

V. On some synthetic methods for preparation of polyolefin – polyolefin compositions

Multicomponent, PO-based polymer blends represent the most abundant group of PPC; most often, they serve as materials for recycling. This group of polymer compositions comprises blends of normal PE and high-molecular-mass or ultrahigh-molecular-mass HDPE, blends of different types of PE (LDPE, medium density PE and HDPE), *etc*.[84,85] These materials exhibit some valuable properties, such as improved impact toughness, resistance to external factors including cold resistance, have good optical and rheological characteristics, high crystallisation rate, *etc*.[86,87] These parameters of the PPC are nonlinear functions of their chemical composition, which is due to the influence of the interfacial layer and to the changes in the structure and properties of the constituent phases in the blends caused by the interaction with other components. One of the main goals of research into such PPC is the development of methods for improvement of processability of PO.

1. Systems based on different types of polyethylene

Design of novel materials with improved properties involves the preparation of microheterogeneous composites as an integral part. Microheterogeneous composites represent (i) PPC based on different types of PE (high density and low density PE) and (ii) highly oriented systems containing LDPE and HDPE.[88] Low density PE, with its long-chain branchings, and linear HDPE (LHDPE) are of similar chemical nature. Therefore, one could expect that they will form homogeneous blends which, nevertheless, represent microheterogeneous systems. An increase in the concentration of HDPE in the blend leads to a decrease in the crystallite size and to an improvement of the structural homogeneity of PPC. If the content of HDPE exceeds 30%, phase separation occurs, HDPE forms a dispersed phase and interfacial interaction between the polymeric constituents is observed. Further increase in the concentration of HDPE causes the formation of ordered HDPE domains that are structurally similar to the HDPE crystallites. Polymer – polymer compositions containing 80% HDPE have superiority in mechanical properties compared to the starting components. This is thought to be a result of the highest possible structural homogeneity of the polymer compositions due to the maximum compatibility of the components. Neutron scattering studies showed that the melts of HDPE and LDPE are compatible in the whole range of their concentrations.[89] A key factor that governs the extent of co-crystallisation of HDPE and LDPE is the similarity of crystallisation rates of each component. The amount of co-crystallisate formed increases as the isothermal crystallisation temperature reduces under quenching conditions.[90] The co-crystallisation is also influenced by the branching composition of the constituent macromolecules, as was shown taking a blend of linear PE (1% to 20%) and branched PE as an example.[91] These systems can also exhibit partial compatibility like, *e.g*., a blend of LLDPE (1-octene co-monomer), HDPE and LDPE.[92]

As the content of LDPE in its blends with the ethylene – propylene – 1,4-hexadiene terpolymer increases, the T_g value is shifted towards higher temperatures (*i.e*., towards the region of β-relaxation of PE, which is due to an increase in the mobility of small independent structural fragments of the macromolecules).[93] This confirms that the blend components are miscible on the molecular level. In addition, LDPE and ethylene/propylene copolymers are characterised by close values of the density of cohesive energy in the amorphous phase; these polymers also seem to be compatible on the molecular level. The addition of small amounts of LDPE (merely 2.5%) to LLDPE (1-hexene co-monomer with a density of 0.900 g cm^{-3}) leads to the formation of well-defined spherulites and to a substantial decrease in their size.[94] Hence, LDPE is a nucleating agent for the crystallisation of LLDPE and the addition of LDPE shifts the α-relaxational processes towards higher temperatures or longer times. The table presented below lists the melting temperatures (T_m), densities (ρ), crystallite volume fractions (x) and spherulite radii (r) for individual LLDPE and for the LLDPE component of the LLDPE – LDPE composition containing 2.5% LDPE.[94]

Sample	T_m/K	ρ/g cm^{-3}	x(%)	r/μm
LLDPE	370.3	0.9031	33.2	6.5
LLDPE – LDPE	372.5	0.9048	34.3	0.7

Linear LDPE has superiority in mechanical properties (*e.g*., elongation at break) compared to LDPE. LLDPE-based blends exhibit intermediate properties (*e.g*., torque[95]) between those of the starting polymers. Studies on both film and melt behavior of such blends revealed no severe problems originating from polymer incompatibility. On the other hand, non-polar and low-polar crystalline polymers are poorly miscible with one another and with non-crystalline polymers. In this respect, a classical example is provided by blends of PE and PIB.[96]

Polymer – polymer compositions prepared from solutions of polyolefins are also used, though much more rarely. For instance, linear PE (M_w = 53 000, M_n = 16 000) and branched PE (M_w = 76 800, M_n = 11 300) are mixed in predetermined ratios from 1% solution in xylene and then precipitated with methanol.[91] Studies on the properties of such PPC allows the development of methods for compatibilisation of these polymers for their blending, processing and further use of the material.

Crystallisation of blends of HDPE and LLDPE has been the subject of intensive research (see, *e.g*., Refs 97 and 98). The morphology and mechanical properties of films prepared from blends of UMMPE with a viscosity-average molecular mass of 6×10^6 and low-molecular-mass PE (4×10^4) by gelation§ or crystallisation from solutions are determined by the degree of entanglement of the macromolecules of both polymers. Here, LDPE has no time to form crystals since it crystallises at a much lower rate than HDPE. The modulus of elongation of such PPC is as high as 50 GPa, which is a quite appropriate value for conventional usage. These PPC exhibit lower viscosity, which favours substantial improvement of the performance of the equipment used for fabrication of blend-based films.

Structural peculiarities of the blend-based PPC under consideration determine[99–101] the tensile strength of the PE blends,[102] their operating characteristics[103] and dielectric and other properties. For instance, isothermal crystallisation of blends of the linear and branched PE at 397 K results in compact branched structures. Carrying out the process at 288 K leads to the formation of open, lamellar spherulite structures; quenching favours the appearance of a continuous spherulite texture.[91] The dielectric properties of PPC depend, first of all, on their morphology, heat treatment conditions and the content of linear PE. This also concerns the PPC based on industrially used LDPE and LLDPE.[104] At the same time, HDPE and LLDPE are compatible in the whole range of their concentrations provided that quenching occurs at low melt cooling rate.[105] In the presence of HDPE the blend morphology is governed by the distribution of lamellae (crystallites), which is due to higher mobility of the HDPE molecules. The macromolecules of LLDPE form mixed crystals (co-crystallise) with the HDPE molecules. The lattice parameters of the crystalline phase increase as the number of side chain branchings increases. Vol'fson[16] constructed a 'map' of the morphology behaviour of the LDPE – LLDPE blends with the predominant 'shish-kebab'-like morphology, containing 0.5% to 5.0% LDPE and quenched at different temperatures in the range from 393 to 463 K. Polymer – polymer compositions with low content of LDPE are characterised by a higher degree of crystallinity of LLDPE, higher melting temperature and rigidity.[94] The ultimate strength decreases while the yield stress increases as the content of LDPE increases (Fig. 6).

§ For gelation, polymer solutions in decalin, prepared at 408 K, are poured in an aluminium pan and the solvent is evaporated.

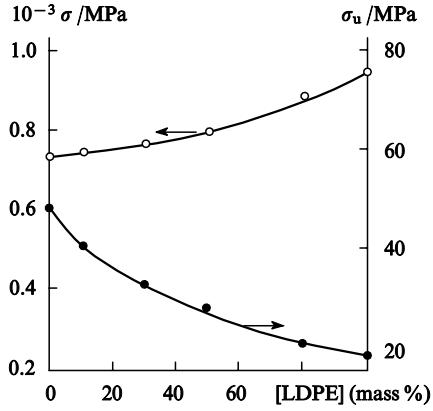


Figure 6. Yield stress (σ) and ultimate strength (σ_u) of compositions LLDPE – LDPE as functions of the component ratio at 296 K.[94]

Information on 'ternary' PE-based PPC is scarce. Donatelli[99] studied ternary films prepared from low, medium and high density PE and showed that two polymers can be compatible within rather narrow limits of the content of branched units while they separate into individual crystalline phases at higher concentration of branchings.

2. Polyethylene – polypropylene systems and other compositions

Low-temperature impact brittleness of PP originates from the relatively high glass transition temperature of this compound (~263 K). An increase in the cold resistance of PP-based materials is a topical problem. Blends of PP and HDPE have been studied in most detail. At particular chemical compositions, these PPC are characterised by high breaking strength, modulus of elasticity and impact toughness and low brittleness temperature. The structural-dynamical parameters of the amorphous domains, the supramolecular structure and physicomechanical properties of such systems consisting of polymeric constituents with different molecular-mass characteristics have been studied. The properties of PPC prepared from isotactic PP and PE also depend on which catalyst was used for the polymerisation of ethylene, namely, a heterogeneous (Ziegler – Natta type) or a one-centre homogeneous metallocene catalyst.[106] Isotactic PP and HDPE are thermodynamically incompatible and form different types of crystal lattices. Since the melting temperatures of these polymers are different, they form individual structures.[107]

In situ preparation of PPC from HDPE and PP by polymerisation at low pressure involves immobilisation of the catalyst components on either PP or PE. (This procedure was used in the polymerisation of, *e.g.*, propylene with the product of co-grinding of HDPE and $TiCl_3$ as the catalyst component.[46]) The newly formed PPC can have virtually any chemical composition and exhibits improved strain – stress properties and cold resistance as compared to conventional polymer blends. It should be noted that the polymerisation method allows one to control the properties of the PP polymerisate, its stereosequence and molecular-mass parameters. Not only PE, but also other polymers and copolymers can be used for the preparation of the catalyst component. In particular, blends of PE and synthetic ethylene – propylene rubber (SKEP), PP and polybutene, PP and poly(4-methylpentene), *etc.*, were prepared. The structure of this type of PPC is shown in Fig. 7. Co-grinding of the catalyst (MCl_3) and HDPE leads to coating each catalyst submicroparticle with the polymer layer ('skin'). Probably, sub-microcrystals (*e.g.*, $TiCl_3$) are inserted into the amorphous phase of PE. Nucleation of the PP phase with the globular structure gradually transforming into a lamellar one occurs in the bulk of the catalyst component particle. Microheterogeneous mixing of the growing PP phase with the PE phase is thought to result in the formation of IPN.

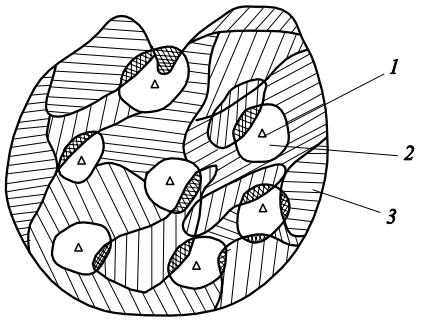


Figure 7. Structure of a submicroparticle of composition HDPE – PP. (*1*) Catalyst microparticle; (*2*) HDPE 'skin'; (*3*) PP phase.

Binary compositions containing PP (70%) and HDPE (30%) are prepared by *in situ* polymerisation on binuclear metal complex catalysts immobilised on the SiO_2 surface.[108] The mechanical characteristics of this material (Young's modulus, tensile strength) are 1.5 to 2 times higher than the corresponding characteristics of 'pure' PP. This is due to the very complex and unusual morphology of the material.

Considerable attention has been given to the studies of polymer blends based on PP and some other polymers such as elastomers, different crystalline and amorphous thermoplastics [PETP, polycarbonates, PS and acrylonitrile – butadiene – styrene (ABS) terpolymers]. Gupta *et al.*[109] analysed the rheological properties of binary and ternary blends of PP with ABS and LDPE. Ethylene/propylene block copolymers exhibit improved impact toughness and low brittleness temperature (down to 256 K).

At the same time, the strain – stress properties of such blends prepared from, *e.g.*, isotactic PP and LDPE[110,111] are to a great extent dependent on the blending temperature and duration of blending of the components. The diffraction patterns of the HDPE – PP blends with different chemical compositions represent superpositions of the diffraction patterns of the starting components, which indicates that no co-crystallisation occurs. The average crystallite size in the blends is nearly the same as those in the non-blended components (150 and 170 Å, respectively).[112] However, the specific volume of the blend exceeds the value obtained using the additivity scheme. This points to the formation of a loose structure resulting from an increase in the content of the amorphous phase. This conclusion was also confirmed by the results of radiothermoluminescence studies, according to which the glass transition temperatures of the components in blends of LDPE and PP decrease (Fig. 8). Such a negative synergistic effect of the blend components can be rationalised by different rates and

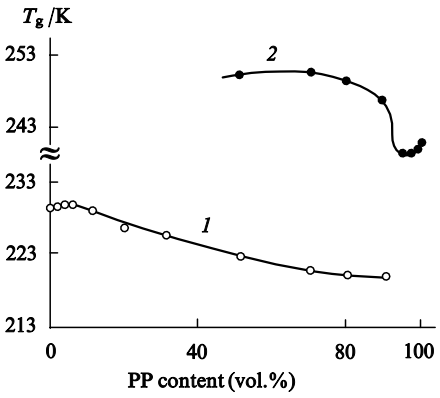


Figure 8. Glass transition temperature of the LDPE (*1*) and PP (*2*) phase as a function of the component ratio of LDPE –PP blend.[112]

temperatures of their crystallisation, by their thermodynamic incompatibility and by the absence of co-crystallisation in the blend. The rate of crystallisation of isotactic PP blended with LLDPE insignificantly decreases as the content of LLDPE increases.[113] Dissolution of chain segments leads to the formation of an extended amorphous interfacial layer which precludes crystallisation of PP. The LDPE phase can be considered as a poor solvent for the PP phase (and *vice versa*).[3]

High density PE is incompatible with isotactic PP under steady-state conditions. However, compositions prepared from these polymers (PP : HDPE = 60 : 40) by injection moulding form a phase with regularly separated structure and an identity period of 0.15 μm. The regular structure cannot be formed by simple melt mixing but only by the spinodal decomposition (at zero shear rate).[114] In the compositions consisting of isotactic PP and HDPE (0.1% – 3%), phase separation occurs on gradual cooling from 473 down to 443 K.[115] The average spherulite diameter is less than 10 μm for HDPE and greater than 100 μm for PP.[24] The proportion of ordered polymer chains in the amorphous phase of PP increases upon the addition of HDPE (10 mass % to 20 mass %) even for isotropic blends of these polymers prepared by melt mixing.[116] The modulus of elasticity of the blends exhibits a synergistic effect due to the strengthening of the intercrystallite links in both the PP phase and in the interfacial layer.

It is interesting that, unlike the PPC based on syndiotactic PP and random ethylene/propylene copolymer¶ (a 80 : 20 blend, 4.9 mass % ethylene units), isotactic and syndiotactic PP synthesised on zirconocene catalysts are incompatible even upon heating up to 513 K (a 50 : 50 blend).[118]

The mechanical properties of PP – PE compositions can be substantially improved by using UMMPE instead of conventional PE.[119] Such blends were prepared by coprecipitation of polymers from 1% xylene solutions at 398 K with excess methanol. Improved compatibility of PP and UMMPE can be most likely rationalised by the interpenetration of polymer chains in the amorphous phase due to the low degree of crystallinity of UMMPE.

A study on the morphology of blends of amorphous-crystalline block copolymers with amorphous homopolymers carried out taking the system consisting of ethylene/propylene diblock copolymer and atactic PP as an example showed that blending of the block copolymer responsible for the formation of the lamellar structure of microdomains and atactic PP leads to changes in the morphology of the microdomain structures and to microphase separation.[120, 121] If the atactic PP chains are shorter than the block length, morphological transformations from lamellar structure into a bicontinuous cylindrical one, then into a discrete cylindrical and, finally, into a spherical structure occur. If the PP chain is longer than the block length, microphase separation occurs and a morphological change from lamellar to bicontinuous cylindrical structure is observed. In melts, these morphological transformations are accompanied by changes in the blend crystallisation kinetics.

In the blend of isotactic PP and SKEP the morphology of the ethylene domains depends only slightly on the viscosity ratio of the blend components and exhibits a strong dependence on the content of ethylene.[122] The microstructure and chemical composition of SKEP (the dispersed phase) affect the rheology, morphology and properties of such compositions prepared by injection moulding.[123] The microstructure of a composition of isotactic PP and SKEP (60 : 40) essentially depends on which (a titanium- or vanadium-containing) catalyst it was prepared. Blends of isotactic PP and random SKEP, synthesised on vanadium-containing catalysts exhibit substantially improved impact toughness at low temperatures. The structure of the SKEP component affects both the crystallisation kinetics and the internal structure of spherulites of isotactic PP (the thickness of the crystalline lamellae and amorphous layer).

Among other PO – PO compositions, we will dwell on blends of isotactic PP and PIB. Problems of co-crystallisation and compatibility of blend components were considered by Cham *et al.*[124] Blends of PP and PIB are compatible in the amorphous phase and can even undergo co-crystallisation. Figure 9 presents the glass transition temperature and the Flory – Huggins interfacial interaction parameter of the PE – PIB compositions as functions of their chemical composition.[125] The maximum shift of T_g is 8.6 K for PE and 5.9 K for PIB (at 90% PE). This means that the solubility of PIB in PE is higher than that of PE in PIB. According to calculations, the solubility of PIB in the PE phase of the PE – PIB (10 : 90) composition is ~17% by mass, whereas the content of the PE phase in the PIB phase of the PE – PIB (90 : 10) composition is only 6 mass %. Low values of the Flory – Huggins interaction parameters χ_{12} and χ_{21} (see Fig. 9*b*) point to some degree of compatibility of the blend components despite the absence of specific interactions between their macromolecules. For unknown reasons, the χ_{12} value differs from χ_{21}.†

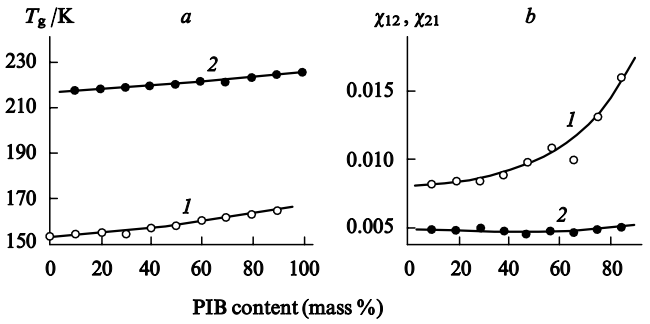


Figure 9. Glass transition temperatures (*a*) and Flory – Huggins parameters (*b*) of compositions PE – PIB as a function of the component ratio: (*1*) PE phase; (*2*) PIB phase.

Interesting results were obtained in studies of PIB – PS polymer networks containing from 10% to 70% PS.[127] Such blends were prepared by radical polymerisation of styrene preliminarily swollen in the PIB matrix. Electron microscopy studies did not reveal the formation of PS particles; however, cloudiness and rougher surfaces of the samples observed with increasing the content of PS are evidence of phase separation. Mechanical properties of PS are strongly dependent on its molecular mass. A decrease in the molecular mass probably favours compatibility of PS and PIB and an increase in the degree of grafting of the PS chains onto PIB, which manifests itself as increased ultimate strength, elongation at break and the fracture energy of the samples (at close PS content).

Information on polymer blends based on higher PO is scarce and fragmentary.

3. Preparation of polyolefin – polyolefin compositions by consecutive polymerisation

In the preceding section of this review we considered the formation of PPC in the course of the synthesis of one of the components. However, the *in situ* approach is also efficient if two or more polyolefin components are formed during the synthesis. This type of PPC is prepared by consecutive polymerisation of monomers on metal complex catalysts, which can be done

¶ For comparison, mention may be made that a study on the texture of a blend of syndiotactic and atactic PS revealed that the density of cross-link points strongly depends on temperature and exhibits relatively weak dependence on the initial chemical composition of noncrystallisable materials and on the degree of crystallinity of lamellar stacks.[117]

† This was also observed for polymer – polymer compositions PS – PMMA (the Flory – Huggins parameter for this system is 0.035 ± 0.010).[126]

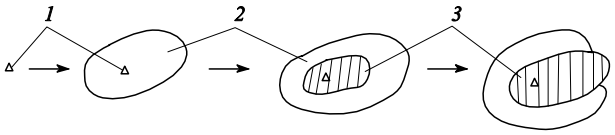


Figure 10. Formation of nascent morphology in the preparation of polyolefin compositions under conditions of polymerisation compatibility.
(*1*) Catalyst subparticle; (*2*) polymer prepared in the first stage of polymerisation (phase 1); (*3*) polymer prepared in the second stage of polymerisation (phase 2).[128]

immediately in the polymerisation reactor using the Ziegler – Natta catalysts. The dispersity of the polyolefin compositions obtained is determined by both the size of the catalytic species (most often, $TiCl_3$) and peculiarities of the polymer morphology. Salient features of such PPC, differing from polymer blends of identical chemical compositions, are high molecular masses of the components and the presence of corresponding random and block copolymers localised within the interfacial layers.[128]

A scheme illustrating the preparation of this type of PPC is presented in Fig. 10. The growing PP chains linked into crystalline fibrillae form a specific 'skin' around the $TiCl_3$ microcrystal. For instance, after completion of the polymerisation of propylene and removal of excess PP down to the specified post-polymerisation content, the reactor is filled with ethylene and then copolymerisation of ethylene with propylene on 'living' PP chains is carried out, followed by the homopolymerisation of ethylene. In this case, nucleation of the polymeric phase of PE occurs in the bulk of the globular PP particles formed in the first stage. The growing PE phase causes deformation of the 'skin' of the first submicroparticle and penetrates the PP layer. High-molecular-mass PE dispersed in the PP matrix represents particles of submicron size and is strongly amorphised. Hence, compatibilisation *via* polymerisation involves fine mixing of the components, which is accompanied by the formation of interpenetrating phases. The properties of the resultant product are determined by balance between its rigidity and strength (impact toughness). Semicrystallinity of the phase of isotactic PP has a crucial effect on the mechanical properties of these materials. The chemical composition of the elastomeric component and its content in particular PPC is also of great importance. Polymer – polymer compositions prepared using this approach consist of crystallisable polymers and are called polyallomers.[129] Studies on the morphology of polyolefins synthesised by consecutive polymerisation of propylene and ethylene in the presence of the $TiCl_3 - AlEt_2Cl$ catalytic system showed [130, 131] that the PE phase formed in the second stage causes deformation of the preliminarily formed PP layer followed by its disturbance and penetrates to the particle surface. A similar phenomenon was also observed for the polymerisation of propylene in the second stage of the process. Here, the PP phase penetrates the PE or SKEP layer formed in the first stage.[132] The same is true for polymerisation of the butene – ethylene pair. Consecutive polymerisation also allows preparation of homogeneous ternary polyallomers containing, *e.g.*, the PP, PE and PB phases.[133]

VI. Improvement of compatibility of polymeric components by introduction of compatibilisers

The most widely used strategies of improvement of the compatibility of immiscible polymeric components involve such approaches that initiate strong specific interactions (ion – ion and ion – dipole interactions, hydrogen bonds, *etc.*), formation of IPN, cross-linking, *etc*. Compatibility of the blend components is improved due to strengthening of the interfacial layers. Compatibilisation of different classes of polymers is achieved by introducing polymeric additives (specific 'concentrates' of the interface phases) that favour manifestation of the above-mentioned compatibilising factors. These additives favour the formation of different types of bonds between the blend components and improvement of microheterogeneity of the systems in the stage of dispersion blending. Compatibilisers represent reactive copolymers containing chain segments that are compatible or miscible with both components of the PPC. These additives are of considerable interest as an alternative to conventional or graft copolymers. They can both be synthesised in the polymerisation stage and provide a means for *in situ* modification of the systems under study. This approach allows controlling the surface tension at the interface and the interfacial adhesion, thus providing more homogeneous distribution of the dispersed phase. The third component also acts as plasticiser.

It has been known for long [134] that block copolymers (in regard to polymer blends, they are often considered as 'oil-in-oil'-type emulsifying agents [135]) can emulsify polymer dispersions. This prevents phase separation. For instance, the addition of an AB diblock copolymer to a binary blend of polymers A and B causes a marked compatibilisation effect.[136] Moreover, a diblock copolymer AC can be used as a link between immiscible polymers A and B provided that polymer C is miscible with polymer B.[137] Yet another version of this approach involves blending of two incompatible polymers A and B using a diblock copolymer CD provided that both A and B are miscible with both C and D.[138, 139] Blending of the diblock copolymer with the homopolymers having identical monomer units is a thermal process. However, if blending of a diblock copolymer consisting of blocks with different chemical nature with two immiscible polymers is accompanied by exothemic interaction between the blending pairs of polymers, this interaction can become an additional factor of compatibility of the immiscible components.

The most widely used compatibilisers represent additives containing anhydride (most often, maleic anhydride, or MA),[140 – 145] carboxylic,[146, 147] epoxy [148, 149] and oxazoline [150] functional groups which react with the amino or carboxy groups of various thermoplastic polymers. Binary or ternary blends are also compatibilised using commercial products. Most often, these are PE-g-poly(maleic anhydride), ethylene – butyl acrylate – MA terpolymers (91 : 8 : 1) or poly(ethylene-co-vinyl acetate) (91 : 9) modified by grafting of MA (1%). Here, we restricted ourselves to the typical examples.

1. Compatibilisation of polyolefin blends

Weak interfacial interaction deteriorates the properties of composite materials based on PO blends. Compatibilisation of PO – PO block copolymers allows improvement of the miscibility of blend components and affects the properties of the interfacial layer in heterogeneous PO blends. If the molecular mass of a block copolymer is sufficiently large, it can act as an anchor at both sides of the interface. In particular, compatibility of a blend of isotactic PP and PE is often improved by using SKEP as the interfacial modifier.[151 – 153] The cohesive energies of LDPE and ethylene/propylene copolymers in the amorphous phase are similar;[93] therefore, they are miscible on the molecular level. The addition (even in small amounts) of a random ethylene/propylene copolymer to the blend of HDPE and PP improves the impact toughness of the PPC;[154] that is, a portion of SKEP is dissolved in the amorphous domains of PE and PP, thus forming the interface layer. Multicomponent blends of LDPE, HDPE, isotactic PP, PB and poly(methylpentene) and recycled PO – PO blends can also be compatibilised by melt blending with ethylene/propylene block copolymers used as additives. An even more pronounced compatibilising effect is achieved by using synthetic ethylene – propylene – diene terpolymers (SKEPT) as additives to these polymeric compositions.[155] Grafting of compatibilisers onto a particular blend component (PE or PP) is also widely used. This approach allows improvement of blend processing conditions and an increase in the performance of the equipment used.

The mechanical properties of the PPC based on different types of PE (LDPE, HDPE, LLDPE and hydrogenated polybutadiene) and melt-mixed PS exhibit a strong dependence on the content (usually 2% to 10%) and molecular mass (60 000 to 270 000) of copolymer G [G stands for poly(hydrogenated butadiene-b-styrene)] used as an additive (see Fig. 11).[156, 157] The hydrogenated triblock styrene–ethylene–butadiene–styrene terpolymer characterised by the total molecular mass of 35 000, the molecular mass of the central block of 7500 and the PS content of 29% is an efficient interfacial modifier for the HDPE–PS systems.[158–160] Stability of polyolefin blends is often improved using ternary blends. For instance, the ternary blend of PP, polybutene and hydrogenated oligocyclopentadiene (50 : 30 : 20) [35] has one glass transition temperature, 289 K (*cf.* a value of 286 K obtained from calculations using the Fox equation), which confirms compatibility of the blend components.

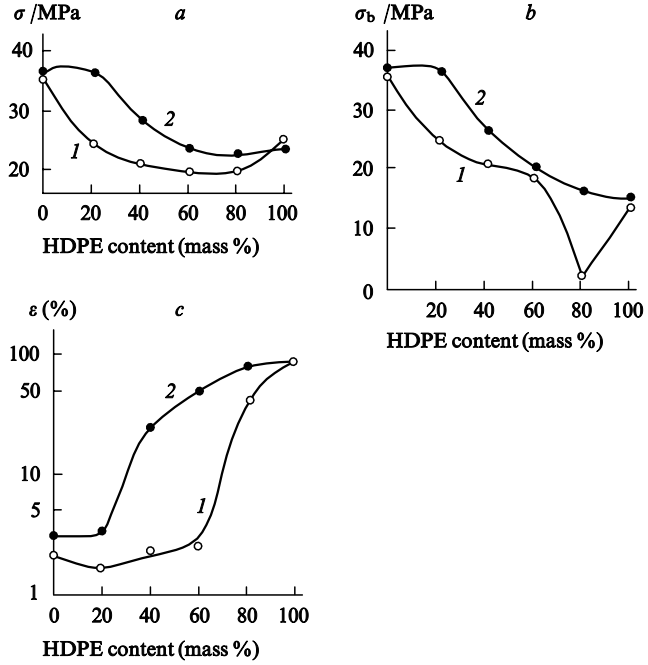


Figure 11. Yield stress (*a*), tensile strength (*b*) and relative elongation at break (*c*) plotted as functions of the component ratio of composition HDPE–PS without (*1*) and with addition of 10% copolymer G (*2*).

Graft, triblock and star copolymers have high emulsifying ability and are even more efficient compatibilisers. These types of blends based on PP, HDPE and SKEPT (as a rule, with ethylidene-2-norbornene as the third monomer) are of commercial value and have therefore been the subject of intensive research.[161–163]

If some fraction of the elastomeric constituent (SKEPT) of the blend of PP, SKEPT and PE is replaced by PE, this system can exhibit a higher or lower impact toughness depending on the blending conditions of the components, their rheological properties and viscosities.[164] Sometimes, the interfacial adhesion is improved by carrying out the reactions of dynamic selective cross-linking (see below).[165]

2. Compatibility of polyolefin–polyamide systems

Polyamides (PA-6, PA-66, PA-12, *etc.*) exhibit high mechanical strength, rigidity and good processability and are therefore widely used in the automotive industry and for production of textile fibres. They have high melting temperatures and oil resistance. However, PA are characterised by ready deformation at low temperatures, cracking and high moisture absorption, which imposes limitations on possible applications of these materials. Polyamides are often used in the form of blends with low-module polymers, such as PO and, in particular, LDPE, which exhibits excellent elastic properties at low temperatures and low moisture absorption. Using such blends reduces the cost of materials. The high commercial value of the systems based on PA-6 and LDPE has attracted considerable attention.[166] Interest in the compatibility problem of PO and PA is also due to the fact that the polyolefins and polyamides represent two main groups of materials for recycling.[167, 168]

The components of the two-phase system LDPE–PA-6 are incompatible; therefore, this blend is characterised by weak interfacial adhesion and high dispersity of the LDPE domains. The properties of such PPC are determined by the size and shape of the dispersed phase; it should be noted that these parameters depend on the elasticity of the components.[10, 169] The addition of interfacial modifiers, *viz.*, block or graft copolymers (their content is 0.5% to 1%) leads to a decrease in both the degree of crystallinity of LDPE and the crystal lattice parameters and to improvement of the mechanical properties (especially, yield stress, Young's modulus, impact toughness, relative deformation). The components of this system were compatibilised by the introduction of the block copolymer of styrene, ethylene and butylene to the modified extrudate.[170] Based on the analysis of the shape of thermomechanical curves of the blends, it was suggested that PA-6 was nearly molecularly dispersed in the LDPE matrix in the presence of 5% of the ternary block copolymer.

In the case of melt mixing of blend components the introduction of a third component can facilitate the blending and improve the mutual solubility of the components, thus providing predominant interaction of functional groups with a particular component. The most detailed studies on the problems of graft functionalisation of PO with MA or acrylic acid were carried out taking compositions of PO and PA as examples.[171–173] *In situ* grafting in the extruder at 473 K in the presence of dicumyl peroxide (DP) (PP : MA : DP = 94 : 6 : 0.3) was followed by granulation. Free-radical melt grafting of MA, glycidyl methacrylate and diethyl maleate (DEM) onto PO was also studied in detail.[174, 175] *In situ* preparation of PPC based on PA-6 and LDPE that was graft functionalised with MA or DEM led to interesting results.[176] The addition of PP–MA compatibilisers improved the interfacial adhesion and the impact toughness of the compositions of PP and PA-6.[177, 178] Probably, the interfacial adhesion becomes stronger due to the formation of hydrogen bonds between the end amino groups of PA and grafted MA; this leads to nearly complete homogeneity of polymer blends.[141] It is appropriate to use functionalised PO, *e.g.*, carboxy derivatives for compatibilisation of polyamide matrices and the dispersed PO phase.[179, 180] As a rule, grafting of carboxy or anhydride groups onto the PO chains is performed during melt mixing. Reactions of the amino or amido groups of the PA phase with functional groups of the PO phase result in the formation of *in situ* prepared copolymers characterised by weakened interfacial tension and improved interfacial adhesion of their components.[181]

Improvement of fracture toughness is often achieved by energy dissipation within the interfacial layer of immiscible components of PPC. The introduction of a block copolymer additive should result in a decrease in both the interfacial tension and phase dispersity; in many instances this depends on the number of 'stitches' between the two phases.[182] Nearly perfect compatibility was observed, *e.g.*, upon addition of small amounts of the PP/MA copolymer to blends of PE and PA-6.[183] Park *et al.*[184] studied the morphology, thermal and rheological properties of the composition of PP, PA-6 and PP/MA (5%) including the dependence of its viscosity on the chemical composition at low shear rate (Fig. 12). The results obtained point to the negative deviations from the additivity rule for the simple system PP–PA-6 and to positive deviations for the blends of PP, PA-6 and PP/MA. These results were used for assessing the texture of the PPC and evaluating the chemical interaction between the starting polymers. Currently, the composition of SKEP, PA-6 and the melt-prepared

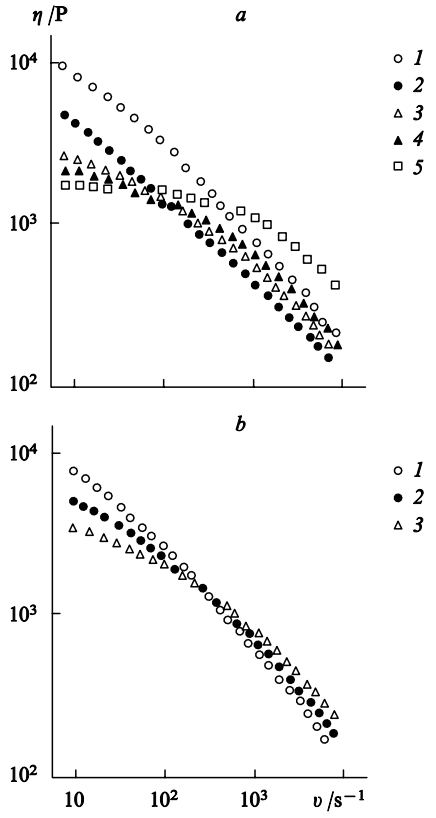
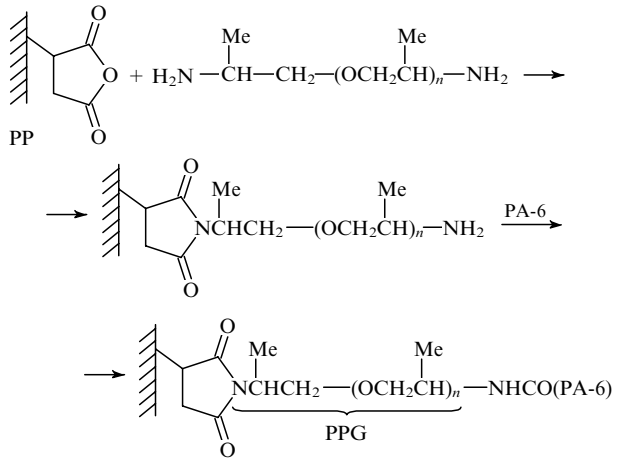


Figure 12. Shear viscosity (η) of compositions PP – PA-6 (*a*) and PP – PA-6 – (PP/MA) (*b*) plotted *vs.* shear rate.
(*a*) PP (*1*), PP – PA-6 = 75 : 25 (*2*), PP – PA-6 = 50 : 50 (*3*), PP – PA-6 = 25 : 75 (*4*) and PA-6 (*5*);
(*b*) PP – PA-6 – (PP/MA) = 75 : 25 : 5 (*1*), PP – PA-6 – (PP/MA) = 50 : 50 : 5 (*2*) and PP – PA-6 – (PP – MA) = 25 : 75 : 5 (*3*).

graft copolymer of carboxy- or anhydride-modified SKEP and PA-6 has been the subject of intensive research.

Sometimes, more complex interfacial modifiers are used. For instance, *in situ* modification of the blend of PP and MA (the degree of grafting was 0.3 mass % or 0.8 mass %) with poly(propylene glycol)-bis-(2-propyamine) with M_w = 230, 400 and 2000 was reported.[185, 186] This was done based on the fact that polymers containing ether groups [*e.g.*, poly(ethylene glycol) or poly(propylene glycol) (PEG or PPG)] are compatible with PA due to the formation of hydrogen bonds[187] and resulted in the PP – MA – co-PPG composition which exhibits good compatibility with PA-6 due to hydrophobic-hydrophilic interactions between the ether groups of PPG and amido groups of PA-6. Some characteristics of mechanical properties of the PP – PA-6 compositions prepared in different manner are listed in Table 7. It should be noted that all the compatibilised compositions have lower melt flow indices than the simple polymer blend. Increasing the degree of grafting of MA and the chain length of PPG leads to improvement of the strength properties of the compositions. Schematically, the formation of such a PPC can be represented as follows:



n = 2 – 3, 5 – 6, 33.

The limiting factor in the design of compatible systems with optimum characteristics is the concentration of reactive groups.

Compatibilisation of immiscible polymers using isocyanate groups which react not only with the amino or carboxy groups, but also with hydroxy groups has been rarely reported. For instance, blending of LDPE and PA-6 involves the modification of LDPE by grafting the product of the interaction of 2-hydroxymethyl methacrylate and isophoronediisocyanate (the reaction is carried out in xylene at 393 K in the presence of 1% DP in N_2 atmosphere) followed by mixing the modified LDPE and PA-6 in N_2 atmosphere at 518 K for 4 h.[188] In the course of blending the NCO groups interact with the terminal amino groups. Chemical bonding between the butyl acrylate or MA groups and terminal amino groups is formed in the compositions based on PA-6 and PE – MA, in the ethylene – butyl acrylate – MA (91 : 8 : 1) terpolymer and in the ethylene/vinyl acetate (91 : 9) copolymer modified by grafting MA (1%).[41]

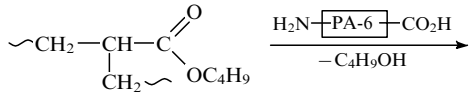
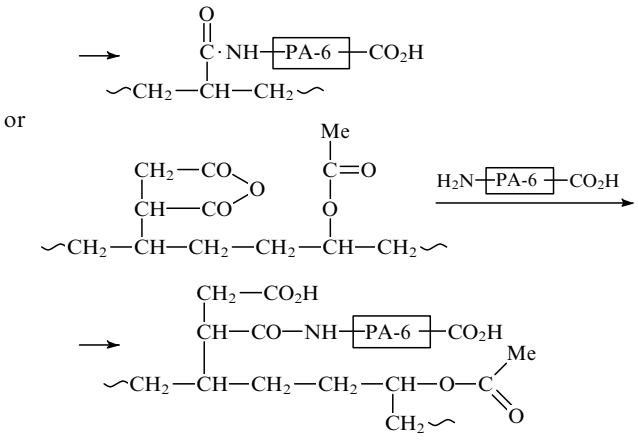


Table 7. Mechanical properties and melt flow indices of PPC modified in a different manner.[94]

PPC	Component ratio (by mass)	Unnotched impact toughness /MPa	Strength properties /MPa		Melt flow index [a]
			tensile strength	fracture toughness	
PA-6 – PP	30 : 70	11.9	25.0	2.2	19.6
PA-6 – PP – PP-g-MA (0.3%)	30 : 70 : 5	13.8	30.2	2.5	9.3
PA-6 – PP – PP-g-MA – co-PPG (400) [b]	30 : 70 : 5	15.3	31.3	3.3	10.0
PA-6 – PP – PP-g-MA – co-PPG (2000) [b]	30 : 70 : 5	19.4	32.3	3.8	6.7
PA-6 – PP – PP-g-MA (0.8%)	30 : 70 : 5	25.6	34.1	7.7	6.7
PA-6 – PP – PP-g-MA – co-PPG (400) [b]	30 : 70 : 5	21.4	34.4	8.0	9.6
PA-6 – PP – PP-g-MA – co-PPG (2000) [b]	30 : 70 : 5	38.6	35.6	11.5	6.4

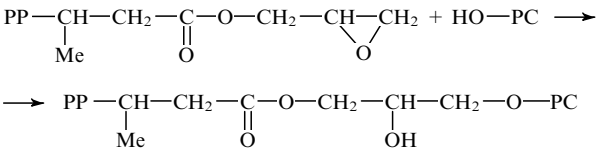
[a] Dimensionality: grammes of polymer flown over a period of 10 min at 513 K and a standard load of 21.2 N. [b] Figures in parentheses denote the molecular mass of PPG.



3. Third component in the compatibilisation reactions of polyolefins with other polymers

Compatibility of PVC and chlorinated PE with ethylene/vinyl acetate copolymers (EVAC) is often used to improve the mechanical properties of PPC.[78] Such a modification can also be performed in the polymerisation stage. For instance, blends of styrene and acrylonitrile or styrene and MMA are selectively grafted onto chlorinated PE using $TiCl_3$.[79] The addition of PE–g-PS (merely 2.5 mass %) to the PE–PS films substantially improves their strain–stress properties.[80]

The LDPE–EVAC–PETP system has considerable advantage over the LDPE–PETP composition, namely, the presence of polar functional groups in the copolymer provides the possibility of controlling the contact reactions, *i.e.*, the chemical interaction at the interface.[189] It is solely the polar interaction of the PP–MA additive (4 mass % MA) and the carbonyl groups of the blend of PP and the liquid-crystalline polymer that is responsible for improvement of the mechanical properties of this system.[190] A number of reaction compatible blends of PO [with PE–g-poly(glycidyl methacrylate) or PE–glycidyl acrylate (GA) as compatibiliser] and polycarbonate (PC), PETP and other polymers was reported.[142, 191, 192] The composition of PP and PC can be compatibilised using the PP–GA graft copolymer (2.5%–20%), which favours weakening of the interfacial interaction, improves the mechanical properties of the composition, increases the crystallisation temperature of PP and changes the blend morphology. In the molten state (in both the internal blending chamber and twin screw extruder) the epoxy groups of the third component react with the terminal groups of PC by the mechanism shown below



Interestingly, the coupling reaction between the polymeric constituents makes extraction of the entire PC phase from the ternary blend impossible, as in the case of compositions of PE and PMMA, PE and PVC, LLDPE and PA-6, *etc.*

This method allows compatibilisation of LLDPE modified by grafting MA[193] and PVAlc (the component ratio is 70:30). Another example is provided by the analogously modified composition of PP and liquid-crystalline polymer, which exhibits improved strength, deformation characteristics and the modulus of elasticity.[194]

Numerous methods for the introduction of reactive polymeric reagents capable of *in situ* compatibilising of PO and PS have been reported.[149, 195] One of them involves generation of reactive radicals on the surface of PO or PS to form the grafted layer[196, 197] (detailed consideration of this approach is presented below).

The morphology and properties of PPC based on PP and ethylene/dimethylaminoethyl methacrylate copolymers containing up to 27 mass % dimethylaminoethyl methacrylate units by mass have been studied in detail.[198] The components of this PPC are incompatible and form two-phase structures. As the content of the copolymer increases, the compositions become brittle and the interfacial adhesion between the constituent phases weakens substantially.

The third component, *e.g.*, PS–b-poly(ethylene-co-butene)–b-PS (PSBECB) is often used as plasticiser, especially for improvement of the impact toughness of brittle polymers.[199] This compatibiliser represents a microheterogeneous thermoplastic elastomer in which the PS end blocks (as a rule, le sethan 35 mass %) are linked into rigid domains that form a lattice in the flexible matrix of the ethylene/butene copolymer (EBC). It is used if one component of a PPC is compatible with the EBC blocks while the other component is compatible with the PS blocks. This additive allows the preparation of polymer blends containing not only PP, HDPE, LHDPE, but also the ABS plastics and other components.[200, 201]

In studies of ternary systems containing, *e.g.*, PA, a modified additive, PSBECB–MA, is used.[202] It is thought that the EBC blocks are compatible with PP and the interfacial adhesion between PA and PSBECB is provided by the formation of imides in the reaction of the terminal amino groups with anhydride. In this case, the formation of domains with rigid polyamide core and flexible elastomer 'skin', which favours improvement of the strength and viscosity without changing the polymer rigidity, cannot also be ruled out.[203] Finally, the PSBECB constituent of ternary blends containing impact-resistant PS reduces the degree of crystallinity of PP.[204] The modulus of elasticity and yield stress of PP–PSBECB blends decrease as the content of the block copolymer increases.[205] Good compatibility of PSBECB and PP can be due to the random nature of the copolymer in the EBC block. The effect of repulsion[206] between different polymer chain segments in EBC (though the repulsion between the ethylene and butene segments must be very weak) can improve the compatibility of the PE–PP pair. It was shown that PSBECB is a good compatibiliser for polymer blends based not only on isotactic PP, but also syndiotactic PP.[207] In both cases, the additive, PSBECB, favours a decrease in the modulus of elasticity, yield plateau and an increase in the yield stress. The use of the compatibiliser consising of PSBECB and MA allows reduction of the tear resistance for the block copolymer and isotactic PP.

Summing up, we considered the most widely used strategies of using polymeric compatibilisers for improvement of compatibility of polymer blend components. It shoud be mentioned that polymeric supports for metal complex catalysts, obtained by the grafting of corresponding, *in situ* polymerisable monomers onto PO (see the grafting scheme presented in Section III.1) contain the interfacial modifier which improves compatibility of the components of PPC.

VII. Polyolefin-based polymer blends prepared by reactive blending

Many polymeric compositions considered above are prepared by reactive blending in extruder reactors. Since this process is accompanied by numerous chemical reactions between the components or specially introduced compatibilisers, it would be reasonable to call the blends obtained 'reactor blends' or 'extrusion blends'. However, in this review we will use the term 'reactor blends' in a somewhat narrower sense.

As a rule, functionalisation of polymers by graft polymerisation represents an individual stage of the process and is followed by their blending. Currently, extruder reactors are widely used as continuous reactors combining the stages of dispersion of blend components and chemical reactions between

them.[180, 208–210] In particular, chemical modification of thermoplastics in a twin screw extruder is thought to be a promising procedure for production of novel materials.

Extrusion combines the *in situ* functionalisation of blend components and the formation of block or graft copolymers at the interface. Inter-chain copolymers prepared by extrusion are often used *in statu nascendi* for compatibilisation of thermodynamically incompatible blend components; this particularly concerns the PE – PA-6 blends modified using the third component.[211] In these cases, at low concentrations of the interfacial modifier and initiator the additives favouring improvement of the relative elongation at break and the impact toughness perform three functions. First, they act as reactive interfacial modifiers that improve compatibility of the components in the molten state. Second, they are grafted onto PO by the radical mechanism. Third, their functional groups react with the terminal groups of the components (*e.g.*, PA), thus forming covalent or hydrogen bonds. Most often, reactive blending is performed in the presence of peroxide (0.5% to 2.0%) with MA, bifunctional or multifunctional monomers as interfacial modifiers. The additives having long hydrocarbon chains (*e.g.*, alkylmaleic monoamide or alkylmaleic monoether) are more efficient compatibilisers than the short-chain additives. Non-monomeric additives are used more rarely. For instance, the addition of stearic acid (5%) to the blend of LDPE and PA-6 (75 : 25) allows control of the phase morphology.[212]

The effect of *in situ* reactive blending in an extruder reactor was also observed in studies of blends of LLDPE modified by grafting of maleic acid or MA with PA-6 or PA-11.[213–215]

In situ mechanochemical preparation of self-compatible polymer blends by solid-phase extrusion grinding of immiscible polyolefin constituents represents a variant of the approach in question.[16, 216, 217] The process is accompanied by scission of polymer chains and, hence, generation of free radicals capable of entering the reactions with another polymer chain or undergoing recombination with other macroradicals (this was experimentally proved taking the PE – PP system as an example), thus forming a block copolymer or a graft copolymer. The latter acts as an *in situ* generated compatibiliser. This procedure is particularly convenient when performing recycling since the process proceeds at a low temperature, so both the mechanical and oxidative degradation are reduced to a minimum.

Nearly three decades ago a new product, *viz.*, a thermoplastic blend based on SKEP finely dispersed in the PP matrix appeared in the world market. Such polyolefin blends are prepared by dynamic vulcanisation and called thermoplastic elastomers or thermoplastic vulcanisates.[218] They represent multicomponent polymer blends which possess the mechanical properties of elastomers at room temperature and the rheological properties of thermoplastic polymers at elevated temperatures. A salient feature of the procedure for their preparation is the combination of blending and vulcanisation (with SKEPT as the third component). This leads to the formation of PPC with specific morphology, namely, two-phase systems in which the particles of the cross-linked elastomer of size 1 to 10 μm are dispersed in a continuous thermoplastic polymer matrix and the content of the elastomeric component exceeds that of the thermoplastic polymer. Usually, such systems are cured with DP. Dynamic vulcanisation can be performed in two ways (Fig. 13). Thermoplastic elastomers offer improved processability, *e.g.*, their melts behave as thermoplastics despite the presence of the cross-linked elastomeric constituent.[219] The thermoplastic nature of the blend can be due to the curing dynamics features which prevent the formation of a three-dimensional rubber network in the dispersed phase. However, the melt viscosity of the PPC enriched with PP increases as the content of SKEPT increases up to 25%. The crystal structure of the starting PP can either change or remain unchanged depending on the procedure for preparation. The structure and properties of this type of dynamically cured polymer blends, peculiarities of their

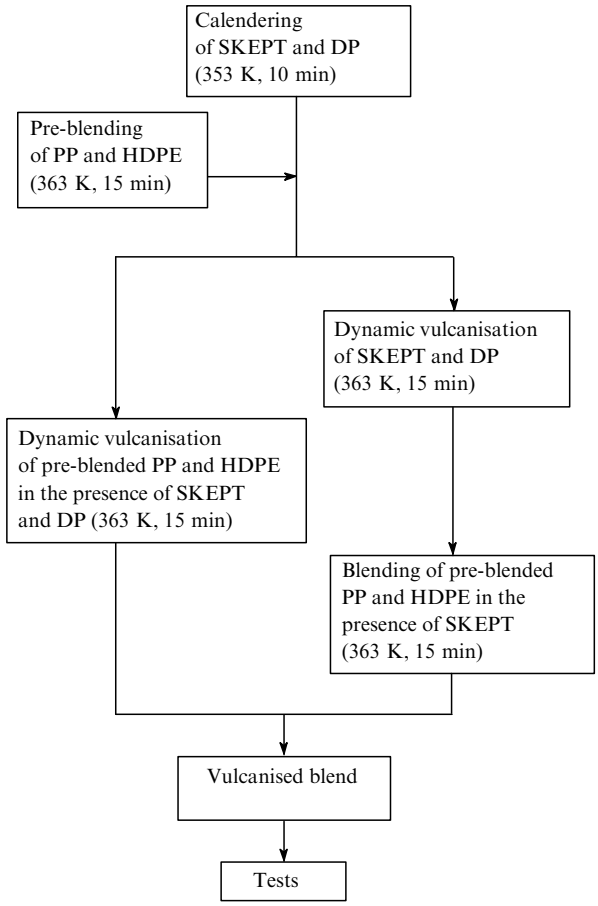


Figure 13. A scheme of dynamic vulcanisation process.

rheology and structural characteristics have been the subject of detailed studies (see, *e.g.*, Refs 220 and 221). The deformation mechanism of thermoplastic elastomers based on isotactic PP and SKEPT involves the deformation of the structure of the composition in the first stage followed by simultaneous deformation of both the cross-linked SKEPT domains and PP macromolecules; the strength and elongation at break are determined by the tension of the cross-linked elastomer.[222]

Blends of PO and SKEPT can be prepared using numerous methods that are not only of scientific, but also practical value. One of these procedures involves the formation of blends of cross-linked SKEPT (ternary SKEP) and PO using roll mills or peroxide-initiated dynamic vulcanisation in an extruder. This method was first proposed for PPC;[223] however, at present it has found wide industrial application for production of plastics and thermoplastic elastomers. It offers such advantages as short blending time, short-term processing cycle, small energy expenditure for recycling and the possibility of easy control over the properties of products by varying the component ratio.

Main conditions for the preparation of materials based on dynamically vulcanised polymer blends with optimum properties have been formulated and a number of factors determining the structure and properties of such blends were pointed out.[224] For instance, polymeric compositions with high content of rubber can be used as thermoplastic elastomers, while polymer blends with high content of plastic can be used as rigid plastics 'enriched' with rubber. Peculiarities of their morphology improve processability despite the presence of the cross-linked elastomeric component.[199] Dynamic vulcanisation also allows the preparation of such PPC as, *e.g.*, SKEPT – PP, SKEPT – PP – HDPE, LDPE – SKEPT, *etc.*[225, 226]

VIII. *In situ* preparation of diblock chemical hybrids

In this section we will consider diblock polymeric compositions in which one of the block materials does not belong to the polyolefins. From the standpoint of structure and properties this group of PPC comprises diblock copolymers, namely, graft copolymers in which one component (the polymeric support) represents a macromolecular organometallic compound. These copolymers can be prepared using the Ziegler–Natta catalysts and by consecutive polymerisation of olefins.

Lithium-containing block copolymers of ethylene and butadiene[227] and of ethylene and isoprene[228] seem to be the first representatives of this group of PPC. The molecular mass of the PE blocks varied from 13 000 to 36 000. Since ethylene polymerisation was accompanied by cross-linking of 1,2-butadiene units, this method was found to be more appropriate for the preparation of ethylene/styrene diblock copolymers[229] or blends consisting of PS blocks and blocks of ethylene/propylene copolymer (EPC).[230, 231] The synthetic procedure involves treatment of the organolithium compound with $TiCl_4$ to replace lithium by titanium, reduction of titanium and the formation of the catalyst component for polymerisation of ethylene (the molecular mass was 7000–33 000 for PE blocks, 10 000–11 000 for PS blocks and 33 000 for EPC blocks).

The PS–b-poly(ethylene-co-propylene) composition was also synthesised using the PS–Li macroanion and $TiCl_4$.[232] The molecular mass of the EPC blocks was as high as 500 000, the $M_w : M_n$ ratio was 2.24 to 4.23, the degree of crystallinity varied from 7% to 20% and the content of ethylene units in the block was 70% to 80%.

The efficiency of the catalyst, expressed as the number of polymer chains per Ti–C bond was rather high (0.88). According to the results of differential scanning calorimetry (DSC) studies, the thermogram (Fig. 14) exhibits a small peak of PS at T_g = 369 K. Both the melting temperature (410 K) and relatively low molecular mass (M_n = 63 000, $M_w : M_n$ = 1.4) point to a linear structure of the PE blocks.‡

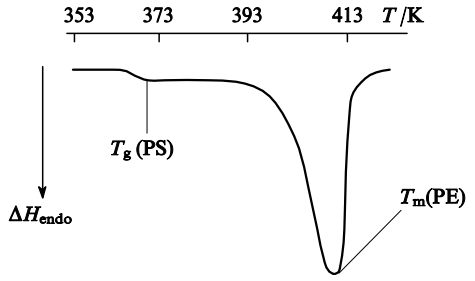


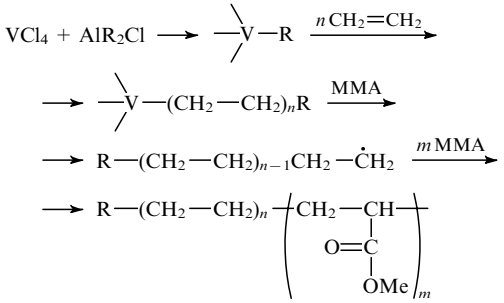
Figure 14. A DSC scan of block copolymer PS–PE.[232]

Among numerous methods for the *in situ* preparation of diblock PPC in the radical polymerisation of a particular component, two procedures are most widely used. The first method (preparation of IPN) is in essence a radical polymerisation of vinyl monomers in the presence of soluble or swollen polymers (here, a typical example is provided by the polymerisation of styrene in the presence of polybutadiene). The second procedure involves the use of polymeric peroxide or azo initiators (see, *e.g.*, Refs 235 and 236) whose concentrations are comparable with those of the components.

In situ preparation of diblock PPC can proceed either by conventional polymerisation mechanisms or as a stepwise (consecutive) process involving 'switching' of the polymer formation mechanisms (in this case, each block is formed on the active centres of different chemical nature). The latter can be exemplified by the preparation of diblock copolymers based on olefins and vinyl monomers in the presence of the $TiCl_3–AlEt_3–ZnEt_2$ system.[237] The stage of ethylene polymerisation involves the formation of polymer chains with terminal zinc–carbon bonds that provide the possibility for the next stage, $TiCl_3$-catalysed polymerisation of vinyl monomers, to proceed. By choosing the most appropriate combinations of the olefin and vinyl monomers one can prepare block, graft or block/graft copolymers representing either the end products (PPC) or compatibilisers of PO and vinyl polymers.

Methods for the preparation of modified poly-α-olefins by switching of polymerisation mechanisms (anionic-coordination mechanism changes to cationic or anionic mechanism, anionic mechanism is replaced by the radical one, *etc.*) have long been developed. A typical example is as follows:[238] first, polymerisation of propylene is performed on the $TiCl_3–Et_2AlCl$ catalytic system. After some time, the unreacted monomer is separated and 4-vinylpyridine and $SnCl_4$ or Bu^nLi are added. This procedure can also be used for preparation of polyolefin chains with the MMA, vinyl ketone, acrolein and other fragments. Isotactic PP synthesised on the ethylenebis(tetrahydroindenyl)zirconium dichloride ($C_2H_4[H_4Ind]_2ZrCl_2$)–methylalumoxane catalytic system by successive treatment with the borane–dimethyl sulfide complex and pentane-1,2-diyldimagnesium dibromide was transformed into PP with the MgBr terminal groups.[239] The modified PP was then used as anionic initiator of polymerisation of MMA at temperatures between 195 and 318 K. ^1H NMR and gel permeation chromatography studies confirmed the formation of the PP–b-PMMA system (M_n = 5300–3000) which can be used as polymeric additive to blends of PP and PMMA.

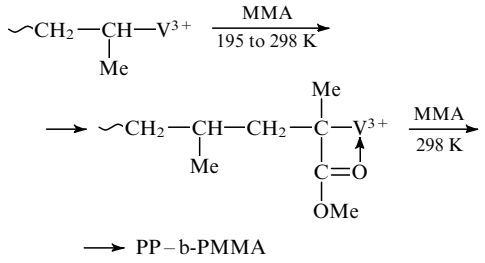
It was established experimentally that the polymerisation mechanism changes from anionic-coordination to radical during the preparation of diblock copolymers of PE and PMMA.[240] The addition of MMA to the $VCl_4–AlR_2Cl$ catalytic system in the course of anionic-coordination polymerisation of ethylene leads to its inhibition and initiation of the polymerisation of MMA (probably, as a result of radical induced cleavage of the V–C bond). The process results in the PE–b-PMMA system.



It is known that both homopolymerisation and copolymerisation of polar monomers on metal complex catalysts proceed solely by the coordination mechanism in the absence of electron-donor additives and can follow both coordination and radical pathways in the presence of such additives. It cannot be ruled out that in many instances the polar monomer itself acts as electron donor.

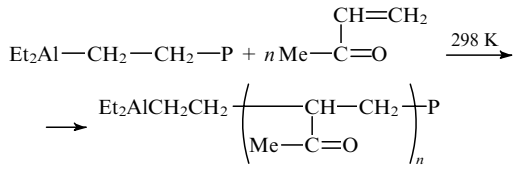
‡ For comparison, mention may be made that consecutive anionic copolymerisation of equivalent amounts of styrene and 4-vinylpyridine on LiBu at 195 K resulted in a PS–b-P4VP (PS : P4VP = 59 : 41) composition (M_n = 62 300),[80] which was used as compatibiliser for blends of polar and non-polar polymers belonging to different classes. Anionic polymerisation of styrene in the presence of polymers is accompanied by chain entanglement of newly formed linear macromolecules and the polymer network of cross-linked chains[233] and results in macroscopically heterogeneous gels. The formation of cross-linked or grafted chains was also observed in the anionic polymerisation (using LiBu, $AlEt_3$) of diisocyanates in the presence of butadiene, isoprene and butadiene-styrene rubbers.[234] In the last-named case the formation of graft polymers occurs due to the involvement of the side double bonds in positions 3 and 4.

Kinetic studies confirmed that graft copolymerisation of MMA is radical initiated. 'Living'[§] coordination polymerisation of propylene on the $V(acac)_3 - AlEt_2Cl$ system was used for the synthesis of a diblock copolymer of PP and PMMA.[241] The polymerisation proceeds at 195 K; raising the temperature up to 298 K in the presence of MMA leads to the formation of a radical centre as a result of homolytic cleavage of the V – C bond.



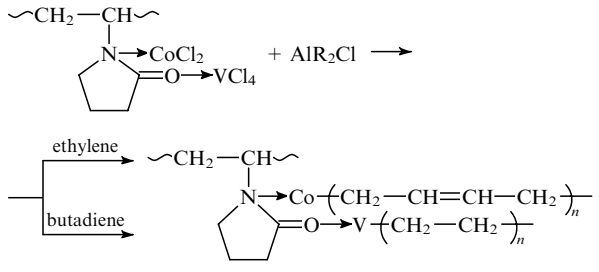
The macroradical is stabilised by the vanadium ion, which provides the possibility for 'living' polymerisation of syndiotactic PMMA blocks to proceed; chain termination in the radical polymerisation occurs on the organoaluminium compound.

Diblock copolymers of propylene and methyl vinyl ketone were synthesised using the stereospecific Ziegler – Natta catalysts.[238] In first stage, a conventional anionic-coordination polymerisation of propylene proceeds, while the second stage of the process (in contrast to the radical polymerisation of MMA) represents an anionic polymerisation of methyl vinyl ketone catalysed by terminal alkylaluminium groups.



No additional treatment is required to 'switch' between the catalytically active centres in the schemes presented above since MMA itself acts as the 'switching' agent. Transformation of the anionic process into a radical one was also observed by Souel *et al.*[242] who studied polymerisation of isoprene in the presence of butyllithium. Treatment of the product, 'living' oligomeric isopropenyllithium, with Me_3PbCl results in an adduct whose decomposition in the presence of styrene leads to the formation of PI – b-PS.

Let us consider yet another procedure for *in situ* preparation of PPC based on polymers belonging to different classes, namely, polyolefins and polydienes. We will dwell on the copolymerisation of olefin and diene monomers under the action of bifunctional immobilised catalysts. For instance, copolymerisation of ethylene and butadiene can be performed using complexes of Co^{2+} and V^{4+} immobilised on the PE – g-poly(vinylpyrrolidone) (PE – g-PVP) system.[46] Alkylation of this heterometallic complex with AlR_2Cl leads to the formation of active centres initiating the polymerisation of ethylene (V-centres) and butadiene (Co-centres).



§ Polymerisation proceeds until complete consumption of monomer; however, the addition of a fresh portion of the monomer leads to a restart of the process at the same rate.

In the text below the combination of Co- and V-centres will be shown in a simplified form as $\begin{pmatrix} Co-P' \\ V-P'' \end{pmatrix}$. These active centres coexist in the presence of ethylene and butadiene and retain their catalytic activity despite essential modification. Butadiene is known to be a strong inhibitor of ethylene polymerisation. The rate of copolymerisation of ethylene and butadiene on vanadium-containing active centres is low. Indeed, the rate of ethylene polymerisation decreases in the presence of butadiene (Fig. 15); however, inhibition of the reaction proceeding in the presence of heterometallic cobalt – vanadium catalysts is less pronounced. In turn, the rate of butadiene polymerisation on the Co-centres also somewhat decreases in the presence of ethylene[243] whose molecules undergo insertion into the polymer chain (1 or 2 ethylene molecules per macromolecule), thus reducing the molecular mass of polybutadiene. The mechanism of this process is similar to that of chain transfer to polymer and consists in decomposition of the less stable σ-alkyl cobalt derivative that is formed from the π-allylic product upon addition of ethylene.

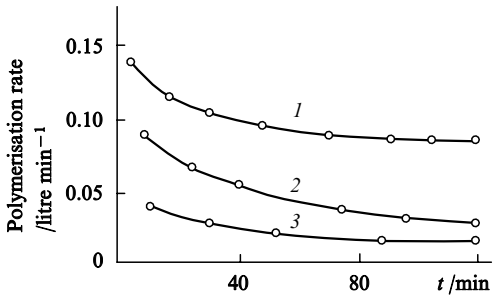
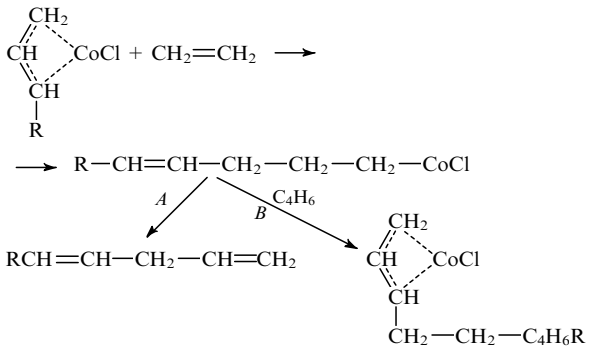
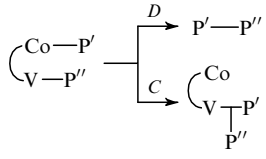


Figure 15. Kinetic curves for the synthesis of HDPE – PBd compositions under comparable conditions.
(*1*) Ethylene polymerisation on monometallic catalyst; (*2*) copolymerisation of ethylene and butadiene on bimetallic catalyst; (*3*) copolymerisation of ethylene and butadiene on monometallic catalyst.



Here, route *A* corresponds to chain transfer while route *B* corresponds to copolymerisation of ethylene and butadiene. However, spatial proximity of both active centres and co-operative chain propagation processes make migrations by, *e.g.*, the inter-chain exchange mechanism[244] *via* transfer of the polybutadiene chain to PE (route *C*) or recombination of polymer chains (*D*) quite probable.



If these reactions are accompanied by chain disproportionation, the $P'-P''$ diblock copolymer is formed; persistence of

Table 8. Formation of PE – polybutadiene block copolymers in the PPC prepared by copolymerisation of ethylene and butadiene on bifunctional cobalt – vanadium catalyst.[46]

Ethylene consumption for polymerisation /g	Content of polybutadiene units [a] in product (mass %)
0.5 [b]	2.7 (–)
0.5	38 (95)
1.0	24 (90)
2.0	14 (90)

[a] The value in parentheses is the content of 1,4-cis units. [b] For copolymerisation of ethylene and butadiene on monofunctional catalyst (VCl_4 on PE – g-PVP).

ethylene polymerisation after chain transfer results in a polyblock copolymer. Such a reaction mechanism is few and far between. Obtaining convincing proof of this mechanism presents considerable difficulties, since analysis of the structure of such 'chemical hybrids' characterised by possible formation of interpenetrating polymer chains is a rather complicated problem. However, experiments with ^{14}C-labelled butadiene allowed one to collect proof of the formation of block copolymers (Table 8). Quantitatively, the formation of the random copolymer was estimated by comparing its radioactivity with that of the ethylene/butadiene copolymer synthesised on the Co-containing monometallic catalyst. The stereosequence of polybutadiene units (mostly 1,4-*cis*-butadiene) in the block copolymers is such that mutual influence of the monomers is weak. Probably, this method for *in situ* preparation of diblock chemical hybrids will appear to be useful in the case of PPC based on polyolefins and polyallene and on other polymers.¶

Synthesis of binary polymer networks belongs to new avenues of current research. Binary networks consist of two chemically different polymer chains linked by one covalent bond, whereas IPN comprise two independent networks that cannot be separated without cleavage of covalent bonds.[246] The distinctions between these systems are illustrated in Fig. 16.

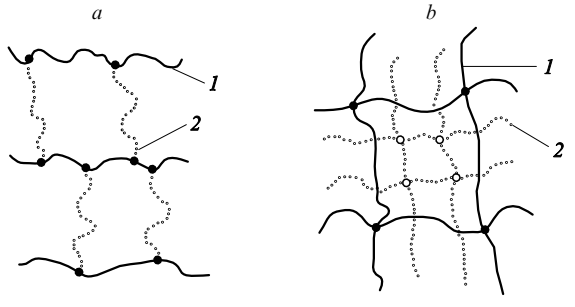


Figure 16. The structure of two-component (*a*) and interpenetrating (*b*) polymer networks;
polymer A (*1*) and polymer B (*2*).

As applied to polyolefins, binary polymer networks were prepared for, *e.g.*, the poly(isobutylene) – poly(dimethylsiloxane) system.[247] Allyl-tritelechelic PIB was synthesised by 'living' polymerisation of isobutylene at 193 K using the tricumyl chloride – $TiCl_4$ – *N*,*N*-dimethylacetamide catalytic system. Allylation at the end groups was performed using allyltrimethylsilane. Allyl-tritelechelic PIB undergoes cross-linking with SiH-ditelechelic poly(dimethylsiloxane) by hydrosilylation under the action of Pt-containing catalysts. This method was used for preparation of novel thermoplastic elastomers PS – b-PIB.[248]

Thus, *in situ* prepared PPC can be synthesised from various classes of incompatible monomers following any polymer formation mechanism. The diblock copolymers considered in this section are most often used as polymeric additives that improve compatibility of immiscible polymers rather than individually.

IX. Preparation of conducting composites using the principle 'compatibilisation *via* polymerisation'

Mixing of conducting and dielectric particles is a well known procedure used for preparation of conducting polymers.[249] The synthesis of a conducting polymer surrounded by a dielectric matrix is often used to improve the strength and electrical conductivity of polymeric materials.[250, 251] According to percolation theory,[252] an increase in the content of the conducting polymer to a particular critical value causes a sharp decrease in its electrical resistance (the so-called percolation threshold is reached).

The method for *in situ* preparation of molecular compositions containing a polyolefin as one component can also be extended to the conjugated polymers (in particular, doped PAc). Conducting PAc films are very brittle, which is detrimental to their operating characteristics, and unstable (film destruction occurs with time). Therefore, the preparation of materials that can be processed in a conventional manner requires modification of such films.

An attempt at preparing a composite material with good electrical properties by simple dispersion of powdered PAc obtained by catalytic polymerisation of acetylene according to Shirakava using the $Ti(OBu)_4 - AlEt_3$ system in the PE matrix failed,[253] since only large PAc aggregates of size 10 to 100 μm were formed. Blending of components on a molecular level can be achieved by performing direct polymerisation of acetylene on any surfaces moistened with the catalyst solution. In particular, such a polymerisation can be carried out on 300 μm-thick LDPE films impregnated with $Ti(OBu)_4$ and alkylated with AlR_3.[253] The reaction on the surface of the PE powder impregnated with the same catalytic system is carried out in the liquid phase (in dibutyl ether) [254] or in the gas phase.[255] Sometimes, polymerisation is performed from the gas phase in viscous media (*e.g.*, silicon oil) in the presence of PE-supported catalysts.[256, 257] Polystyrene solutions (5% – 20%) in toluene can be considered as examples of such high-viscosity (10 – 400 sP) media. Suspension polymerisation allows the preparation of materials with good electrical and mechanical properties. High density PE films containing PAc (6 mass % – 10 mass %) remain flexible and elastic and exhibit high strength. The conductivity of the compositions prepared by doping such films with iodine or lithium lies between 10 and 100 Ω^{-1} cm^{-1} and increases upon film drawing due to alignment effects.[255] Polyacetylene obtained by polymerisation of acetylene on a PE matrix at 383 K has a *trans*-structure stereosequence and undergoes cross-linking with time, thus forming a three-dimensional structure in the bulk of the PE matrix. Such composite materials are characterised by a conductivity of 1 to 5 Ω^{-1} cm^{-1}. High-molecular-mass PAc latex particles are formed on the Luttinger catalysts in the presence of surfactants, mainly copolymers of styrene or PE blends and poly(ethylene oxide) (PEO).[258]

To improve the adhesion between the conducting components and the polymeric support (*i.e.*, films based on PE, PP, SKEP, PS, *etc.*, and shaped as necessary), the latter is modified by grafting of functional groups [poly(acrylic acid) (PAAc) or poly(allyl alcohol) (PAA)] that serve as 'immobilisers' of the catalyst of acetylene polymerisation.[58] After polymerisation these supports become coated with a dark PAc film 10 – 50 μm thick, which acquires conducting properties (see Table 9) after treatment with iodine vapours or other electron acceptor dopants such as SbF_5, AsF_5, $FeCl_3$ and perchlorates.

¶ It should be noted that copolymerisation is also performed using other catalytic systems. For instance, the microblock copolymer of butadiene and styrene is formed when the system LiR – KOR is used.[245] In this case, butadiene undergoes polymerisation of the Li centres, while styrene is polymerised on the K centres. The microblock size is determined by the frequency of C – Li ⇄ C – K transitions.

Table 9. Properties of conducting films prepared by polymerisation of acetylene in the presence of catalytic system $Ti(OBu)_4 - AlEt_3$ and immobilised on dielectric supports.[58]

Support	Titanium content /mmol g^{-1}	Polymerisation time /h	PAc film thickness /mm	Specific conductivity [a]
PE	traces	3	–	1×10^{-7}
PE – g-PAA	0.04	2	0.05	6.2
PE – g-PAAc	0.06	2	0.016	4.2
PE – g-PAAc	0.10	1	0.02	14.4
PE – g-PAA	0.115	3	0.025	6.7
PTFE – g-PAA	0.4	3	0.01	2.4
PVAlc	0.20	2	0.02	3.9

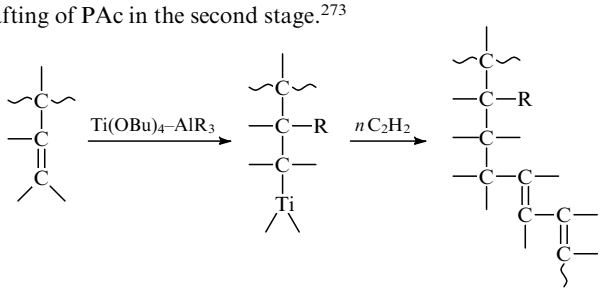
[a] Dimensionality is Ω^{-1} cm^{-1}.

In this case, we deal with the surface conductivity of the *in situ* prepared PPC, while the polymeric supports remain dielectrics. This method can also be used for the preparation of multi-layered PPC containing a conducting layer with controllable conductivity parameters. Materials based on this type of PPC are relatively easy to produce and retain their properties on long storage (more than three years). Probably, improved stability of these materials is due to the presence of a barrier preventing the oxidation of PAc.

High-conductivity compositions, namely, block copolymers of PAc and PS are also prepared by 'switching' the polymerisation mechanisms,[259, 260] that is, the polymerisation of the styrene oligomer (M_n = 1000) obtained on LiBu in the presence of $AlCl_3$ and $Ti(OBu)_4$ additives is followed by the polymerisation of acetylene or propyne. It is noteworthy that an increase in the content of acetylene units in the copolymer leads to changes in its morphology, *viz*., fibrillar structures typical of PAc disappear and the polymer acquires a *trans*-structure. The syntheses of soluble block copolymers consisting of PAc blocks and polymeric support blocks (PS or polyisoprene) were reported.[261, 262] In this case, $CuCl_2$ in anhydrous THF at 193 K is used as catalyst. Polymeric support blocks exhibit dielectric properties; however, doping of the block copolymers allows the preparation of materials whose conductivity is comparable with the metal conductivity. This type of conducting composition can be synthesised using a terpolymer of, *e.g*., diene, ethylene and propylene and blends of thermoplastic elastomers as well.[253, 255, 263]

Bolognesi *et al*.[264] reported an interesting method for preparation of a comb-like copolymer in which the *trans*-PAc chains are grafted onto a polybutadiene or polyisoprene matrix [this was done using the $Ti(OBu)_4$ catalytic system and a mixture of tetramethylenediamine and *sec*-butyllithium].[264] A large body of patent literature exists on this subject. For instance, the procedure for preparation of a readily processable composition of PE and PAc involved treatment of a thin PE film with the catalyst followed by polymerisation of acetylene.[265] The conductivity of the material obtained was 5 Ω^{-1} cm^{-1}. To obtain doped, high-conductivity compositions based on PO and oriented PAc, plastic fibres or ribbons were washed with a solution of the Ziegler – Natta catalyst and placed stretched in a vessel filled with acetylene gas.[266, 267] Polymer blends based on conducting material were also prepared in another manner using porous films or membranes.[268, 269] The newly formed macromolecules that fill porous matrices with uniaxially oriented pores were found to have a preferential orientation along the pore axis. The approach based on the use of porous HDPE films obtained by uniaxial drawing of the polymer in liquid media *via* delocalised crazing was used for the preparation of PE – PAc compositions.[270] The content of PAc was at most 8 mass % and the results obtained after selective extraction of PE indicated the formation of a rigid three-dimensional PAc network reinforcing the PE matrix. However, the formation of PAc chains grafted onto PE in such systems also cannot be ruled out. This will cause the orientation of both phases, *viz*., the finely dispersed porous PE matrix and rigid-chain PAc macromolecules. Doping the polymer blend with iodine led to an increase in the bulk conductivity by 14 to 16 orders of magnitude, which points to a low percolation threshold for the conductivity of the structures with marked anisotropy of the mechanical and electrophysical properties. The conductivity of compositions containing up to 3% doped PAc was described in the framework of the simple percolation model.

The structure and various (including electrical) properties of films based on PAc and polybutadiene have been studied in detail.[271, 272] It is appropriate to prepare these compositions from diene – ethylene – propylene terpolymers and PAc.[255] Polymerisation of acetylene in the elastomeric matrix results in a product which exhibits not only high conductivity and resistance to aggressive media, but also reasonable operating characteristics. Cross-linking of these compositions leads to immobilisation of PAc. Graft polymers consisting of polydiene and PAc are relatively easy to prepare. In this case, the metal – carbon bonds formed with participation of vinyl groups of the 1,2-polybutadiene units in the first stage of the process are then involved in grafting of PAc in the second stage.[273]



Soluble graft block copolymers of PAc (up to 5%) and atactic PS, soluble block copolymers of PAc and polyisoprene (including doped block copolymers)[274] and the PAc – b-poly(norbornene) – b-PAc triblock copolymers with different block lengths were synthesised. Graft copolymers are characterised by microphase separation.

Polymer – polymer compositions based on polyolefins and conjugated polymers can be prepared using not only PAc, but also such components as polyphenylacetylene, poly(propargyl alcohol) and poly(propargylamine), which are obtained by polymerisation of the corresponding monomers on the Mo(V) complexes immobilised on PE, PP or PS.[275] Polymerisations of crystalline diacetylenes in a microporous polymeric matrix resulted in compositions of isotactic PP and substituted polydiacetylenes.[276] Drawing the PP film in 20% solutions of substituted 2,4-hexadiynes followed by removal of the solvent allowed the preparation of a film containing up to 20% diacetylene units. Studies on the γ-radiation-induced, solid-phase polymerisation revealed an increase in the degree of conversion of the monomer in the PP matrix as compared to the reaction in solution. This was explained by a higher initiation rate rather than the mechanical effect of the matrix. A method for 'internal' doping of the polyconjugated system with iodine that is partially separated during the polymerisation of the iodine-containing monomer was reported.[277]

Preparation of blends of polyconjugated polymers and UMMPE by gelation[278 – 280] is also of interest. For instance, a UMMPE – poly[2-butyl-5-(2-ethylhexyl)-1,4-phenylenevinylene] (70 : 30) composition was prepared from solution (more correctly, a gel) in *p*-xylene. No information on the conducting properties of such PPC was reported.

Products of the *in situ* polymerisation of pyrrole are also used as components of conducting PPC. The procedure for preparation of such PPC as PE – PAc involves immobilisation of the catalyst on the surface of functionalised PE films. This method was also used for the synthesis of PE – polypyrrole (PPr) compositions.[281] To this end, a film consisting of PE and sulfonated PS was immersed in a solution containing $FeCl_2$ and $FeCl_3$ and then polymerisation of pyrrole was performed at 275 K for 30 min in

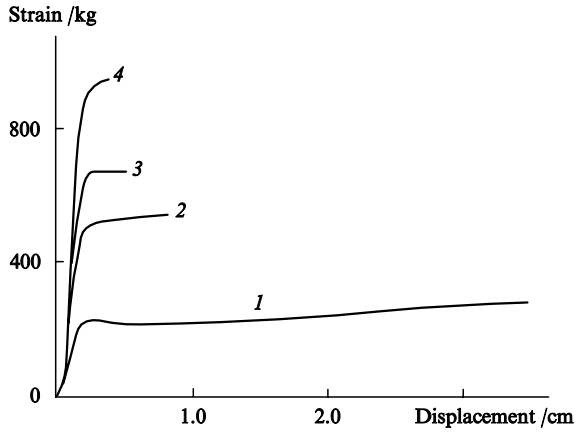


Figure 17. 'Strain – displacement' curves for double film PE – sulfonated PS (without PPr) (*1*) and ternary films PE – sulfonated PS – PPr (*2–4*) with different conductivities prepared by electrochemical polymerisation.[281] Conductivities (Ω^{-1} cm^{-1}): (*2*) 3.8; (*3*) 7.5; (*4*) 14.9.

the dark followed by post-polymerisation doping. The surface conductivity of the polymerisation product was $\sim 250\ \Omega^{-1}$ cm^{-1}. Films prepared from this material exhibit good mechanical properties; however, the films characterised by higher conductivity are less elastic and more rigid (Fig. 17).

Conventional methods for the synthesis of conducting compositions have some inherent drawbacks, such as high rigidity and dark colour of products, a complicated procedure for preparation of samples with specified conductivity and long duration of the formation of films thicker than 10 μm. To eliminate these drawbacks, it was proposed to prepare this kind of PPC in the form of PPr-based polymer alloys by chemical[282] or electrochemical[283] polymerisation of pyrrole on polymer supports. The method involves coating an electrode with a polymeric support film ~ 20 μm thick. The PPr chains begin to grow from the film side adjacent to the electrode surface. Therefore, initially only the 'electrode' side of the film is conducting. The opposite, 'surface' side of the film acquires conducting properties only after being penetrated by the PPr chains. Polymer alloys prepared in this manner exhibit some attractive properties including high conductivity (more than 300 Ω^{-1} cm^{-1}), stability in air, good film-forming ability and high homogeneity. Werner[284] reported the synthesis of a number of PPr-based, conducting, thermoplastic and elastic *in situ* prepared PPC including those containing PB. Methods based on the use of monomers (*e.g.*, pyrrole or aniline) as solvents for the polymerisation have also been developed.[285–287]

Conducting compositions containing tailor-made PO can be prepared by the blending of components. In particular, microporous PE films synthesised by rapid melt extrusion followed by annealing exhibit a well-developed surface and can be used as supports for composite materials prepared by coating these films with a thin layer (4–7 μm) of conducting polyaniline (PAn) from aqueous dispersion.[288] This kind of material is characterised by strong adhesion between their components. Despite its very small thickness, the PAn layer has the same conductivity (0.2 Ω^{-1} cm^{-1}) as that of a much thicker film cast from the PAn dispersion.

PAn-Based conducting compositions are also prepared by polymerisation of monomers in porous polymeric matrices obtained by cold drawing of polymer films (including HDPE films) in reactive liquid media by a delocalised crazing mechanism.[289,290] Electrochemical polymerisation in thin pores of the PE matrix in the acid-aqueous electrolytes results in the formation of oxidised PAn (emeraldine salt). The specific surface conductivity of the undoped product is $9 \times 10^{-3}\ \Omega^{-1}$ cm^{-1} (the conductivity of undoped PAn is only $10^{-10}\ \Omega^{-1}$ cm^{-1}, see Ref. 291). Doped PAn exhibits a conductivity of 5 Ω^{-1} cm^{-1} (see Ref. 292). In finely dispersed porous matrices, PAn forms spherulites 60–100 nm in diameter (*cf.* 300 nm in diameter fibrillae formed outside the matrices). The films are characterised by uniform dispersion of the PAn phase in the bulk and by complete phase separation of the components. It is noteworthy that the content of non-extractable (insoluble) PE retained as the constituent of the polymer blend upon selective extraction of PE in decalin at 418 K and in xylene at 408 K lies between 20% and 30% PE. A possible explanation is as follows. Since the growing polymer particles are much larger than the effective pore diameter of the matrix (4–15 nm), the fibrillae of the matrix phase penetrate the particles of the PAn phase, thus preventing them from being accessed by the solvent molecules.

In situ synthesis of conducting compositions can also be performed in the reverse order. In this case, the catalyst or initiator of polymerisation of the corresponding monomer is immobilised on the conducting component. For instance, doping of PAc with dihydronaphthalide sodium results in the formation of a charge-transfer complex[293] $[Na_{0.057}(CH)]_x$ which is used as initiator for grafting of blocks of PS, polyisoprene, PMMA, PEO, *etc.*, onto the PA chains.[294]

The possibility of immobilisation of metal complex catalysts on graphite followed by the *in situ* preparation of conducting PPC[295] makes this approach be particularly attractive. Here, the height of the potential barrier to the charge carriers injected into the dielectric polymeric component of the PPC reduces.[296] The PE – soot composition also exhibits conducting properties;[297] a sharp decrease in the electrical resistance begins as the content of soot reaches 6 vol.%. The conductivity of this PPC is independent of the soot particle size (on the average, 62 nm in diameter) and the melt flow index of PE. As the content of soot changes from 16 vol.% to 28 vol.%, the maximum conductivity increases from 1 to 3 Ω^{-1} cm^{-1} at a current density of up to 15 A cm^{-2}. The current-*vs.*-voltage curve passes through an extremum. The decrease in the electric current is due to stress relaxation and to scission of soot chains caused by the Coulomb forces at high voltages. The HDPE-based composition exhibits higher conductivity compared to the LDPE-based PPC; this is probably due to the lower volume fraction of the amorphous phase characterised by high concentration of soot in the former case.

Thus, different synthetic procedures developed in the framework of the *in situ* approach to preparation of PPC are convenient and promising for the synthesis of conducting composite materials.

X. Formation mechanism and the structure of *in situ* prepared polymer – polymer compositions

In the preceding sections of this review we have considered many aspects of the mechanism of formation of the *in situ* prepared PPC. In this section, we will sum up information on the morphology, formation mechanism of polyolefin molecular compositions and the role played by the interfacial layers.

The strength of adhesive interaction between the components of PPC is an important characteristic determining their mechanical properties and operating characteristics. The properties of various two-phase polyolefin – polymer compositions can essentially (and even abnormally) change irrespective of the nature of the polymeric constituents. Most often, the parameters of PPC are determined by peculiarities of the boundary (interfacial) layers characterised by effective interactions between the components of the PPC. In principle, the morphology of the interfacial layer can follow two patterns.[7] First, the interfacial layer can comprise two regions adjacent to the one and only interface and having specific structures different from the structure of the bulk phases of each component (A and B). Second, a situation with two interfaces is possible. General and more detailed schemes illustrating the structure of the interfacial layers are shown in Fig. 18. If PPC are prepared by blending polymeric components that can be even virtually immiscible, the first pattern can be followed; however, in

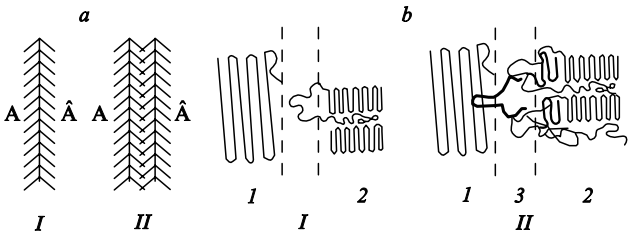


Figure 18. The structure of intermediate layers in the formation of polymer blends (*I*) and synthetic (*II*) compositions (*a*) and the structure of the intermediate layers in polymer blends (*I*) and in synthetic (*II*) compositions iso-PP (*1*), triblock copolymer (*2*) and PE (*3*) (*b*).

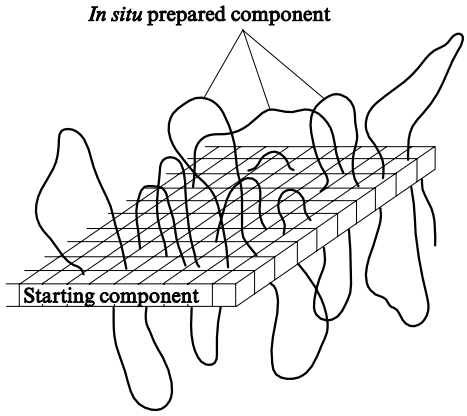


Figure 19. A scheme illustrating interpenetration of polymer chains in compositions prepared by *in situ* polymerisation.

this case the interfacial layers are formed due to the physical interparticle interactions and self-diffusion of macromolecular segments. The latter process is a kind of segmental dissolution of polymers accompanied by migration of the low-molecular-mass homologues-components towards the interface (this provides an explanation for the important role of the molecular mass distribution of the starting polymers in the formation of PPC).

As mentioned above, considerable attention is given to the methods for weakening the interface stress and improving adhesion between the immiscible phases.[298] In the course of reactive blending (polymerisation of one monomer in the presence of the other component) such boundary layers are formed as a result of the appearance of interpenetrating polymer chains and, possibly, pseudointerpenetrating polymer networks, which favours the improvement of compatibility of the components.

Often, the interface is represented as a conventional, two-dimensional geometrical surface. However, in real binary compositions the interface can be rather thick and exhibit specific properties that differ from the properties of the bulk phases. These are not only lowered segmental mobility of macromolecules, reduced number of possible macromolecular conformations and loosened macromolecular packing, but also violation of identity of the chain building blocks and changes in the translational dislocation vectors and character of relaxation processes, *etc*. The properties of PPC are strongly dependent on how the interfacial layer is distributed within the compositions, *i.e*., is it localised only at the interface or does it extend to the bulk phases of the polymeric constituents? The interfacial layer has a complex structure. It includes the adsorbed near-surface layer with specific properties and some transition layers in which the degree of ordering of the macromolecular packing varies with the distance from the surface of the polymeric matrix. If the content of one component is low (5% to 10%), the so-called threshold space of the interfacial layer takes on particular significance, since in this case the phase continuity can be violated, thus providing the possibility of direct contact between the macromolecules of the polymeric constituents. Under certain conditions, one bulk phase can 'penetrate' through the second bulk phase (Fig. 19), which leads to the formation of interfacial structures with improved adhesion.

As a rule, the mechanical characteristics of the interfacial layer are related to its adhesive properties, that is, an increase in the modulus of elasticity corresponds to an increase in the adhesive energy and to thinning down of the interfacial layer. When estimating the contribution of the boundary layers to the properties of a multiphase system, one should know the distance from the interface at which deviation of local properties from the bulk properties can be considered insignificant; an important point is, however, that the thickness of the interfacial layer determined by different methods depends on the sensitivity of a particular method.[8] Nevertheless, the thermodynamic approach allows one to evaluate the minimum thickness of the interfacial layer (δ_{min}), which meets the criterion for its stability.[299]

The density of the interfacial layer changes exponentially with the distance from the interface and can be controlled in a targeted manner. The volume of the interfacial layer, V_1, can be found using the following equation [300]

$$V_1 = \frac{\rho}{\rho_1} V(1 - e^{\alpha N}),$$

where ρ and V are the density and volume of the polymer matrix, respectively; ρ_1 is the effective density of the interfacial layer; α is the coefficient of proportionality; and N is the number of particles of a particular component.

The density of the interfacial layers in the composition of HDPE and PVC was qualitatively assessed using positron annihilation technique.[65] It was found that the *in situ* prepared PPC are characterised by dispersion of the PVC particles in disordered PE domains. A decrease in the density of macromolecular packing upon the formation of the interface was also pointed out by Chalykh *et al*.[301] The PE component of this PPC was found to form one crystalline phase and two amorphous phases (the surface phase and the intermediate phase).[302] NMR studies revealed the existence of domains characterised by different free induction decay parameters and relaxation times in the bulk of the PPC. The interaction between these domains is weaker than within each of them. The formation of the transition layer leads to loosening of the near-surface layer of the PE phase. The mean correlation time of intermolecular motions in this layer is 10^{-8} s.

Similarly to the filled systems, the interfacial layer in polymer – polymer compositions serves three main interrelated functions.[1] These are (i) stress redistribution from the phase contact region to the bulk phases (reduction of stress concentration in the more flexible component), or operation as a specific structural stress concentrator during the degradation of PPC; (ii) changes in the elastic and viscoelastic properties of PPC; and (iii) suppression of both cracking and formation of other defects (the interfaces prevent the samples from microcracking).

The type of the phase structure and the sizes of corresponding structural domains depend on the nature of the polymers under study (the surface tension at the interface and the viscosities of the components and their ratios, the volume fraction of the components and blending conditions). It is these characteristics that determine the properties of PPC. In particular, the formation of amorphous-crystalline structure leads to improvement of the impact toughness (see, *e.g*., Ref. 303); PPC with fibrillar structure exhibit higher strength and improved strain – stress properties (see, *e.g*., Refs 304 and 305); polymer compositions with lamellar structure are characterised by improved barrier properties [306] while continuous structure favours achievement of an optimum combination of the properties of both components.[307]

If the formation of dispersed structures has been studied in much detail, the conditions for the appearance of domains with

continuous morphology have been little studied except, probably, for the PE – PS system.[308] Recently, Tseng *et al.*[186] reported the results of scanning electron microscopy studies of the changes in the morphology of compatible and compatibilised incompatible PP – PA-6 (30 : 70) systems. The incompatible PPC were characterised by high surface tension at the interface, which led to the formation of a coarse-grained product. Even the addition of a rather large amount of the PP/MA phase (5 parts by mass) was insufficient for inhibition of the formation of this structure. On the other hand, the addition of the PP/MA – co-PPG copolymer (5 parts by mass) led to substantial reduction of the domain size of PA-6. The reduction magnitude was found to be a function of the diamine-modified PPG chain length. Finally, the reactions involving compatibilisers containing grafted MA (0.8 mass %) followed by the formation of the PP/MA – co-PPG copolymer result in the compatible compositions for which the longer the PPG chains, the higher the dispersity. Similar results were also obtained in studies of a compatible system PP – (PP/MA) – PA-12 (65 : 10 : 25), in which all the MA groups enter into reactions with the terminal NH_2 groups of PA-12 and the particle size lies between 0.1 and 0.5 μm or less.[309]

It should be noted that the particle size distribution of the dispersed phase in compatible systems is much narrower than in incompatible systems. In the latter, coarse-grained particles of PA-12 grow in the course of annealing at 453 K. This is accompanied by grafting a larger number of the PA-12 molecules onto the PP/MA phase and by an increase in the thickness of the interfacial layer. An increase in the content of the PP/MA phase favours an increase in the dispersity of PA-12. Despite the presence of excess MA groups, the (PP/MA) – g-PA-12 system is formed in these compositions. However, it should be kept in mind that thermomechanical treatment during processing of polymers has a strong effect on the mechanochemical processes in and, hence, on the morphology of these heterogeneous systems.

In addition to the interaction between the functional groups of different components (including grafted ones) of an *in situ* prepared PPC, grafting of the newly formed polymeric constituent (a polyolefin, polydiene or polyacetylene) of the PPC onto the surface of the polar component also plays an important role in the formation of the interfacial layer in this type of PPC. Grafting can occur, first, in the initiation stage of polymerisation (the multiple bonds of the surface reactive groups can be cleaved and these groups can undergo insertion into macromolecules in the form of end groups); second, in the growth stage, when the multiple bonds of a particular component are involved in the copolymerisation; and, third, in the stage of chain transfer to the surface of the polar component (the reaction between the propagating chain end or a functional group of the polymer and the specific surface group, resulting in the formation of a covalent bond). Specific reaction mechanisms and the relative contributions of particular reaction stages depend on the nature of the constituents of PPC.

Improvement of the properties of the PO – PO compositions prepared using the principle 'compatibilisation *via* polymerisation' as compared to polymer blends of the same chemical composition is rationalised by higher ordering of their morphology.[128] The synthesis of the PO – PO compositions involves coating of the catalyst with the polymeric constituents in rigorous order, that is, PP, SKEP and, finally, PE. In this case the adhesive, SKEP, is localised at the interface (*cf.* polymer blends with the same structural elements, in which SKEP is much more dispersed within the bulk of the dispersed phase). Therefore, the brittleness temperature of the compatibilised composition is reduced by 16 °.

As a rule, one component of a polymer blend presents no obstacles to crystallisation of the other blend component.[99] Nevertheless, there are some exceptions. For instance, the crystallisation temperature of the PA-6 phase in the PP – PA-6 compositions is 2 – 3 ° lower than that of the starting polymer, which points to a lower nucleation rate.[186] In other words, the product of *in situ* polymerisaton, PP – (PP/MA) – PA-6, prevents crystallisation of PA-6.[310, 311] On the other hand, the crystallisation temperature of the PP phase of the composition is appreciably higher (by 6 – 9 °) than the crystallisation temperature of the individual polymer. This means that PA-6 acts as a promoter for crystallisation of PP in the composition under consideration. No substantial changes in the melting temperatures of these semicrystalline polymers in both compatible (437.5 K) and incompatible (494.5 K) PPC occur; however, the degree of crystallinity of the PA-6 phase in the compositions decreases. Probably, the presence of copolymers within the interfacial layer makes the crystallisation of PA-6 more difficult to proceed. On the other hand, the degree of crystallinity of the PP phase in compatible PP – PA-6 compositions remains unchanged.

Finally, yet another important structural feature of the interfacial layer should be pointed out. The macromolecules located within this layer adopt an extended conformation due to the orientational effect of the matrix. For instance, the macromolecular segments adjacent to the PVC phase in the molecular compositions of PE and PVC are oriented.[312] This can be rationalised by the effect of the PE chain growth conditions, namely, by high density of the growing PE chains in the thin near-surface layer. Polymer chains growing in this case in a co-operative manner adopt an extended conformation. It is assumed [7, 8] that crystallisation of one component near the phase boundary of the other component is accompanied by the formation of transcrystallites that are stronger and more rigid than spherulites. Interpenetration of the polymer blocks into the interfacial layer provides the possibility for the adhesive interaction (anchoring) between the constituent phases to occur. Such a submicrostructure contributes largely to improvement of the impact toughness of PPC.

Orientation of macromolecules at the interface between glassy polymers leads to transition of the polymers into a state typical of liquid-crystalline polymers.[313] Rigorous control of crystallisation conditions also allows the preparation of highly crystalline PE films (in this case, the polar component can act as nucleating agent for crystallisation) and polymer alloys. In particular, PE can undergo epitaxial crystallisation on oriented poly(oxymethylene) in spite of different crystal structures, macromolecular conformations and polarity of both polymers.[314] However, this is impossible if PP, cellulose, PVAlc or PA-6 are used instead of poly(oxymethylene). The formation rate of the *in situ* prepared PPC also plays a significant role. If macromolecules leave the reaction medium at a rate comparable with the chain propagation rate, no stacking occurs; rather, structures with extended conformations of the macromolecules are formed.[315] The so-called occlusion effect responsible for occlusion of the growing polymer chains within the 'dead' polymer domains should also be taken into account. Thus, by using the 'compatibilisation *via* polymerisation' strategy one can prepare structures with the nonequilibrium orientation of macromolecules.

From the aforesaid it follows that the interactions between the components of PPC at the interface, especially between crystalline polymers, should be considered in close relation to the changes in the molecular and supramolecular structure and taking into account the unique topology of such polymers. Not only physical immobilisation and chain entanglement, but also chemical interactions between different-type polymeric constituents can occur in the molecular compositions. The net effect of these factors leads to the formation of a common co-operative system, which includes several types of bonds and is characterised by additional structuralisation of PPC, which favours the achievement of a high degree of homogenisation. This complex system of interactions at the interface in the *in situ* prepared PPC takes over the breaking load in the case of destruction of the composite material.

Nevertheless, an ideal type of structural organisation of the PPC in question is provided by the IPN that represent molecular compositions formed in the *in situ* polymerisation of monomer 2 in preliminarily swollen polymer 1. The major difference between the classical IPN and the *in situ* prepared compositions based on crystalline polymers lies in the fact that the formation of IPN

involves substantial swelling of the polymer in the monomer. One of the most important features of the IPN consists in extremely strong (in essence, on the molecular level) mutual dispersion of the components.

The size, D, of the polymer 1 phase domains formed in the semi-IPN in the polymerisation of monomer 2 with the molecular mass M_2 can be estimated using the semiempirical Donatelli equation.[316] This equation takes into account the changes in the free energy of the system and is written as follows:

$$D = \frac{2\gamma\omega_2}{RTv_1[(1-\omega_2)^{-2/3} + \omega_2/v_1M_2 - 1/2]},$$

where γ is the surface tension at the interface, ω_2 is the mass fraction of the monomer and v_1 is the density of cross-links in polymer 1.

Under some assumptions we can estimate the domain size of the PS phase in the blends with PP, prepared by the *in situ* polymerisation of styrene in PP deformed *via* delocalised crazing.[75] This size is nearly 100 nm, which is in agreement with the results of electron microscopy studies. The aggregative stability of these systems is provided by the strong system of entanglements between two macromolecular networks (the so-called catenane links), *i.e.*, by a specific type of anchoring. Under optimum conditions this method allows one to achieve complete interpenetration of the components on the molecular level even for thermodynamically incompatible polymers.

Morphologically, the systems under study are also relatively close to the IPN. The point is that the second polymer phase is formed in the intercrystallite domains of partially crystalline PO. At temperatures below the melting temperature, PO exhibit rather high resistance to the action of the surface forces that cause phase separation, thus stabilising the newly formed structure. In other words, the crystal structure of PO, which plays the role of cross-links in the first network, reduces the possibility of the formation of extended phase domains of the second component and determines the dispersity of the system. Indeed, the synthesis of the HDPE – PMMA compositions *via* delocalised crazing [76] resulted in the formation of the structures characterised by phase co-continuity (selective extraction of the components led to the formation of a continuous porous framework rather than to phase separation of the composition). The formation of the PO phase within the amorphous polar component occurs in a more complex manner. In this case, release of heat (its amount can be rather large) in the formation zone of the PO component leads to softening of the matrix and to penetration of the PO phase into the polar component matrix under the action of mechanical stress.

A salient feature of the formation of IPN is the imposition of microphase separation that is due to the thermodynamic incompatibility of the polymer networks formed on the chemical reactions.[12] The chemical compositions of the separating phases depend on both the stoichiometry of the components and the IPN formation rate. The microphase structure is characterised by the degree of segregation of the two-component system in which phase separation into the polymeric constituents occurred (usually, no equilibrium phase separation is reached and the phases with variable chemical composition are formed). The most sensitive characteristic of the phase separation in polymer blends is the relative elongation at break.[84] Often, passage from compatibility to incompatibility is very sharp and occurs at a particular ratio of the components. Even if specific interactions between the macromolecules of PPC can occur at ambient temperatures, their thermodynamic compatibility deteriorates on heating and they are characterised by the lower critical solution temperature.

Since the components of molecular PPC are thermodynamically incompatible, the compositions prepared from them belong to nonequilibrium systems. To convince oneself that this is true, it is sufficient to give, *e.g.*, the PE – PMMA system molecular mobility (by annealing), which leads to melting of the PE phase and devitrification of the PMMA phase and is exactly the same as what occurs usually in the case of mixing of polymer melts.

Thus, polyolefin-based PPC prepared by *in situ* polymerisation of one component do not represent typical interpenetrating polymer networks since they can be dissolved in appropriate solvents and are characterised by a wide range of variations in the yielding and creep. On the other hand, they also differ from conventional polymer blends. These PPC can be called molecular, pseudointerpenetrating, thermoplastic chemical polymer blends [317] that exhibit homogeneity on a microscopic level. Combinations of some specific properties of their components can lead to positive synergistic effects.

XI. Fields of application of *in situ* prepared polymer – polymer compositions

Almost without exception PPC and their individual polymeric constituents have found the same fields of application, the use of the former being often more advantageous. Polymer – polymer compositions belong to the class of hybrid composite materials with improved breaking strength. A salient feature of PPC is nonlinear dependence of their properties on the chemical composition due to unique structural peculiarities. As a rule, these materials are characterised by improved impact toughness (cold resistance), strength, wear resistance and exhibit good dispersability and processability. Many of them (*e.g.*, PVC – PE compositions) are suitable for production of plastic pipes and sheets, various profiles, moulded products and antifriction materials. Polymer compositions based on syndiotactic PP exhibit radiation-damage stability and can be used instead of plasticised PVC.[116] Improved thermal stability of the *in situ* prepared HDPE – PVC compositions is rather unusual and sets them apart from polymer blends or untreated PVC.[49, 318] This property, which is also characteristic of the PVC – PS graft copolymers,[319] is thought to be due to the fact that the mobile chlorine atoms present in the allyl groups as impurities or bound to the tertiary carbon atoms of PVC are removed in the course of grafting. This again confirms the formation mechanism of the structure of interfacial layers in the *in situ* prepared PPC. Polymer – polymer compositions PVC – HDPE can find applications as high-strength, cold resistant polymer films for enclosing greenhouses.[63] These materials exhibit improved thermal stability and UV and IR radiation stability, *i.e.*, they favour the 'greenhouse effect'. The ability of the PE films used for enclosing greenhouses to keep unsweated and retain transparency for long periods under conditions of excess moisture content is also of great importance.

Modification of PP with elastomeric and thermoplastic elastomer additives allows substantial improvement of the impact toughness of the materials and reduction of the brittleness temperature. Among conventional additives are PIB, butyl rubber, SKEP, SKEPT, polybutadiene rubbers, divinylstyrene-based thermoplastic elastomers, *etc*. Polymer – polymer compositions based on PP and ternary SKEPT have superiority in cold resistance (down to 223 K) and impact toughness compared to the untreated PP.[320] The rheological characteristics of these PPC allow them to be processed using conventional methods for processing of thermoplastics, *viz*., extrusion, injection moulding, blow moulding and pressing.

Blends of different types of PE exhibit improved processability and higher impact toughness compared to the individual components. Often, this leads to enhancement of the performance of production equipment. The PE – PB and PP – PB compositions prepared using the method of 'compatibilisation *via* polymerisation' are characterised by high modulus of elasticity, strength, thermal stability, crack resistance and tensile creep. These materials are promising for production of hot water supply pipes, heat exchangers and cable plasticates. In addition, blends of engineering polymers and commercially available thermoplastics are used for production of, *e.g.*, bumpers.

The thickness of the LDPE film used for production of containers should be at least 50 to 60 μm; these values are mainly determined by the low strength of the polymer. Compatibilisation of several types of polyolefins (*e.g.*, LDPE and HDPE) allows substantial improvement of the properties of the polymer films and reduction of their thickness down to 20 to 30 μm without deterioration of the film strength. This result in more than doubling the performance of extruder reactors and reducing the specific consumption of materials.[321] Packaging films are also produced from PPC based on blends of PE with atactic PP, PIB, *etc*. The content of the recycled materials used for production of PE packaging films and containers reaches 50%.[16] Recycled materials are used for production in those cases where no heavy demands are placed on the structural strength of products, but their environmental safety characteristics should meet stringent requirements (*e.g.*, decorative, insulating and sound-absorbing panels, *etc*.). To this end, one can use wood–polymer compositions based on wood waste and recycled thermoplastics (in particular, sawdust mixed with SKEPT-modified recycled LDPE).[322]

Polyolefins, and first of all HDPE, LLDPE, LDPE, PP and its copolymers, as well as PB are the main components of the PPC used for production of pressure pipelines. The properties of polymer–polymer compositions have a strong effect on the strength characteristics of pipes and the operating conditions. New types of LLDPE-based PPC were recommended[323] for production of hot water supply pipelines (323 K, a pressure of 5 MPa) with a service life of 50 years. Compositions based on UMMPE ($M_w = 4.5 \times 10^6$) and low-molecular-mass PE ($M_w = 8.0 \times 10^4$) are used for production of high-strength, high-modulus fibres by single-stage and two-stage drawing techniques.[324, 325]

Dilution of the blend with the main component is also used for recycling of multicomponent compositions.[326] For instance, homogenisation of blends of LDPE, HDPE, PP and PVC followed by the addition of PP ($\sim$50%) resulted in phase inversion, so that the properties of the end product were mainly determined by the properties of multifilled PP.

As mentioned above, PO and PA, with somewhat different polarities, represent a typical example of immiscible polymers. Blending of PO and PA in the presence of appropriate compatibilisers improves the impact toughness of materials and provides a means of protecting the polymer surface from attack by atmospheric moisture and oxygen. The latter can be illustrated taking the *in situ* prepared PPC formed immediately on polymeric fibres as an example.[49] The PETP or PA fibres become covered with a specific kind of PE 'coat', which protects them from wear, thus improving the wear resistance of the materials, from moisture absorption, *etc*. (Fig. 20). *In situ* prepared polymer–polymer compositions have found an unusual field of application as supports for metal complex catalysts.[53] Specific properties of PPC based on HDPE and metal-containing polymers, *e.g.*, titanium, nickel, cobalt and other metal polyacrylates should also be pointed out.[327] Interpenetrating polymer networks can be formed not only within the interfacial layer, but also in the bulk of these PPC. This is due to the fact that not all unsaturated groups are consumed in the polymerisation of metal diacrylates in PE melts. Since the PPC are processed at temperatures above the polymerisation temperature, the unreacted functional groups can be involved in the chemical interaction to form IPN. *In situ* prepared polymer compositions can combine the advantages of thermoplastics and thermosetting polymers. Often, the *in situ* method allows recycling of thermoplastics. The use of filled PPC, *e.g.*, a ternary system PP–LDPE–short glass fibres (up to 30%–40%) whose morphology was studied by Avalos *et al.*,[328] is also expected to provide a way to substantially improve their properties.

Stable conductivity, good mechanical characteristics, high homogeneity, protective effect of the matrix and good processability of the compositions of PAc and PO open the possibility of their use for production of moulded products, *e.g.*, semiconductor relays, thermistors, solar batteries, *etc*.[329]

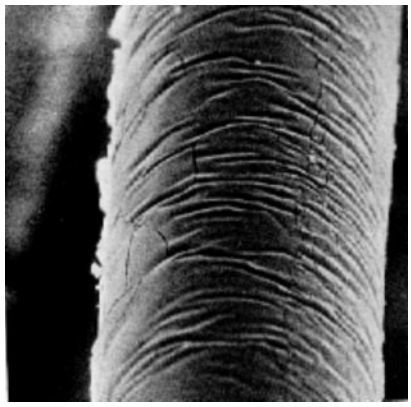


Figure 20. A SEM image of the surface of PETP fibre coated with a HDPE 'skin'.

The operating characteristics of PPC including their photodegradation and photo-oxidation behaviour under natural conditions have been the subject of intensive research. For instance, it was found that the rate of ozone oxidation of oriented HDPE–PP compositions decreases as the content of PP increases.[330] In studies of the blend of isotactic PP and SKEPT† it was shown that an increase in the content of PP leads to enrichment of the interfacial layer with rubber and that the structure of the interfacial layer is the determining factor in the thermal oxidation of blends and vulcanisates.[331] This manifests itself as changes in both the mechanism and kinetics of radical steps in the initial stage of oxidation which can affect inhibition of the oxidation process. Photo-induced oxidation of PPC based on commercially available LDPE and LLDPE is accompanied by scission of the polymer chains and cross-linking of the molecules, as indicated by the changes in the molecular mass and molecular mass distribution. If PPC contain polymeric sensitiser constituents, chain scission reactions become more important, while cross-linking of polymer chains, which can also occur, appears to be less significant. No preferential degradation of a particular component was observed in studies of the blends of LLDPE[332] or LDPE[333, 334] and styrene–butadiene copolymer.

A unique possibility of controlling the properties of polymers has arisen after the preparation of blends of PO with non-olefin components by reactive blending. In particular, polyolefins co-calendered with PVC without using volatile plasticisers can be given such useful properties as elasticity and strength.[335]

Of course, the entire spectrum of applications of molecular polyolefin–polymer compositions is much broader.

XII. Conclusion

The use of molecular polyolefin–polymer compositions allows to a great extent the increasing industrial demands for novel materials to be met with reasonable cost : property ratio. Studies on interrelations between the compatibility of polymeric constituents, structure and properties of these PPC are of great theoretical and practical importance. In addition, the preparation of this type of PPC by reactive blending opens the possibility of re-use of plastic waste and degraded polymeric materials. Compatibilisation of the components of PPC requires improvement of interfacial adhesion and an increase in the phase dispersity, which can often be achieved by using interfacial modifiers. PO-Based compositions prepared by *in situ* polymerisation of one component do not belong to typical representatives of interpenetrating polymer

† SKEPT composition is ethylidenenorbornene (4.0 mol %), propylene (32 mol %) and ethylene (the rest).

networks; on the other hand, they differ from conventional polymer blends. They can be classified as molecular, pseudointerpenetrating, thermoplastic chemical polymer blends.[317] In some optimum cases the *in situ* prepared PPC are characterised by homogeneity on a microscopic level, a valuable combination of specific properties of their constituents and by positive synergistic effects.

The structure of a real particle of the *in situ* prepared PPC is shown in Fig. 21. The particle is composed of the catalyst component or another precursor (*1*) coated with the newly formed polymer (*3*) and the interfacial layer (*2*). The topology and phase structure of the PPC can be controlled in the design stage. Determination of the structure of the PPC and finding out the methods for its control will allow targeted design of polyolefin-based composite materials with desired properties. Unfortunately, no analytical expressions relating the molecular parameters and the composition of a system to its properties have been derived as yet. Would they be proposed, this will favour the refinement and generalisation of the experimental relationships and the development of a well-substantiated approach to the preparation of PO compositions with desired properties.

A great advantage of the methods for preparation of PPC considered in this review is that they allow one to prepare operationally compatible polymer compositions from thermodynamically incompatible components. These compositions exhibit stable properties and have superiority in some characteristics compared to traditionally used polymer blends. This approach follows a recent trend, according to which polymeric materials are given the desired properties by choosing appropriate combinations of the known components rather than by polymerisation of new monomers, since the potential of the organic synthesis of new monomers and polymers based on them are, after all, limited.

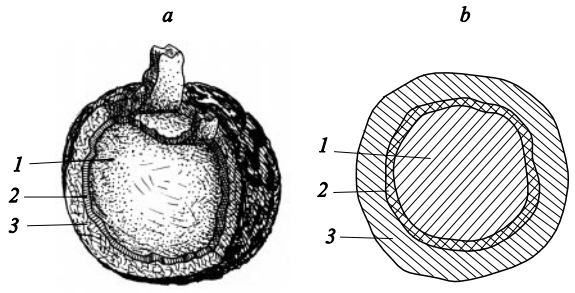


Figure 21. General view (*a*) and simplified scheme (*b*) of the structure of a particle of molecular PPC (for details, see text).

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