

# STRATEGIES FOR COMPATIBILIZATION OF POLYMER BLENDS

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## **Nomenclature**

ABS	acrylonitrile-butadiene-styrene terpolymer
aPP	atactic PP
CPE	chlorinated PE
EPDM	ethylene propylene-diene terpolymer
EPM	poly(ethylene-co-propylene)
EVA	poly(ethylene-co-vinylacetate)
HDPE	high density PE
HIPS	high impact PS
HPB	hydrogenated PB
LDPE	low density PE
NBR	poly(acrylonitrile-co-butadiene) (= nitrile rubber)
NR	natural rubber
PA	polyamide
PAr	polyarylate
PB	polybutadiene (= butadiene rubber)
PBA	poly(butylacrylate)
PBAD	poly(1,4-butylene adipate)
PBMA	poly(butyl methacrylate)
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCDS	poly(1,4-cyclohexane dimethylene succinate)
PCHMA	poly(cyclohexyl methacrylate)
PCL	poly( $\epsilon$ -caprolactone)
PDMS	poly(dimethylsiloxane)
PE	polyethylene
PEA	poly(ethylacrylate)
PECH	poly(epichlorohydrin)
PEMA	poly(ethylmethacrylate)
PEO	poly(ethylene oxide)
PEs	polyester
PET	poly(ethylene terephthalate)
PF	phenol-formaldehyde resin
Phenoxy	poly(hydroxyether of bisphenol-A)
PI	polyisoprene (= isoprene rubber)
PIB	polyisobutylene (= butyl rubber)
PMMA	poly(methyl methacrylate)
PMS	poly( $\alpha$ -methylstyrene)

PP	polypropylene
PPO	poly(dimethylphenylene oxide)
PPrO	poly(propylene oxide)
PPS	poly(phenylene sulphide)
PS	polystyrene
PSU	poly(arylether sulphone)
PVC	poly(vinyl chloride)
PVF <sub>2</sub> , PVDF	poly(vinylidene fluoride)
PVME	poly(vinylmethylether)
PVP	poly(4-vinylpyridine)
SAN	poly(styrene-co-acrylonitrile)
SBR	poly(styrene-co-butadiene) (= styrene rubber)
SBS	styrene-butadiene-styrene triblock copolymer
SEBS	hydrogenated SBS
SMA	poly(styrene-co-maleic anhydride)
SMAA	poly(styrene-co-methacrylic acid)
sPMMA	syndiotactic PMMA

## 1. SCOPE

The blending of polymers provides a powerful route for obtaining materials with improved property/cost performances. Since most blended polymers are immiscible, compatibilization is required to obtain maximum synergy. Several excellent reviews on the compatibilization of polymer blends exist.<sup>[1-10]</sup> However, our approach is to present **all** known compatibilization techniques as a kind of toolbox for blend compatibilization: what can be added to an incompatible blend, or how should we modify the blend components to obtain a compatible blend? The principles of **all** these techniques **will** be illustrated with a limited number of rather detailed examples, and, when possible, commercial applications will be listed. The compatibilization techniques described in Section 3 will be limited to those routes which result in heterogeneous, compatibilized blends. Techniques which result in the homogenization of mixtures of two polymers, such as the so-called "copolymer effect" (for a nice example, see ref.<sup>[11]</sup>) have been omitted. We will not discuss reactor blends for which one polymer is polymerized from its monomer in the presence of the other polymer, thereby generating a compatible blend; such as HIPS, ABS and PP/EPM/PE ternary blends. (Semi-) interpenetrating networks will not be discussed either.

## 2. BASIC PRINCIPLES

### 2.1. Polymer blends

Polymer blending is a convenient route for the development of new polymeric materials, which combine the excellent properties of more than one existing polymer. This strategy is usually cheaper and less time-consuming than the development of new monomers and/or new polymerization routes, as the basis for entirely new polymeric materials. Polymer blending usually takes place in processing machines, such as twin-screw extruders, which are considered standard industrial equipment. So the financial risk inherent to the development of new materials is limited in case of polymer blends.

An additional advantage of polymer blends is that a wide range of material properties is within reach by merely changing the blend composition. A significant drawback is, however, the difficult recyclability of these materials in comparison with neat or just-reinforced resins.

Nevertheless, the market for polymer blend based materials has increased continuously during the past two decades, and is expected to increase by 8-10% in the coming decade. The major markets are automotive, electrical and electronic, packaging, building and household. Nowadays, the total market for polymer blends is estimated to be *ca.* 1.5 million tonnes per year.

Let us recall that polymer blends are either homogeneous or heterogeneous. In homogeneous blends, both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components. In heterogeneous blends, the properties of all blend components are present. Weaknesses of one polymer can to a certain extent be camouflaged by strengths of the other. In a few exceptional cases, (some) properties of the either homogeneous or heterogeneous blend can be better than those of the individual components. This synergism is unfortunately hard to predict.

Heterogeneous blends appear in a variety of morphologies. The best known and most frequently observed morphologies are: (i) a dispersion of one polymer in the matrix of the other polymer; and (ii) a co-continuous two-phase morphology. Which type of morphology is obtained is dependent on the nature of the blend components, the viscosity and the viscosity ratio of both polymers at the blending temperature, and the blend composition. Avgeropoulos<sup>[12]</sup> has proposed a very useful plot for EPDM/PB blends, which predicts in a qualitative way the phase morphology as a function of the blend composition and the viscosity (or torque) ratio (Fig. 1).

Another type of heterogeneous blend, the so called laminates, falls beyond the scope of this chapter. For a comprehensive report on polymer blends, the reader is referred to the excellent book by Utracki<sup>[1]</sup>.

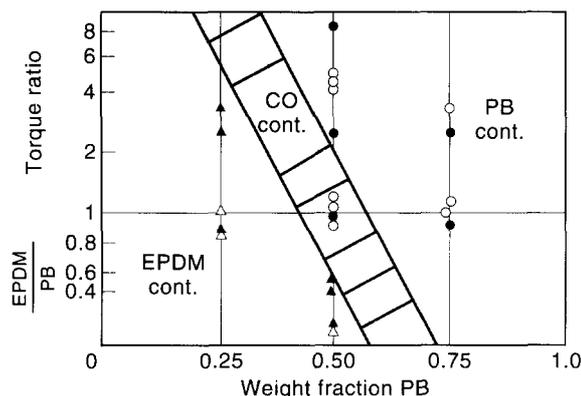


Fig. 1. Dependence of morphology on composition and viscosity (or torque) ratio for a binary EPDM/PB blend.

## 2.2. Miscibility of polymers<sup>[13]</sup>

Homogeneous miscibility in polymer blends requires a negative free energy of mixing:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

However, if two high molecular weight polymers are blended, the gain in entropy,  $\Delta S_{\text{mix}}$ , is negligible, and the free energy of mixing can only be negative if the heat of mixing,  $\Delta H_{\text{mix}}$ , is negative. In other words, the mixing must be exothermic, which requires specific interactions between the blend components. These interactions may range from strongly ionic to weak and nonbonding interactions, such as hydrogen bonding, ion-dipole, dipole-dipole and donor-acceptor interactions. Usually, only Van der Waals interactions occur, which explains why polymer miscibility is the exception rather than the rule.

The miscibility behaviour of two polymers is strongly dependent on temperature. Each polymer pair is characterized by an interaction parameter, which usually exhibits such a temperature dependence that possible miscibility at lower temperatures is lost at higher temperatures, e.g. during processing.

## 2.3. Types of blends

Basically, three different types of blends can be distinguished.

In *completely miscible blends*, for which  $\Delta H_{\text{mix}} < 0$  due to specific interactions, homogeneity is observed at least on a nanometer scale, if not on the molecular level. A well known example of a blend which is miscible over a very wide temperature range and in all compositions is **PS/PPO**, that combines the heat resistance, the inflammability and the toughness of **PPO** with the good processability and the low cost of **PS**. This type of blend exhibits only one glass transition temperature ( $T_g$ ), which is between the  $T_g$ s of both blend components in a close relation to the blend composition.

In *partially miscible blends* a (small) part of one blend component is dissolved in the other. This type of blend, which exhibits a fine phase morphology and satisfactory properties, is referred to as *compatible*. Both blend phases (one being rich in polymer 1, the other phase being rich in polymer 2) are homogeneous, and have their own  $T_g$ . Both  $T_g$ s are shifted from the values for the pure blend

components towards the  $T_g$  of the other blend component. An example is the PC/ABS blends, which combine the heat resistance and toughness of PC with the low temperature impact, processability, stress cracking resistance and low cost of ABS. In these blends, PC and the SAN phase of ABS partially dissolve in one another. In this case, the interphase is wide and the interfacial adhesion is good.

By far most blends are *fully immiscible*. They have a coarse phase morphology, the interface is sharp, and the adhesion between both blend phases (each exhibiting the  $T_g$  of the pure blend components) is poor, so that these blends are useless without being *compatibilized*.

Examples of fully immiscible blends are PA/ABS, PA/EPDM, PA/PPO and PP/PA. All of these blends have become commercially successful, but only after being efficiently *compatibilized*. In PA 6/ABS, the polyamide provides good heat and chemical resistance, good tensile properties, good flow and good paintability. ABS lowers the moisture absorption, improves the dimensional stability, and provides a lower price and good low temperature impact. PA 6.6 (or 6)/EPDM blends are the so-called "supertough nylons". In PA 6 or 6.6/ PPO blends, the polyamide provides good processability (as such, PPO is intractable), good chemical resistance and paintability, while the PPO exhibits low moisture absorption, good dimensional stability and stiffness at higher temperatures. In PA 6/PP blends, the contribution of PA is as described above, and PP lowers both moisture absorption and price. In this chapter, a blend is called compatible if it exhibits a set of properties which are desirable and useful, from a commercial point of view, either by complete or partial miscibility, or by the application of a suitable compatibilization technique. An emphasis will be on blends which need to be compatibilized.

## 2.4. Blending process and role of compatibilizers

### 2.4.1. Blending process

#### 2.4.1.1. Rheology

- It is essential to know the viscoelastic behaviour of polymer blends, not only for reaching optimum processing conditions, but also for collecting valuable information on the flow mechanism and its effect on both phase morphology and ultimate mechanical properties. It is worth recalling that the shear viscosity ( $\eta$ ) of polymers is usually observed to increase as the shear rate ( $\dot{\gamma}$ ) is decreased, until reaching the Newtonian plateau. The nonlinear part of this viscosity dependence may be approximated by a power law:  $\eta = K_1 \cdot \dot{\gamma}^{m-1}$ , [14] where  $K_1$  is a viscosity constant, and  $m$  the rheofluidity index. Moreover, the thermal dependence of the melt viscosity measured at a constant shear rate can be expressed by a modified Arrhenius law:  $\eta = K_2 \exp(\dot{\gamma}E/RT)$ , [15] where  $E$  is the activation energy and  $K_2$  is a viscosity constant. Compared with these classical relationships, the melt viscosity of immiscible polymer blends depends on the interactions at the interface and the phase morphology, in a strong dependence on the addition of an interfacial agent.

As a rule, polymer blends can be classified into four categories defined by the melt viscosity-composition dependence with respect to the log-additivity rule (eqn (1)).

$$\log(\eta) = \sum_i \phi_i \log(\eta_i) \quad (1)$$

where  $\phi_i$  and  $\eta_i$  are volume fraction and viscosity of component  $i$ , respectively. The four classes of polyblends are: additive blends, whose melt viscosity follows eqn (1). Some blends, and particularly immiscible blends with strong interfacial interactions, show a positive deviation from the log-additivity rule. The opposite effect is observed when the interactions are weak. Blends in which the phase structure changes with composition exhibit both positive and negative deviations. Nevertheless, the experimental dependence of viscosity on blend composition is not typical of the polymer pair under consideration, but rather of the mechanism of flow that prevails under the processing and/or testing conditions. In the case of immiscible blends, two mechanisms are assumed to be operative, (i) The "emulsion effect": an increase in the relative blend viscosity is observed as a result of the addition of the second phase. The effect is at a maximum ( $\eta_{mix}$ ) at the phase inversion composition, (ii) The "interlayer slip", whose effect ( $\beta$  slip factor) increases with temperature and with shear stress. Utracki has proposed a relationship for calculating the  $\eta$  vs composition dependence for immiscible polymer blends. Experimental data for more than 30 blends have been well described by a two-parameter ( $\eta_{max}$  and  $\beta$ ) equation. [16] An easy, although qualitative, way to prove the efficiency of an

interfacial agent (prefabricated or in-situ generated block or grafted copolymer) is to compare the viscosities of the modified and the original blends. An increase in viscosity would be an indication of the interfacial activity of the additive. The interfacial adhesion, and thus the blend viscosity, usually increases with increasing amounts of interfacial agent, until the interface is saturated.

2.4.1.2. *Morphology development* - Control of the phase morphology during blend processing is a key issue for the production of new materials with improved properties compared with the constitutive immiscible polymers. The shape, size and spatial distribution of the phases result from a complex interplay between viscosity (and elasticity) of the phases, interfacial properties, blend composition and processing conditions.

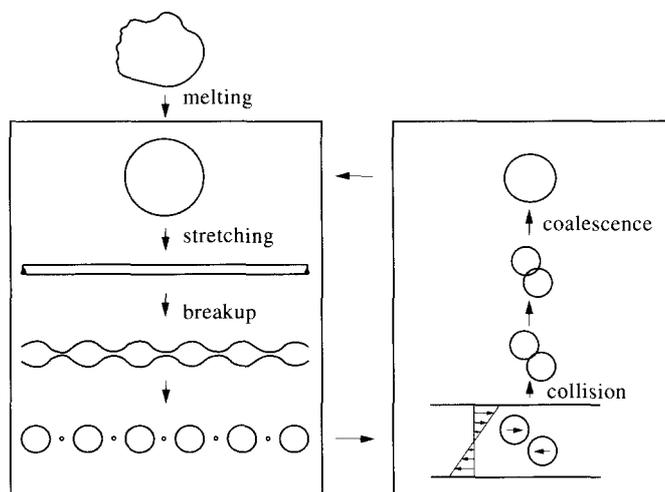


Fig. 2. Schematic representation of the processes occurring during the melt blending of two polymers .

Fig. 2 summarizes the processes that occur when two polymers are blended in the melt, particularly when polymer 1 (with melt viscosity  $\eta_d$  and volume fraction  $\phi_d$ ) is dispersed in the continuous phase of polymer 2 (with melt viscosity  $\eta_c$  and volume fraction  $\phi_c$ ).

An elementary step is the deformation of dispersed drops in the flow field. The interfacial area is accordingly increased and the local dimensions are decreased perpendicular to the flow direction. In the case of two viscous polymers, drop deformation is mainly governed by the capillary number,  $Ca$ , i.e. the ratio of the (deforming) shear stress  $\tau$  exerted on the drop by the external flow field and the spherical shape conserving interfacial stress  $s/R$  (with  $s$  the interfacial tension and  $R$  the local radius):

$$Ca = \frac{\tau}{\sigma/R} = \frac{\eta_c \dot{\gamma} R}{\sigma} \quad (2)$$

For small capillary numbers, the interfacial stress withstands the shear stress, and an ellipsoid drop shape persists. Above a critical value,  $Ca_{crit}$ , typically in the initial stage of mixing when the dispersed domains are large, the shear stress dominates the interfacial stress, and drops are stretched affinely with the matrix into long thin threads. If the local radius of the thread becomes sufficiently small, interfacial ("Rayleigh") disturbances grow on the thread and result in the breakup of these liquid threads into small drops. Above a certain diameter, these small drops may be stretched and broken again. For very small drops,  $s/R$  is high enough to prevent further stretching and breakup.  $Ca$  is actually the upper limit for the particle dimension.<sup>[17,18]</sup> In the case of viscoelastic systems, Wu<sup>[19]</sup> has proposed an empirical relationship between the capillary number and the relative melt viscosity of the dispersed and continuous phases ( $\eta_d/\eta_c$ ) (eqn (3)).

$$Ca = \eta_c \cdot \dot{\gamma} R / s = 4(\eta_d / \eta_c)^k \quad (3)$$

with  $k = 0.84$  for  $(\eta_d/\eta_c) \geq 1$  and  $k = -0.84$  for  $(\eta_d/\eta_c) \leq 1$ . From the  $Ca$  vs  $(\eta_d/\eta_c)$  plot the average particle size can be predicted as a function of the processing parameters. These predictions have proved to be valid at low and constant volume fractions of the dispersed phase. As a result, the finest phase dispersion is predicted for equiviscous polymer blends. This conclusion relies upon the assumption of the so-called stepwise equilibrium mechanism of repeated breakup. A stepwise increase in shear stress is assumed to occur with the repeated breakup of drops under quasi-equilibrium conditions at  $Ca_{crit}$  until the machine-dependent maximum shear stress is reached.

If, conversely, a transient mechanism is assumed to exert the same maximum shear stress directly to

the original drop, thus inducing a one-step thread breakup during stretching (as shown in Fig. 2 and described in ref. [20]), then a finer phase morphology should result from a higher difference in viscosity of the two phases.[21]

In order to account for an increase in the average particle size with the dispersed phase concentration, Serpe et al.[15] have completed Wu's equation with an additional empirical factor. Moreover, the viscosity of the blend ( $\eta_b$ ) has been substituted for the matrix viscosity ( $\eta_c$ ), which is valid for diluted systems. Eqn (4) has accordingly been proposed:

$$Ca = \eta_b \cdot \dot{\gamma} R (1 - (4\phi_d \cdot \phi_c)^{0.8}) / \sigma = 4(\eta_d / \eta_b)^k \quad (4)$$

In regions of low  $\dot{\gamma}$  in the mixing equipment, coalescence of non-stabilized dispersed droplets occurs and results in the coarsening of the phase morphology.[22]

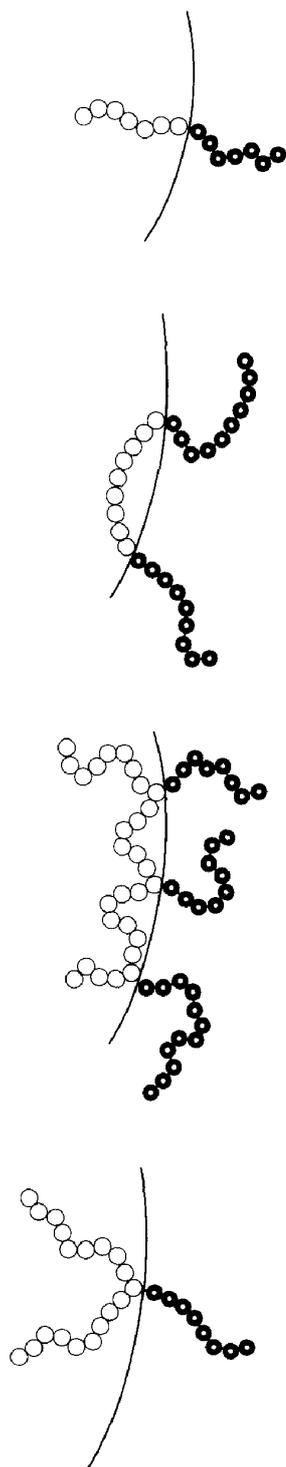
The coalescence of the dispersed particles is supposed to be included in the composition-dependent factor  $(1 - (4\phi_d \cdot \phi_c)^{0.8})$  in eqn (4). Actually, at relatively high concentrations of the minor phase, the final morphology results from a competition between breakup and coalescence, whereas, at low enough concentrations, drop breakup is the dominant effect that dictates the lower limit of particle size. Luciani and Jarrin have observed that dispersed particles and fibrils can coexist in a certain composition range. The fate of the phase morphology then depends on the fibril stability, either the formation of nodules by the Rayleigh mechanism or phase inversion by coalescence of stable fibrils.[23]

Until now, no equation can predict the effect of interfacial agents on the phase breakup-coalescence mechanism. When the volume fraction of the minor phase is low (a few percent of the blend volume) the phase coalescence process is so slow that it may be neglected. Then, some differences between modified and unmodified blends mainly result from changes in the interfacial tension. In addition, coalescence is retarded if the viscosity of both the continuous and the dispersed phases is high. Furthermore, it is obvious that the processing conditions (temperature, screw speed, residence time, screw type) play an important role in the development of the phase morphology. In practice, co-rotating twin-screw extruders have proven to be the most effective blending machines.

#### 2.4.2. Role of compatibilizers in blending processes

Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and a second block miscible with the other blend component. These blocky structures can be pre-made and added to the immiscible polymer blend, but they can also be generated in-situ during the blending process. The latter procedure is called reactive compatibilization, and mutual reactivity of both blend components is required. In Section 3 of this paper, illustrative examples of both techniques will be presented. In fact, we will give a comprehensive overview of all known compatibilization techniques, which nearly all, in one way or another, result in the formation of blocky structures with interfacial activity.

Fig. 3 presents a schematic picture of the supposed conformation of some compatibilizer molecules at the interface of a heterogeneous polymer blend. Shown are triblock, diblock, multigrafted and singlegrafted copolymers. A heterogeneous blend of polymers A and B can be compatibilized by a diblock copolymer poly (C-b-D), provided that block C is miscible with polymer A (therefore block C can also be polymer A) and that block D is miscible with polymer B (so block D can also be polymer B). Since phases A and B are merely  $\theta$ -solvents for blocks A and B, respectively, whereas the mutual miscibility of phase A with block C (and phase B with block D) implies specific interactions between A and C (and B and D), a poly(C-b-D) is usually the more effective compatibilizer for blend A/B. The role of compatibilizers in the blending process is firstly to retard the formation of the Rayleigh disturbances on the generated threads of polymer 1 (Fig. 2), as the result of a decreased interfacial tension.



*Fig. 3. Schematic picture of conformations for diblock, triblock, multigraft and singlegraft copolymers at the interface of a heterogeneous polymer blend.*

The lower the interfacial tension, the longer the deformation tension exceeds the interfacial tension, the longer the stretching of the thread will proceed, the smaller the diameter of the resulting thread will become, and, consequently, the smaller the size of the generated droplets of polymer 1 will be. Usually, an average particle size in the sub-micron range can be achieved. In addition, the presence of compatibilizer molecules at the surface of the small generated particles prevent coalescence from occurring during subsequent processing (Fig. 2). Compatibilizers are thus able to generate and to stabilize a finer morphology.

Finally, provided that each block of a poly(A-b-B) compatibilizer penetrates the parent phase (A and B, respectively) deeply enough to be entangled with the constitutive chains, the interfacial adhesion is enhanced. Good interfacial adhesion is essential for stress transfer from one phase to the other one to be efficient and for cracks initiated at the interface to be prevented from growth until catastrophic failure occurs. Refinement and stabilization of the phase morphology and the enhancement of the interfacial adhesion usually upgrade an inferior and useless immiscible polymer blend to an interesting material in which the beneficial properties of both blend components are united and the "Achilles' heel" of the pure blend components are effectively camouflaged.

### **3. Strategies for compatibilization of polymer blends**

#### *3.1. Addition of premade grafted and block copolymers*

##### 3.1.1. General information

The emulsification of polymer blends has been proposed as the most efficient tool for obtaining a fine phase morphology and good mechanical properties. The best way to validate that concept is to tailor block and grafted copolymers and to investigate the beneficial effects that they can have on immiscible polymer blends. That approach allows the main molecular characteristic features of block and grafted copolymers to be changed in a systematic way, e.g. molecular architecture, composition and molecular weight, so that basic relationships can be drawn between the structural characteristics of these additives and the general properties of the polyblends. These relationships are the most desirable guidelines for the emulsification of polyblends, as will be discussed in Section 4.

The remarkable progress reported in living anionic and coordinative polymerization during the last two decades has largely contributed to the tailoring of block copolymers by sequential living polymerization of the constitutive monomers.<sup>[24]</sup> The most controlled technique for the synthesis of grafted copolymers relies upon the radical (co)polymerization of so-called macromonomers.<sup>[25,26]</sup>

##### 3.1.2. Types of compatibilized blends (Table 1)

Early efforts were concentrated on blends of (di)block copolymers with homopolymers possessing repeat units identical or chemically similar to each segment of the copolymer. This type of compatibilized blend will be designated as a "A/B/A-**B**" system, where the A-B diblock is an "entropic acting copolymer".

Table 1. *Compatibility by premade copolymers*

Type of blend	Major component	Minor component	Compatibilizer	References
A/B/A—B block	PE or PS	PS or PE	HPB-b-PS, HPB-b-PI-b-PS, SBS, SEBS	27,39-48
	PE or HIPS	PE or HIPS	HPB-b-PS	49,50
	PBT or PS	PBT or PS	PS-b-PET or PS-b-PBT	51
A/B/A—C block	PPO or PBT	PPO or PBT	PS-b-PET or PS-b-PBT	51
	SAN	SBS (Solprene)	PS-b-PMMA or PB-b-PMMA	45,52
	PVF <sub>2</sub> or PMS	PMS or PVF <sub>2</sub>	PMS-b-PMMA	53
	PVF <sub>2</sub>	HIPS	PS-b-PMMA	45,54
	PVF <sub>2</sub>	PE or PP	HPB-b-PMMA, HPI-b-PMMA	55
	PET or PS	PS or PET	PS-b-PCL	56
	PS/PPO or PBT	PBT or PS/PPO	PS-b-PET or PS-b-PBT	51
	PVC	PS	PCL-b-PS or PMMA-b-PS	45,57,58
	ABS	PE	HPB-b-PMMA	59
	PVF <sub>2</sub>	PS	PS-b-PMMA	45
	PVC	SEBS	HPB-b-PMMA	45
	PET	HDPE	S-EB-S	60,61
	PS or PC	PC or PS	PS-b-PCL	62
A/B/C-D block	Phenoxy	PPO	PS-b-PMMA	63
	Surllyn	PPO	PS-b-PVP	64
	PPO	SAN	PS-b-PMMA	65
	SAN	PPO	PS-b-PMMA	66
A/B/A-B graft	EPDM	PMMA	EPDM-g-MMA	67
	PF	PMMA or PS	PF-g-MMA or PF-g-PS	68
	PBT	PS	PBT-g-PS	37
	PS or PE	PE or PS	PS-g-PE	69-71

The emulsification of PE and PS blends by copolymers consisting of HPB (miscible with PE) and PS has been extensively studied by Teyssey et al.<sup>[27]</sup> More recently, this approach has been extended to A-C (di)block copolymers, for filling the incompatibility gap between some A/B pairs, provided that C is miscible with B, so that the diblock is an "enthalpic acting copolymer". sPMMA containing (di)blocks are among the most "universal" compatibilizers for this type of "A/B/A-C system". sPMMA is indeed quite miscible with a number of important polymers [PVC, PVDF, random copolymers of styrene and acrylonitrile (SAN), etc.], and it can be copolymerized in a two-step living polymerization with styrene and dienes.<sup>[28]</sup> Another valuable family of (di)block copolymers is based on PCL,<sup>[29]</sup> which is miscible with phenoxy, SAN, PVC, nitrocellulose, PECH, chlorinated polyether,<sup>[30,31]</sup> Saran [copolymers of vinylidene chloride with either acrylonitrile (Saran F), vinyl chloride (Saran B), or vinyl acetate (Saran C)],<sup>[32]</sup> chlorinated polypropylene, chlorinated polystyrene,<sup>[33]</sup> CPE,<sup>[34]</sup> and PC.<sup>[35]</sup> This list could be extended to various aliphatic polyesters and aromatic polyesters, such as PET and PBT.<sup>[36]</sup> Finally, there are a few reports on blends of two immiscible polymers (A and B) compatibilized with a C-D diblock copolymer, where A and B are miscible with C and D, respectively ("A/B/C-D system").

The use of grafted copolymers is another possible route for the control of the phase morphology and the mechanical properties of immiscible polymer blends. In addition to polymer-polymer or polymer—monomer reactions, a large variety of macromonomers has been prepared as precursors of grafted copolymers<sup>[25,26]</sup> with some control on the copolymer structure, since the length and number of grafts are dictated by the macromonomer molecular weight, the comonomer feed and the comonomer

reactivity ratios. Recently,  $\omega$ -dihydroxy PS has been synthesized as a macromonomer for the synthesis of poly(PBT-g-styrene). The SEM analysis of fracture surfaces of blends containing PBT/PS 70/30 by weight shows spherical PS domains with diameters ranging from 1 to 4  $\mu\text{m}$ . In addition, during the fracture process, many domains are pulled away from their previous positions and the surfaces of holes left by removed PS spheres appear to be very smooth. These observations suggest a poor compatibility between PBT and PS. As PBT-g-PS is added (10%) to the incompatible blend, the domain sizes of PS are reduced and the interface between the two phases becomes more diffuse. These features demonstrate the compatibilizing effect of PBT-g-PS in the PBT/PS blend. Furthermore, increases in modulus, elongation at break, and impact strength have been observed in PBT/PS (70/30) blends as a result of the compatibilizing effect of increasing amounts of PBT-g-PS up to 10%.<sup>[37]</sup>

A recent report by Braun et al. has shown that a PS-b-(PB-g-PCHMA) block-grafted copolymer is a suitable compatibilizer for PS/PVC multiphase blends. This copolymer has been prepared by radical grafting of cyclohexylmethacrylate onto the PB block of a PS-b-PB copolymer. As a result, a long PS block is connected to PCHMA blocks through short PB segments. This copolymer has been observed by TEM to form an interfacial layer in an immiscible PS/PVC 50/50 blend.<sup>[38]</sup>

### 3.1.3. Representative examples and commercial blends

As convincing examples of the practical interest of polyblend compatibilization or emulsification, toughened thermoplastics have been produced with mechanical performances possibly higher than commercial resins having comparable compositions.<sup>[45,49,50,52,59]</sup> Teyssié et al.<sup>[49]</sup> have studied the emulsification of LDPE and commercial HIPS blends by a hydro-genated tapered block copolymer of butadiene and styrene ( $MW = 80,000$ ). In this diblock, there is a smooth transition from the pure PB block ( $MW = 32,000$ ) to the pure PS block ( $MW = 26,000$ ), through an intermediate section of  $MW = 22,000$ .<sup>[72]</sup> As expected, the phase morphology of neat LDPE/HIPS blends is coarse and heterogeneous whatever the blend composition, and the interfacial adhesion is very poor. Upon the addition of the block copolymer (5 wt%) there is a marked decrease in the particle size and a significant enhancement of the interfacial adhesion. It is worth noting that HIPS is *per se* a dispersion of rubber particles emulsified within a PS matrix by an in-situ formed grafted copolymer. Fig. 4a illustrates the dispersion of HIPS (and its internal structure) in LDPE. Upon the addition of the hydrogenated poly-(butadiene-b-styrene), PS becomes finely dispersed within LDPE, whereas the PB particles still coated by an adherent layer of PS become anchored within the LDPE matrix by the diblock copolymer (Fig. 4b). This assumption is convincingly supported by the stability of the phase morphology and particularly the stability of the rubber particles against coalescence when the LDPE content is decreased. Furthermore, there is a general improvement of the ultimate mechanical properties of the LDPE/HIPS blends when the diblock copolymer is added. For instance, the elongation at break of the LDPE/HIPS 40/60 blend is increased by one order of magnitude and becomes higher than the value characteristic of HIPS.

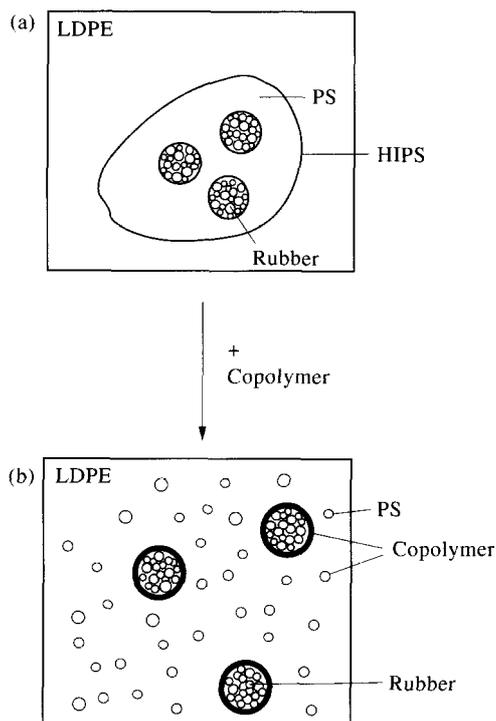


Fig. 4. Effect of the HPB-b-PS diblock copolymer on the dispersion of HIPS in a PE matrix.

As far as the Charpy impact energy is concerned, the effect of the diblock is quite remarkable. Indeed, the impact energy of HIPS ( $10\text{kJ/m}^2$ ) is rapidly decreased by the addition of increasing amounts of LDPE. In sharp contrast, that property is greatly enhanced when these HIPS/ LDPE blends (e.g. containing 20 wt% LDPE and less) are compatibilized by 5% diblock. For instance, the Charpy impact resistance of the HIPS/LDPE 80/20 blend, which is as small as  $5.3\text{kJ/m}^2$ , is increased up to  $16.3\text{kJ/m}^2$  with the addition of the emulsifier. It is thus clear that unexpected synergistic effects can be imparted to polyblends by emulsification; particularly, the ductility of HIPS can be very much improved by an appropriate combination with LDPE and a suitable diblock copolymer.

In the same vein, ABS resins have been successfully mimicked by melt blending a SAN resin with a suitable rubber and a compatibilizer (or emulsifier) such as PB-b-PMMA.<sup>[55]</sup> A thermoplastic elastomer of the SBS type has been used as the rubber phase in order to overcome the difficulty to properly control the rubber crosslinking (usually required for high impact performances) during the blending process. Depending on the total rubber content and molecular weight of the diblock copolymer (of a 50/50 composition), Charpy impact energies as high as  $35\text{kJ/m}^2$  have been reported compared to  $19\text{kJ/m}^2$  for "Cyclocac GSM<sup>®</sup>", i.e. a commercially available ABS resin. However, these blends have to be optimized, particularly the flow properties which are not suitable for an injection moulding process.

For the time being and to our best knowledge, no blend compatibilized by premade block or grafted copolymers has been made available on the market place. One of the main reasons is that the low volume production of specific block or grafted copolymers is often too expensive to be of a viable business interest.

### 3.2. Addition of reactive polymers

#### 3.2.1. General principles

The addition of a reactive polymer, miscible with one blend component and reactive towards functional groups attached to the second blend component results in the "in-situ" formation of block or grafted copolymers. This technique has certain advantages over the addition of premade block or grafted copolymers. Usually reactive polymers can be generated by free radical copolymerization or by melt

grafting of reactive groups on to chemically inert polymer chains. Furthermore, reactive polymers only generate block or grafted copolymers at the site where they are needed, i.e. at the interface of an immiscible polymer blend. Although grafted and (especially) block copolymers may form micelles after being added to or formed in a blend, the chance that the critical micelle concentration is exceeded is actually higher in the case of pre-made structures. This is a drawback with respect to the efficiency of the compatibilizer. Finally, the melt viscosity of a (linear) reactive polymer is lower than that of a pre-made block or grafted copolymer, at least if the blocks of the pre-made copolymer and the reactive "blocks" are of similar molecular weights. Lower molecular weight polymers will diffuse at a higher rate towards the interface. This is of utmost importance in view of the short processing times used in reactive blending which may be on the order of a minute or less.

In order to successfully apply reactive polymers as block or grafted copolymer precursors, the functionalities must have a suitable reactivity in order to react across the melt phase boundary during the short blending time. In addition, the generated covalent bond must be sufficiently stable to survive subsequent processing conditions.

Fig. 5 illustrates the different block and grafted copolymer precursors that can be added to a blend of immiscible polymer (A) and polymer (B), as well as the type of copolymer formed. The unmodified polymer (A) is assumed to be unreactive towards polymer (B). The reactive, polymeric additive (left column in scheme) may be either an X-functionalized polymer (A) or an X-functionalized polymer (C), provided that polymer (C) is miscible with polymer (A). Polymer (B) is supposed to have either end-reactive or pendant-reactive groups (e.g. amine and carboxylic acid groups if B is a PA, or succinic anhydride if B is a styrene-maleic anhydride copolymer, respectively).

In view of the higher possible concentrations of pendant-reactive groups X and Y with respect to end-reactive groups, alternatives II and III in Fig. 5 are generally preferred over I, since the rate of copolymer formation is given by the general equation for a second-order reaction.

$$v_{\text{copolymer formation}} = k \cdot [X] \cdot [Y] \quad (5)$$

In fact, the concentration of co-reactive groups is even higher in the case of alternative IV. For too high concentrations of pendant groups, however, alternative IV may result in a crosslinked network, which (depending on the amount of reactive polymer (A)\* or (C)\* and on the number of functional groups per polymer chain) may have a deleterious effect on processability.

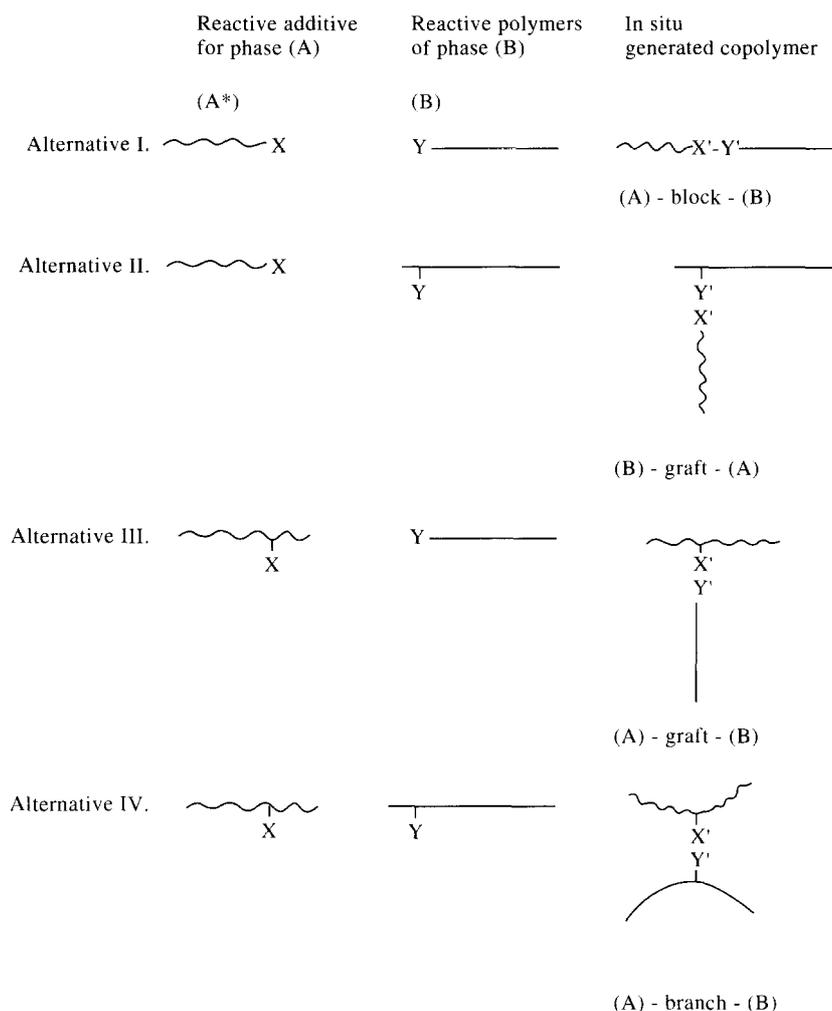


Fig. 5. Block and graft copolymer precursors and type of copolymer formed during reactive processing.

In some blends, neither of the blend components (A) nor (B) contain reactive groups in their polymeric chains. Examples are blends of PE and PP. Then, both an X-functionalized polymer (A) [or (C)] and a Y-functionalized polymer (B) [or (D), miscible with (B)] have to be added to compatibilize the blend (Fig. 6).

### 3.2.2. Representative examples

#### 3.2.2.1. Addition of end-reactive polymers generating block copolymers

(Fig. 5, alternative I) — Because of the reactivity of epoxide end groups with, for example, carboxylic acid end groups of PBT, a modified PPO has successfully been used as a reactive compatibilizer for PPO/PBT blends (Fig. 7).<sup>[73]</sup>

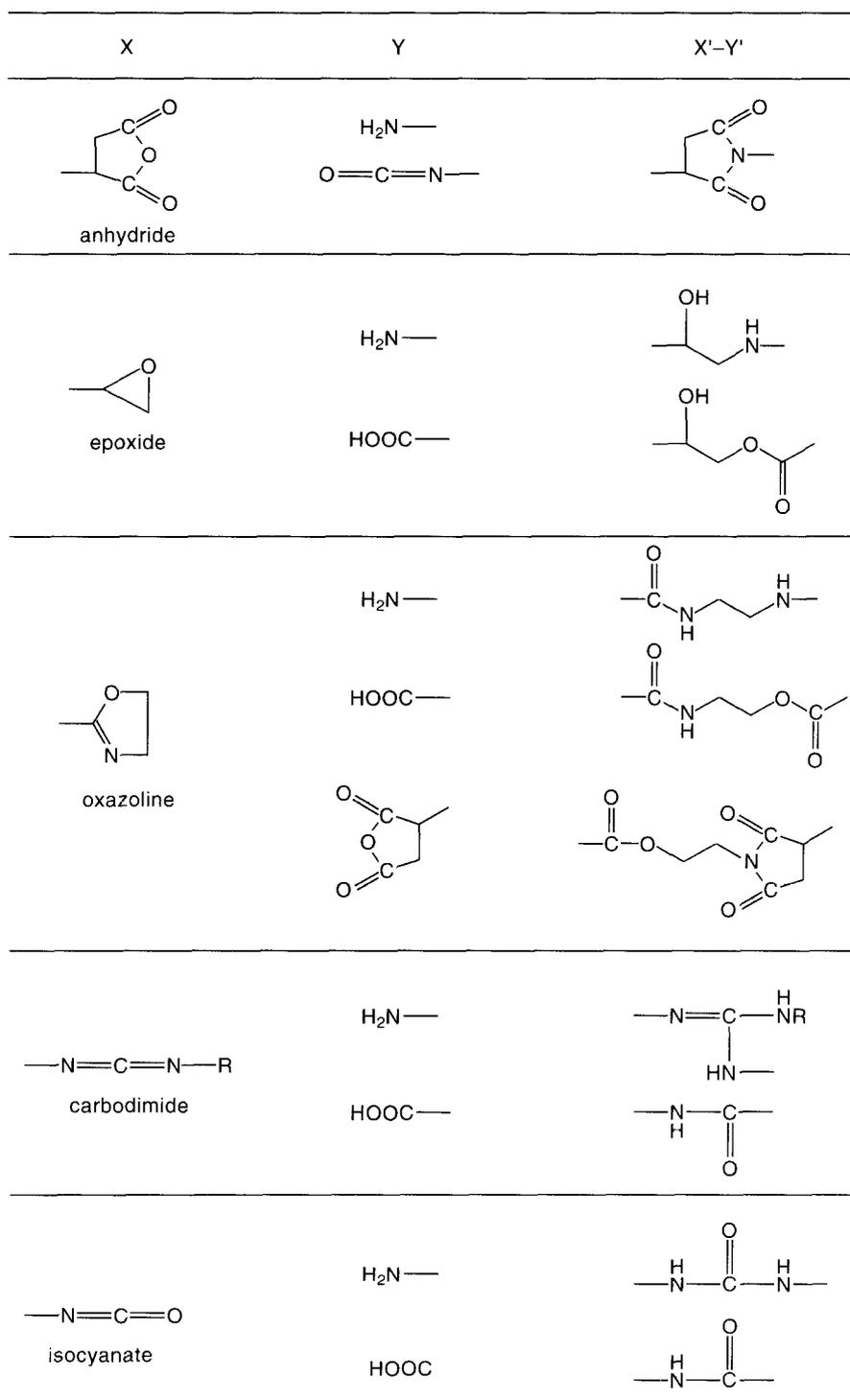


Fig. 6. Reactive groups involved in reactive processing.

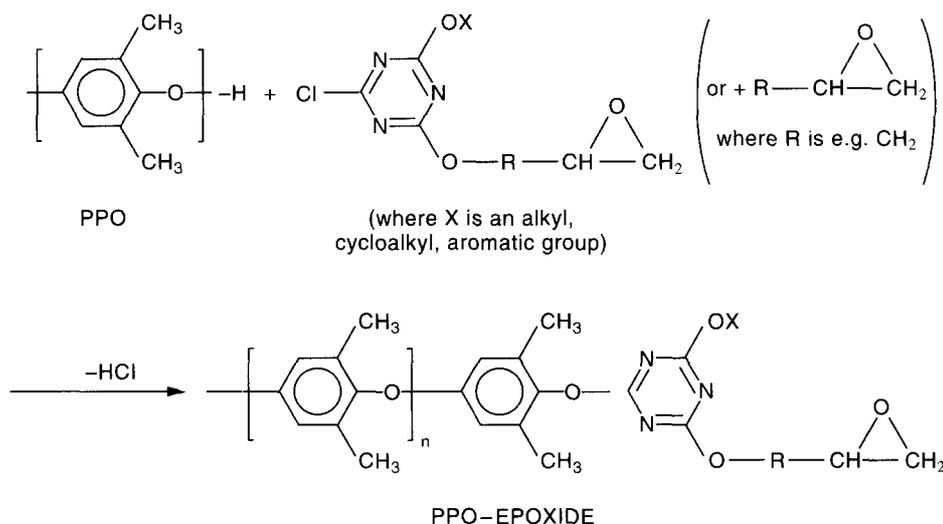


Fig. 7. Epoxide end-capped PPO compatibilizer for PPO/PBT reactive blends.

In this case PPO-b-PBT copolymers are generated at the interface during melt blending. As indicated in Fig. 6, the PPO blocks and the PBT blocks will be linked together by ester bonds. A patent-example describes a compatible blend of 30 parts by weight (pbw) of an epoxy capped PPO, 60 pbw of PBT and 10 pbw of the SBS impact modifier. This blend exhibits a notched Izod impact of *ca.* 85 kJ/m<sup>2</sup> and an elongation at break of 41%.

Another good example is the work of Aycock and Ting.<sup>[74,75]</sup> PPO is end-capped in solution with trimellitic anhydride chloride, as shown in Fig. 8.

During melt blending with PA 6.6, the anhydride end groups of PPO react with the amine end groups of PA 6.6, generating a PPO-b-PA 6.6 copolymer, whose blocks are linked by an imide-bond (Fig. 6). The presence of PPO-b-PA 6.6 copolymer is confirmed by solubility measurements in formic acid and toluene. The very same concept has successfully been applied to PPO/PA 4.6 blends,<sup>[76]</sup> to which SEBS-MA, i.e. a hydrogenated SBS copolymer grafted by maleic anhydride on the PS blocks, has been added as an impact modifier. For comparison, PA 6.6 based blends with the same composition have been prepared as well.

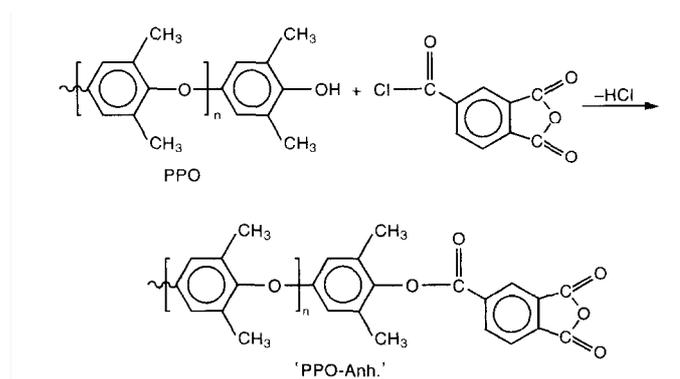


Fig. 8. Anhydride end-capped PPO compatibilizer for PPO/PBT reactive blends.

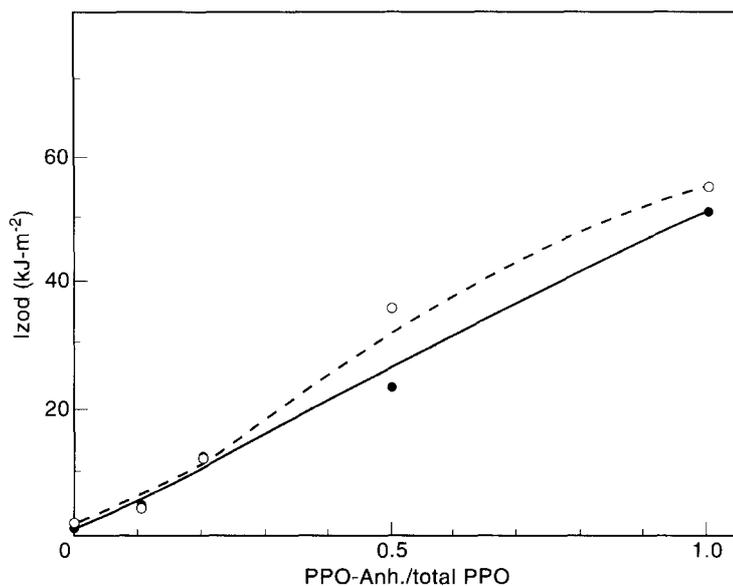


Fig. 9. Izod impact strength at 23°C as a function of PPO-Anh./total PPO for PA/PPO/SEBS-g-MA 60/30/10 blends (•, PA 6.6; ◦, PA 4.6).

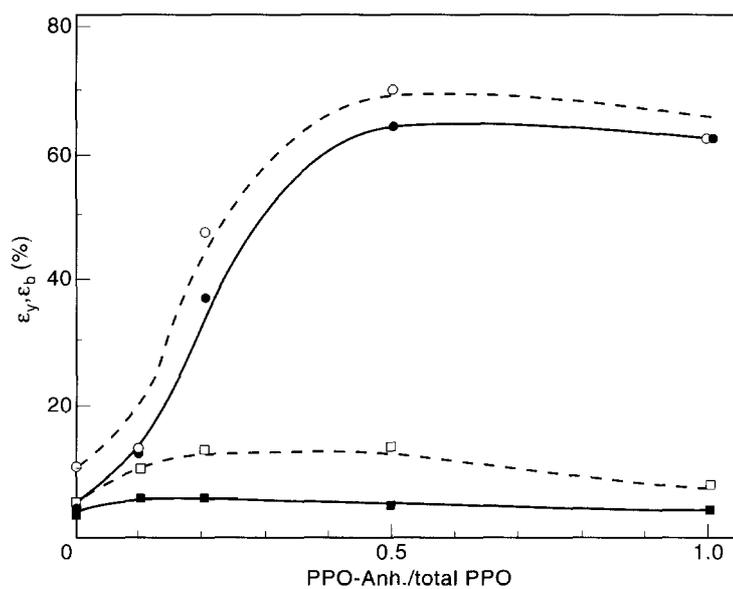


Fig. 10. Yield strain ( $\epsilon_y$ ) and strain at break ( $\epsilon_b$ ) as a function of PPO to Anh./total PPO for PA/PPO/SEBS-g-MA 60/30/10 blends (■,  $\epsilon_y$  for PA 6.6; □,  $\epsilon_y$  for PA 4.6; •,  $\epsilon_b$  for PA 6.6; ◦,  $\epsilon_b$  for PA 4.6).

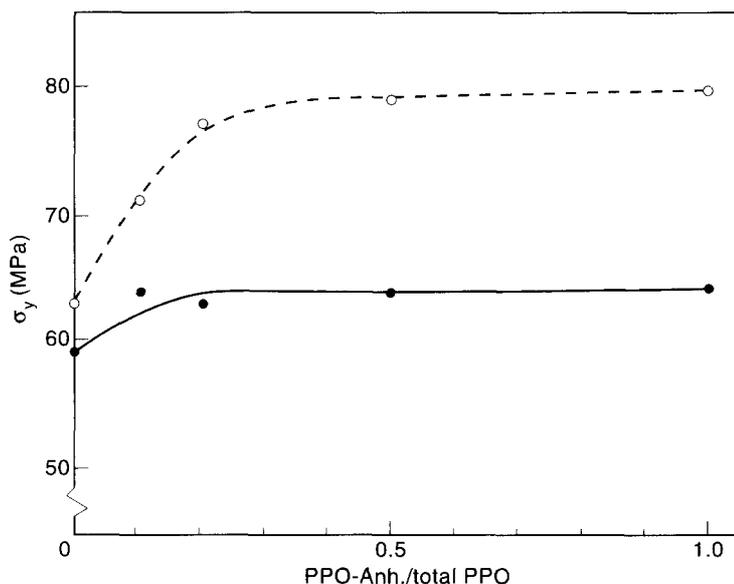


Fig. 11. Yield stress ( $\sigma_y$ ) as a function of PPO-Anh./total PPO for PA/PPO/SEBS-g-MA 60/30/10 blends (•, PA 6.6; °, PA 4.6).

The effect of an increasing PPO-anhydride/total PPO ratio on notched Izod impact, elongation at break and yield, and yield stress is shown in Figs 9-11. The better performance of the PA 4.6 based blends with respect to yield stress can be explained by a higher degree of crystallinity of the polyamide phase. As expected, an increasing amount of anhydride end-capped PPO results in a continuously decreasing particle size of the dispersed PPO phase, in which the SEBS-MA impact modifier is present.

### 3.2.2.2. Addition of end-reactive polymers generating grafted copolymers (Fig. 5, alternative II)

Koning et al.<sup>[77]</sup> have prepared primary amine end-capped PS (PS-NH<sub>2</sub>) according to a method described by Bronstert<sup>[78]</sup> for the reactive compatibilization of a blend of PPO and SMA with a MA content of 28 wt%. During melt blending the amine end groups of PS-NH<sub>2</sub> react with anhydride groups of the SMA, thereby generating a grafted copolymer SMA-g-PS, the presence of which is confirmed by a careful GPC/LALLS analysis. The generated PS grafts are homogeneously miscible with PPO. In order to obtain tough blends, the PPO phase has been impact modified by SEBS, whose PS blocks are miscible with PPO, and the SMA phase has been toughened by ABS, where the SAN phase is miscible with SMA. So this complex blend consists of a homogeneous SMA/SAN blend containing PB spheres introduced by ABS, and a second phase being a homogeneous PPO/PS phase carrying HPB domains introduced by SEBS. Even in this four component blend, the addition of PS-NH<sub>2</sub> results in a finer phase morphology and in an improved notched Izod impact strength, presumably due to the formation of SMA-g-PS copolymers at the interface between SMA/SAN and PPO/PS. Fig. 12 illustrates the effect of the presence of 10 wt% of PS-NH<sub>2</sub> with  $MW = 37,000$  g/mol on the notched Izod impact strength of a SMA/ABS/PPO/SEBS/PS-NH<sub>2</sub> blend with a weight composition of 35/30/17.5/7.5/10.

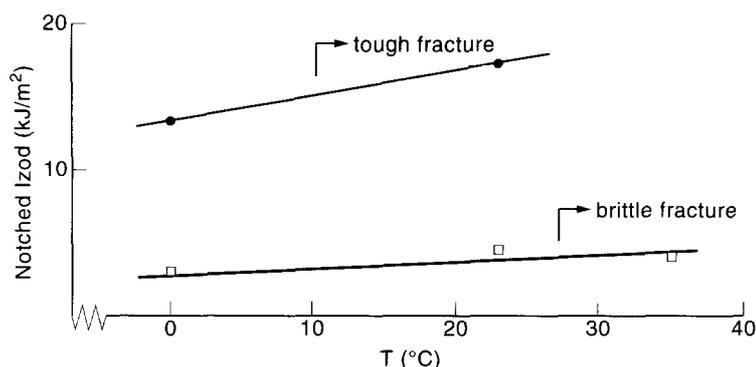


Fig. 12. Temperature dependence of notched Izod impact for SMA/ABS/PPO/SEBS/PS 35/30/17.5/7.5/10 blends. (●) PS—NH<sub>2</sub> with MW = 37,000 g/mol; (□) non-reactive PS with MW = 31,500 g/mol.

### 3.2.2.3. Addition of polymers carrying pendant reactive groups as precursors to grafted copolymers (Fig. 5, alternative III)

Although there are numerous known examples, this approach will be illustrated with a few selected systems only. A Monsanto patent by Lavengood<sup>[79]</sup> describes the free radical copolymerization of styrene (S), acrylonitrile (AN) and maleic anhydride (MA). These terpolymers have been used for the reactive compatibilization of PA 6/ABS blends. During melt blending, the amine end groups of PA 6 chains and the MA groups along the S-AN-MA terpolymer react, generating a grafted copolymer at the interface. The link between the SAN-like main chain and the PA 6 grafts is again a stable imide. Fig. 13 illustrates the influence of the MA content of the added S-AN-MA polymer on the notched Izod impact strength of an ABS/PA 6/S-AN-MA: 50/44/6 blend. Fig. 13 shows a sharp maximum around *ca.* 1 mol% MA in the S-AN-MA additive. It is thought that for lower MA contents, the number of reactive groups in the system is too small to generate a sufficient amount of grafted copolymer. For MA contents exceeding 1 mol%, the number of PA 6 grafts per S-AN-MA main chain may become so high that the PA rich grafted copolymers leave the interface and form a kind of micelle in the PA phase. This phenomenon is nicely illustrated in a drawing by Majumdar et al. (Fig. 14).<sup>[80]</sup> Pendant reactive groups can be introduced into a polymer chain not only by copolymer-ization (like in the aforementioned S-AN-MA example), but also by free radical grafting onto a polymer chain. Numerous examples have been mentioned, both in the patent and the scientific literature. The following example may serve as a representative one. Ide and Hasegawa<sup>[81]</sup> have melt grafted PP with 1.15 wt% of MA in the presence of a peroxide. The addition of 3.6 wt% of this PP-MA to a PP/PA 6 80/20 blend results in a raise of the yield stress from *ca.* 23 MPa for the non-compatibilized blend to *ca.* 38 MPa for the compatibilized blend. At the same time, the elongation at break increases from 5 to 28%.

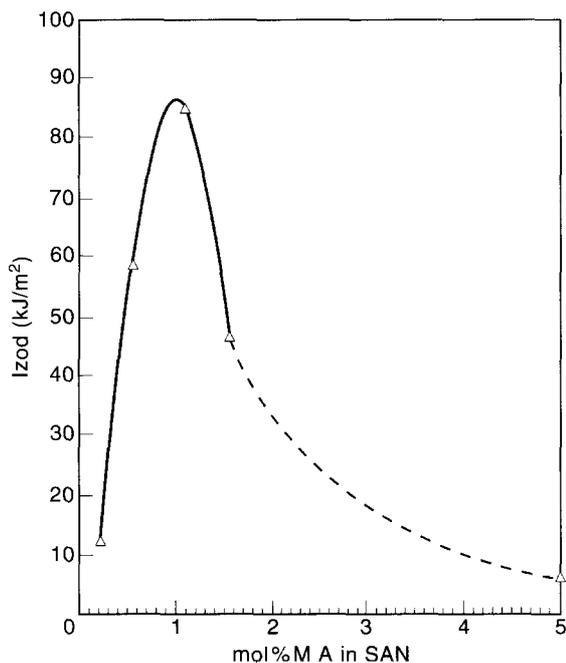


Fig. 13. Effect of MA content of *S-co-AN-co-MA* compatibilizer on notched Izod impact strength for ABS/PA 6/*S-co-AN-co-MA* 50/44/6 blends.

Analysis of the residual amine groups in the PA phase shows a decreasing content with respect to a control blend without PP-MA, indicating the formation of a PP-g-PA 6 copolymer by the earlier mentioned anhydride-amine reaction. Similarly, MA modified EPM, or EPDM have been prepared and used as impact modifiers for polyamides.<sup>[82-84]</sup>

Other reactive and unsaturated monomers, such as glycidylmethacrylate (epoxy functionality), isopropenyl-oxazoline (oxazoline functionality), (meth)acrylic acid (carboxylic acid functionality) are also examples of frequently grafted or copolymerized monomers utilized for reactive compatibilization.

#### 3.2.2.4. Addition of polymers carrying pendant reactive groups as precursors of branched copolymers (Fig. 5, alternative IV)

It is also a valuable strategy to combine a pendant-reactive additive with a pendant reactive blend component (alternative IV in Fig. 5). If the concentration of co-reactive pendant groups is relatively high, a crosslinked network may be formed across the interface.

Datta and coworkers<sup>[85,86]</sup> have described blends of SMA (*MW* of ca. 200,000) containing 8 or 14 wt% of MA (SMA-8 and SMA-14, respectively) and primary amine-modified EPM (EPM-NH<sub>2</sub>) containing 0–3 mol% amine. The latter corresponds to ca. six amine groups per EPM chain. Since both the SMA and the modified EPM contain several pendant reactive groups per polymer chain, a branch/graft copolymer can be formed as shown in Fig. 5. A SMA-8/EPM 70/30 blend is brittle, the notched Izod at 21°C is close to the value for neat SMA-8, being ca. 1.6 kJ/m<sup>2</sup>, and the EPM domains are 25(±15) μm long and 5 μm wide.

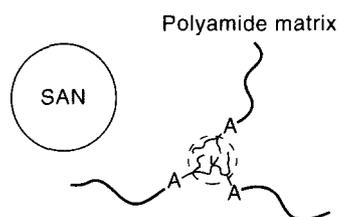


Fig. 14. Schematic representation of the possible migration of SAN-g-PA 6 from the interface towards the PA 6 phase, for *S-co-AN-co-MA* compatibilizers carrying too many

### MA groups per chain.

In sharp contrast, a SMA-8/EPM—NH<sub>2</sub> 70/30 blend has a notched Izod impact strength at 21°C of *ca.* 30 kJ/m<sup>2</sup>. In this toughened blend, the dispersed rubber particles are elongated in the moulding direction, but the length of the particles is much smaller (0.2 to 4 μm). The formation of SMA-branch/graft-EPM has been confirmed by selective solvent extractions. Unbound SMA has been extracted with acetone, and unbound EPM with isooctane. In the insoluble residue, which may be partially crosslinked, imide bonds have been observed by IR spectroscopy. The authors have also reported that the notched Izod impact of a ternary SMA-8/EPM-NH<sub>2</sub>/HDPE 65/20/15 blend is *ca.* 32 kJ/m<sup>2</sup>. Interestingly enough, significant amounts of functionalized EPM can be replaced by non-functionalized HDPE without a detrimental loss of impact.

England et al.<sup>[87]</sup> have described blends of EPDM-g-MA containing 4 wt% of MA, and terpolymers of styrene, AN and {1-methyl-1-[3-(1-methylethenyl)-phenyl]ethyl}, carbamic acid 1,1-dimethylethyl ester (Fig. 15).

In a specific example, 50 wt% of a terpolymer containing 1 mol% of the carbamic acid ester is melt blended at *ca.* 230°C with 50 wt% of EPDM-MA. Extractions show that 7.8 wt% of the carbamate functionalized SAN is chemically linked to the EPDM-g-MA. The reactivity between both blend components can be explained by a decomposition reaction of the carbamate groups during blending, with the release of isobutene and CO<sub>2</sub>. The cumylamine groups then form the well-known imide linkage with the MA grafted EPDM. In a second processing step, 50 wt% of the reaction mixture described above is melt blended with 50 wt% SAN, again at *ca.* 230°C. This SAN/EPDM 75/25 blend thus contains 3.9 wt% of EPDM-bound SAN. This blend has a notched Izod impact strength of *ca.* 43 kJ/m', and the size of the dispersed EPDM particles is 0.5-1 mm. A SAN/EPDM 75/25 blend containing no branch/graft copolymer has a notched Izod impact strength of only *ca.* 1.6 kJ/m<sup>2</sup> and an EPDM particle size of 20 mm.

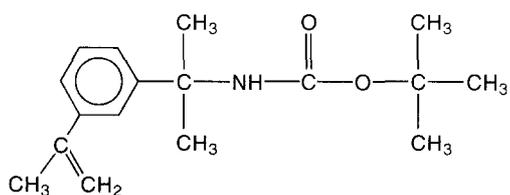


Fig. 15. {1-methyl-1-[3-(1-methylethenyl)-phenyl]ethyl} carbamic acid 1,1-dimethylethyl ester.

### 3.2.3. Commercial blends

It is common knowledge that Noryl GTX<sup>®</sup>, General Electric's PPO/PA 6.6/S(E)BS blend, is compatibilized by reactive processing. It is possible that the method described by Aycock and Ting,<sup>[74,75]</sup> i.e. end-capping of PPO chains with anhydride groups as described in Fig. 8, is applied on a commercial scale. Another possibility is the well documented melt modification of PPO (in combination with an impact modifier) with 0.6-3.1 parts MA. A very tough material results from the blending of the MA modified PPO and an impact modifier with PA 6.6.<sup>[88]</sup> In view of the earlier mentioned Monsanto patent on ABS/PA 6 blends, it is more likely that Monsanto uses S-AN-MA terpolymers to compatibilize the commercially available Triax<sup>®</sup> PA 6/ABS blend. It is known that Monsanto is producing S-AN-MA on a commercial scale (Cadon<sup>®</sup>). In the commercial PP/PA blend of DSM (Akuloy<sup>®</sup>), a PP-g-MA is used as a reactive compatibilizer. DuPont's supertough PA, Zytel ST<sup>®</sup>, is impact modified with MA grafted EPDM.

## 3.3. Addition of low molecular weight chemicals

### 3.3.1. General principles

A completely different strategy for polymer blend compatibilization relies upon the addition of a (mixture of) low molecular weight chemical(s). The actual compatibilizer, a branched, block or grafted copolymer, is formed during a reactive blending process. Various procedures may be distinguished, depending on the added chemical(s):

- a peroxide, that activates inert polyolefins and results in the formation of branched copolymers (Fig. 16a);
- a Afunctional chemical that forms block copolymers (Fig. 16b);
- a mixture of a peroxide and a Afunctional chemical, which leads to the formation of branch/graft copolymers (Fig. 16c and d).

The addition of selective crosslinking agents, reactive towards one blend component only, i.e. dynamic vulcanization, is discussed in Section 3.6, since compatibilization is then achieved not by reducing the interfacial tension, but by freezing in a non-equilibrium morphology.

### 3.3.2. Peroxides and related chemicals

Recently, a seemingly simple and attractive procedure for the compatibilization of polymer blends has drawn some attention. It involves the addition of just one chemical, i.e. a peroxide, to an incompatible blend. Up to now, studies have been limited to rheology,<sup>[89-91]</sup> morphology<sup>[92,93]</sup> and mechanical properties.<sup>[91,93-95]</sup> Thorough analyses of the involved processes and the formed polymer structures have not been published yet. With a PE/PP blend as an example,<sup>[89,90]</sup> it is assumed that the radicals derived from the peroxide activate the chemically inert polyolefins via hydrogen abstraction.

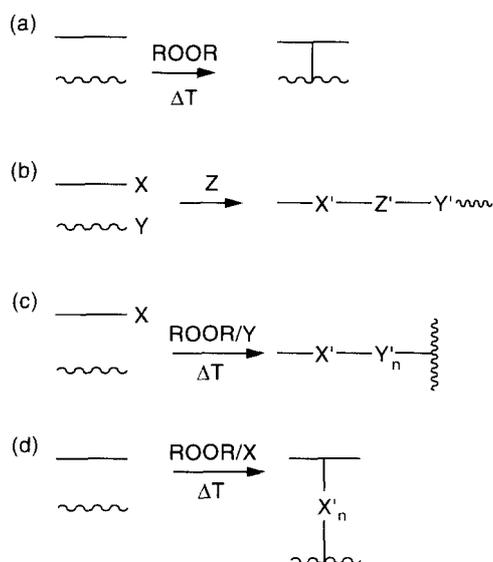


Fig. 16. Addition of low molecular weight chemicals and the type of copolymer formed during the reactive blending process.

In a next step, the PE and PP macroradicals combine and form a branched PE-PP copolymer, which acts as compatibilizer (Fig. 16a). In addition to this in-situ compatibilizer formation, the crosslinking of PE and/or the degradation of PP also occur. These phenomena affect the viscosity match of the two blend components, and thus the blend morphology. In addition, crystallization of the blend components can be affected.<sup>[94]</sup>

This compatibilization strategy seems to be quite simple, but the lack of chemical selectivity is quite a problem. Competition between in-situ compatibilization, crosslinking and degradation makes the control of blend properties very difficult, which is illustrated by the lack of convincing examples in the literature. Grafting, enhancement of phase dispersion and/ or small improvements of properties have been reported for PE/PP,<sup>[89,90]</sup> PE/PS,<sup>[92]</sup> LDPE/ EVA<sup>[94]</sup> and poly( $\beta$ -hydroxybutyrate)/PBA<sup>[93]</sup> blends. Although industrial applications have not been reported yet, this simple compatibilization procedure might find applications in the future for upgrading polymer waste mixtures. Addition of 1 wt% peroxide to a representative LDPE/HDPE/PVC/PS/HIPS/PP/PET: 45/15/15/7.5/7.5/5/5 blend

results in an increase in the unnotched Izod from 133 to 465 J/m, the stress at break from 10.2 to 16.9 MPa and the elongation at yield from 3.9 to 6.8%.<sup>[91]</sup>

No surprising synergy has been reported up to now, except for the study by Radusch et al.<sup>[95]</sup> Indeed, the addition of 1-2 wt% of an organic sulfonylazide, a chemical of a reactivity similar to peroxides, to a PS/PB 80/20 blend results in large improvements of the elongation at break and the impact resistance (Fig. 17). The formation of PS-g-PB copolymers has been demonstrated by selective extractions and IR, whereas the improved blend dispersion has been shown by SEM.

Only when the peroxide is somehow forced to be present at the polymer interface is the chance for grafted copolymer formation maximized, and can blends with significantly improved properties be expected. In this case, Campbell<sup>[92]</sup> has claimed that a peroxide with a silicon tail is effective for the compatibilization of a PE/PS 80/20 blend.

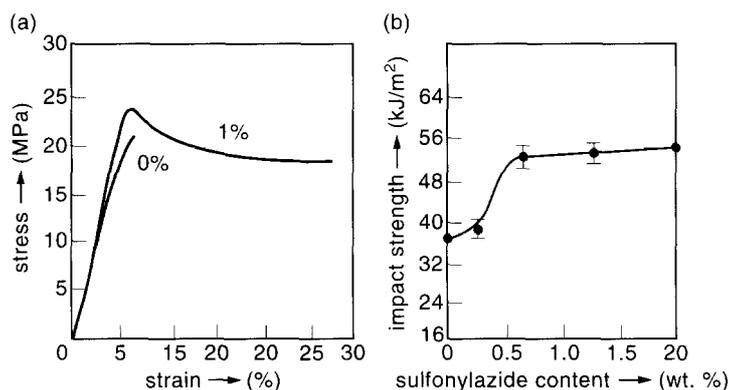


Fig. 17. Effect of an organic sulphonylazide on a PS/PB 80/20 blend: A, stress-strain behaviour (1 wt% sulphonylazide); B, impact strength.

It is argued that the interfacial tension drives this special peroxide towards the PE/PS interface. SEM micrographs show that the addition of this peroxide results in a smaller size of the dispersed phase from 10-12  $\mu\text{m}$  down to 3-5  $\mu\text{m}$  and in the prevention of coalescence. However, no data on mechanical properties are available.

### 3.3.3. Bifunctional chemicals

According to this approach, the low molecular weight, bifunctional chemical forms a chemical link between the two constitutive polymer chains resulting in a block copolymer compatibilizer (Fig. 16b). Two categories of bifunctional chemicals can be distinguished, i.e. those containing two identical functionalities and those with two different reactive groups. The first approach is a chain extension process, since the end groups of two different polymers are linked to each other. Typical examples are the application of bisepoxides, such as bisphenol glycidylethers and cycloaliphatic diepoxides, in PPS/PC, PPS/PA, PC/PA and PA/ polyestercarbonate blends.<sup>[96-99]</sup> The epoxide groups more likely react with the end groups of the various polycondensates, resulting in block copolymers. Maleic anhydride (MA) or citric acid (or its hydrate) are typical examples of chemicals with two different functionalities used to compatibilize PPO/PA(rubber) blends. MA is reactive with the phenolic end groups of the PPO chains (ether formation by addition of hydroxyl to unsaturation or ester formation by reaction with anhydride) and with the amine end groups of the PA chains (addition of amine to unsaturation or reaction with anhydride to imide). As a result, PPO-PA block copolymers are formed at the interface. Extrusion at 290°C of a PPO/PA 6 50/50 blend in the presence of 0.5 wt% MA results in an increase in drop impact strength from below 25 to 46-61 J. <sup>[100]</sup> When citric acid is used instead of MA, extrusion at *ca.* 300°C is thought to result in dehydration of the activated  $\beta$ -hydroxyl group with the formation of unsaturation<sup>101</sup> (Fig. 18). Furthermore, the  $\alpha,\beta$ - or  $\alpha,\gamma$ -dicarboxylic acid moieties are converted to cyclic anhydrides, a well known reaction for succinic, maleic and glutaric acid.

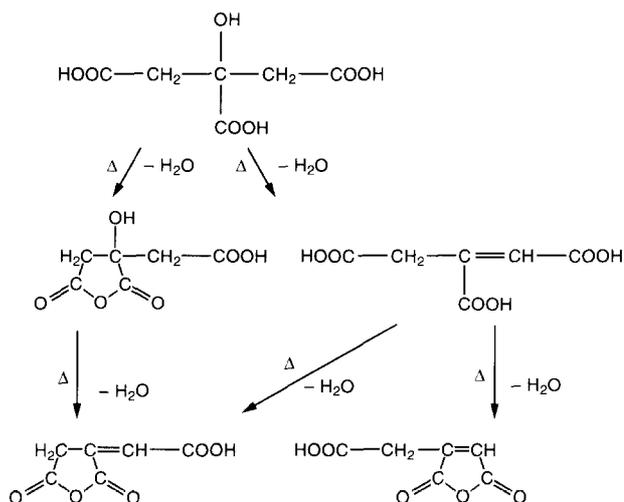


Fig. 18. Dehydration of the activated  $\beta$ -hydroxyl group of citric acid during extrusion with formation of unsaturation,

The (mixture of) chemicals finally produced behave like MA. The addition of 0.25 part citric acid to a PPO/PA 6.6/SEBS 49/41/10 blend results in an increase of the elongation at break from 8 to 33% and a change in the notched Izod impact strength from 4 to 13kJ/m<sup>2</sup>.<sup>[102]</sup>

### 3.3.4. Mixtures of peroxides and multifunctional chemicals

The compatibilization routes discussed in Section 3.3.2 and Section 3.3.3 can be advantageously combined. A peroxide is used to activate the reaction between one polymer and at least one of the functionalities of the chemical. The multifunctional chemical ultimately links the constitutive polymer chains in branch/graft copolymers, which is the actual compatibilizer (Fig. 16c and d, respectively). Unsaturated chemicals, such as styrene,<sup>[103,104]</sup> hydroxypropylmethacrylate,<sup>[105]</sup> triallyl isocyanurate,<sup>[103,106]</sup> an undefined silane<sup>[104]</sup> or a low molecular weight unsaturated rubber<sup>[104]</sup> have been used in combination with suitable peroxides for the compatibilization of PS/PE blends. The two polymers are activated by hydrogen abstraction and are finally linked to each other through oligomers/polymers of the unsaturated chemical. Formation of the compatibilizer has been confirmed by toluene extraction of PS and by reductions in particle size.<sup>[104]</sup> A combination of a peroxide with unsaturated monomers is actually identical to the peroxide/coagent systems, which are frequently used for the crosslinking of polyolefins, such as EP(D)M or PE and unsaturated polyesters. For all these systems, the main advantage over adding just the peroxide is an increase in the reaction rate and in the efficiency of the peroxide. However, as for compatibilization just by adding peroxides, this strategy suffers from a lack of chemical selectivity and the improvement in properties is not remarkable. A branched copolymer structure is also expected to result from the addition of hydroquinone(HQ)/peroxide to LDPE/PP blends.<sup>[107]</sup> Hydrogen abstraction from the polymer chains and from HQ molecules provides various radicals that contribute to PE-PP branching through HQ linking units. The HQ/peroxide system is rather unusual, since it does not involve PP chain scission, but rather PP (crosslinking).<sup>[108]</sup> The chemical nature of this route closely resembles the action of phenolic antioxidants for the stabilization of polyolefins and the use of HQ as a scorch retardant in the course of PE or EPDM crosslinking by peroxide. For a LDPE/PP 50/50 blend, the impact strength dramatically increases from 13 to at least 110 kJ/m<sup>2</sup> upon addition of a HQ/ peroxide 3/0.5 mixture. The three-point bending test with notched samples shows that the deformation, when the crack starts to grow, increases from 1.4-1.7 mm up to 6.3-10.0 mm. The subsequent rate of notch growth decreases from 0.95-1.5 mm/s to 0.11-0.21 mm/s. Mixtures of MA and a peroxide have been used for the compatibilization of blends of PA 6 or PA 11 with PE, PP or EPM.<sup>[109,110]</sup> The peroxide is only needed to activate the polyolefin, which

subsequently reacts with the unsaturation of MA (Fig. 16d). The reaction of the grafted anhydride and PA, results in a polyolefin-PA grafted copolymer, as described in Section 3.3.3. Actually, this route for the compatibilization of PA blends can be seen as a single step procedure, combining the preparation of a MA grafted polyolefin with the subsequent, reactive blending of PA. Addition of only 0.1/0.02 MA/peroxide to a PA 6/EPM 80/20 blend is responsible for a severe reduction of the particle size of the EPM dispersion down to *ca.* 1  $\mu\text{m}$ . This observation is consistent with the increase of the notched Izod impact strength to values above 60  $\text{kJ/m}^2$  (cf. Section 3.3.3). Problems of process and product reproducibility may explain why this one-step compatibilization procedure has not yet replaced the common, industrial two step grafting/blending process.

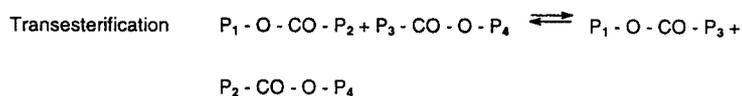
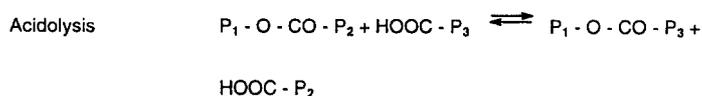
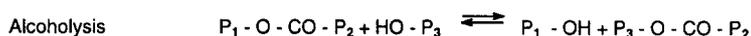
### 3.4. Interchange reactions

#### 3.4.1. Interchange chemistry

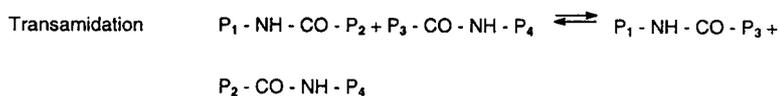
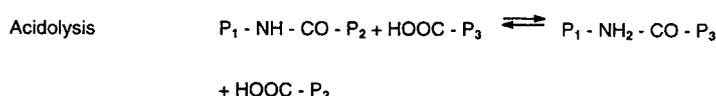
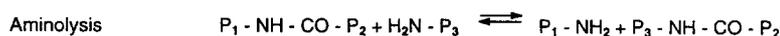
When two or more polycondensates are blended in the melt, several interchange reactions can occur to an extent that depends on type of polymers, nature and concentration of the reactive groups (either in the main chain or as end-groups), blending temperature, moisture content, residence time in the melt and the presence and concentration of an interchange catalyst. Fig. 19 shows the possible interchange reactions during the melt blending of two polyesters (PEs), two polyamides (PA) and a polyester and a polyamide (PEs + PA). In Fig. 19, the -O-CO- bond stands for both an ester and a carbonate bond (-O-CO-O-).

Wilfong<sup>112</sup> has reported numerous interchange catalysts. In the case of polyesters, tetra-butoxy titanate has proved to be a very active catalyst,<sup>[112]</sup> whereas, for example, aromatic phosphites are recommended for transreactions between polyamides." During melt blending, complete interchange with formation of a random copolycondensate can occur at high processing temperatures (e.g. > 300°C), for long residence times in the melt (sometimes even several hours) and/or in the presence of interchange catalysts. Usually this outcome is undesirable, because the amorphous product has lost the beneficial properties of both blend components. More useful is the approach that limits the interchange reactions to a small extent, i.e. to the point where only a small amount of block copolymer is formed during melt blending at the interface of two immiscible polycondensates. This process requires relatively low processing temperatures, rather short residence times in the melt and only traces of catalyst, if any. Then, the physical properties of both blend components, such as crystallinity, are retained.

PEs + PEs



PA + PA



PEs + PA

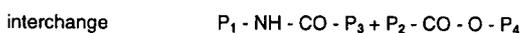
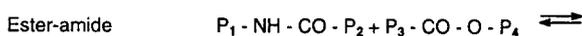
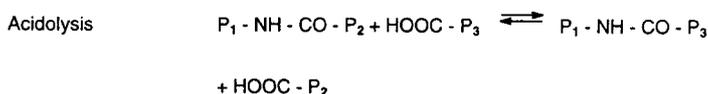
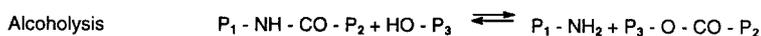
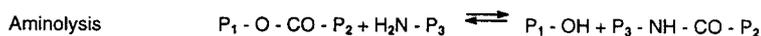


Fig. 19. Interchange reactions between polycondensates.

### 3.4.2. Compatibilization via interchange reactions

For an extensive review of the interchange reactions in polyesters, the reader is referred to a paper by Porter and Wang.<sup>[114]</sup> Transamidation reactions between two PAs have been studied by, for example, Kricheldorf,<sup>[115,116]</sup> whereas Kotliar<sup>[117]</sup> has written an excellent general review paper on interchange reactions involving condensation polymers. The work by Pillon and Utracki<sup>[118,119]</sup> nicely demonstrates the efficiency of compatibilization by (limited) interchange reactions. Equimolar blends of PET and PA 6.6 were prepared in a twin screw extruder. 0.2 wt% of *p*-toluene sulphonic acid (*p*-TSA) was used as an ester-amide interchange catalyst with a residence time of 4 min at 305-325°C and 10 r.p.m. This resulted in 2.3% interchange product, as determined by <sup>1</sup>H NMR. No copolymer was detected under the following processing conditions: no *p*-TSA, 10r.p.m. at 310-330°C for 4 min, and 0.2 wt% *p*-TSA, 10 r.p.m. at 290-310°C for 4 min. The neat equimolar PET/PA 6.6 blend consists of PA 6.6 spheres with a diameter up to 14 μm in a PET matrix. Limited interchange reactions (a few

percent) reduce the maximum PA 6.6 particle size down to 8  $\mu\text{m}$ . The enhancement of the elongation at break is however disappointing. In a non-reacted PET/PA 6.6 90/10 blend, the diameter of the dispersed PA 6.6 spheres is 0.5-5  $\mu\text{m}$ , which is reduced to at most 0.2  $\mu\text{m}$  as result of ca. 2% interchange. So, although the enhancement of mechanical properties is only marginal, compatibilization of PET/PA 6.6 blends by ester-amide interchange reactions is clearly demonstrated. The work by Eguizabal et al. [120] on a PAr/PET 50/50 blend, prepared by coprecipitation from a phenolic solution into methanol, and reacted for 0-90 min at 297°C, is also worth mentioning. Fig. 20 illustrates the solubility of these blends in chloroform as a function of the residence time. PAr is soluble in chloroform, whereas PET is not. For reaction times shorter than 20 min, the solubility is rather poor because of the formation of block copolymers containing long PET blocks, which are insoluble in chloroform. After a few minutes of reaction, the chloroform insoluble part already contains PAr-parts (FT-IR analysis). For longer reaction times, multiblock copolymers with shorter PET blocks or even random copolymers are generated, and the solubility is increased.

### 3.4.3. Commercial blends of polycondensates

In commercial blends of polycondensates, transreactions are carefully controlled, or even prevented. Examples of commercial blends of polycondensates are PET/PBT (Valox<sup>®</sup> 800), PC/PET (Makroblend<sup>®</sup>) and PC/PBT (Xenoy<sup>®</sup>), the latter being used in car bumpers. By nature, PC and PBT are partially miscible, so that additional interchange reactions promoted by the tetrabutoxytitanate polymerization catalyst present in the PBT are undesirable. These ester-carbonate transreactions would deteriorate both the toughness of PC and the gasoline resistance provided by crystallinity of PBT. PC/PBT blends are stabilized with respect to interchange reactions by blocking the titanate catalyst, particularly by phosphorous containing compounds, such as  $\text{NaH}_2\text{PO}_4$  and diphenylphosphite. [121] Van der Velden et al. [122] have demonstrated the stability of Xenoy<sup>®</sup> CL-100 by  $^{13}\text{C}$  NMR and FT-IR. Transesterification products are not detected in this commercial blend. After 16 h at 270°C, some ester-carbonate interchange reactions are observed.

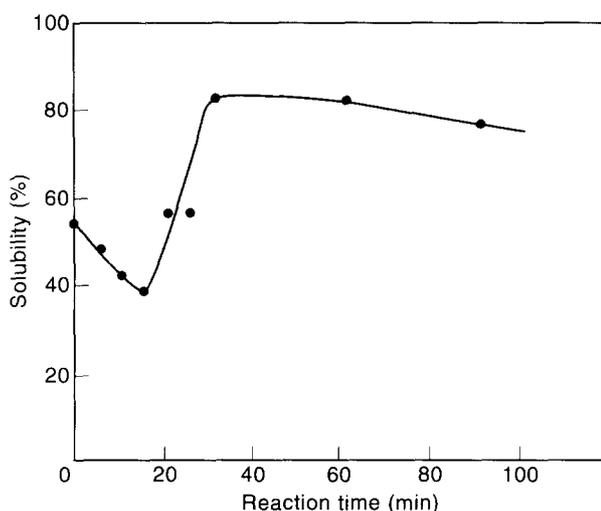


Fig. 20. Time dependence of solubility in chloroform for a PAr/PET 50/50 blend treated at 297°C.

### 3.5. Mechanochemistry

During the melt processing of polymers in kneaders or extruders under high shear forces, mechanodegradation can occur, i.e. chain scission resulting in polymer chains with radical sites at the chain ends. Moreover, macroradicals can be formed at high processing temperatures and/or in the presence of oxygen due to thermal and/or oxidative degradation. The various polymer radicals may recombine or add to unsaturated bonds when present. Mechanodegradation might be advantageous for specific polymer blends, since it can result in compatibilization without adding any additional polymers or chemicals. Macroradicals of the two immiscible polymers can cross-combine at the interface and

form grafted- or block copolymers. In this sense, compatibilizer formation via mechanodegradation is similar to the addition of a peroxide (cf. Section 3.3.2; Fig. 16a).

Since elastomers are rather prone to mechanodegradation ("mastication"), this compatibilization technique is usually studied for rubber/rubber or thermoplastic/rubber blends; the latter especially for toughening the thermoplastic. Casale and Porter<sup>[123]</sup> have reviewed these applications for a variety of blends, such as those of NR or PS with PB, NBR or SBR. Mastication of blends based on thermoplastics only (PE, PS and PMMA) has been shown to result in three-dimensional, intertwined networks of homopolymer strands with diameters of 1 -50  $\mu\text{m}$ .<sup>[124]</sup> These structures are largely unaffected by annealing. Although compatibilization can be carried out, the practical potential of this approach is questionable.

### 3.6. Addition of selective crosslinking agents

#### 3.6.1. Principles of dynamic vulcanization

Compatibilization of blends by the addition of low molecular weight chemicals (Section 3.3) requires that both blend components participate in chemical reactions. Branched, grafted or block copolymers are formed, which affect the development of the blend morphology by reducing the interfacial tension.

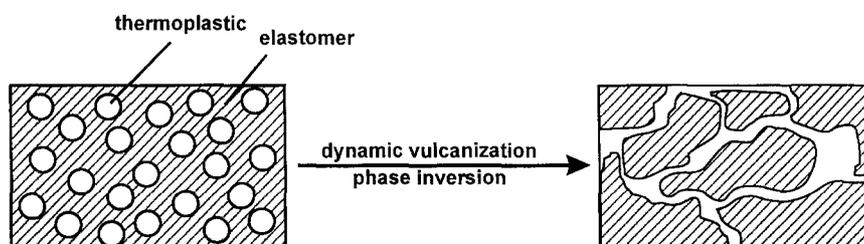


Fig. 21. Morphology of a thermoplastic/rubber blend before and after dynamic vulcanization.

However, when blend compatibilization by crosslinking is concerned, only one of the blend components may react, otherwise a fully crosslinked material is obtained, which has no thermoplastic properties and cannot be processed after production. Dynamic vulcanization, i.e. the selective crosslinking of the dispersed phase, prevents it from undergoing coalescence, which of course affects the kinetics of the blend morphology development. For blends of polymers with similar polarities, a fine morphology is frozen in during dynamic vulcanization and no additional compatibilizer is needed (Section 3.6.2). Dynamic vulcanization of incompatible blends results in a coarse morphology. Therefore, useful blends with a fine morphology require the addition of an extra compatibilizing agent (Section 3.6.3).

Dynamic vulcanization is frequently applied to the compatibilization of blends containing a rubber as the main blend constituent in combination with a (semi-)crystalline thermoplastic. Since an excess of rubber is used and the viscosities of the thermoplastic and the rubber at the processing temperature do not deviate too much, the physical blend is a dispersion of the thermoplastic in a rubber matrix (Fig. 21). Upon addition of the crosslinking agent, the viscosity of the rubber phase increases and at a sufficient degree of curing phase inversion occurs.<sup>[125]</sup> In the plot shown in Fig. 1, this modification corresponds to a vertical cross-section through the co-continuous regime. The high degree of crosslinking of the rubber phase inhibits the processes of strand break into smaller particles, the reduction of interfacial area by formation of smooth spheres and also the coalescence of the dispersed particles. As a result, the dispersion in a thermoplastic/rubber dynamic vulcanizate is very irregular (Fig. 21). The thin thermoplastic layers between the crosslinked rubber particles are somehow elastic and act as a kind of glue between the crosslinked rubber domains.<sup>[126]</sup>

Thermoplastic/rubber dynamic vulcanizates combine thermoplastic and elastic properties as a result of the final morphology, and are superior to thermoset rubbers obtained by static vulcanization, with respect to processability and recycling. These blends are called thermoplastic vulcanizates (TPVs) and belong to the same class of thermoplastic elastomers (TPEs) as, for instance, hard/soft segmented block copolymers and elastomeric ionomers.

### 3.6.2. Dynamic vulcanization of PP/EPDM blends

Sulphur/accelerator combinations, the most abundant crosslinking systems for static vulcanization of elastomers, have been demonstrated to be applicable to dynamic vulcanization of PP/EPDM blends.[127]

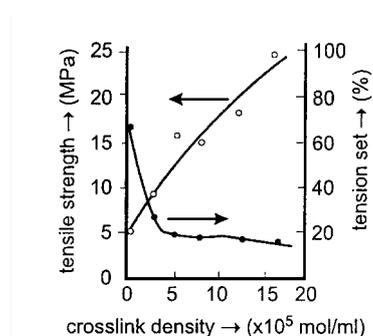


Fig. 22. Effect of crosslink density of the EPDM phase on tensile strength and tension set for PP/EPDM 40/60 blends dynamically vulcanized with a sulphur cure system .

An increase in the amount of sulphur from 0 to 2.0 phr in combination with a standard zinc oxide/stearic acid/tetramethyl thiuramdisulphide/ mercaptobenzothiazole vulcanization recipe has resulted in a dramatic improvement of the elasticity of a PP/EPDM 40/60 blend. The tensile strength increases from 4.9 to 24.3 MPa, the elongation at break increases from 190 to 530% and the tension set decreases from 66 to 16% (Fig. 22). However, sulphur crosslinking systems are not used in commercial PP/EPDM TPVs, since PP has a relatively high melting point and the crosslinks lack thermal stability. Moreover, the production and processing of these TPVs suffer from severe stench problems. In the case of PP based TPVs, PP degradation by  $\beta$ -scission may be initiated by the peroxide/ coagent cure system and this results in inferior properties.

A specific crosslinking system, i.e. PF resins prepared at high pH (resoles), is used in the commercial PP/EPDM dynamic vulcanization. The main reasons for using these crosslinking agents are their activities at temperatures above 200°C and the formation of thermally stable carbon-carbon bonds. Usually catalysts are added, such as stannous chloride dihydrate or a halogen donor, for instance PVC or CPE, in combination with zinc oxide. The acidity of these catalysts allows the ether linkages and/or the alcohol end groups of the resole to be activated. The chemical structure of the crosslinked rubber has recently been elucidated by using low molecular weight models, and was shown to consist mainly of mono- and bisphenol units linked to the elastomer by methylene or cyclic chroman bridges.[128] Dynamic vulcanization of a PP/EPDM blend by increasing the amounts of resole results in improvements of tensile strength and, to a lesser extent, of elongation at break.[129]

In addition to the selective crosslinking of the rubber phase, a small rubber particle size of *ca.* 1-2  $\mu\text{m}$  is required for optimum TPV properties. An increase of the blending shear rate from 300 to 1400  $\text{s}^{-1}$  in the dynamic vulcanization of a PP/EPDM 40/60 blend with a resole has resulted in a decreased size of the dispersed, crosslinked EPDM phase and thus in an increased tensile strength from 13 to 15 MPa and an increased elongation at break from 390 to 490%.[125]

### 3.6.3. Dynamic vulcanization and in-situ compatibilization of immiscible blends

The continuous use temperature (CUT) of TPVs depends on the melting point of the thermoplastic phase. PP/EPDM TPVs are usually used up to 120°C. Other (semi-)crystalline thermoplastics, such as PAs or polyesters, have been studied in order to increase the CUT of TPVs.

Table 2. Effect of dynamic vulcanization using a peroxide cure and/or addition of a EPM-g-MA compatibilizer on the properties of a PA 6/EP(D)M 50/50 blend

Rubber phase composition (wt%)		Peroxide (phr)	Tensile strength (MPa)	Elongation at break (%)	Hardness Shore D
EP(D)M	EPM-g-MA				
50	0	0	4.6	25	27
50	0	10	11.1	35	52
25	25	10	18.7	200	49

EPDM, which is used for good thermal and oxidative stability, is however immiscible with the PAs or polyesters. Therefore, an additional, compatibilizing agent is needed for optimum TPV properties. EP(D)M-g-MA is usually added to dynamically vulcanized PA/EPDM blends. The in-situ formation of EP(D)M-PA grafted copolymers as compatibilization agents has been explained in Section 3.2.2. Resoles cannot be used in PA/EPDM blends, since not only the EPDM phase, but also the PA phase is crosslinked. Usually, these blends are peroxide cured. The beneficial effects of dynamic vulcanization together with an additional compatibilizer are illustrated in Table 2 for a PA 6/EP(D)M 50/50 blend.<sup>[130]</sup> A similar approach has been used in case of a polyester based TPV.<sup>[131]</sup> Optimum properties are obtained, when EPDM grafted with glycidyl methacrylate (GMA) is used for compatibilization with PBT, and a peroxide is added for dynamic vulcanization: a tension set of 15% is observed for a PBT/EPDM-g-GMA 50/50 blend with 0.5 wt% peroxide.

PP/NBR blends, dynamically vulcanized with resole, have been developed as oil resistant TPVs.<sup>[132]</sup> Various routes for compatibilization have proved to be successful. The addition of a resole modified PP has some beneficial effects, especially in combination with the substitution of part of the NBR by an amine terminated NBR. Other routes for compatibilization are the in-situ formation of PP-NBR grafted copolymers from PP-g-MA and amine terminated NBR or from PP containing amine functionalities and carboxylic acid terminated NBR. A last alternative is the application of chlorinated PP in combination with some amine terminated NBR. Optimum TPVs have tension set of 40-50%, elongation at break of 150-400% and tensile strength of 15—25 Mpa.

#### 3.6.4. Commercial examples

It is thought that TPEs (with TPVs as one of the main representatives) have a future, due to advantages over the classical thermoset rubbers regarding recycling and thermoplastic processing, e.g. injection moulding. It has been argued that TPEs cannot compete with thermoset rubbers, particularly with respect to elastic properties, such as compression set. However, it is now accepted that a large number of thermoset rubber applications are overspecified and in the long term TPEs might take over. It must be noted that TPEs are the fastest growing part of the elastomer market (12% per year). The world use of TPVs in 1995 was about 60 kton.

The most important, commercially available, dynamic vulcanizates are those based on compatible PP/EPDM blends as produced by AES (Santoprene<sup>®</sup>), DSM (Sarlink<sup>®</sup> 3000 and 4000), Softer SpA (Forprene<sup>®</sup>), Himont (Dutralene<sup>®</sup>) and Mitsui (Milastomer<sup>®</sup>). A whole range of grades of varying hardness is made available by changing the PP/EPDM ratio and adding an extender oil. These TPVs offer a good performance/price compromise. Typical applications of PP/EPDM TPVs are automotive, window and door profiles, grips for tools and small industrial and medical rubber parts, such as tubes, seals, stoppers etc. PP/NR TPVs are sometimes applied as a low cost alternative for PP/EPDM TPVs (AES: Vyram 6000<sup>®</sup> and Vitacom: DVNR<sup>®</sup>). In addition to these general purpose TPVs, special types have been developed. Commercially available examples include PP/NBR TPVs with improved oil resistance (AES: Geolast<sup>®</sup>), PVC/NBR TPVs with excellent oil resistance (DSM: Sarlink<sup>®</sup> 1000 and LVM: Marvylex<sup>®</sup>) and PP/PIB TPVs with low gas

impermeability (AES: Trefsin<sup>®</sup>; DSM: Sarlink<sup>®</sup> 2000). TPVs based on incompatible thermoplastic/rubber blends are not commercially available.

### 3.7. Introduction of specific interactions

#### 3.7.1. Influence of specific interactions on compatibility

Achieving compatibility via specific interactions differs from the compatibilization strategies discussed in the preceding sections. Specific interactions are introduced into the blend by chemical modification of the blend components with suitable functional groups. No third polymeric or low molecular weight material is added to the polymer blend.

It has previously been discussed that introduction of specific interactions between polymer chains results in a change in the enthalpy of mixing. In addition, a drop in the interfacial tension and an increase in the interphase thickness are observed. Even for polymer combinations with very large differences in polarity, a certain degree of compatibility between the two phases can be induced, resulting in a refinement of the phase morphology. When the interaction energy is too high and not localized, the interfacial tension may decrease to the point where molecular miscibility is observed. This demonstrates that specific interactions operate via a different mechanism than the addition or in-situ formation of block or grafted copolymers. Both the number of interactions per polymer chain and the strength of the individual interactions are of importance. The energy of interaction between polymer units increases in the following order: van der Waals interactions < dipole-dipole interactions < electron donor-acceptor complex formation  $\approx$  hydrogen bonding  $\approx$  ion-dipole interactions < ion-ion interactions. The five Coulombic types of interaction correspond to increased electron or proton transfer between donor and acceptor sites, and so to increased charge separation. The effects of the various types of non-bonding interactions on polymer blends is discussed below.

#### 3.7.2. Electron donor-acceptor complex formation

PECH/PPO blends have been compatibilized by grafting electron donor and acceptor groups onto the original polymers.<sup>[133]</sup> Carbazolyl donor groups have been attached to PPO and 3,5-dinitrobenzyl acceptor groups to PECH. When the functionalization degree exceeds 25 mol%, DSC analysis indicates complete miscibility (one  $T_g$ ). Mechanical properties and compatible, heterogeneous blends have not been studied.

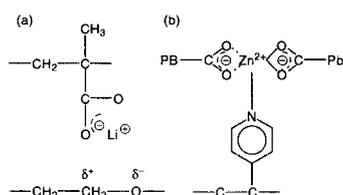


Fig. 23. Compatibilization via ion-dipole interactions.

#### 3.7.3. Hydrogen bonding

Blends of the commodity polymer PS are of commercial interest. The compatibility of PS with a variety of hydrogen acceptor containing polymers, such as PMMA, PEMA, SAN, PC, PPO, PVME, PSU, PET, PAs and PDMS can be improved by the copolymer-ization of styrene with *p*-(hexafluoro-2-hydroxy-isopropyl)styrene.<sup>[134]</sup> The electron withdrawing effect of the six fluorine atoms results in a relatively strong acidic character of the hydroxyl group. As a result, the hydrogen bonding of this modified PS with hydrogen acceptor containing polymers is possible, resulting in complete miscibility for PS with a high hydroxyl content (one  $T_g$  and transparent films). For lower hydroxyl contents, partially miscible or compatible, heterogeneous blends are expected to be formed. These have not been studied.

### 3.7.4. Ion-dipole interactions

Eisenberg et al. have been particularly active in polymer blend compatibilization via the introduction of ionic interactions (see also Section 3.8). They have studied for instance incompatible PS/PEO and PS/PPrO blends. The copolymerization of styrene and methyl-methacrylic acid and the subsequent neutralization of the methacrylic acid units of SMAA with lithium hydroxide results in ion-dipole interactions (Fig. 23a), which enhance miscibility as demonstrated by DMA.<sup>[135,136]</sup> The cloud point curve is shifted towards higher temperatures when the degree of interaction is increased by the addition of more salt and/or salts with a smaller cation. Again, careful control of the polymer modification is expected to provide immiscible polymer blends with some compatibility and improved mechanical properties.

Compatibilization of PS/PB blends is achieved by the functionalization of both blend components, e.g. by copolymerization of styrene with a few mol% 4-vinylpyridine (VP) and the preparation of  $\alpha,\omega$ -carboxylic acid PB.<sup>[137]</sup> The PB carboxylic acid end groups are neutralized with zinc ethoxide and the parent zinc carboxylates are coordinated to the pyridine moieties of VP (Fig. 23b). The DSC shows a third  $T_g$  in between the  $T_g$ s of the two blend components, which suggests the formation of an interphase between the two immiscible phases. The mechanical properties of these materials have not been studied.

### 3.7.5. Ion-ion interactions

Ion-ion interactions have been used to compatibilize PS/PEA 50/50 blends.<sup>[138,139]</sup> Styrene has been copolymerized with sulphonated styrene and poly(ethylacrylate-co-VP) has been used instead of PEA. Since sulphonic acid is a strong acid, not just hydrogen bonding but proton transfer from the sulphonic acid to VP occurs with the formation of vinylpyridinium sulphonate salts.

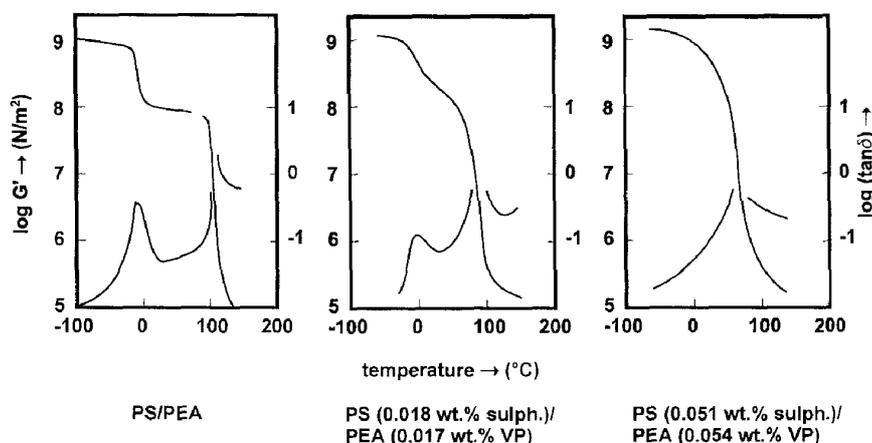


Fig. 24. Effect of PS sulphonation and ethylacrylate copolymerization with 4-vinyl-pyridine upon the temperature dependence of shear storage modulus ( $G'$ ) and loss angle ( $\tan \delta$ ) for a PS/PEA 50/50 blend.

Upon increasing the degree of functionalization of both polymers, the incompatible PS/PEA blend (two  $T_g$ s) changes into a partially miscible blend (two  $T_g$ s shifted towards the  $T_g$ s of PEA and PS) and, finally, into a miscible blend (single  $T_g$ ) (Fig. 24). The same approach has been used for compatibilization of poly(styrene-co-sulphonated styrene)/ poly(methylacrylate-co-VP)<sup>[140]</sup> and poly(styrene-co-VP)/sulphonated PI blends.<sup>[138]</sup> Again, the mechanical properties have not been measured.

Similarly, solution cast mixtures of telechelic polymers end-capped with tertiary amines and telechelic polymers terminated by either sulphonate or carboxylate moieties have a morphology that closely resembles that seen in block copolymers formed by the covalent bonding of the two dissimilar chain segments.<sup>[141]</sup>

### 3.8. Addition of ionomers

#### 3.8.1. Compatibilization using ionomers

Ionomers are polymeric species carrying a relatively low number of pendant ionic groups per molecule. Usually, the ionic groups result from neutralization of sulphonic acid or carboxylic acid groups. Either monovalent (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ) or divalent (e.g.  $\text{Zn}^{2+}$ ) metal cations are used as counterions. Sulphonic acid or carboxylic acid groups are introduced into the polymer chains by copolymerization or chemical modification of existing polymers. Whatever the cation, the ionic groups tend to associate into multiplets, which at sufficiently high concentrations can associate into clusters. Multiplets and clusters act as physical crosslinks between polymer chains. At elevated temperatures, these ionic crosslinks become reversible. Now, if two different ionomers, based on two different and immiscible polymers, are intensively mixed in the melt, the ionic domains may reorganize. The newly formed clusters may contain ionic species of both immiscible polymers. As a result, branched copolymers in which the link between both polymer chains is an ionic bond, are generated at the interface, and a stable compatibilized multiphase blend is generated. As in case of the addition of premade block or grafted copolymers or reactive compatibilizers, limited amounts of ionomers based on polymers A or/and B are required for the compatibilization of a polymer A/ polymer B blend. If both blend components A and B are apolar, such as PPO and EPDM, then both PPO and EPDM based ionomers are required for compatibilization. However, if one of the blend components contains highly polar groups, such as PA in a PE/PA blend, then the addition of a PE based ionomer should be sufficient for obtaining a compatible blend since the interactions between the ionic groups of PE and the polar functional groups of the polyamide are strong enough to generate a kind of a grafted copolymer at the interface.

#### 3.8.2. Representative examples

Two examples are discussed below, which clearly illustrate the principle of ionomeric compatibilization. Various studies<sup>[142-144]</sup> describe the compatibilization of blends of PS, PPO and the EPDM based ionomer  $\text{EPDM-SO}_3^-(\text{Zn}^{2+})_{1/2}$  by the addition of a PPO based ionomer  $\text{PPO-SO}_3^-(\text{Zn}^{2+})_{1/2}$ . Because of the miscibility of PPO and PS, a PS based ionomer can be used as well. Both zinc stearate and triphenyl phosphate are added as plasticizers, in order to facilitate the redistribution of the ionic crosslinks in both the PPO and the EPDM based ionomers. In a specific patent example, 52 parts of PPO, 13 parts of  $\text{PPO-SO}_3^-(\text{Zn}^{2+})_{1/2}$ , 23.3 parts of PS, 11.7 parts of  $\text{EPDM-SO}_3^-(\text{Zn}^{2+})_{1/2}$ , 11.7 parts of zinc stearate and 18.2 parts of triphenyl phosphate were melt blended in a twin screw extruder up to 270°C. Test bars show a notched Izod impact strength of *ca.* 50 kJ/m<sup>2</sup>. The PPO ionomer provides the dispersed EPDM particles with a rather uniform diameter between 0.2 and 1.5 µm. In comparison with a control blend without  $\text{PPO-SO}_3^-(\text{Zn}^{2+})_{1/2}$  and consisting of 55 parts of PPO, 36.7 parts of PS, 8.3 parts of  $\text{EPDM-SO}_3^-(\text{Zn}^{2+})_{1/2}$  and the standard amount of plasticizers, the compatibilized blend shows a reduced tendency to delamination. The notched Izod impact of the non-compatibilized blend is extremely low, i.e. 1 kJ/m<sup>2</sup>, which is 50 times lower than in the case of the PPO ionomer addition. Although, the composition of both blends is not entirely the same, the improvement in toughness is impressive.

So far, the compatibilization of a blend of two apolar polymers (PPO and EPDM) requires two different types of ionomers. The last example in this paragraph however concerns a blend of PE and PA 6.6. In this case, only a PE based ionomer is required because the ionic groups sufficiently interact with the polar functional groups of PA6.6. According to a DuPont patent,<sup>[145]</sup> a PA 6.6/PE 80/20 blend exhibits a notched Izod impact strength of *ca.* 3 kJ/m<sup>2</sup>, whereas a PA 6.6/PE/Surlyn® 80/15/5 blend has a notched Izod impact value of *ca.* 7 kJ/m<sup>2</sup>. The Surlyn® used in this example is a commercially available ethylene-methacrylic acid based ionomer with the structure illustrated in Fig. 25.

Although ionomers are commercially available, to our knowledge no commercial blends consisting of a matrix-dispersed phase or a co-continuous two-phase morphology have been compatibilized by ionomers. Sometimes, Surlyn® is used as an impact modifier for polyamides.

### 3.9. Addition of a third polymer (partially) miscible with all blend phases

#### 3.9.1. General principles

This section considers the case where a polymer C is (partially) miscible with the two constitutive polymers (A and B) of a two-phase binary blend.

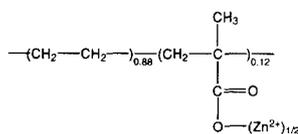


Fig. 25. Commercially available ethylene-methacrylic based inomer used in blending studies.

C is actually a common solvent for A and B, and it can accordingly promote the complete or the partial miscibility of the originally immiscible polymers. This strategy may thus be a convenient way to produce a variety of potentially useful blends. Indeed, the two-phase morphology can be preserved in a certain domain of composition, although the interface characteristics then depend on the composition of the segregated phases. Otherwise, a monophasic ternary blend is formed, whose properties are dictated by the blend composition. The knowledge of the phase diagram of the ternary blends is more than helpful to know the composition range in which phase separation occurs and monophasic material is formed. The characterization of the ternary blends by dynamic mechanical analysis might be instrumental for this purpose, particularly if the characteristic transition temperatures of A, B and C are sufficiently different from each other. Most often the binary interaction parameters,  $B_{ij}$ , (where  $i$  and  $j$  refer to the A, B and C polymers) are determined, e.g. by the melting point depression in case of a semi-crystalline polymer (PCL, refs. [146,147]), and used to predict the phase diagram. The authors assume that the free energy of mixing can be approximated to the heat of mixing, since the entropic contribution is negligible if the molecular weight of the blended polymers is high. Eqn (6) is the usual expression for  $\Delta H_{mix}$ .

$$\Delta H_{mix}/V = \sum_i \sum_j B_{ij} \phi_i \phi_j \quad (6)$$

where  $\phi_i$  is the volume fraction of species  $i$  in the multicomponent mixture and  $V$  is the system volume.  $\Delta H_{mix} = 0$  is then the thermodynamic criterion for the boundary between the single phase domain and multiphase systems. The choice of polymers A, B and C is such that the binary interaction parameter is negative for the A/C and B/C pairs and positive for the A/B pair. The relative magnitude of the binary A/C and B/C interaction parameters determines the shape (symmetry) and position of the boundary curve between monophasic and multiphase blends in the phase diagram. A ternary blend of PC (A), Phenoxy (B) and PCL (C)[148] is an example where B interacts more strongly with C than A does, as a result of hydrogen bonding between B and C.[149] This suggests that the transition from two-phase blends to monophasic blends will occur upon the addition of smaller amounts of PCL in case of PC/Phenoxy blends rich in Phenoxy. Shah et al. [150] have compared the compatibilization efficiencies of various polyesters PBAD, PCDS and PCL in binary blends of PC and SAN. They have concluded that these polyesters are more effective in solubilizing SAN (25% AN)-rich blends compared to PC-rich blends, in agreement with the stronger SAN-polyester interactions than the PC-polyester interactions. The solubilization efficiency has also been observed to decrease from PCDS to PBAD and finally to PCL. As a rule, a large amount of the compatibilizer C is required for the complete miscibility of the originally immiscible polymers A and B. Thus the addition of moderate amounts of C preserves the phase separation while promoting a finer phase dispersion, as a consequence of a lower interfacial tension. In parallel, an improvement in the interphase adhesion and ultimate properties might be expected.

#### 3.9.2. Representative examples and commercial blends

The tensile properties and phase morphology of a 90/10 Phenoxy/SAN blend compatibilized by PCL

have been reported by Jo.<sup>[147]</sup> Upon the addition of 5 wt% PCL, the tensile modulus is increased by *ca.* 10%. This observation agrees with the phase morphology that shows a finer dispersion, which may be a clue for an improved interfacial adhesion. When the PCL concentration is increased up to 10 wt%, further improvements in phase dispersion do not trigger a parallel improvement in tensile properties. The explanation has to be found in the plasticization of the phases by PCL, which results in lower tensile modulus and tensile strength, whereas a slight increase in elongation at break and fracture energy is observed.

A number of elastomer-based modifiers have been blended with PVC for improving its impact resistance. PVC is however immiscible with most apolar elastomers, so these blends have to be compatibilized. Yu-Der Lee et al.<sup>[151]</sup> have investigated tricomponent blends of PVC/CPE/EPDM where EPDM is the low temperature impact modifier, and CPE is the compatibilizer, as a result of similarity in chemical structure with PVC and EPDM. CPE indeed consists of randomly distributed chlorinated blocks and ethylene segments. Compatibilization of PVC/EPDM blends by CPE has been proved by the analysis of the phase morphology and mechanical properties. From TEM observations, a structural model has been proposed for the PVC/CPE/EPDM ternary blends as shown in Fig. 26. The EPDM domains are dispersed in the PVC matrix and surrounded by CPE which may also be dispersed in the PVC matrix. The fraction of EPDM domains encapsulated by CPE appears to increase with the CPE/EPDM ratio. Thus the localization of CPE between PVC and EPDM helps to enhance the compatibility of the originally immiscible polymers as supported by the improvement in the mechanical properties. The elongation at break and the impact strength at both room and low temperatures significantly increase upon the addition of CPE to PVC/EPDM blends, indicating that CPE is not only a compatibilizer but also an impact modifier (Table 3).

DSM has developed a ternary polymer blend (SAN/CPE/EPDM) which is based on the concept reported in this sub-section, but whose composition is somewhat different from the system reported by Yu-Der Lee et al.<sup>[151]</sup> (Ronfalyo<sup>®</sup>E with a SAN/CPE/EPDM composition ranging from 75/12.5/12.5 to 75/15/10).

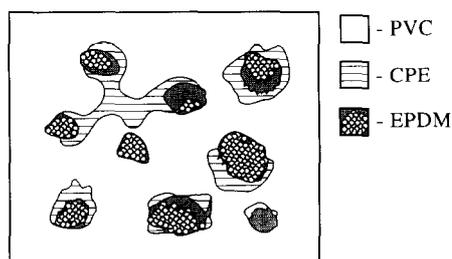


Fig. 26. Sketch of the PVC/CPE/EPDM (100/10/10) phr morphology .

Table 3. Notched impact strengths of PVC, PVC/EPDM, PVC/CPE and PVC/CPE/EPDM blends measured at room temperature and at  $-12^{\circ}\text{C}$

Polyblend	Room temp, impact strength (J/m)	Low temp. ( $-12^{\circ}\text{C}$ ) impact strength (J/m)
PVC	25	27.5
PVC/EPDM 100/10 (PHR)	12.5	22.5
PVC/CPE25 <sup>a</sup> 100/10 (PHR)	50	30
PVC/CPE25 100/20 (PHR)	112.5	50
PVC/CPE36 <sup>a</sup> 100/10 (PHR)	75	30
PVC/CPE36 100/20 (PHR)	837.5	80
PVC/CPE42 <sup>a</sup> 100/10 (PHR)	75	30
PVC/CPE42 100/20 (PHR)	100.0	47.5
PVC/CPE25 <sup>a</sup> EPDM 100/10/10 (PHR)	325.0	77.5
PVC/CPE25/EPDM 100/20/10 (PHR)	637.5	145.0
PVC/CPE36 <sup>a</sup> EPDM 100/10/10 (PHR)	125.0	70.0
PVC/CPE36/EPDM 100/20/10 (PHR)	737.5	155.0
PVC/CPE42 <sup>a</sup> EPDM 100/10/10 (PHR)	62.5	38.75
PVC/CPE42/EPDM 100/20/10 (PHR)	512.5	52.5

<sup>a</sup>Chlorine content (%) of CPE. Data taken from figures 6-8 of ref. [151].

### 3.10. Miscellaneous routes to compatibilization

#### 3.10.1. Common solvent method

Two incompatible polymers are dissolved in a common solvent, either under ambient or elevated pressures and temperatures. After the complete dissolution, the solvent is removed, e.g. by freeze-drying or sublimation. This technique creates a very large interfacial area which allows even very weak polymer/polymer interactions to stabilize a pseudo-homogeneous system. In this way much finer dispersions can be obtained in comparison with the more conventional melt blending techniques. When polymers are dissolved under high pressures and high temperatures, and when the solvent is removed very quickly, the technique is called "compositional quenching". Cangelosi<sup>[152]</sup> has demonstrated the usefulness of the common solvent method for a system with weak hydrogen bonding. However, if this technique is used without compatibilizers, coalescence phenomena resulting in a coarsening of morphology cannot be precluded. To our knowledge, the common solvent method has not been applied to prepare blends on a commercial scale.

#### 3.10.2. Addition of reactive fillers as compatibilizers

##### 3.10.2.1. General principles

-Section 3.9 has shown that the immiscibility of two polymers can be tuned by a third polymer miscible with each of them. Similarly Shifrin et al.<sup>[153]</sup> have proposed an alternative approach that consists of substituting a mineral filler for the third polymer as a compatibilizer for a two-phase polymer blend. The selective localization of the filler at the interface is a prerequisite, which is fulfilled (or not) depending on the balance of interactions between the filler and each constitutive polymer.<sup>[154]</sup> In the case of a comparable affinity of the filler for each blended polymer, the filler may be expected to accumulate in the interfacial region and provide the immiscible polymer blend with an enhanced stability. Otherwise, the filler will preferably concentrate in the polymer phase which more strongly interacts with it.

##### 3.10.2.2. Representative examples and commercial blends

The effect of a filler (kaolin) on the thermodynamic interaction parameter ( $\chi_{23}$ ) between PBMA (polymer 2) and PMMA (polymer 3) has been investigated by reverse gas chromatography over a broad range of temperatures and compositions.<sup>[153]</sup> It has been reported that the concentration dependence of  $\chi_{23}$  is shifted towards smaller values of  $\chi_{23}$  as the kaolin content is increased. A positive value of  $\chi_{23}$  indicates that the neat PMMA-PBMA pair is completely immiscible in the melt (at 475 K), whatever the PMMA volume fraction. The addition of kaolin results in a marked reduction of  $\chi_{23}$  and thus in the immiscibility degree of the two polymers. When the kaolin content is high enough (40%), miscibility is predicted for blends containing more than 60% PMMA. The observed dependence of  $\chi_{23}$  on the filler content is supposed to reflect the formation of an increasingly more diffuse interphase between the originally immiscible polymers. The mineral filler is then a compatibilizer for the two immiscible polymers.

Although this strategy is attractive because of a straightforward implementation and low cost, no commercial applications have been reported (to our knowledge), which might suggest some limitations in the availability of a filler that is able to provide the required balance of interactions.

## 4. FUNDAMENTAL GUIDELINES FOR POLYMER BLEND COMPATIBILIZATION

As previously mentioned, the basic interest in preformed block and grafted copolymers is found in the unique opportunity to change their molecular characteristic features in a controlled way and to identify

the key criteria that: (1) allow the interfacial tension to be largely decreased; and more importantly (2) impart a strong mutual anchoring to the phases.

#### 4.1. Effect of molecular architecture of the compatibilizer

PE/PS blends have been modified by hydrogenated PB-*b*-PS copolymers of various molecular architectures. This general A/B/A-B system has been extensively studied by Teyssié et al., in order to clear up the fundamental dependence of the blend properties on the molecular structure of the amphipatic copolymer.<sup>[27]</sup> On the basis of LDPE/PS blends of two extreme compositions (80/20 and 20/80), Table 4<sup>[27]</sup> shows that the efficiency of hydro-genated PB-*g*-PS is poor, particularly when the elongation at break is concerned (Table 4).<sup>[155]</sup> Triblock copolymers of a radial or linear structure, with a major central HPB block, are either more efficient or less efficient than the grafted copolymer depending on the binary blend composition. When LDPE forms the continuous phase (LDPE/PS 80/20), these copolymers have some beneficial effect on both  $\sigma_B$  and  $E_B$  (Table 4). Diblock copolymers are far more efficient in compatibilizing LDPE and PS over the whole composition range (Table 4). This superiority is usually accounted for by less drastic conformational restraints at the interface and the opportunity for each block to penetrate deeply into the parent homopolymer phase and to be intimately intermingled with the homopolymer chains. This condition is essential to impart high elongations at break and impact energies which result from the strong mutual anchoring of the phases.

Table 4. Maximum improvement in ultimate tensile strength ( $\Delta\sigma_B$ ) and elongation at break ( $\Delta\varepsilon_B$ ) for LDPE/PS blends modified with 6% grafted and 10% block copolymers

Copolymer structure	LDPE/PS/20/80		LDPE/PS 80/20	
	$\Delta\sigma_B$ (%)	$\Delta\varepsilon_B$ i%)	$\Delta\sigma_B$ (%)	$\Delta\varepsilon_B$ (%)
Graft <sup>a</sup>	55	0	75	0
Linear triblock <sup>b</sup>	20	0	30	40
Star-shaped multiblock <sup>c</sup>	20	0	10	130
Pure diblock <sup>d</sup>	25	900	60	1000
Tapered diblock <sup>e</sup>	100	100	60	1000

<sup>a</sup>Data taken from figures in ref. [155]. <sup>b</sup>Kraton G 1651 (Shell). <sup>c</sup>Hydrogenated Solprene 415 (Philips).  
<sup>d</sup>MW: 155,000 (49 wt% of PS). <sup>e</sup>MW: 80,000 (33 wt% of PS).

Finally, the internal structures of diblock copolymers also have an effect on the ultimate properties of polyblends when all the other conditions are the same. Although there is a sharp transition from one block to the other one when diblock copolymers are prepared by the sequential addition of the two monomers, this transition may be made more progressive by changing the copolymerization recipe, and the final copolymer is then referred to as a "tapered" copolymer. Table 4 confirms the superiority of a tapered variant of HPB-*b*-PS over the parent pure diblock.<sup>[27]</sup> Moreover, the lower melt viscosity of the tapered diblock allows the final morphology and properties to be reached in a much shorter processing time, which is an additional advantage. The discussion will concentrate now essentially on diblock copolymers recognized as the most efficient interfacial agents.

#### 4.2. Effect of relative length of homopolymers and parent constitutive blocks of diblocks

The relative length of the constitutive blocks has been found to be an important molecular parameter for the emulsification of polymer blends by diblocks. Mixing of A-B diblock copolymers with A and B immiscible homopolymers is typically athermal. In this case, it is generally accepted that the molecular weight of the copolymer blocks should be higher than the molecular weights of the corresponding homopolymers, so as to maximize segmental repulsion between the individual blocks compared with the parent homopolymers.<sup>[156,157]</sup> This "molecular weight rule" must however be used as a qualitative guideline, since it is less stringent for blends prepared in the melt (thus far from the thermodynamic equilibrium) rather than by solvent casting.<sup>[158]</sup> It must also be emphasized that very high molecular weights are not recommended, since they are responsible for high melt viscosities and low diffusion rates. At a constant weight content, the number of diblock molecules available to cover

the interface is also smaller, which is an additional drawback.<sup>[159]</sup> In sharp contrast, when at least one block of the diblock copolymer is chemically different from but miscible with the corresponding homopolymer (A/B/A-C and A/B/C-D systems), exothermic interactions may develop and provide additional driving force for the block to be anchored into the parent miscible homopolymer. Then strong interphase adhesion can be promoted independently of the relative molecular weight of the block/homopolymer pairs.<sup>[160]</sup> Nevertheless, the balance of interactions for each block/polymer pair must be such that the copolymer has no marked tendency to form micelles in one homopolymer phase. In this respect, if the relative length of the two blocks in A/B/C-D systems is properly balanced with the intrinsic A/C and B/D interactions, the C-D diblock will spontaneously migrate to and accumulate at the interface. Immiscible PPO and Phenoxo have been compatibilized by a PS-b-PMMA copolymer,<sup>[63]</sup> in which PPO/PS and Phenoxo/PMMA are the miscible pairs.<sup>[161,162]</sup> From thermal analysis, it is clear that a copolymer with a PMMA block twice as short as the Phenoxo homopolymer (and PS block with a similar *MW* to that of the PPO homopolymer) is localized at the interface. More regular and finer phase dispersions are observed by SEM when small amounts of this diblock are added. Furthermore, the toughness of the modified blends is remarkably improved, in agreement with an enhanced *interfacial adhesion*. For instance, when 10 wt% diblock is added to the PPO/Phenoxo 30/70 blend, a ductile fracture is observed until *ca.* 85% strain, which corresponds to a threefold increase in fracture energy. This compatibilization activity of the diblock is more likely due to a favourable exothermic mixing of each homo-polymer with the miscible block. This suggests that the interfacial activity of PS-b-PMMA copolymers is higher when PPO and SAN are substituted for PS and PMMA as immiscible homopolymers. In the first instance, the PS-b-PMMA is an entropic acting copolymer, which behaves as an enthalpic acting one towards the PPO/SAN polyblend. The swelling of PPO by a deuterated PS block has been observed by forward recoil spectroscopy<sup>[163]</sup> and dynamic mechanical analysis (DMA).<sup>[66]</sup>

Heuschen et al.<sup>[57]</sup> have also used a 50/50 PS-b-PCL copolymer in order to compatibilize PS/PVC blends (A/B/A-C system). At least when the blocks are longer than the homo-polymers, the copolymer is localized at the interface, as shown by a sub- $T_g$  for PVC assigned to an external layer of the PVC phases plasticized by the PCL blocks of the copolymer. The PS/PVC adhesion is also improved compared to the neat binary blends. When the blocks are shorter than the homopolymers, the 50/50 diblock seems to preferably form micelles in the PVC phase.

#### 4.3. Amount of added copolymer

In the case of A/B/A-B systems, the ultimate tensile properties are improved upon the addition of increasing amounts of the diblock copolymer until the interfacial area is saturated and the copolymer starts to form micelles in at least one polymer phase. Beyond that concentration, which is usually in the range of a few wt%, a plateau is observed in the ultimate mechanical properties.<sup>[164-166]</sup> SEM micrographs convincingly confirm that the more drastic change in the PS/PE phase morphology occurs when as low as 0.5 wt% of HPB-b-PS is added, and that no further significant modification is observed above 2 wt%. This conclusion also holds when the ultimate mechanical properties are concerned<sup>[27]</sup>. This behaviour strongly contrasts with A/B/C-D systems, i.e. for enthalpic acting copolymers (SAN/PPO/PS-b-PMMA)<sup>[66]</sup>. The affinity of each individual block for the miscible homopolymer is then responsible for the preferential localization of the copolymer at the interface and micelle formation can be delayed up to copolymer concentrations as high as 20%.

#### 4.4. Morphology-mechanical properties relationships

The toughening of thermoplastics by rubber dispersions is an important achievement, whose success depends on the phase morphology in close connection with the brittle/ductile behaviour of the matrix. In the particular case of a matrix where the predominant failure mechanism is crazing rather than shear yielding, the interfacial adhesion is also of the utmost importance. It has been shown that a prerequisite for the rubber toughening is a thick interface,<sup>[167]</sup> which can be achieved by adding to the binary thermoplastic/rubber blend a properly tailored block copolymer. A twofold increase in the interfacial thickness (2-5 nm) has, for instance, been observed as a result of the block copolymer addition.<sup>[158]</sup> Although the toughness of thermoplastics is usually improved by dispersions of discrete elastomeric

particles, a co-continuous two-phase morphology can also have a beneficial effect on some ultimate properties (e.g. ultimate tensile strength,  $\sigma_B$ ). It might be tentatively explained that the need for a high interphase adhesion is less stringent when each phase is continuously connected throughout the blend. For example, a high  $\sigma_B$  has been imparted to PS/PE blends by the addition of a tapered hydrogenated PB-b-PS copolymer.<sup>[168]</sup> A synergistic effect has been observed in some composition ranges, in spite of blocks shorter than the parent homopolymers. This unexpected effect has been correlated with a co-continuous two-phase morphology, which would however account for a fragile-type failure under tensile testing. This observation indicates that LDPE is more efficient in imparting a high toughness when it is dispersed as discrete particles rather than as a continuous phase. This illustrates the critical importance of the phase morphology on the mechanical properties. Although a rather low molecular weight hydrogenated PB-b-PS copolymer (60-80 K) promotes a synergy in  $\sigma_B$ , a higher molecular weight diblock (155-275 K) is required for a maximum in the elongation at break, more likely as result of the enhanced anchoring of each block within the parent homopolymer.<sup>[27]</sup> From this very brief overview, it appears that a delicate balance of interactions between each homopolymer and the parent block of the copolymer dictates the particular localization and conformation of the copolymer at the interface. This balance primarily depends on the type of blends (A/B/A-B, A/B/A-C or A/B/C-D), which indicates that each system is a special case in itself. Moreover, the balance required for the optimization of one property (e.g. ultimate tensile strength,  $\sigma_B$ ) does not necessarily provide for an optimum in another property (e.g. elongation at break,  $\epsilon_B$ ) in many of these systems.

## 5. CONCLUDING REMARKS

Compatibilization of immiscible polymer blends is by far the most general and efficient strategy to convert usually poor multiphase blends into high performance alloys. The implementation of this strategy is very straightforward, since it relies upon commercially available polymers and/or existing processing equipment. As a rule, the suitability of compatibilization techniques to industrial development depends on the complex interplay of several factors, such as cost, final performance, recyclability and possibly biodegradability.

Block and grafted copolymers are typically used as interfacial agents. These can be synthesized, either in a preliminary and thus independent step (Section 3.1) or in the course of reactive processing (Section 3.2). Although the second process is more attractive and less expensive, the question is whether the way of incorporating the block or grafted copolymer (preformed or formed in-situ) has an effect on the properties of the polyblends.

Table 5. Particle size and block copolymer content in PS/PMMA 70/30 blend

Blend	Particle size ( $\mu\text{m}$ )	Block copolymer content (wt%)
Non reactive	1.1	0
Non reactive + copo.	1	5
Reactive (pellets)	0.75	1.6 <sup>a</sup>
Reactive (powder)	0.5	1.7 <sup>a</sup>

<sup>a</sup>Determined by GPC.

Reference is often made to Nakayama et al.,<sup>[169]</sup> who compared a PS/PMMA 70/30 blend modified with a preformed PS-b-PMMA (50/50) diblock with a reactive blend of a carboxylic acid-terminated PS (PS-COOH) and epoxy-terminated PMMA (70/30). All the PS and PMMA constitutive components (blocks or homopolymers) are of the same molecular weight (40,000). It must however be clear that although PS-COOH is capped with only one reactive group, PMMA is capped by several epoxy groups, so that "Y" shaped and/or "fork" shaped block copolymers are expected to be formed in the reactive blend compared to the linear preformed diblock. Table 5 compares the average size of the dispersed phase measured by light scattering for the different types of PS/PMMA blend. A finer phase dispersion with a narrower size distribution is observed for the reactive system, which however contains a much smaller content of block copolymer. It might be argued that the preformed diblock is preferably dispersed as micelles in one (or both) polymer phase(s) compared to the copolymer which is formed in-situ and is thus unavoidably at the interface. This difference in localization is of course of a kinetic origin and merely indicates that the two systems are not frozen in the same situation. Would the

two copolymers (premade and formed in-situ) be exactly of the same structure, molecular weight and composition, they should exhibit the same distribution between the interface and the polymer phases when the thermodynamic equilibrium is reached. Unfortunately in the example reported by Nakayama et al., the two PS/PMMA copolymers are of different compositions, i.e. 50/50 for the premade diblock and at least 66.6/33.3 (and/or higher) in the reactive system. Since PMMA-PMMA interactions are stronger than the PS-PS interactions, the preformed diblock must have a higher propensity to reside in the PMMA phase than the "Y" and/or "fork" shaped counterpart. In addition to unavoidable kinetic control factors, the difference in molecular structure of the two copolymers is a thermodynamic factor, that contributes to the differences between the reactive and non reactive blends reported in Table 5. That non-equilibrium situations prevail in most polyblends prepared in the melt has to be kept in mind, since it can account for differences in polyblends of the same composition but compatibilized differently, e.g. by changing the processing conditions or the addition order of homopolymers and a premade block copolymer,<sup>[170]</sup> etc. Since a rigorous comparison between the reactive and non-reactive compatibilization is often difficult, it may be concluded that reactive processing is basically more attractive and fits better with industrial requirements. The main problem is of course the kinetic tuning of the reactive system which has to be carried out under stringent conditions of time and temperature. In spite of this possible limitation, reactive blending is at the origin of several compatibilized blends produced on a commercial scale. Further progress may thus be expected as a result of improved insight and control over the kinetics of the underlying reactions. The most straightforward compatibilization strategy relies upon the addition of low molecular weight chemicals, and particularly peroxides. The lack of chemical selectivity and poor control of competitive degradation reactions are severe limitations, which explains why no industrial breakthrough has been reported up to now. Nevertheless, treatment of polymer waste mixtures by this very cheap technique might be considered in the future. Dynamic vulcanization of thermoplastic/rubber blends of the polyolefin type (PP/EPDM) might be viewed as a very successful extension of the aforementioned strategy, where chemical selectivity has been achieved. As a result, the thermoplastic vulcanizates (TPV) accordingly produced have a position in the market place which is continuously growing. This type of thermoplastic elastomer is superior to the classical thermoset rubbers, with respect to processability and recycling. When the TPV composition is, however, such that a compatibilizer has to be used in addition to the cross-linking agents, the final cost becomes prohibitively high and no commercial development is known. Special attention has also been paid to the interchange reactions between poly-condensates, because these polymers can be engaged in a reactive blending process without the need for functionalization. Although the cost of this technique may be low enough, commercial success is strongly dependent on how accurate the control of the reaction extent can be. Indeed, "randomization" of the original chemical structures can result from excessive transreactions and thus be responsible for a deleterious effect on the final properties. Playing with mutual cross-interactions between immiscible polymers is actually an extension of the above-discussed strategy, that however requires the suitable functionalization of these polymers. Reactivity and content of the mutually reactive groups are of the utmost importance and reaching this desirable balance may limit industrial applications. For instance, compatibilization by ionomers has been patented, but no commercial outcomes are known.

Undoubtedly, the science and technology of polymer blends and their compatibilization continue to grow in the future. Efforts will continue to predict miscibility in relation to composition, temperature, pressure and specific interactions. A better understanding of the interphase, including the calculation of interfacial tension and interfacial thickness, is highly desirable, particularly for predicting the effects of interfacial agents and interphase modifications. Although thermodynamic studies are useful guidelines for polymer blend compatibilization, this general strategy provides materials far from the thermodynamic equilibrium, which addresses the question of rheology, kinetic control of morphology development and stabilization of morphology against any post-treatment, including recycling. In this respect, the roles of the molecular characteristic features of the interfacial agent (premade or not), i.e. molecular architecture, molecular weight and composition, must be cleared up further in relation to micelle formation, diffusion rates to the interface, rheology, flow-induced modification of morphology and ultimate mechanical properties. The interest in compatibilization by premade block copolymers should certainly be renewed by the availability of short-length "enthalpic acting" copolymers prepared at low cost. The remarkable progress recently reported for controlled radical (co)polymerization allows for optimistic forecasts in this field.

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