Compatibilization of Polymer Blends

Utracki, Leszek A.

National Research Council Canada   Conseil national de recherches Canada

Canada

COMPATIBILIZATION OF POLYMER BLENDS

L. A. Utracki, NRCC/IMI, 75, de Mortagne, Boucherville, QC, Canada J4B 6Y4; leszek.utracki@nrc.ca

ABSTRACT

Most polymer blends are immiscible and need to be compatibilized. The compatibilization must accomplish: (i) optimization of the interfacial tension, *i.e.*, the degree of dispersion; (ii) stabilize the morphology against high stresses during forming, and (iii) enhance adhesion between the phases in the solid state. Compatibilization is accomplished either by addition of a compatibilizer or by reactive processing. The presentation will focus on the fundamental aspects, *viz.* description of the interphase, compatibilization by addition and reactive compatibilization.

INTRODUCTION

There are several hundred reported cases of polymer/polymer miscibility limited to a specific set of conditions, *viz.* configuration of polymeric molecules, molecular weight and molecular weight distribution, composition, temperature, pressure, stress field, additives, etc. However, the immiscibility dominates. Alloying polymer blends involves several operations that should produce alloys with *stable* and *reproducible* properties. Since the material performance depends on morphology, the requirement for alloying means that the morphology must be optimized for the desired performance, *i.e.*, during forming to be either stable or reproducibly modifiable (*e.g.*, into lamellae during biaxial stretching).

There are three goals for the compatibilization process: (1) to adjust the interfacial tension, thus engender optimum dispersion, (2) to make certain that the morphology generated during the alloying stage will yield optimum structure during the forming stage, and (3) to enhance adhesion between the phases in the solid state, facilitating the stress transfer hence improving performance. The compatibilization methods can be divided into two categories:

1. *By addition* of: (i) a small quantity of third component that is miscible with both phases (co-solvent, *e.g., Phenoxy*), (ii) a small quantity of copolymer whose one part is miscible with one phase and another with another phase (*e.g.*, 0.5-2 wt% of usually tapered block copolymer), (iii) a large amount of a core-shell, multi-purpose compatibilizer-*cum*-impact modifier.

2. *By reactive compatibilization*, which uses such strategies as: (i) Trans-reactions, (ii) Reactive formation of graft, block or lightly crosslinked copolymer, (iii) Formation of ionically bonded structures, (v) Mechano-chemical blending that may lead to chains' break and recombination, thus generation of copolymers (even at liquid nitrogen temperatures), etc.

Different strategies lead to blends with different sets of properties. For example, addition of a small amount of copolymer (block-, graft-, random-copolymer or co-solvent) mainly affects the interfacial tension coefficient hence the size of dispersion, but normally it has little effect on either the shear sensitivity of the blends' morphology or their solid-state behavior. In most studies of blends' compatibilization, di- or tri- block copolymers have been used — the first type is more efficient in reducing the interfacial tension coefficient, v_{ij}, but the second type frequently in improving the mechanical performance. Addition of large quantities of core-shell copolymer is particularly useful in blends of two brittle, immiscible polymers, *e.g.*, polyamide (PA) with either thermoplastic polyester (PEST) or polyphenylene ether (PPE).

The solid-state compounding requires intensive mechanical mixing of immiscible blend components, then stabilization of obtained morphology. The stabilization can be achieved either by chemical (*e.g.*, recombination of free radicals, crosslinking by electron beam irradiation) or physical means (e.g., by

controlled crystallization). These alloys have high a modulus and a different fracture mechanism than that observed for melt-mixed ones.

The present day commercial alloys may comprise up to six polymeric ingredients. The increased number of components, n, means that the number of interfaces between them is: $N = n(n-1)/2$. Thus, compatibilization of multicomponent polymer blend may pose serious problems —improperly designed interface may be a source of fracture initiation. One of the adopted strategies involves addition of at least one ingredient having functional groups that react with several polymeric components; for example, a multicomponent copolymer that plays the dual role of compatibilizer and impact modifier, or a low molecular weight additive that at different stages of reactive blending binds to different components, viz., ethylene-glycidyl methacrylate, triglycidyl-isocyanurate, etc. The preferred method of compatibilization of such complex systems is sequential reactive processing.

THE INTERPHASE

In polymer blends' technology, the interface/interphase is of key interest. Compatibilization can be regarded as modification of the interphasial properties. In 1971, Helfand and Tagami calculated that the density profile across the interface follows the exponential decay (see Figure 1). The intercepts of the steepest tangential (at the place of the steepest decline or incline for the other component) with the horizontal lines defining the volume fraction of either one of the two polymeric ingredients, $\phi = 0$ and 1, defines the thickness of the interphase, Δl. Experimentally (see Table 1), Δl varies from 2 to 60 nm; the first value being valid for antagonistically immiscible polymer pairs, the second for reactively compatibilized polymer alloys. Addition of block copolymers only slightly increased the interphasial thickness, to 6-8 nm [Inoue, 1993]. Thus, any immiscible, two-component system has at least three phases. As the degree of dispersion and/or the thickness of the interphase increase so does the importance of the latter phase; the volume fraction of the interphase will be larger than that of the dispersed phase when the interphase thickness: $\Delta l > 0.26R$ (R = radius of the dispersed drop).

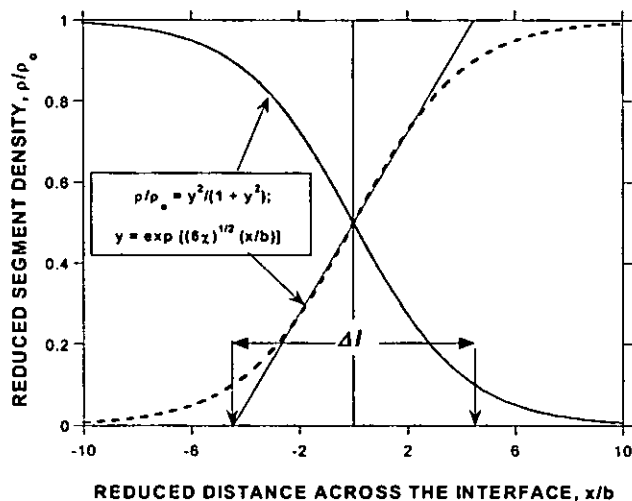Figure 1. Density profile across the interface, defining thickness of the interphase

$$\rho/\rho_o = y^2/(1 + y^2);$$
$$y = \exp{[(6\chi)^{1/2} (x/b)]}$$

Table 1. Interphase Thickness

TYPE OF BLEND	THICKNESS (nm)
Immiscible	2
Block copolymer	4 to 6
Polymer/Copolymer	30
Reactive Compatibilization	30 to 60
(Radius of gyration	5 to 35)

Helfand-Tagami lattice theory is based on the mean-field approach: (i) the two homopolymers were assumed to have the same degree of polymerization, (ii) the complex set of equations derived for the segmental density profile, ρ_i where i = A or B, was solved for entangled macromolecules, $M_w \to \infty$, (iii) the isothermal compressibility was assumed negligibly small, (iv) there was no volume change upon blending. The theory predicts that (i) the product, $\Delta l_{\rho\infty} v_\infty$, is independent of the thermodynamic binary interaction parameter, χ; (ii) the surface free energy is proportional to $\chi^{1/2}$; (iii) the chain-ends of both polymers concentrate at the interface; and (iv) low molecular weight third components are repulsed to the

interface. Theoretically, the interfacial tension coefficient, v_{ij}, can be calculated from the molecular structure of two polymers by means of Hansen's solubility parameters [Luciani et al., 1996].

According to Leibler [1988], for the most efficient reduction of the interfacial tension coefficient between two immiscible homopolymers, A and B, the two blocks of an A-B block copolymer should be equally long. When the interface becomes saturated with copolymer, v_{ij} reaches its lower plateau, $v_{ij} = v_{CMC}$, and the copolymer macromolecules start forming micelles, i.e., the critical micelle concentration, CMC, has been reached, $\phi = \phi_{CMC}^{+}$. Concentration dependence of v_{ij}, also know as the "copolymer titration curve", can be described by a semi-empirical relation, [Tang and Huang, 1994]:

$$v = v_{CMC} + (v_o - v_{CMC})\exp\{a\chi Z_c\phi\}$$
$$d = d_{CMC} + (d_o - d_{CMC})\exp\{a_1\chi Z_c\phi\}$$

(1)

where a and a_1 are adjustable parameters, and Z_C is the copolymer's degree of polymerization. Tang and Huang suggested that diameter of the dispersed drop, d, may follow the same "titration curve" as v_{ij}. The dependencies of Eq 1 well describe the experimental data — see Figures 2 and 3.
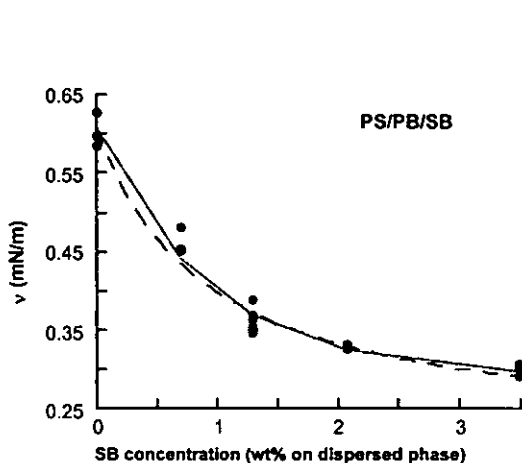

Figure 2. Interfacial tension coefficient vs. SB concentration. Data Anastasiadis [1988]; solid line Tang-Huang equation.
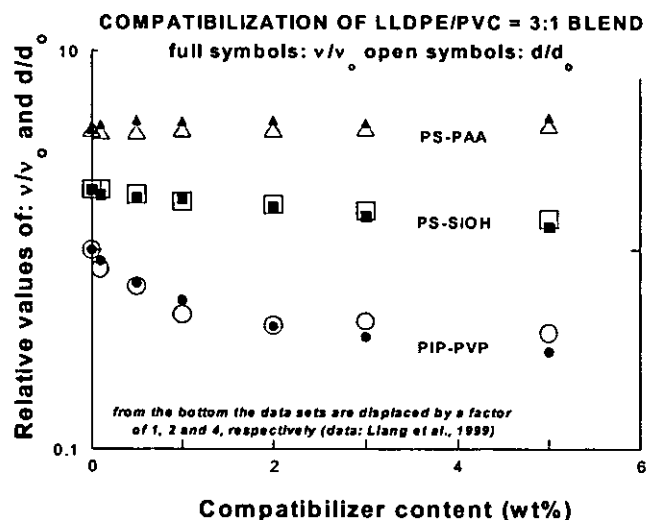
Figure 3. Relative interfacial tension coefficient in LLDPE/PVC blends vs. compatibilizer concentration. Note the superposition of the relative diameter of the dispersed PVC drops. Data Liang et al. [1999]

Assuming that compatibilizer is only located at the interface (i.e., no dissolution or micellization), its amount required for saturation is: $w_{cr} = K\phi/d$, where ϕ is the volume fraction of the dispersed phase, d is the drop diameter. The factor K depends whether the compatibilizing molecules only once intersect the interface or they coil on the surface of the dispersed phase. The first assumption leads to proportionality between compatibilizer molecular weight (MW) and w_{cr}, whereas the second removes such proportionality. The reality is somewhere in between these two ideal cases.

The methods of determination of the interfacial tension coefficient in industrially interesting polymer blends are few. Deformed drop retraction [Luciani et al., 1996], liquid thread break-up, rotating drop, and pendant or sessile drop have been used with a decreasing order of success. Even fewer methods are available to measure the interphase thickness, viz. ellipsometry, microscopy, or diffraction. So far, the interfacial tension coefficient and the interphase thickness have not been measured for the same blends.

COMPATIBILIZATION BY ADDITION OF A COPOLYMER

Historically, the most popular method of immiscible blends compatibilization has been by addition of a third component. In most cases, such an additive was either a block or graft copolymer. Since the key requirement is *miscibility*, it was not necessary for the copolymer to have identical chain segments as those of the main polymers, but this approach has been frequently used. It suffice that the copolymer has segments having specific interactions with the main polymeric components, viz., hydrogen bonding, dipole-dipole, dipole-ionic, Lewis acid-base, etc. Theoretical calculations suggest that efficiency of a compatibilizer increases with its MW. However, thermodynamics requires that the added copolymer not only concentrates in the interphase, but also dissolves in both phases, where (at higher concentration) it may form its own micellar structures. Thus, it is essential that the compatibilizer be designed to migrate to the interface, broadening of the segmental concentration profile, experimentally expressed as Δl. Addition of a block or graft copolymer reduces the interfacial tension and alters the molecular structure at the interface. Thus, compatibilization-by-addition changes not only the interfacial properties. The compatibilization may strongly affect the flow behavior (hence processability) and performance.

One of the disadvantages of the addition method is the tendency of the added copolymers to form micelles. These reduce the efficiency of the compatibilizer, increase the blend viscosity and may lessen the mechanical performance. For these reasons, the copolymer must be designed in such a way as to: (i) maximize miscibility of the appropriate part of its macromolecule with the specific polymeric component of the blends, (ii) minimize its molecular weight just to about the entanglement molecular weight for each interacting block, and (iii) minimize copolymer concentration in the blend. Addition of 0.5-2 wt% of well-designed, tapered block copolymer has been found sufficient [H. R. Brown, 1989; Cho *et al.*, 1990].

While reduction of the interfacial tension is relatively simple, the two other functions (stabilization of morphology and improvement of inter-phasial adhesion in the solid state) rarely are simultaneously achieved. Often, a combination of compatibilizers, or use of other strategies, e.g., crosslinking of one of the three phases (by chemical, thermal or irradiation treatment), may be more appropriate. Morphology stabilization may also involve addition of a small quantity of a third polymer-C to a binary A/B blend. The added polymer should have limited miscibility with either principal component of the blend. In the ternary system: A-matrix, B-dispersed, C-interphase when $v_{AB} > v_{CA} + v_{CB}$ polymer C migrates to the A-B interphase, improving morphological stabilization of the blend. The third aim of compatibilization, the enhancement of adhesion in the solid state, can be accomplished either by ascertaining that an appropriate concentration of covalent bonds crosses the interface, by introducing a compatibilizer that can act as an adhesive between two polymers, and/or by control of morphology, especially by inducing the phase co-continuity.

Nowadays, only a few commercial alloys are prepared using the compatibilizer-addition method. For example, according to the basic patent the blending of polyamide (PA) with polycarbonate of bisphenol-A (PC) involves compatibilization by addition of a polyesteramide elastomer and a maleated polypropylene or EP rubber (*Dexcarb®*) [Perron, 1984; 1988]. Commercial blends of PE/PS (*Neopolen®* for blister packaging) are compatibilized by addition of hydrogenated, tapered S-B copolymer (exclusively prepared for the in-house use). Numerous binary blends of PVC or PC with ABS or ASA (*e.g.*, *Cycovin®* or *Geloy®* and *Cycoloy®* or *Bayblend®*) can also be considered as non-reactively compatibilized by appropriately formulated latter component. These blends are at least three component systems with, *e.g.*, PVC, SAN-grafted elastomer and SAN, which may be considered a co-solvent. Polypropylene/polycarbonate, PP/PC, blends were compatibilized by addition of hydrogenated styrene-*b*-butadiene-*b*-styrene tri-block copolymer, SEBS. In blends comprising 10-20 wt% PC with the PP/SEBS ratio = 95/5 to 90/10, SEBS was found to envelop PC drops embedded in PP, indicating better interfacial affinity of SEBS to PP than that existing between PC and PP [Srinivasan and Gupta, 1994].

REACTIVE COMPATIBILIZATION

The second and today the dominant method of compatibilization is based on specific chemical reaction between two polymeric components during mechanical blending in a twin-screw extruder (TSE). As a result of the process, the chemical reaction takes place within the interphase hence the interfacial agent is produced *in situ*, with segments from the two homopolymers. Formation of a copolymer at the interface immediately suggests that, by contrast with the compatibilization-by-addition, here the highest MW copolymer is the most desirable – the copolymer is formed within the interphase where it should stay. From the economic as well as performance point of view, the technique is more interesting than the previously discussed by copolymer addition.

The reactive blending engenders a thick interphase that results in high stability of morphology during the forming stage, *e.g.*, during injection molding under high stress and strain, but also in increased viscosity. In some cases, as for example in polycarbonate/polybutyleneterephthalate (PC/PBT) blends, transesterification seems to be the easiest compatibilization strategy. However, since PBT crystallinity is of utmost importance, the method is neither easy to control nor of great advantage.

Reactive processing is an integration of fine polymer chemistry with precisely executed polymer processing (melting, compounding, extruding and forming). It combines the chemical kinetics with flow and thermal properties of the reaction ingredients and products. The conditions for reactive processing require that there is: (i) sufficient dispersive and distributive mixing to ascertain required renewal of the interface, (ii) presence of a reactive functionality, capable to react across the interphase, (iii) sufficient reaction rate making it possible to produce sufficient quantity of the compatibilizing copolymer within the residence time of the processing unit, (iv) stability of the formed chemical structures, and (v) stability of the morphology. During the reactive processing, in extrusion or injection molding, block or graft copolymers are usually formed. The chemical reaction leads to covalent or, less frequently, ionic bonds.

HISTORY

From the very beginning, blending involved both chemical and physical aspects. The very first patent on polymer blends [Parkes, 1846] describes mixing two polyisoprene isomers, natural rubber (NR) and gutta percha (GP) in the presence of SCl_2 that at the milling temperature partially co-vulcanized the ingredients. In 1939, I. G. Farbenindustrie patented blends of polyvinyl alcohol (PVAl) with acrylic copolymers containing maleic anhydride (MAH), thus describing what is know today as reactive blend. In the 1948 patent from du Pont de Nemours, polyvinylacetate (PVAc) was first maleated, and then reactively blended with PA-66. Starting in the mid-1960, the reactive extrusion began to be used for toughening and general modification of such engineering resins as PA, PET, PC, or PBT. For example, in the 1966 Bayer patent, PA-6/PVAl blends were obtained by polymerizing ε-caprolactam in the presence of PVAl. In 1969, the first reactive grafting of PPE was patented.

In 1971, Tokyo-Shibaura patented a two-step reactive extrusion leading to PC/SAN-grafted chlorinated polyethylene, CPE blends. The same year, Exxon patented reactive modification of polyolefins, PO (*e.g.*, maleation of PP) by reacting poly PE or PP with olefinic monomer in the presence of peroxides. A year later, styrene-grafted PE, obtained in reactive extrusion, was blended with PPE for improved processability and engendering a set of desired properties. In 1975, du Pont de Nemours started to manufacture the super-tough PA, *Zytel-ST*™, by reactive blending of PA-66 with maleated ethylene-propylene-diene elastomer, EPDM-MA.

In 1977 Ueno and Maruyama deposited the basic patent on reactive compatibilization of the PPE with PA [patent granted in 1979]. General Electric developed several strategies for the preparation of *Noryl*™ GTX. Initially, the hydroxyl-terminated PPE was end-capped in solution with trimellitic anhydride acid chloride, then extruded at 290°C with 41 wt% of PA-6,6 to give PPE-PA copolymer that subsequently was used as compatibilizer for the PPE/PA blends. Furthermore, to improve impact strength of the blends, 10 parts of SEBS was added. Molded parts showed higher impact and tensile strength than those containing only non-functionalized PPE or PPE grafted with MA [Aycock and Ting, 1986, 1987]. Blends of PC/PA (commercialized in 1988) were also produced by reactive compounding.

Reactive processing makes it possible not only to develop new blends, but also to generate old blends with new sets of properties, viz., blends with specialty resins or new PVC/acrylics compositions. The technology makes it possible to intelligently combine properties of several polymers into complex, multicomponent alloys. In 1985, Toray introduced PPE/PET/PC/EGMA blends for high performance automotive applications. In 1987, GEC patented PPE/PBT/PC/SEBS blends (*Gemax®*) [Campbell *et al.*, 1990]. These commercial activities find a broad base of support in the open literature.

In many systems, the first step of the reactive processing involves modification of a polyolefin (PO) resin, usually by grafting it with either maleic anhydride or glycidylmethacrylate. Compounding the product with PA, PEST or PC may follow. Finally, the resulting copolymer may be compounded with a blend of main components, possibly having different molecular characteristics (*e.g.*, MW, MWD, etc.). As this and other cited above examples indicate, the reactive compatibilization may be carried out in one, two or three compounding steps. Historically, the first and easiest to perform was the 3-step compatibilization process, *e.g.*, maleation, reaction and blending as three independent processing operations. Conceptually, it was still "compatibilization-by-addition", with a desired copolymer separately prepared using (frequently lower MW) homologues of the main components of the blend. The 2-step reactive compatibilization is more efficient, since here the compatibilizing copolymer is prepared in a single step (*e.g.*, maleation and reaction), followed by compounding. The most difficult, but the most effective is the reactive compatibilization in a single step, involving a cascade of coordinated processing steps in often more than a single processing unit.

REACTIVE COMPATIBILIZATION CHEMISTRY

The basic method for generation of a well-structured copolymer is through inter-polymer reactions. The process may be defined as a reaction between two or more polymers to form a copolymer. The five basic chemical processes by which interchain copolymer formation has been achieved in an extruder are summarized in Table 2 [Brown, 1992, 2002]. Interchain block copolymer formation by reactive extrusion is particularly useful.

Table 2. Bruce Brown's classification of the reactive compatibilization strategies [2002]

1	**Redistribution or Trans-reactions** $\Rightarrow$ Block & Random Copolymers
1a	Reactive end-groups of polymer-1 (P-1) attack main chain of polymer-2 (P-2)
1b	Chain cleavage/recombination involving all polymers
2	**Graft Copolymer Formation** $\Rightarrow$ Graft Copolymers
2a	Direct reaction of end-group of P-1 with pendent groups of P-2
2b	Reaction of end-group of P-1 with pendent group of P-2 in the presence of a condensing agent
2c	Reaction of end-group of P-1 with pendent group of P-2 in presence of a coupling agent ("c")
2d	Reaction of pendent groups of P-1 with main chain of P-2 in a degradative process
3	**Block Copolymer Formation** $\Rightarrow$ Block Copolymers
3a	Direct reaction of end-group of P-1 with end-group of P-2
3b	Reaction of end-group of P-1 with end-group of P-2 in the presence of a condensing agent
3c	Reaction of end-group of P-1 with end-group of P-2 in the presence of a coupling agent ("c")
3d	Reaction of end-group of P-1 with main chain of the P-2 in a degradative process
4	**Crosslinked Copolymer Formation** $\Rightarrow$ Crosslinked Structures
4a	Direct reaction of pendent functionality of P-1 with pendent functionality of P-2
4b	Reaction between pendent functionalities of P-1 and P-2 in the presence of a condensing agent
4c	Main chain of P-1 reacts with main chain of P-2 in the presence of a radical initiator
4d	Reaction between pendent functionalities of P-1 and P-2 in presence of a coupling agent ("c")
5	**Ionic Bond Formation** $\Rightarrow$ Block, Graft or Crosslinked Structures
5a	ion-ion association mediated by metal cations as linking agents ("c")
5b	ion-neutral donor group association mediated by metal cations
5c	ion-ion association mediated by interchain protonation of a basic polymer by an acidic polymer

As indicated in Table 2, block copolymers can be preferentially formed in reactions involving end-groups of two polymers. Since the probability of two end-groups reacting within typical residence time in an extruder is low, highly reactive functionalities, a catalyst and/or high concentration of end-group (i.e., low molecular weight polymers) may have to be to be employed. The majority of polymers modified by reactive processing have nucleophilic end-groups, such as carboxylic acid, anhydride, amine, or hydroxyl group. These groups readily form covalent bonds with suitable electrophilic functionalities, such as epoxide, oxazoline, isocyanate, or carbo-di-imide, generating the desired copolymer.

Redistribution is a slow statistical process in the melt between: (1) ester groups, (2) amide groups, or (3) amide-ester groups. It may lead to destruction of crystallinity and/or lowering of T_g — as observed for PET/PC or PET/PA-6. Transesterification is observed in PEST/PC, PEST/LCP, LCP/PC, PAr/LCP, PET or PETG with EVAc, etc. It can be catalyzed by di-butyl tin oxide, SnO_2 or $Ti(OBu)_4$, and hindered by tri-phenyl phosphite (TPPite). The reaction between ester groups may involve these of the main chain or side chain or groups, viz. of PMMA, EVAc, acrylic impact modifiers, etc. Controlled redistribution has been used to induce compatibilization (PET/LCP) and/or impact modification (PET/MABS).

Transamidation is a slow, reversible process that may randomize composition of melt-blended PA's. Since a mixture of aliphatic and aromatic PA's is immiscible, controlled transamidation followed by impact modification has been used. Similarly, ester-amide exchange reaction (catalyzed by, *e.g.*, *p*-tolueno sulfonic acid or tertiary phosphite esters,) has been employed to compatibilize, *e.g.*, PA/PEST or PA/EAA blends [Pillon and Utracki, 1984, 1986; Aharoni *et al.*, 1984]. As shown in Fig. 4, the reaction is sensitive to temperature. It is more difficult to reactively compatibilize blends of PC with PA. To enhance reactivity the hydroxy-terminated PC was end-capped with trimellitic anhydride acid chloride, then extruder-blended at 277°C with PA-6 and an acrylate-styrene core/shell impact modifier [Hathaway and Pyles, 1988, 1989].
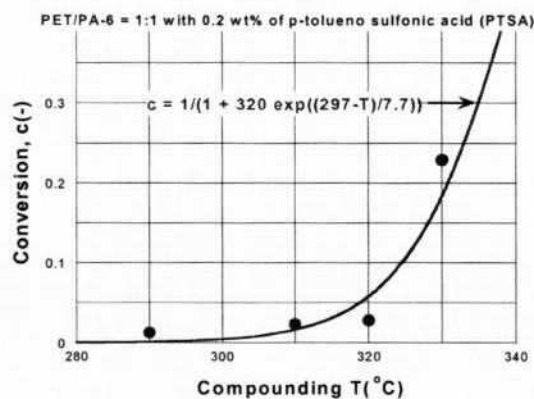

Figure 4. Conversion vs. compounding temperature is TSE during PET/PA-6 reactive compatibilization in the presence of p-tolueno sulfonic acid.
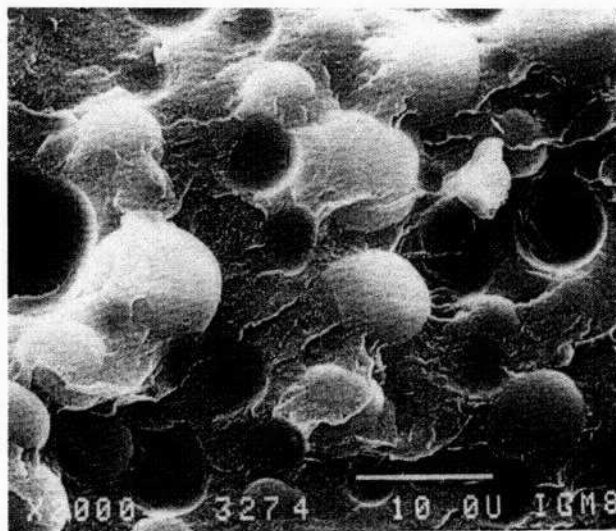
Figure 5. SEM micrograph of reactively compatibilized PET/PA-6 blend [Pillon and Utracki, 1984, 1986].

Reactive blends have thicker interphase than blends with added copolymer. The interfacial thickness in blends of amorphous polyamide, PARA, with a styrenic copolymer, either SMA or SAN was measured by time-resolved ellipsometric method during annealing [Yukioka and Inoue, 1993; 1994]. The interphase thickness increased with time to a plateau, whose value depended on the temperature and net concentration of the reactive sites. The interface was thick, $\Delta l = 10$–60 nm, larger than the radius of gyration of the copolymer. Reactive compatibilization most frequently increases viscosity of the blends, especially at the low deformation rates (yield stress).

COMPATIBILIZATION TECHNOLOGY

Reactive compatibilization is usually conducted in a TSE. As illustrated in Fig. 6, the process involves several functions, e.g., feeding the polymer, melting it, injection of peroxide solution, injection of monomer, reaction within the pressurized zone, mixing, devolatilization, then building the pressure to push the product through a die. The sequence of addition of initiator and monomer is critical. Depending on the system, the initiator may be introduced before (even directly with the main polymer) or after the monomer (especially when the latter is miscible with molten polymer).
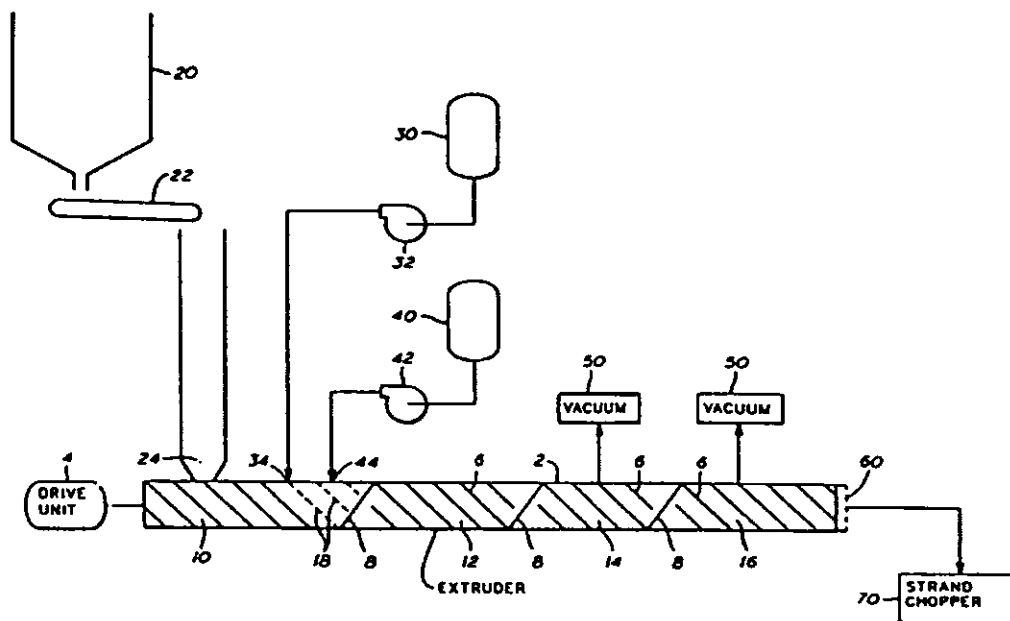
Figures 6. Maleic anhydride (MAH) grafting of LDPE was conducted at T = 220-260°C in a TSE separated into 4 zones by reversed flights.

- *Zone-1, T = 215°C, feeder: LDPE, port 34: solution of MAH in MEK*
- *Zone-2, T = 228°C, port 44: solution of peroxide in MEK - reaction*
- *Zone-3, T = 233°C, homogenization, port 50: devolatilization*
- *Zone-4, T = 235°C, devolatilization and pressure buildup.*

The residence time was t_r = 5 min. The initiator had large effect on MAH level in the product [Strait et al., 1988].

The reactive compatibilization requires judicious selection of the ingredients, the suitable chemical process, appropriate sequence of ingredients' addition and precise control of the processing parameters. The choice must ascertain the desired total residence time within the extruder, as well as the residence time within each of the principal zones, e.g., melting, reaction and devolatilization. In TSE the residence time is mainly determined by the "degree of screw fill" that controls the throughput, Q (kg/h). For example, at the screw speed of 100 to 500 rpm the residence time, t_r, decreased from 400 to 15 s when Q increased from 1 to 20 kg/h. The required residence time within the reaction zone depends on the interrelated kinetic and thermal effects, which are sensitive to temperature (T) and pressure (P). The latter parameters in turn depend on the screw configuration, processing parameters and the degree of dispersion these generate. The process is usually optimized by trial and error. Once the parameters are selected, computer control is essential.

Evidently, the reactive compatibilization is more complex than compatibilization-by-addition. Mathematical modeling of it is in an early stage of development. It should involve three integrated parts: (1) the hydrodynamic description of TSE (providing the T, P, t_r and the stress fields), (2) description of the morphology evolution, and (3) chemical and thermal effects of the reactive compatibilization.

CONCLUSIONS AND OUTLOOK

During 160 years since the first compatibilized blends of Alexander Parkes were commercialized, the compatibilization technology evolved along with new resins, equipment and the knowledge of the process. For the thermoplastic resins the original co-reaction or co-vulcanization method was replaced by compatibilizer addition. At the beginning, for blends of polymer-A with polymer-B, A-B block copolymers were used, later copolymers X-Y, where the branches X and Y would be miscible but not chemically identical to resins A and B have been applied. At the next stage it was the preparation of universal compatibilizer-*cum*-impact modifier that by virtue of different interactive groups would engender the desired performance. Only during the last 25 years or so the reactive compatibilization evolved into the dominant method.

Nowadays, the blend technology is fully integrated into the main stream – the industry knows how to alloy polymers for the desired set of performance characteristics. The attention seems to be shifting to other challenges. However, as this short review indicates there are still many difficult unsolved problems left in the polymer alloys and blend science and technology, including compatibilization.

One of the most important fundamental problems is the departure from the equilibrium state. All principal aspects of the polymer blend technology, viz. rheology, thermodynamics, microrheology, morphology, or kinetics, assume existence of a steady state or equilibrium. The laboratory tests may afford sufficient time for the signals to reach constant value. However, as the speed of the processing line continues to increase (TSE with screw speed of 1,500 rpm is a reality, while these with 3,000 rpm are being developed) for the industry this fundamental assumption is getting less and less real. Even at the "normal" screw speeds in a TSE, due to heterogeneity of stress field the morphology of specimen collected within one second is totally different (large quantity of sub-micron droplets) from that in sample collected within one minute (absence of the sub-micron droplets). If one would want to describe the reactive compatibilization that take place within the interphase a "zero time" morphology should be used, but this is illusive. Microrheology is able to predict variation of "equilibrium" morphology in dilute, non-reactive blends. However, how to describe the evolution of the "zero time" morphology and incorporate the chemical reactions there, is a serious problem.

Another area of activity that falls into the blend compatibilization category is the development of new, commercially valuable poly mer blends comprising polymer-A/polymer-B. Few examples of binary blends that await development are listed in Table 3. Assuming additivity of properties many of these (as well as several additional binary systems and many multi-polymeric ones) are good candidates for industrial development. As always, economic compatibilization toward optimum morphology is the key.

Table 3. Examples of binary blends that need development

Polymer-A	Polymer-B
PO (PE, PP, EPR)	PS, ABS, PMMA, PVC, PPE, PSF
PS, ABS	PMMA, PVC, PSF, PA
PMMA	PS, EPR, PPE, PA
POM	PC, PEST, PAr, PA, PPE, PPS, PSF, PEI, ...

REFERENCES

(For topical references consult the following books on polymer blends by the author):

Polymer Alloys and Blends, Hanser, Munich (1989); Tokyo Kagaku Dozin, (1991); *Encyclopaedic Dictionary of Commercial Polymer Blends,* ChemTec, Toronto (1994); *Commercial Polymer Blends,* Chapman & Hall, London (1998); *Polymer Blends Handbook,* Kluver, Dordrecht (2002).