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Compatibilization phenomenon in polymer science and technology: Chemical aspects

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ABSTRACT

Polymer blends are mixtures of two or more macromolecular species − polymers and/or copolymers. They are used to increase the range of properties available from existing polymers without synthesizing new ones, which is time consuming and expensive. But most blends are immiscible, and need to be compatibilized. The compatibilization must not only insure improvement in performance, it must be clearly defined with regard to the method and objective. Keeping this view in focus, the present review classifies the main approaches that are available into four well-defined "routes" to compatibilization for various types of polymers and copolymers. Further, the possibility of using an innovative combination of *in-situ* polymerization and *in-situ* compatibilization as a new route to polymeric nano-blends is explained. While most of the present narrative deals with different types of binary polymer/copolymer blends, pathways for extension of some of the methods to ternary or multicomponent blending and the significance of the novel *composite compatibilizers* in this context are also highlighted.

1. Introduction

Since in blending of two high molecular weight polymers the gain in entropy (ΔS_{mix}) is negligible, a negative free energy of mixing (ΔG_{mix}), required for miscibility, can be achieved only if the heat of mixing (ΔH_{mix}) is negative, according to the equation: $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$. In other words, the blending must be exothermic, and that requires specific interaction/chemical reaction between the blend components, such as, acid−base reaction, ion−dipole interaction, hydrogen bonding, metal complexation, etc. Since only van der Waals interactions occur in most polymer blends, compatibility in blending is clearly an exception rather than the rule. This incompatibility is an important issue as it influences significantly the properties of polymer blends and alloys, as also polymer melts, solutions, and dispersion of additives, such as fillers and reinforcing agents, in a polymer matrix. Compatibilization is thus required to obtain useful materials by blending two or more polymers and also for blending polymers with other materials [1].

In practice, polymer immiscibility results in phase-separated blend morphology that is controlled by a host of parameters, with the best known and most frequently observed morphologies

being (a) dispersion of one polymer in the matrix of the other and (b) a co-continuous two-phase morphology. Which type of morphology is obtained for a given pair of polymers depends, however, on the blend composition, melt viscosity, viscosity ratio, and the degree of miscibility of the polymers — leaving aside the effects of molding and processing variables. While the best known example of a completely miscible blend is PS/PPO, which is miscible in all compositions over a wide temperature range, most other blends are fully immiscible, displaying coarse morphology, sharp interface, poor adhesion between blend phases, and non-uniform physical properties throughout whole volume.

The problem of polymer immiscibility and phase separation being rooted in the lack of favorable interaction between the blending polymers, linking them chemically at the interface or coupling suitably functionalized polymers across the interface would appear to be a simple and convenient route to compatibilization of immiscible polymers. Block or graft copolymers can be generated *in situ* at the interface by reaction between co-reactive functional groups, either pre-existing in the polymers or introduced before blending. These can both stabilize morphology, enhance adhesion and reduce interfacial tension. However, besides the inherent reactivity of functional polymers, several other non-chemical factors may also influence the interfacial reaction, such

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as thermodynamic interaction between polymers, functional group location along the chain, and the effects of processing flows.

Block and/or graft copolymers may also be pre-formed separately and then added to the blending polymer mixture. Such externally added polymers, possessing segments with chemical structures identical with those of the polymers to be blended, are effective compatibilizing agents. Block and/or graft copolymers may also be generated *in situ* by polymerization of a monomer in the presence of a non-propagating polymer chain, or even by subjecting a mixture of incompatible polymers to shearing forces so as to rupture the polymer chains, thereby generating radicals to facilitate coupling.

Block or graft copolymers with segments either miscible or chemically identical to segments of blending polymers can act as mediating entities and can be considered as "interfacial agents" since they tend to concentrate at the interface of the blending polymers and act as an emulsifier. The application of this concept about the role of chemical similarity in polymer compatibility can be illustrated with many well-known examples [2]. It is important to note, in this context, that random copolymers do not compatibilize homopolymers, which may be attributed to the fact that polymer properties are derived from finite length segments of a particular structure. Thus, block/graft copolymer segments with 10−15 monomer units are considered to be effective for compatibilization [2], the assumption being based on the fact that only chain segments of 10−15 monomer units can have reasonably similar characteristics as larger chain segments. On the other hand, a copolymer that has segments of molecular weight > 150,000 are also likely to compatibilize poorly, since chain entanglements may reduce their accessibility to the blending polymers. Besides segment length, solubility parameter is also an important consideration in polymer compatibility. Thus, polymers and copolymers with solubility parameter differing by 0.5 unit are considered compatible, even though their structures may differ significantly, and for relatively low molecular weight polymers, even larger differences in solubility parameter (as much as one unit) may qualify for compatibility [2].

Since the problem of polymer immiscibility and phase separation arises from the lack of favorable interaction between the blending polymers, their miscibility or compatibility may be improved by promoting mediation between them with an added polymer that has structural similarity and/or mutual solubility, by promoting interchain exchange of segments via catalysis leading to copolymer formation, by linking segments with chemical bridging agents, and by allowing reaction between functional groups in the polymer pair during melt blending, with or without external addition of a functionalized polymer.

2. Routes to compatibilization of binary polymer blends

In light of the above discussion, broadly four routes to compatibilization in binary polymer blending can be defined: (a) *molecular mediation*; (b) *catalysis and short-chain bridging*; (c) *co-reactive melt blending*; and (d) *external addition of a functionalized polymer*.

2.1. Molecular mediation

A mediating polymer may be added that is either miscible with both the blending polymers (i.e., co-solvent) or is a copolymer whose one part is miscible with one blend component and second with the other. Thus, block or graft copolymers possessing segments with chemical structures identical with those of the polymers to be blended are effective compatibilizing agents. There are many such examples in the literature some of which have been mentioned above and some more are included in Table 1.

2.2. Catalysis and short-chain bridging

There are instances in the literature where a low molecular weight compound through its catalytic or bridging effects promote significant compatibilization. Since the interchangeable characteristic of polyester groups [3] enables *in situ* formation of block copolymers, catalysts which promote such reaction are particularly useful for compatibilization of polymer blends. However, a precise control of molten interchange reactions must be maintained for obtaining suitable blends. This calls for special attention to the selection of appropriate interchange catalysts. A host of catalysts have been suggested [4], which include Lewis acids, nitrogen compounds, sodium stearate, sodium octadecanoate, alkoxides, phenolates, borates, hydrides, hydrogen phosphates, ammonium and phosphonium salts. However, catalysts are not essential for the exchange reaction to take place.

Four types of exchange reactions (Fig. 1) that polyester blends can undergo in the molten state are alcoholysis (reaction between

Table 1
Compatibilization by species acting as mediators (Route 1) and catalysts or coupling agents (Route 2).

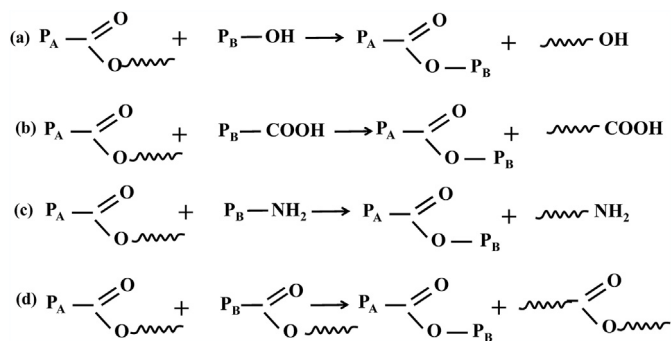| Compatibilizing mechanism	Polymer blend	Compatibilizer	Ref.
Mediation via chemical and/or structural similarity miscibility, minimizing interface energy	PS/PB	PB-*g*-PS	[2]
	P(SAN)/PB	PB-*g*-P(SAN)	[2]
	PLA/PCL	Graphene	[11]
Interchange reaction/trans-esterification (catalyzed)	PET/PA-6,6, PLA/PA11	p-Toluene-sulfonic acid,	[12]
		Triphenyl phosphite	[13]
	PLA/PBAT	Tetrabutyl titanate	[14]
Free-radical recombination	PE/PP	Peroxide	[15,16]
Chemical coupling	poly(*l*-lactide)/PBS poly(*l*-lactide)/poly-urethane	GLYMO	[17]
		Diisocyanate	[18]
	PLA/TPE	Diisocyanate	[19]
	PPC/PBS	Triisocyanate	[19,20]
	PET/PA6	Bisoxazoline	[21,22]
	(PET, PEt, PVa, PSi)/PA	1,1′-Carbonyl-bis-caprolactam	[23]
	PA6/PPE	Epoxides	[24,25]
	PA6/PBT	TGDDM	[25]
	PLA/PHB	Maleic anhydride	[26]

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Fig. 1. Interchange reactions of polymer blends: (a) alcoholysis; (b) acidolysis; (c) aminolysis; (d) transesterification.

hydroxyl/phenol and ester/carbonate), acidolysis (reaction between carboxyl and ester/carbonate groups), aminolysis (reaction between ester and amine groups) [5,6], and transesterification (reaction between ester groups) [7−9]. Transesterification occurs spontaneously during melt processing of polyester blends. Since this is often associated with decrease in molecular weight or degradation, it is important to control the interchange reactions during melt blending of polyesters. Use of coupling agents (such as anhydride and epoxy) and transesterification catalyst (such as, tetrabutyl titanate, TBT) have been reported (Table 1). For PLA/PBAT binary blends that have significant potential as being fully biodegradable, Lin et al. [10] reported TBT to be one of the highly effective transesterification catalysts with only 0.5 wt% producing significant increments in ductility and toughness, and reducing PBAT particle size to 0.5 μm. Several other examples from literature are cited in Table 1.

It is recognized that compatibilized blending of PLA with bio-based PA11 is an attractive way to get biodegradable materials with better thermomechanical properties compared to PLA. The two polymers being immiscible, p-toluene sulphonic acid (TsOH) was used [12] as a catalyst to induce exchange reactions at the interface of the polymers. The resulting copolymer having chemical structure of both the blend components can reduce interfacial tension, resulting in smaller domains or even a co-continuous morphology at the interface. The morphology, chemical structure analysis, and tensile measurements [6] supported that such copolymerization occurred, resulting in improved bonding between PLA and PA11 with 0.5 wt% TsOH catalyst, but higher catalyst loading (>2%) promoted depolymerization. Similarly, it has been shown [13] that when reacted for periods of 5−10 min at temperatures of 280−300° in the presence of organic phosphites, such as triphenyl phosphite, polymers that contain available carbonyl and aliphatic amine undergo amidation. Therefore, this reaction can both increase the molecular weight of many aliphatic polyamides by their self-reaction in an extruder and also can form block or graft copolymers by reacting polymers that contain aliphatic amines with polymers that contain carboxyl, as in PLA/PA11, to promote compatibilization.

There are basically two compatibilization approaches for polymer blends containing polyolefins, namely, using polyolefin-based mediating agents that have good miscibility with both the blending polymers (Route 1) or creating active sites on the polyolefin chains by means of free radicals (Route 2). Free-radicals generated by the cleavage of O−O bonds in organic peroxides by heat and/or aided by a coagent can promote compatibilization through formation of copolymers via re-combination of the formed macroradicals. Interesting examples of such peroxide-initiated compatibilization are found in the literature [15,16]. Zhao et al. [16], for example,

reported triple-shape memory effects of cross-linked blends with co-continuous architecture obtained by using a peroxide initiator.

The ability of silane compounds to hydrolyze in the presence of moisture and react with the hydroxyl groups of substrates to form covalent bonds (Fig. 2) opens up several possibilities of compatibilization in polymer blends. The application can be facilitated by grafting a low MW silane onto an organic intermediate. As an example, Chen et al. [17] treated the organo-clays *Cloisite 25A* (a phyllosilicate flame retardant) with 3-glycidoxypropyl trimethoxysilane (GLYMO) (Fig. 2) and effectively used the treated clay (up to 10 wt%) as a bridging agent for compatibilization of PLA/PBS blends. Again, as an example, where a silane-grafted polymer can be used as a bridging agent, Zhang et al. [18] used vinyl trimethoxy silane (VTMS) grafted EVA as a bridging agent for EPDM/methyl vinyl silicone rubber blends and reported substantial improvements in mechanical properties and thermal stability with addition of only 10 phr of the bridging agent.

Since isocyanates are reactive toward functional groups which are electron-rich, such as amine, hydroxyl, and carbonyl, isocyanates would be suitable as coupling agents for polymers having amine or hydroxyl groups to form covalent linkages (Fig. 3). A polymer that contains hydroxyl and carboxyl groups on the chain can undergo chain extension in the presence of isocyanates. Thus, the addition of diisocyanates into PLA results in increased molecular weight by chain extension, while in the presence of another polymer with the above type of end-functional groups, compatibilization can be achieved by chain extension. As an example, for a blend of PLA and a thermoplastic polyester elastomer that had a carboxyl content of 33 eq/10^6 g, addition of 5 wt% MDI (Fig. 3) was found to produce a 7-fold increase of relative ductility and 325%
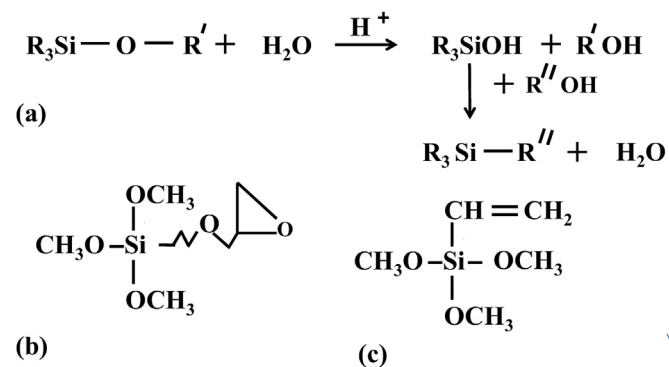

Fig. 2. (a) Hydrolysis of silane followed by reaction with hydroxyl function; (b) chemical structure of 3-glycidoxypropyl-trimethoxy silane (GLYMO); (c) chemical structure of vinyl trimethoxy silane (VTMS).
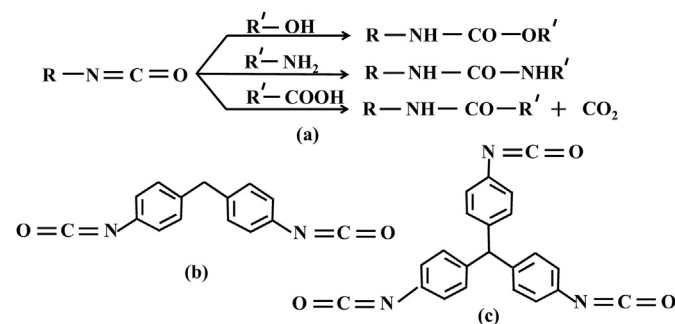

Fig. 3. (a) Reaction of isocyanate with hydroxyl, amine, and carboxyl groups; (b) chemical structure of 4,4′-methylene-bis(phenyl isocyanate) (MDI); (c) chemical structure of triphenyl methane triisocyanate (TTI).

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higher elongation at break without any loss of tensile strength and modulus [19]. On the other hand, using TTI (see Fig. 3) in polymer blends of PPC and PBS, Chen et al. [20] observed that the addition of as little as 0.36 wt% TTI led to doubling of the impact strength, which indicated an increase of the coupling efficiency with an increase in the number of isocyanate groups per molecule, though, however, use of a higher quantity of TTI only led to a drop in impact strength.

Bisoxazolines, which belong to the family of cyclic imino ethers, are capable of reacting rapidly with carboxyl groups (see Fig. 4) within a temperature range of 140−220°, forming ester-amide linkages. This reaction has, therefore, been used both to increase the molecular weight of polymers containing carboxyl groups, such as polyesters and polyamides, and to synthesize polyester-polyamide block copolymers facilitating blend compatibilization [21,22]. Bisoxazolines are thus particularly suitable for compatibilization of both polyester−polyester and polyester−polyamide blends.

Many biscaprolactam derivatives show ability to bring about chain extension of hydroxyl and amine-terminated polymers. They can therefore be employed to improve compatibility of immiscible polymers having hydroxyl and amine groups. Thus, 1,1′-carbonyl-bis-caprolactam (Fig. 5) has been used to compatibilize immiscible blends of polymers having hydroxyl (e.g., polyesters, polyethers, polyvinyl alcohol, polysiloxane, etc.) and amino groups (e.g., polyamide), resulting in notable improvements of certain properties attributable to greater compatibilization [23]. The reactions can be catalyzed by titanate and zirconate alkoxy derivatives leading to acceleration of the compatibilization reaction.

Owing to high reactivity of the epoxide functional group toward nucleophilic agents that lead to a covalent linkage with amine, alcohol, and carboxylic groups through ring opening (Fig. 6), epoxides are widely used as coupling agents. There is thus a wide variety of epoxide coupling agents, ranging from low MW compounds to polymers containing epoxy groups [24,25]. Tetrafunctional epoxy resin N,N,N′,N′-tetraglycidyl-4′,4′-diaminodiphenyl methane (TGDDM) was shown to be a highly efficient reactive coupling agent in blends of PA6 and PPE [25] with only 0.5 phr TGDDM producing a sharp increase of impact strength by 20 times in one-step melt blending. The marked compatibilizing effect of TGDDM, as reflected in the improvement of tensile strength determined by torque measurements, was also observed for PA6/PBT blends [25]. However, in this case, the improvement was more pronounced in PA6-rich blends than in PBT-rich blends, which was attributed to the solubility difference of TGDDM in the two blend components.

Due to the high reactivity of the anhydride functional group (−CO−O−CO−) with water, alcohols, and amines, low MW anhydrides have been extensively used for compatibilization of polymer
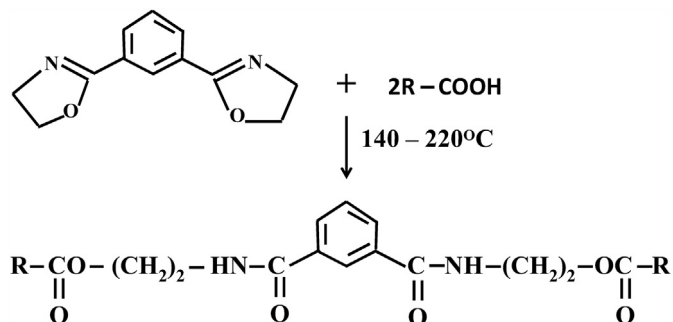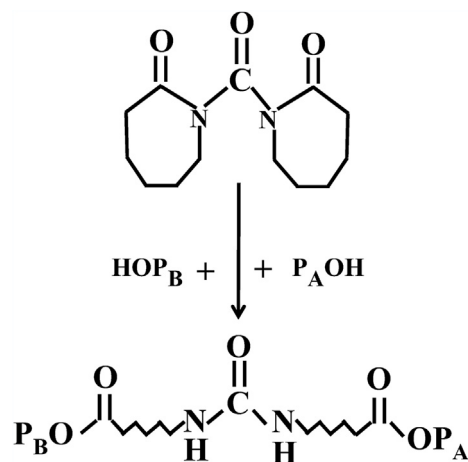

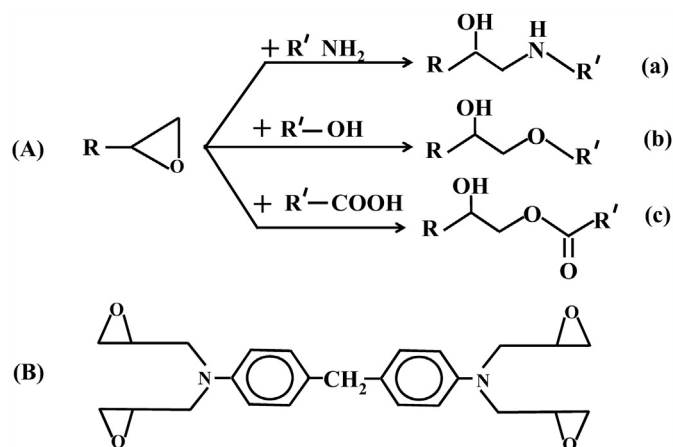**Fig. 5.** Reaction of 1,1′-carbonyl biscaprolactam with hydroxyl-terminated polymers.

Fig. 6. (A) Chemical reaction between epoxide and (a) amine, (b) alcohol, and (c) carboxylic acid; (B) chemical structure of N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM).

blends. Thus, maleic anhydride (MAn) can be added, along with a free-radical generator, such as benzoyl peroxide (BPO) into PLA/PHB melted blends to form *in situ* MAn-grafted polymer chains of both PLA and PHB. Compatibilization can thus be achieved between PLA and PHB by simply adding MAn into the melted blend in the presence of BPO [26].

Pyromellitic dianhydride (PMDA), which has two anhydride groups in one molecule is also widely used for chain extension of polyesters, mostly PET, to improve their mechanical properties. Moreover, the fact that PMDA has relatively high thermal stability is also advantageous in some applications.

2.3. Co-reactive melt blending

Compatibilization by polymers formed *in situ* by reaction between active and co-reactive groups in blending polymers is a commonly used strategy for compatibilization of immiscible polymer blends. The reactively formed polymers (block or graft) both stabilize morphology and enhance adhesion at the interface. However, the block or graft copolymer formation, which takes place by coupling reaction between polymer-bound functional groups (pre-existing or introduced before blending), must occur during a typical processing time, < 5 min [27], in a melt-blending

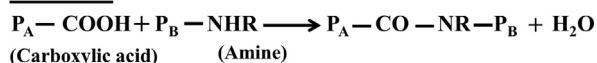**Fig. 4.** Reaction between bisoxazoline and carboxylic acid.

environment, where the reaction rate can be reduced by the restricted diffusional mobility of the functional groups, but can also be greatly accelerated by flow/mixing [28,29].

Early examples of such *in situ* compatibilization have been mostly in the polyblends between various nylons and MAn-grafted polyolefins. The compatibilization in these cases involve reaction between the amine groups of nylons and the anhydride groups of the grafted MAn [30]. Carboxylic acid/epoxy has also been considered as a preferred reactive pair for *in situ* compatibilization [30]. A number of other reactive groups have been suggested [31–33] as well. All of them can be classified into four types, viz., (1) addition/substitution, (2) interchange; (3) ring-opening, and (4) ionic bonding. These reactions are shown by equations in Figs. 7(a)–7(d), in which P_A and P_B represent chain segments of polymers A and B, respectively. To be effective for compatibilization, the coupling reaction has to be fast so that the interface is covered with an amount of reactively formed polymer sufficient to compatibilize and/or to increase adhesion between phases within the processing time in the extruder [33,34].
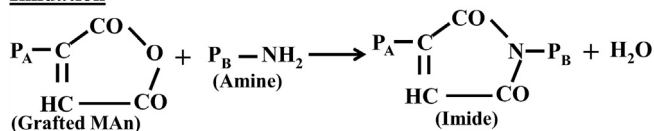
In evaluating the different reactive pairs with regard to *in situ* compatibilization, questions arise about the relation between the reactivities of small molecule analogs and bigger molecules in reality, as also the influence of interface on the polymer melt coupling kinetics. In order to address this issue, Orr et al. [35] measured homogeneous coupling kinetics in polymer blends using a number of narrow distribution end-functional polystyrenes (PS) with different terminal groups. While all the polymers were synthesized by anionic polymerization, the blends were prepared by melt-mixing at 180°. From the kinetic data of reactions, the functional group pairs were arranged in the order of decreasing reactivity as: aliphatic amine/anhydride > aromatic amine/anhydride > acid/epoxy > acid/oxazoline > aliphatic amine/epoxy > hydroxy/(anhydride or acid) > acid/amine, in general agreement with the ranking found for small-molecule analogs in dilute solutions (with solvents of solubility parameter close to that of the polymer) [27].
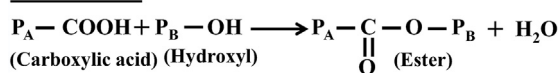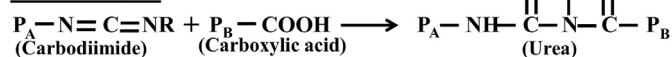
Addition reactions :

Amidation

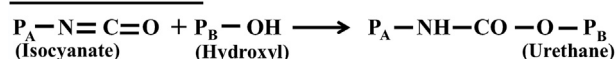$$P_A—COOH + P_B—NHR \longrightarrow P_A—CO—NR—P_B + H_2O$$
(Carboxylic acid)   (Amine)

Imidation

Esterification

$$P_A—COOH + P_B—OH \longrightarrow P_A—\overset{\overset{O}{\|}}{C}—O—P_B + H_2O$$
(Carboxylic acid) (Hydroxyl)   (Ester)

Urea formation

$$P_A—N=C=NR + P_B—COOH \longrightarrow P_A—NH—\overset{\overset{O}{\|}}{C}—\overset{R}{\underset{}{N}}—\overset{\overset{O}{\|}}{C}—P_B$$
(Carbodiimide)   (Carboxylic acid)   (Urea)

Urethane formation

$$P_A—N=C=O + P_B—OH \longrightarrow P_A—NH—CO—O—P_B$$
(Isocyanate)   (Hydroxyl)   (Urethane)

Substitution reaction

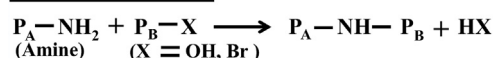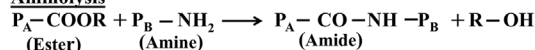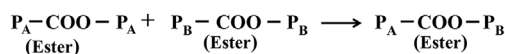$$P_A—NH_2 + P_B—X \longrightarrow P_A—NH—P_B + HX$$
(Amine)   (X = OH, Br)

Fig. 7(a). Addition reactions of reactive groups with co-reactive groups in blending polymers.
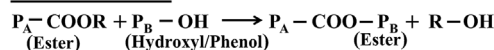
Interchange Reactions

Aminolysis

$$P_A—COOR + P_B—NH_2 \longrightarrow P_A—CO—NH—P_B + R—OH$$
(Ester)   (Amine)   (Amide)

Ester interchange

$$P_A—COO—P_A + P_B—COO—P_B \longrightarrow P_A—COO—P_B$$
(Ester)   (Ester)   (Ester)

Transesterification

$$P_A—COOR + P_B—OH \longrightarrow P_A—COO—P_B + R—OH$$
(Ester)   (Hydroxyl/Phenol)   (Ester)

Amide – ester exchange

$$P_A—CO—NH—P_A + P_B—COO—P_B \longrightarrow P_A—CO—NH—P_B + P_B—COO—P_A$$
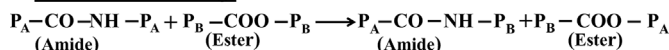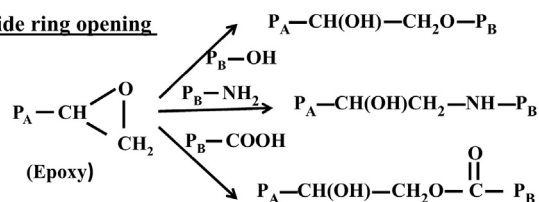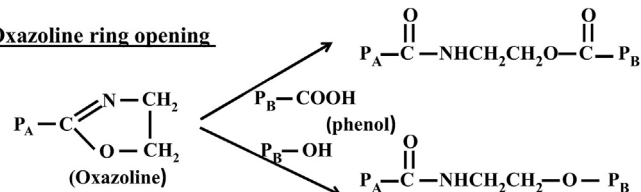(Amide)   (Ester)   (Amide)   (Ester)

Fig. 7(b). *In situ* interchange reactions in melt-blending.

Ring opening reaction

Epoxide ring opening

Oxazoline ring opening

Lactam ring opening

$$P_A—N—CO + P_B—NH_2 \longrightarrow P_A—NH—\overset{\overset{O}{\|}}{C}—(CH_2)_X—NH—P_B$$
$(CH_2)_X$ Amine
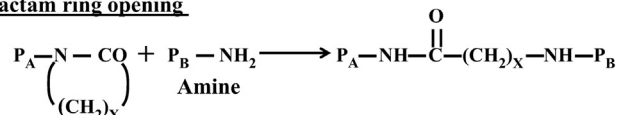
Fig. 7(c). Ring-opening reactions in melt-blending of polymers.

Ionic bonding

(a)   **Pyridine/Amine-acid reaction**

$$P_ANR_3 + P_B—SO_3H \longrightarrow P_A—\overset{+}{N}HR_3 \; \overset{-}{S}O_3—P_B$$
(Pyridine/Amine) (Sulfonic acid)
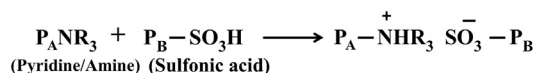
(b)   **Ionomer-Ionomer interchange**

$$(P_A—SO_3^-)_2 \; Zn^{2+} + (P_B—SO_3^-)_2 \; Zn^{2+} \longrightarrow P_A—SO_3^- \; Zn^{2+} \; SO_3^-—P_B$$
(Ionomer)   (Ionomer)
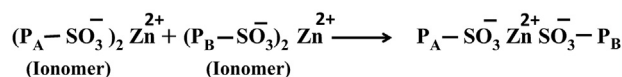
Fig. 7(d). Ionic bond formations in melt-blending of polymers.

While the aliphatic amine/anhydride and aliphatic amine/aromatic isocyanate reactions in the above studies are extremely fast, giving complete conversion in less than 30s [27], aromatic amine/anhydride and carboxylic acid/epoxy rates are also significant. The reactions in all these functional group pairs are considered to be significantly fast for use in commercial blends. Further relevant studies on the kinetics of reactions between functionalized polymers and small molecules in solution and/or in the melt can be found in the literature [36–38].

Since the functional groups are randomly distributed along a polymer chain and as chain-ends in the case of end-functional polymers like polyamides and polyesters, the effect of functional group location on coupling kinetics was investigated by comparing reactions of a mid-functional polymer and those of an end-functional polymer [39]. The study showed that coupling with the mid-functional polymer is slower than with the end-functional polymer, which is attributed to steric hindrance associated with the polymer chain. The reaction taking place typically between functional end-groups of polymers like polyamides and polyesters and functional groups randomly distributed along the chain of a compatibilizer produces graft copolymers rather than block co-polymers, resulting in predominance of the former type.

As mentioned above, compatibilizing polymer (block or graft) formation takes place *in situ* by reaction between polymer-bound functional groups, which may be already present in the polymer chain due to their being part of the monomer in the synthesis process or later introduced into the chain to facilitate reaction with a blending polymer. Some of the well-known examples of such functional polymers, according to the type of active groups are: (a) *Terminal* $-COOH$ or OH, e.g. PET, PBT, PC, PSF, Phenoxy, HTBN, EAA, EMAA, SAA, CTBN; (b) *Terminal* $-NH_2$, e.g. polyamide; (c) *Backbone* $-CO-O-$, e.g. PET, PC; (d) *Backbone* $-CO-NH-$, e.g. polyamide; (e) *Side-chain* $-CO-O-$, e.g. PVAc, polyacrylates, e.g. PMA; (f) *Side-chain* $-C=C-$, e.g. EPDM, PB.

While a variety of chemical reactions may be used for chemically modifying preformed polymers to introduce new functional groups, two types of reactions commonly used for this purpose are the following:

(i) **Addition Reactions**: (a) Free-radical grafting of MAn, where the monomer is introduced directly into a polymer chain, e.g., PE, PP, EPR, EPDM, SEBS, ABS, PPE [40]; (b) grafting of epoxide on NR, EPDM, EPR, PP, PE, PS [41]; (c) lactam on EPR; (d) amine on EPR, PS, PIP, SMA, SAN; (e) hydroxyl on PP, EPR, PVBE; (f) isocyanate on PE, PMMA [42]; and (g) imidazole on PE.

In the case of free-radical grafting in the melt, a key issue is the low grafting yield of vinyl monomers. The use of a comonomer [43,44] or a nano-reactor [44–46] can greatly increase the grafting yield.

(ii) **Substitution Reactions**: (a) Sulfonation and bromination on PS, PPE, and other polymers containing phenyl groups; (b) hydroxyl on EVAc by hydrolysis of acetate group; (c) ring-opening of side or end cyclic groups; (d) terminal substitution, e.g. isocyanate on polyamides, epoxide and carbodiimide on PPE, hydroxyl on PS, PSF and NBR, amine on NBR, SAN; and (e) introducing carboxylic acid group on PE by photo-oxidation [47]. Polar oxidized groups can also be grafted on PE chains through γ-radiation, thereby promoting compatibilization with polymers like polyamides. Such effects were observed in the blending of γ-irradiated PEs of LD, LLD, HD with PA6, which resulted in more uniform and finer distribution of the PE phase in the PA matrix [48].

The grafting of MAn on polymer, mentioned in (ia) above, is usually carried out by melt mixing. The process is triggered by abstraction of hydrogen from the polymer chain by the radicals generated when an organic peroxide decomposes. Being a 1,2-disubstituted alkene, MAn does not homopolymerize and single-unit grafts of succinic anhydride are formed via carbon-carbon double bond (see Fig. 8), which then interacts with a reactive group on the blending polymer.
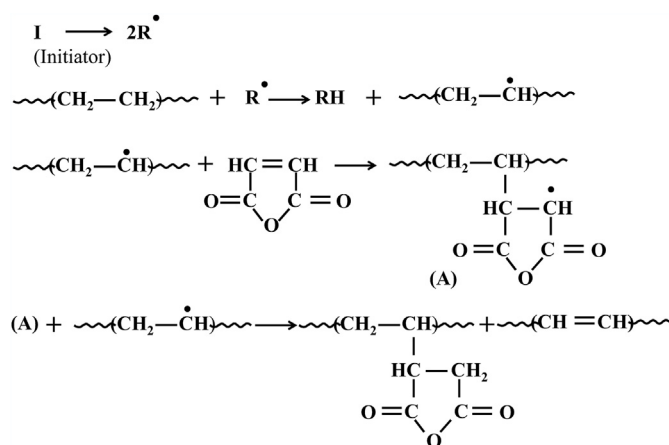

Fig. 8. Maleic anhydride grafting of polyethylene.

MAn-grafted PE and PPs have become increasingly important in recycling of plastics and are also commercially available. For example, blends of polyamide and HDPE, which are commercial blends of interest having adequate properties for a large range of applications, such as in the production of filaments, containers, and molding resins, can be prepared from blends of nylons and recycled HDPE using MAn-grafted polyethylene as a compatibilizer [49].

Similar to MAn, the grafting of epoxide [50,51] also plays an important role in introducing reactive groups into blending polymers. The detailed mechanism of grafting of glycidyl methacrylate on a saturated polymer using BPO as an initiator has been investigated by Huang and Liu [52]. It has been observed, significantly, that the reactivity of the epoxide is not modified due to grafting.

The chemical modification of polymers to introduce reactive functional groups may be carried out either in solution or in the melt [53,54] or in solid state [55,56]. Chemical modification of polymers in the melt avoids using solvents and all associated inconveniences (solvent removal, recovery and losses, safety and environmental issues, etc.). However, it requires rigorous control over (local) residence time distribution [57,58] and (local) mixing [59–61], which is very challenging.

2.4. External addition of a functionalized polymer

Compatibilization can be achieved for a pair of two immiscible polymers by blending with a third polymer which is capable of reacting with both or at least one of the two while being miscible with the other. For example, commonly available styrene-maleic anhydride copolymer (SMA with 8% MAn) has been shown to be a highly effective compatibilizer for blends of PA6 and PPO. Being miscible with PPO, SMA tends to dissolve in the PPO phase during the early stages of melt blending and thus sets a chance to make contact and react (by imidation) with PA6 at the interface to form the desirable SMA-g-PA6 copolymer. This *in situ*-formed copolymer tends to anchor along the interface thereby reducing interfacial tension and resulting in finer phase domains of compatibilized blend with consequent improvement of properties.

In order to achieve successful compatibilization, the third component polymer must have sufficiently reactive functional groups capable of fast, selective and preferably irreversible reaction with the functional group on the blending polymer, while mixing conditions should be such as to minimize mass transfer limitations usually associated with viscous mixing. Some such reactions which can occur at elevated processing temperatures and are frequently utilized for compatibilization are amidation, imidation,

esterification, aminolysis, acid-ester interchange, amide-ester interchange, ring-opening, and ionic bonding. All these reactions are also involved in co-reactive compatibilization (route 3), described earlier, and are presented in Figs. 7(a)–7(d). The reactions lead to copolymer formation across a melt-phase boundary during melt processing of immiscible blends, leading to decrease in immiscibility and interfacial tension, and hence greater compatibility. There are innumerable examples in the literature for blend compatibilization which can be identified as pertaining to the aforesaid Route 4. A few of these are shown in Table 2, in which for each pair of blending polymers, the polymeric compatibilizer used and the type of reaction involved in compatibilization are cited.

Even though Table 2 provides only a limited list of polymer blends and polymeric compatibilizers used in them, it reveals the significant role and extensive application of MAn for polymer blend compatibilization. Four main reasons for the wide use of MAn-functionalized polymers (grafted or copolymerized) are: (a) relative ease with which MAn can be melt-grafted onto many polymers at normal processing temperatures; (b) grafting occurs as single monomeric unit without homopolymerization; (c) can be copolymerized with many monomers by free-radical method; and (d) high reactivity of anhydride. The presence of polar groups in the blending polymers can induce ring-opening and reaction of the grafted or copolymerized anhydride, leading to copolymer formation and compatibilization. Thus, the formation of imide linkage between the amine end-groups of polyamides and the carboxylic groups of grafted or copolymerized MAn (Fig. 7(a)) that contributes to blend compatibilization has been corroborated by spectroscopic studies as well as thermoanalysis experiments. It may be noted that MAn-copolymerized addition polymers are readily available and are widely used as compatibilizers in polymer blending via route 4.

Since the Route 4 process uses a high molecular weight polymer as the compatibilizer, it is essentially a *ternary blending process* and, consequently, in some cases, the mixing sequence of the three polymers can have an effect on the morphology and properties of the blended product, which needs to be taken into account. Considering, for example, the blending of ABS and PA6, for which SMA is an effective compatibilizer, when PA6 is blended with pre-blended ABS/SMA, the SMA-g-PA6 formed during the blending process lies at the interfacial region and acts as a compatibilizer. However, when ABS is blended with pre-blended SMA/PA6, the SMA-g-PA6 formed during the pre-blending remains preferentially in the PA6 domain and notably improves the thermal resistance and modulus of only the PA6-rich domain [84].

3. *In-situ* polymerization and *in-situ* compatibilization

It has been shown experimentally by many workers that, irrespective of the compatibilization method employed, in most polymer blends processed under typical extrusion conditions the particle size of the dispersed phase is rarely below 0.1 μm (or 100 nm). To obtain nanoblends (i.e., where the scale of dispersion of one polymer phase in the other is below 100 nm), Hu et al. [85,86] therefore developed a concept called *in-situ* polymerization and *in-situ* compatibilization that consists in polymerizing a monomer, say B, of one of the polymers, PB, in the presence of the other polymer PA of monomer A, while a fraction of PA bears initiating sites (denoted as PA★), either at the chain end(s) or along the chains. This triggers four phenomena, as shown in Fig. 9, viz., (1) *in-situ* polymerization of B in the presence of PA, producing polymer PB; (2) phase separation between PA and PB; (3) polymerization of B from the active centers on PA★, leading to the formation of copolymers P(A-B) of monomers A and B; and (4) compatibilization of the *in-situ* polymerized blend PA/PB by the *in-situ* formed copolymer P(A-B).

Conceptually, the above *in-situ* polymerization and *in-situ* compatibilization method can allow obtaining a variety of morphologies, including pure block or graft copolymers [87–89], nano-dispersion of one polymer component in the other (nano-blend) by controlling the kinetics of *in-situ* polymerization, phase-separation, and *in-situ* copolymer formation. In order to acquire a nano-blend, both the amount and the rate of formation of the copolymer should be sufficiently high, compared with the rates of polymerization and phase separation, so that the morphology can be stabilized since the early stage of the phase separation [61]. This, however, requires very efficient (local) mixing [90,91] and good control of local residence time distribution [61,92].

4. Ternary polymer blending

While compatibilization of binary or two-component polymer blends has been studied extensively and procedures have been found, compatibilization of ternary or three- and even more-

Table 2
Compatibilization through a reactive polymer added separately.

Polymer blend	Added reactive polymer	Reaction for copolymer formation	Ref.
PP/PBT	PP-g-epoxy	Epoxy-carboxyl	[50]
PP/PBT	PP-g-epoxy	Epoxy-carboxyl	[51]
PS/PA6	PS-isocyanate	Isocyanate-amine	[62]
PS/PA6	PS-isocyanate	Isocyanate-amine	[63]
PP/PA6	PP-g-MAn	Anhydride-amine	[64]
PE/PA6	PP-g-MAn	Anhydride-amine	[31]
PP/PET	PP-g-MAn	Anhydride-hydroxyl	[65]
PP/LDPE	PP-g-MAn with EVAL	Anhydride-hydroxyl	[66]
PE/OPS	PE-g-MAn	Ring opening	[67]
PE/EPDM	PE-g-MAn	Ionic	[68]
PE/NR	PE-g-MAn	Ring opening	[68]
EPR/PA6	EPR-g-MAn	Anhydride-amine	[69,70]
PA6/EPDM	EPDM-g-MAn	Anhydride-amine	[71,72]
PC/ABS	ABS-g-MAn	Anhydride-amine	[73]
PA6/PSF	PSF-g-MAn	Anhydride-amine	[74,75]
PA6/PPE	PS-co-MAn	Anhydride-amine	[76]
PA6/ABS	PS-co-MAn	Anhydride-amine	[77,78]
PA6/SAN	PS-co-MAn	Anhydride-amine	[79]
PA6/PMMA	PS-co-MAn	Anhydride-amine	[80]
PA6/PS	PS-co-MAn	Anhydride-amine	[81]
PS/PA66	PS-co-MAn	Ring opening	[82]
PE/wood flour	Maleated and acrylic acid-grafted PE	Ring opening	[83]
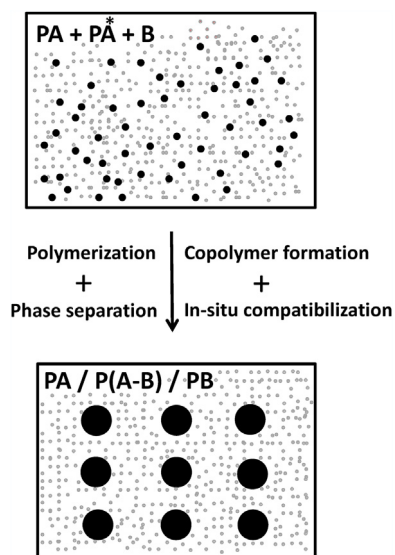
Fig. 9. Schematic description of the *in-situ* polymerization and *in-situ* compatibilization methodology for preparing (nano-)blends of polymer PA of monomer A and polymer PB of monomer B. PA*: polymer PA with some initiating sites either at the chain end(s) or along the chain; P(A-B): copolymer of monomers A and B. (Drawn following Hu et al. [85].)

component polymer blends presents a considerably more complex problem. It is nevertheless important for developing more versatile new polymer materials as also in the context of recycling of plastic wastes which are usually multicomponent.

In a ternary blend of polymers (say, A, B, C), there will generally be three types of polymer-polymer interfaces (A/B, B/C, C/A), though, however, one of these may be missing, e.g., if particles consisting of component A in the core and component B in the shell are formed in the matrix of component C. However, irrespective of the total number of interfaces involved, the issue boils down to dealing with the interface between individual binary pairs for which the possible routes to compatibilization have already been presented above. Thus, in a general case, for compatibilization of a ternary blend of three polymers (A, B, C), attention could be focussed on developing conventional mono-phase compatibilizers that are suitable individually for the three pairs (A/B, B/C, C/A) of the components, for each of which one or more of the routes 1 to 4, discussed above, could be used. Interestingly, in a more recent, novel approach, Wang et al. [93,94] employed a multi-phase *composite compatibilizer* for ternary polymer blending and observed better synergy, as reflected by improved mechanical properties, finer phase dispersion, and stronger interfacial adhesion vis-a-vis the use of conventional mono-phase compatibilizers.

Since waste plastics available for recycling are most commonly mixtures containing polyolefins (PE, PP, etc.), styrene polymers (PS, ABS, etc.) and engineering plastics (PA, PC, etc.). Wang et al. [93,94] studied the blending of PP/PA5/PS as an illustration of ternary blending using the novel strategy of composite compatibilizer. While effective compatibilization of this ternary blend was obtained with conventional mono-phase compatibilizers, such as PP-*g*-MAn and PP-*g*-St, or their mixtures, better compatibilization was, however, observed by using a composite compatibilizer [PP-*g*-(MAn-*co*-St)] prepared by maleic anhydride (MAn) and styrene (St) dual monomers grafting on PP. The higher synergy of the composite compatibilizer was attributed to two factors, one being the *in situ* formation of [PP-*g*-(MAn-*co*-St)]-*g*-PA6 graft copolymer at the PP/PA6 interface and the other being chemical affinity/interaction between homopolymer segments of PS and those of PP. In the

context of the arguments laid out in the present paper, the first factor would be identified as a manifestation of the Route 3 process (co-reactive blending), while the second as that of the Route 1 process (molecular mediation), both embodied in a single composite compatibilizer. This novel composite strategy can be extended to the compatibilization of other ternary blend systems, such as PP/PA/SBS, PE/PA/PS, PP/PC/PS, etc.

5. Conclusion

As the general incompatibility of polymers limits and influences not only the preparation and properties of polymer blends and alloys but also those of polymer melts, solutions and dispersions of additives, the need to use compatibilizing agents in order to reduce interfacial tension and promote adhesion at the polymer-polymer and polymer-additive interface cannot be overemphasized. Compatibilizing agents are usually block or graft copolymers with segments of structure or solubility parameter similar to those of the polymers being mixed. They can be separately synthesized and added or generated *in situ* in the extruder. There may be various ways for the latter option, such as, using catalysts or bridging agents, pre-functionalizing the blending polymers to facilitate grafting or copolymer formation in the extruder, or externally adding a high molecular weight polymer that is suitably pre-functionalized to trigger such activity in the blending mix in the extruder. All these options are classified into four well defined "routes to compatibilization" − namely, (i) molecular mediation, (ii) addition of catalysts or bridging agents; (iii) co-reactive melt blending; and (iv) external addition of a functionalized polymer to a blending pair. A host of diverse polymer blending examples from the literature are discussed in light of this perspective. To these traditional methods a novel method known as *in-situ* polymerization and *in situ* compatibilization has also been added that has the advantage that it can facilitate a variety of morphology including nano-blends, besides pure block or graft copolymers. While the focus in this review has been mainly on the compatibilization of binary polymer blends, ternary blends also are discussed briefly; their compatibilization strategies and the significance of 'composite compatibilizer' are explained in light of the four "routes to compatibilization" highlighted in the present paper.

CRediT authorship contribution statement

Manas Chanda: Writing − review & editing, Writing − original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

List of abbreviations

ABS	Poly(acrylonitrile-co-butadiene-co-styrene)
ATBN	Amine terminated butadiene-acrylonitrile rubber
BPO	Benzoyl peroxide
CTBN	Carboxyl terminated butadiene acrylonitrile rubber
EAA	Poly(ethylene-*co*-acrylic acid)
EAC	Ethylene acrylate copolymer
EMAA	Poly(ethylene-co-methacrylic acid)
EPDM	Poly(ethylene-co-propylene-co-diene)
EPR	Poly(ethylene-co-propylene) elastomer
EVAc	Poly(ethylene-co-vinyl acetate)
EVAL	Poly(ethylene-co-vinyl alcohol)

GMA	Glycidyl methacrylate
HIPS	High impact polystyrene
HTBN	Hydroxyl terminated acrylonitrile-butadiene rubber
LLD	Linear low density
MAn	Maleic anhydride
NBR	Poly(butadiene-co-acrylonitrile) elastomer
NR	Natural rubber
OBC	Olefin block copolymer
OPS	Polystyrene containing oxazoline groups
PA	Polyamide
PB	Polybutadiene
P(B-AN)	Poly(butadiene-co-acrylonitrile)
PBS	Poly(butylene succinate)
PBT	Poly(butylene terephthalate)
PCL	Poly (ϵ-caprolactone)
PE	Polyethylene
PEA	Poly(ethyl acrylate)
PEt	Polyether
PET	Poly(ethylene terephthalate)
PHB	Polyhydroxybutyrate
PIP	Polyisoprene
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PPC	Poly(propylene carbonate)
PPE	Poly(phenylene ether)
PPO	Poly(2,6-dimethyl-*p*-phenylene) oxides
PPS	Poly(phenylene sulfide)
PS	Polystyrene
P(SAN)	Poly(styrene-*co*-acrylonitrile)
PSF	Polysulfone
PSi	Polysiloxane
PUR	Polyurethane
PVa	Poly(vinyl alcohol)
PVBE	Poly(vinyl butyl ether)
PVC	Poly(vinyl chloride)
SAA	Poly(styrene-co-acrylic acid)
SAN	Poly(styrene-co-acrylonitrile)
SEBS	Styrene-ethylene/butylene-styrene triblock copolymer
SMA	Poly(styrene-co-maleic anhydride)
TBT	Tetrabutyl titanate
TPE	Thermoplastic polyester elastomer
TsOH	p-Toluene sulfonic acid

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