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REPORT TO UNIDO

POLYMER BLENDS AND
COMPOSITES: CONCEPTS

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April 1990

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REPORT: POLYMER BLENDS AND COMPOSITES:
AN OUTLINE OF CONCEPTS

I. INTRODUCTION

Plastics of commerce are multicomponent products

Plastics that are in practical use are seldom, if ever, pure polymeric materials. The properties of the latter are of necessity improved in a multiple parameter consideration by the addition of a wide variety of additives. These are of low and/or high molar mass, organic and/or inorganic, soluble (miscible) and/or insoluble (immiscible) and of regular or irregular geometry, and with isomeric or anisomeric configuration.

In the present short survey, we shall for convenience consider two major classes:

1) Polymer-polymer blends, which may be further subdivided into miscible and immiscible alloys, and

2) Polymer-inorganic mixtures, in which the former component is the major constituent: these materials are generally referred to as composites. A major variable in this class is the shape - particulate or fibrous - of the minor component.

This division is not exclusive: many examples can be cited which straddle the above arbitrary division.

For example:

a. There is considerable production of composite materials in which the reinforcing component is a high strength organic polymer fiber.

b. Polymer-polymer blends are often further modified by the addition of

fibrous reinforcement.

Another classical division which has practical significance because of differing industrial practices reflects the glass transition of the principal component: elastomers (rubber) ie. materials with T_g 's (or T_m 's) below ambient temperature, and thermoplastics or thermosets with T_g 's or T_m 's above ambient.

For convenience and expediency we shall, as far as practical, use the polymer-polymer and polymer-filler division in the following report.

II.1. POLYMER-POLYMER BLENDS

We briefly consider the semantics, which have become somewhat confused over time.

A. Miscible, soluble and compatible

We shall define miscible and synonymously, soluble, as a polymer-polymer system which can be regarded as a single phase. In low molar mass situations this is usually obvious from visual inspection.

In polymers, because of high viscosity and other factors, indirect methods, commonly the presence or absence of a single T_g , are employed to perform this differentiation.

A single T_g is held to reflect miscibility on a segmental level. Commonly employed techniques are thermal (change of heat capacity, ΔC_p), dynamic or dielectric mechanical relaxation (observation of loss maxima) and large deformation (static) mechanical measurements (modulus). Optical techniques are also employed (direct visual examination: transparency, or more elaborate scattering

methods). However optical techniques do not necessarily reflect segmental miscibility; they cannot distinguish refractive index inhomogeneities below the 30nm level. In more complex blend systems e.g. of block copolymers with homopolymers, where both micro- and macro-phase separation may occur, these distributions can become important.

Polymer-polymer miscibility is a comparatively rare phenomenon because of thermodynamic factors, see below.

Compatibility is a much more common phenomenon and refers to a blend which is thermodynamically immiscible, i.e. contains multiple phases, but is useful in the technological sense.

Alloy is a term applied to multi-component polymer mixtures, often without distinguishing the phase state.

For an immiscible system to be compatible (a property which in principle could be time and, certainly, temperature, dependent) there must be 1) a practical resistance to macroscopic phase separation (in the limit: to two separate layers) and 2) adhesion between the two dispersed phases. These requirements can be met by a high viscosity and a minimal interfacial free energy.

In practice third components may be used to achieve the latter requirement in modern thermoplastic-thermoplastic blends, while chemical means are used in more traditional systems such as rubber-reinforced brittle thermoplastics.

Thermodynamics

Criteria for miscibility are

$$\Delta G_m(T) \leq 0; \quad \partial^2 \Delta G_m(T) / \partial \phi_2^2 \geq 0 \quad (1)$$

where ΔG_m and ϕ_2 are the free energies of mixing and the volume fraction of component 2 respectively. ΔG_m is usually parameterized in the Flory-Huggins format or elaboration thereof.

Thus:
$$\frac{\Delta G_m}{RT} = \frac{\ln v_1}{n_1} + \frac{\ln v_2}{n_2} + \chi_{12} v_1 v_2 \quad (2)$$

where n_1, n_2 are the degrees of polymerization of the respective components; v_1, v_2 are the volume fractions. The Flory-Huggins segmental interaction parameter, χ_{12} , is a property of the system. It should be emphasized that (except in copolymer cases, see below) it is seldom possible to a priori predict miscibility. Because the first two terms on the RHS (the entropic contribution) are essentially zero for high molecular weight systems, the occurrence of miscibility or immiscibility is largely governed by the sign of χ_{12} . The practical consequences are, since $\chi_{12} > 0$ for most systems (which implies repulsion) that miscibility in homopolymer blends is rare.

It should be noted that χ_{12} is temperature dependent and may change sign within the experimentally accessible temperature range, leading to a change from miscibility to immiscibility or vice-versa. This is an especially important practical consideration in processing polymer blends; a system which may be miscible at lower temperatures in the processing window, may phase separate at higher temperatures.

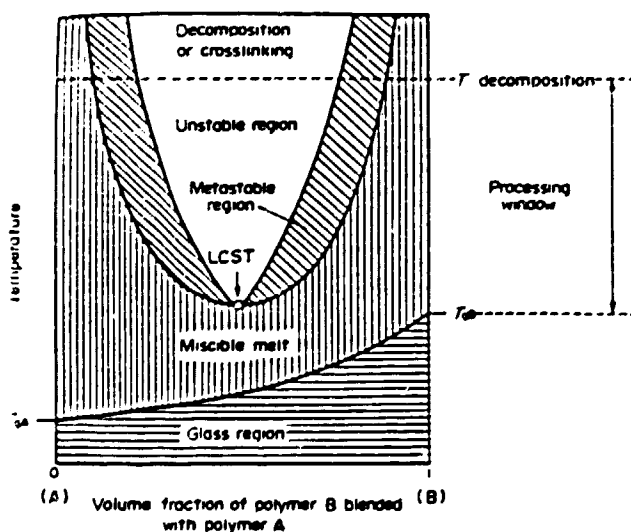
Much effort has been devoted to the a priori calculation of χ_{12} (and possibly its temperature dependency) but because of the absence of significant entropic driving force for miscibility (as occurs in low molecular weight materials) the precision necessary in χ_{12} for prediction is hard to achieve. Many attempts have been made on the basis of solubility parameters which can be related to χ 's and while it is certainly possible to successfully predict immiscibility with this scheme, the opposite is unlikely.

Miscibility in homopolymers is thus empirically associated with the presence of specific (favorable) interactions which include hydrogen bonding, charge transfer interactions, and electrostatic or other polar interactions; in some cases the precise "reason" for miscibility at a molecular level is hard to establish.

Phase Behavior in Polymer Blends

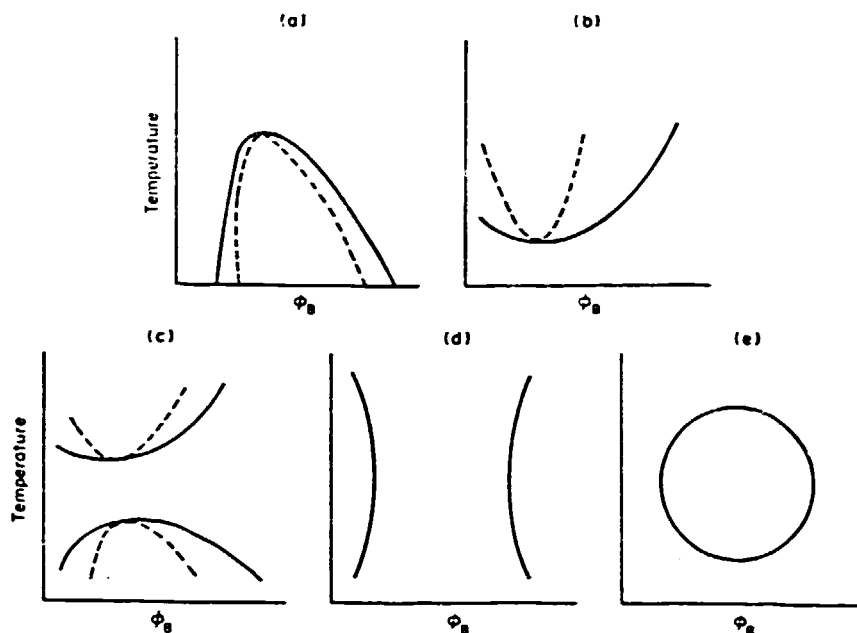
It is important to understand the possible phase behavior which may be found in binary polymer systems (more complicated of course in ternary and higher order cases).

As already stated, in miscible polymer-polymer systems, it is often found that at some higher temperature phase separation takes place. [For thermodynamic reasons, see above]. The resulting minimum in the phase boundary is referred to as the lower critical solution temperature, or LCST, see Figures 1A, B.



A schematic phase diagram for a polymer-polymer blend of the LCST type

Fig. 1A



Schematic phase diagrams for polymer-polymer blends: — binodal lines, --- spinodal lines: (a) a phase diagram of the UCST type; (b) a phase diagram of the LCST type; (c) a phase diagram in which both a UCST and an LCST occur; (d) an 'hourglass' phase diagram; and (e) a phase diagram in which the UCST occurs above the LCST

Fig. 1B

Figure 1A is a schematic generalization of a typical (partially) miscible polymer blend. At low temperatures one phase behavior is found and thus a single line connecting the T_g 's of the pure components represents the T_g of the blend [if the system were immiscible, the more-or-less unchanged T_g 's of the constituents would be found in the blend]. The single T_g is convex downwards to the composition axis; the normal (but not invariable) behavior. At some temperature above the T_g , in the melt [the diagram deals only with amorphous blends] phase separation occurs, and thus above the phase boundary the system separates. Thermodynamically one may recognize a binodal (outer) and a spinodal

(inner) boundary, see below, which are of practical significance in polymers in terms of resulting morphologies. In the Figure 1A schematic, there is also an indication of an upper temperature at which some form of irreversible chemistry occurs; this temperature therefore defines the upper limit of thermoplastic processibility (time factors are of course also to be taken into account). The lower theoretical limit of the processing window is the T_g curve; in practice the lower limit is some tens of degrees above T_g .

Figure 1B shows other possible phase behavior in polymer blends. Diagram (a) with an upper critical solution temperature, (UCST) is typical of polymer-solvent systems, but may also be found in practical elastomeric blends. Diagram (d) is in principle the most common situation in that the majority of the regime represents immiscibility, with limited regions of miscibility occurring only near the pure constituent compositions.

Table 1A lists a few classical polymer pairs known to be miscible over at least some temperature range. Other pairs that have been investigated (Table 1B) are immiscible. There are of course literally thousands of combinations that have been investigated and categorized.

Component 1	Component 2
Poly(vinyl chloride)	Poly(butadiene-co-acrylonitrile)
Poly(vinyl acetate)	Poly(methyl acrylate)
Poly(methyl methacrylate)	Poly(ethyl acrylate)
Polystyrene	Poly(α -methyl styrene)
Polystyrene	Poly(2,6-dimethyl phenylene oxide)
Polystyrene	Isotactic poly(vinyl methyl ether)
Poly(vinyl chloride)	Poly(ϵ -caprolactone)

Table 1A

Polymer 1	Polymer 2
Polyethylene	Polyisobutylene
Poly(methyl methacrylate)	Poly(vinyl acetate)
Natural rubber	Poly(styrene-co-butadiene)
Polystyrene	Polybutadiene
Polystyrene	Poly(vinyl chloride)
Poly(methyl methacrylate)	Polystyrene
Poly(methyl methacrylate)	Cellulose triacetate
Nylon 6	Poly(methyl methacrylate)
Nylon 6.6	Polyethylene terephthalate
Polystyrene	Poly(methyl acrylate)
Polystyrene	Polyisoprene
Polyurethane	Poly(methyl methacrylate)

Table 1B

Morphology of Phase Separation

In polymer-polymer systems the morphology of phase separated systems is a significant issue. Figure 1A, B illustrates the separation of the phase boundary into regions which delineate the so-called spinodal and the nucleated structures which can be obtained by changing the annealing temperature of a miscible polymer blend. This has practical consequences because it is believed that spinodal decomposition can lead to inter-connected morphologies which can lead to enhanced mechanical properties.

Copolymer Effects

Miscibility can often be enhanced by the use of copolymers. A theory is available and a number of practical examples are known (e.g. SAN/PVC; BuAn PVC).

For simplicity we shall deal only with random copolymer/homopolymer blends of the type A/B_xC_{1-x} .

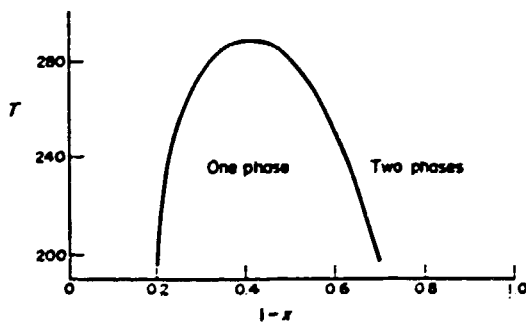
SAN: Styrene-acrylonitrile copolymer
PVC: Polyvinyl chloride
BuAn: Butadiene-acrylonitrile copolymer

In this case the net interaction parameter (χ_{12} in equation 1) is modified as follows:

$$\chi_{net} = x \chi_{AB} + (1-x) \chi_{AC} - x(1-x) \chi_{BC} \quad (3)$$

where the homopolymer contains segments of type A, the random copolymer types B and C, the χ_{ij} are the respective segmental interaction parameters and the x are the volume fractions of B in the copolymer.

The significant point is that intrasegmental repulsion in the copolymer (positive χ_{BC}) if it exists, favours miscibility in the system by tending to make $\chi_{net} < 0$). Clearly this rather non-intuitive result can have a profound practical influence on miscibility in such systems. Many new phenomena are predicted, e.g. "miscibility windows" in which one-phase behavior may be found for certain ranges of copolymer composition, see Fig. 2.



Miscibility window for PPO/poly(o-chlorostyrene-co-p-chlorostyrene) blends

Fig. 2

In Fig. 2 we see a homopolymer, polyphenylene oxide (PPO) mixed with a random copolymer of o- and p- chlorostyrene. The PPO is immiscible with the homopoly-

mers of both of the halostyrene polymer isomers, yet there is a substantial miscibility window, because of the repulsion of the isomers. Notice also that PPO is miscible with homopolystyrene; typically relatively small chemical changes render miscible systems immiscible.

It may be noted that if the respective x 's are known, miscibility may be "designed" into a system. The above treatment has been extended to more elaborate blends systems: copolymer-copolymer, ternary cases, etc. and constitutes one practical method of obtaining polymer miscibilization (see below).

Largely Immiscible Polymer-Polymer Systems

This classification encompasses the vast majority of compatible polymer-polymer blends/alloys.

The bulk behavior of such two phase systems depends on a large array of factors. The chief parameters (in addition to the inherent properties of the constituents) include:

1. state of dispersion (nature of the major, minor phase)
2. adhesion between phases
3. concentration of minor phase

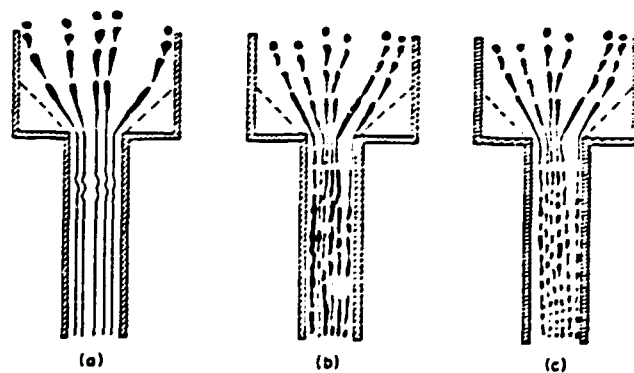
The properties of an immiscible blend in the most general sense may be described in terms of a law of mixtures, for example

$$P_c = \phi_A P_A + \phi_B P_B \quad (4)$$

where P_c represents some property of the composite in terms of the property P_i and volume fraction ϕ_i of components A and B.

Deviations from this "parallel" model are always found and many empirical relationships have been proposed. It is frequently necessary to add a term $K\phi_A\phi_B$ to equ. (4) to take into account interactive effects. In practice these constituent interactions at the interface determine, in a typically unpredictable way, the practical properties of the blend (e.g. modulus, impact strength, fatigue, melt rheology, etc). As already mentioned, the T_g 's in an immiscible blend may be unchanged - except in intensity - relative to the pure constituents.

The rheology of immiscible polymer blends is of great practical importance. In the simplest case the higher T_g component (if it is the minority component) may be regarded in terms of filler particles. Fig. 3 illustrates the effect of viscosity ratio, λ , in a given configuration. Clearly interfacial tension is an important additional parameter.



Phase morphology of blends of varying viscosity ratios: (a) $\lambda < 0.7$; (b) $0.7 < \lambda < 1.7$; and (c) $\lambda > 2.2$

Fig. 3

Modern terminology differentiates between interface and interphase in blends (and also in reinforced systems, see below). The interphase defines a region of intermediate composition (or composition differing from either of the two blend components) and is bounded by two interfaces. This concept may not be meaningful in certain cases, e.g. in polymer-metal systems.

II.2. POLYMER-PARTICULATE/FIBER SYSTEMS

Basic Outline

Such systems, referred to as composites, constitute a very important technological class of plastic materials.

In such systems the polymer necessarily forms the continuous phase and the (usually) inorganic second component is dispersed in the polymer phase. Loadings can vary but are typically in the 10-30 volume percent range.

Classification can logically be made on the basis of filler geometry. Essentially particulate fillers (e.g. glass beads, calcium carbonate, carbon black) may confer some additional rigidity on the system - the particles may be reinforcing or not - but as the geometry becomes anisomeric i.e. to fibrous geometries, greatly improved mechanical and thermal properties are observed.

Fiber reinforcement in a thermoplastic improves stiffness, strength and creep resistance. Non-reinforcing particulate additives (fillers) reduce cost by extension but may also have some secondary effects such as wear resistance, shrinkage reduction and high temperature properties.

Types of Particles/Fibers and Their Properties

We shall consider typical fibers such as E- and S-glass, carbon, boron and the organic polyamides such as kevlar, as well as particulate reinforcers such as carbon black.

E-glass: a borosilicate glass; most commonly used
S-glass: higher strength and modulus, but more expensive than E-glass
Carbon fiber: carbonization of (usually) polyacrylonitrile fiber

Effect of Fiber Reinforcement on Mechanical Properties

Various theoretical mechanical models are available which attempt to predict the following properties in terms of the inherent properties of the constituents. The predictions are always compromised if interfacial adhesion/wetting is less than perfect.

Tensile modulus

Tensile strength

Fracture toughness

Effect of fiber length

Effect of fiber orientation

Effect of loading

Continuous Fiber Reinforcement is a special case of fiber reinforcement.

The performance of a fiber-matrix composite depends ultimately on the constituent materials, the form and arrangement of the constituents, and the interaction between the constituents. Each of these factors can have many degrees of freedom; some have already been alluded to. It is this versatility which, in part, makes composites important. In addition the properties of a composite are controlled by the mechanical, solvent, and thermal histories of the materials i.e. by the processing.

In the case of fibers we may distinguish several factors which affect the properties of the composite:

Nature of fiber

Orientation

Length/diameter ratio

Shape

The matrix serves to hold the fibrous reinforcement in place and to distribute the load to the fibers, under stress. The latter factor depends critically on the coupling.

Matrix-Fiber Interactions

The filler-polymer interface adhesion is a critical aspect of multi-component plastic systems.

A vast technology, somewhat empirical, having to do with adhesion-promoting, coupling agents exists. These surface modifiers do more than promote adhesion; they provide an interphase region which has substantial effect on bulk properties such as rheology and fracture. The most common materials used for thermoplastic - glass systems are organic silanes and titanates. Their chemistry is based on a relatively simple premise: that the Si "end" of the polymer will adsorb/bond to the inorganic glass, while the organic "end" will be solubilized in the polymeric phase.

The effect of humidity and temperature are important parameters.

The enhancement of adhesion between carbon fibers and thermoplastics requires a different technology: oxidation and/or acid treatment of the interface materials is commonly used.

The modification of the matrix-filler interface bond to promote adhesion involve such factors as wettability, surface free energy, polar moieties on the

respective surfaces, surface roughness. In addition interdiffusion effects are relevant. There are in principle two surfaces that can be modified: matrix and filler. Changes in the former usually involve the generation of polar groups on the premise that the reinforcing agents also have polar surfaces. Non polar polymers (PE, PP) may be oxidized chemically by nascent O₂, by corona discharge, UV radiation in the presence of the appropriate gases, or by a variety of plasma treatments. All of these treatments can affect the adhesive properties of the matrix polymer.

Matrices may also be modified by covalently bonding appropriate groups or moieties on to the surface - a method known collectively as graft polymerization. The grafted polymer component is usually immiscible with the bulk material and therefore may be expected to diffuse to the interfacial surface, if it is not already there.

The graft polymerization may be effected by a number of techniques: plasma-induction, radiation polymerization, photografting, etc. In all these modifications, the effect of moisture - positive or negative - is an important consideration. The desired polar groups modifying the surface will tend to be hydrophylic and bonding between the matrix and filler may be very susceptible to water which can enter the interphase by capillary action.

The more usual method of modifying the matrix-filler adhesion is by modification of the reinforcing fiber or filler. The use of coupling agents falls into this general category. Because of the obvious versatility of the chemistries involved this method is most widely used. Silane coupling agents with glass in non polar polymer systems tend to increase strength and rigidity; tita-

PE: polyethylene
PP: polypropylene

nate agents improve processibility. The mechanisms of these effects have been widely investigated.

Another route to obtaining an enhanced matrix-filler bond is by allowing the polymerization (e.g. of PE) to proceed on the surface of the filler on which initiator catalysts have been adsorbed or even covalently attached. This technique can produce (for example) CaCO₃-PE composites with greatly improved properties relative to conventional composites consisting of these materials.

Surface modification of inorganic fibers by a variety of low molecular mass chemistries have been developed. These techniques, again, have the general objective of placing chemical moieties on the surface which have specific (favorable) interactions with the relevant matrix.

Treatment of carbon fiber (typically produced from polyacrylonitrile fiber or pitch) is widespread. The most typical technique is oxidation by high temperature O₂ gas treatments or by wet, acidic, treatments.

III. MIXING

Distributive blending is a low energy process that can be used as a preliminary to dispersive mixing (example: mixing of color additives) or in thermosetting systems when fusion follows in molding processes.

Dispersive mixing is a high energy process that is needed when complete distribution of a second component is required. Examples include cases where large amounts of fillers or other polymers are added, and where little further distribution is attained by the subsequent processing, Figure 4.

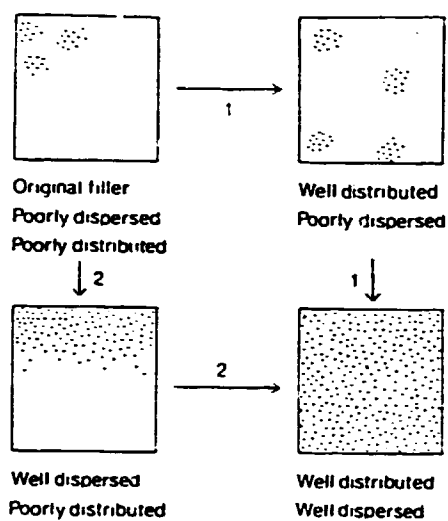


Fig. 4

Machinery for Mixing

This includes tumbler and ribbon blenders; Henschel mixers; two-roll mills; Banbury mixer; single and twin-screw extruders.

The simplest distributive mixing can be accomplished by tumbler action (e.g. as used in PVC processing). The process can be improved by ribbon-like spiral blades (the Henschel mixer) which create vortices of powders in a drum (heated by friction) which can be highly efficient in mixing, again, PVC materials.

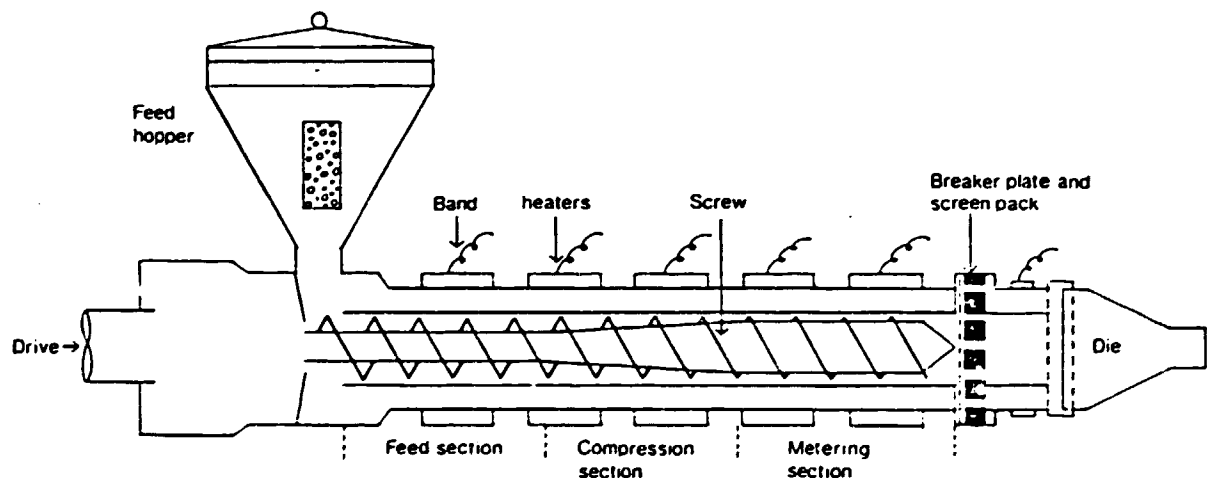
For blends which have a doughy consistency e.g. unsaturated polyester-glass, a different approach is required. A Z-blade mixer (originally developed in the food industry) is typical. Ball mills are also used.

For intensive mixing, high shear machinery is required, with or without external heat. The heat may be generated by internal friction. The simplest of these is a two-roll mill with counter rotating rollers. This device - typically used for melt compounding, at high tem-

perature, or elastomer compounding (ambient or near-ambient) provides good intensive mixing but special precautions must be taken to insure good distribution along the length of the rollers.

A more sophisticated internal high shear device is the Banbury mixer with high throughput and efficiency.

In modern practice, thermoplastics are usually mixed in screw extruders, Fig. 5. These are sophisticated devices with many variations for which considerable theoretical information on screw design, barrel design, etc. is available. The twin-screw extruder possesses considerable advantages (relative to the single screw machine) for mixing and is widely used.



Main features of a single screw extruder.

Fig. 5

For polymer blends the mixer should provide a uniform shear field, controllability of temperature, pressure and residence time and be able to handle polymer melts of greatly different rheological properties.

The twin screw extruder can be optimized for different applications and pro-

vides a uniform high shear stress with short residence times (to minimize degradation). It is self cleaning.

There are many variables in the design of twin-screw extruders. The parameters include co- or counter-rotation, degree of intermeshing, devolatilization capability, additional discs, etc.. The variations are such that essentially different principles apply to each category.

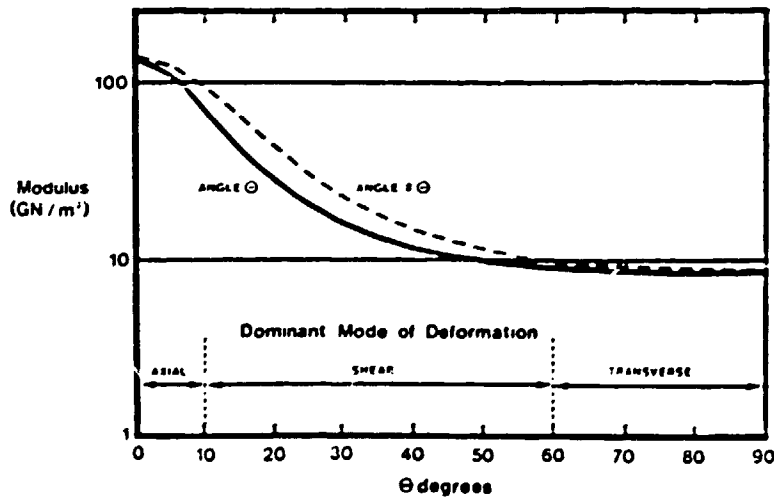
Effect of Processing Variables on Properties

Effect of orientation achieved by different processes

Effect of mixing achieved by different processes

Effect of particle size

These parameters are schematically indicated in Fig. 6. Some effects on properties are shown in Table 2.



The stiffness of an individual ply of APC-I orientated at an angle θ to the loading axis.

Fig. 6

Comparative Mechanical Property Data on Different Types of Composite Compounds

<i>Process</i>	<i>Reinforcement</i>	<i>Matrix</i>	<i>Fiber angle (deg.)</i>	<i>Tensile modulus (GPa)</i>	<i>Tensile strength (MPa)</i>
Injection molding	40 vol. % 3 mm fiberglass	Epoxy	40-60	10.3	48.3
Injection molding	23 vol. % 9 mm fiberglass	Nylon 66	30-40	15.2	221
Injection molding (controlled orientation)	40 vol. % 3 mm fiberglass	Epoxy	19	27	190
Extrusion (prepreg)	40 vol. % 3 mm fiberglass	Epoxy	20	24.1	228
Compression molding (aligned fibers)	57 vol. % 3 mm fiberglass	Epoxy	7	39.3	310

Table 2

IV. COMPATIBILIZATION: POLYMER-POLYMER SYSTEMS

As has already been mentioned, binary polymer blends are usually immiscible; there is much emphasis, nevertheless, on producing compatible, technologically advantageous, materials from such blends. Most homopolymers have been proposed as constituents in blend systems.

The necessary requirements are firstly that the kinetics of the thermodynamically-induced driving force for phase separation are slowed: this can often be achieved by a judicious choice of molecular weights. Beyond this the polymer-polymer surface interaction must be relatively favorable. This can be done by chemically modifying the respective surfaces or by the addition of (usually proprietary) compatibilizing agents.

More and more inherently immiscible combinations of polymers are being used in practical, commercially successful systems.

Miscibilization (compatibilization) agents in some cases can be block copolymers, (on the principle that each arm may be miscible with the respective homopolymers) or they may employ a more sophisticated technology.

The techniques employed vary widely and can be classified generally according to whether they involve reversible or irreversible chemistry. In the latter case stabilization of two essentially immiscible polymers is effected during the processing step. Such cases include interpenetrating networks of various kinds, and inter-component covalent bonding brought about, i.e. initiated, by thermal treatment. It is usually more desirable to compatibilize in such a way that normal processing can be repeatedly and reproducibly carried out.

In practice, polymer blends (miscible/compatible) are produced by (a) mechanical mixing, (b) dissolution in mutual solvent and removal of solvent, (c) production of interpenetrating networks by dissolving polymer A in monomer B followed by polymerization of B.

Compatibilization of immiscible systems can be achieved by:

- (a) addition of copolymers: block, random or graft;
- (b) reaction in blend, (reactive extension) e.g. ester interchange; or random copolymerization;
- (c) cross-linking of constituents;
- (d) chemical modification of constituents to reduce repulsive interaction;
- (e) inter-penetrating network formation

are the main methods.

True miscibilization (to yield one phase systems) can be accomplished by using the copolymer effects described above. In practice this means adjusting copolymer moiety ratios e.g., as in SAN/PVC.

V. EXAMPLES

a. Noryl: Miscible polyphenylene oxide/polystyrene.

This is the prototypical miscible blend, a major commodity plastic. The original driving force for this material was the difficulty of processing PPO; the addition of the miscible PS lowered the (single) T_g and hence increased the processing window.

Many modifications of this original concept now are found: glass-reinforced; flame-retardant; foamed, etc. grades are available.

Commercial PPO/PS blends all contain impact modifiers (usually elastomeric) so in fact practical resins are two (or more) phase components.

Typical properties are shown in Table 3.

Properties of Typical PPO-PA Blends (Noryl GTX 810)	
Property, units*	
Melting point T_m , °F	—
Glass transition temp. T_g , °F	—
Processing temp., °F	500
Molding pressure, 10^3 lb/in ²	15
Mold shrinkage, 10^{-3} in/in	10
Heat deflection temp. under flexural load of 264 lb/in ² , °F	370
Maximum resistance to continuous heat, °F	345
Coefficient of linear expansion, 10^{-6} in/(in · °F)	25
Compressive strength, 10^3 lb/in ²	17
1/2 inch impact strength, ft · lb/in of notch	1.5
Tensile strength, 10^3 lb/in ²	13
Flexural strength, 10^3 lb/in ²	19
Percent elongation	10
Tensile modulus, 10^3 lb/in ²	200
Flexural modulus, 10^3 lb/in ²	225
Rockwell hardness	R119
Specific gravity	1.16
Percent water absorption	0.5
Dielectric constant	4
Dielectric strength, V/mil	500
Resistance to chemicals at 75°F:†	
Nonoxidizing acids (20% H ₂ SO ₄)	Q
Oxidizing acids (10% HNO ₃)	U
Aqueous salt solutions (NaCl)	S
Polar solvents (C ₂ H ₅ OH)	S
Nonpolar solvents (C ₆ H ₆)	Q
Water	S
Aqueous alkaline solutions (NaOH)	S

*lb/(in² · 0.145) = KPa (kilopascals); ft · lb/(in of notch · 0.0187) = cm · N/cm of notch.
 †S = satisfactory; Q = questionable; U = unsatisfactory.

Table 3

b. Noryl GTX:

This is a PPO-polyamide (nylon) immiscible blend which is compatibilized and involves a dispersion of the PPO in a continuous nylon matrix.

The compatibilization is a sophisticated molecular engineering feat. Several approaches have been patented. In one a core-shell impact acrylic modifier core and a styrenic shell (miscible with PPO) is used. Other intermediaries include styrene-butadiene-styrene block copolymers and/or reagents to modify the major constituents.

Properties are shown in Table 4.

Properties of Typical Modified PPO

Property, units*	High-PS blend	Low-PS blend	PA blend	PPO-PS + 30% fiberglass
Melting point T_m , °F	—	—	—	—
Glass transition temp. T_g , °F	105	130	135	120
Processing temp., °F	500	500	500	500
Molding pressure, 10^3 lb/in ²	15	15	12	25
Mold shrinkage, 10^{-3} in/in	6	7	6	3
Heat deflection temp. under flexural load of 264 lb/in ² , °F	200	245	240	290
Maximum resistance to continuous heat, °F	180	230	220	265
Coefficient of linear expansion, 10^{-6} in/(in · °F)	25	25	—	12
Compressive strength, 10^3 lb/in ²	14	16	—	18
Izod impact strength, ft · lb/in of notch	5	5	7	20
Tensile strength, 10^3 lb/in ²	8	10	7	17
Flexural strength, 10^3 lb/in ²	10	11	10	20
Percent elongation	50	60	—	3
Tensile modulus, 10^2 lb/in ²	350	365	350	1200
Flexural modulus, 10^2 lb/in ²	350	350	325	1100
Rockwell hardness	R115	R120	M93	R115
Specific gravity	1.08	1.07	1.3	1.3
Percent water absorption	0.08	0.1	0.1	0.08
Dielectric constant	2	2	2	2
Dielectric strength, V/mil	200	200	200	200
Resistance to chemicals at 75°F:†				
Nonoxidizing acids (20% H ₂ SO ₄)	S	S	Q	S
Oxidizing acids (10% HNO ₃)	Q	Q	Q	Q
Aqueous salt solutions (NaCl)	S	S	S	S
Polar solvents (C ₂ H ₅ OH)	S	S	S	S
Nonpolar solvents (C ₆ H ₆)	U	U	Q	U
Water	S	S	S	S
Aqueous alkaline solutions (NaOH)	S	S	S	S

*lb/(in² · 0.145) = KPa (kilopascals); ft · lb/in of notch · 0.0187) = cm · N/cm of notch.
 †S = satisfactory; Q = questionable; U = unsatisfactory.

Table 4

c. Reinforced Polycarbonate:

Bisphenol-A based polycarbonate is used in the "neat" transparent state, but can be advantageously reinforced with glass or carbon fiber by standard technologies. Such materials are widely used. They show improved rigidity, hardness, and dimensional stability compared to the neat resin.

Typical properties are shown in Table 5.

Properties of Typical Polycarbonates					
Property, units*	PC	PC foam	PC-polyester	PC + 30% fiberglass	PC + 40% graphite
Melting point T_m , °F	—	—	—	—	—
Glass transition temp. T_g , °F	300	—	175	150	150
Processing temp., °F	550	—	650	600	600
Molding pressure, 10^3 lb/in ²	15	—	15	20	15
Mold shrinkage, 10^{-3} in/in	3.5	—	2	1	1.5
Heat deflection temp. under flexural load of 264 lb/in ² , °F	270	260	310	300	290
Maximum resistance to continuous heat, °F	250	240	300	280	275
Coefficient of linear expansion, 10^{-6} in/(in · °F)	70	—	40	10	5
Compressive strength, 10^3 lb/in ²	12.5	—	11.5	19	23
Izod impact strength, ft · lb/in of notch	16	6.5	8	2.5	2
Tensile strength, 10^3 lb/in ²	9.5	5	10.5	19.5	22
Flexural strength, 10^3 lb/in ²	13.5	—	13.5	24	33
Percent elongation	110	5	90	3	3
Tensile modulus, 10^3 lb/in ²	345	290	250	130	1500
Flexural modulus, 10^3 lb/in ²	340	10	300	960	1200
Rockwell hardness	M70	—	M85	M92	R118
Specific gravity	1.2	—	1.2	1.4	1.32
Percent water absorption	0.15	—	0.2	0.2	0.05
Dielectric constant	3.2	—	3	3	—
Dielectric strength, V/mil	380	—	510	475	—
Resistance to chemicals at 75°F:†					
Nonoxidizing acids (20% H ₂ SO ₄)	Q	Q	Q	Q	Q
Oxidizing acids (10% HNO ₃)	U	U	U	U	U
Aqueous salt solutions (NaCl)	S	S	S	S	S
Polar solvents (C ₂ H ₅ OH)	S	S	S	S	S
Nonpolar solvents (C ₆ H ₆)	U	U	U	U	U
Water	S	S	S	S	S
Aqueous alkaline solutions (NaOH)	U	U	Q	U	Q

*lb/(in² · 0.145) = KPa (kilopascals); ft · lb/(in of notch · 0.0187) = cm · N/cm of notch.
 †S = satisfactory; Q = questionable; U = unsatisfactory.

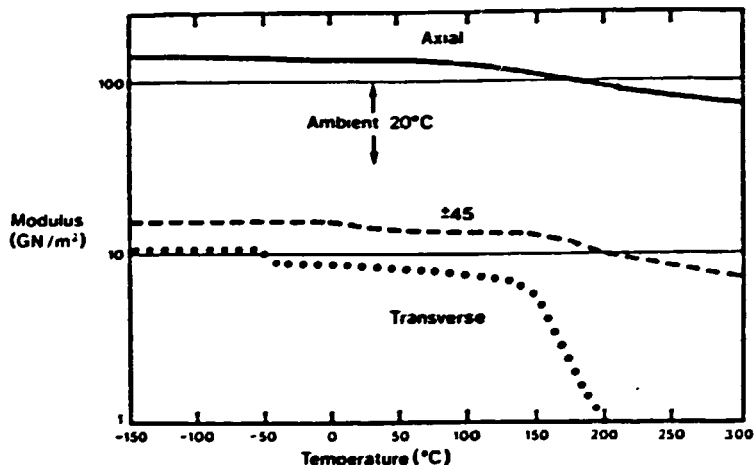
Table 5

d. Reinforced PEEK

PEEK (polyether ether ketone) is an advanced relatively expensive thermoplastic which is an important contender for major aerospace use. PEEK is a high temperature matrix for carbon fiber systems (often continuous or long staple fiber) which greatly enhances the applicability.

The carbon fiber has a modulus of -240 GN/m^2 ; PEEK has a modulus of -4 GN/m^2 .

The stiffness is shown in Fig. 6 and the temperature effects in Fig. 7.



The variation of modulus with temperature for APC-1.

Fig. 7

The PEEK polymers (there are several minor variants) have high oxidative and radiation stability, high chemical resistance and excellent mechanical properties.

e. Polycarbonate/polybutylene terephthalate

This is the basis of another commercial blend ("Xenny") with complicated phase behavior. The two components (PC/PBT) are partially miscible in melt-

formed blends (T_g criterion) and there is copolymerization through ester interchange during processing. This can be inhibited by the addition of phosphite esters. The PBT will crystallize in the coded blend. To improve impact strength a proprietary core-shell modifier is added which is located in the isolated PC phase.

The effect on impact strength is to lower the ductile-brittle transition to -20°C. (+10° for PBT) This low temperature impact strength is important in the use of this blend in the automobile industry.

VI. PROCESSING

The normal thermoplastic processing technologies may be used with blends and, with some modification, with composites.

Extrusion

Blow molding

Injection molding

Compression molding

Etc.

The essential elements of these are described in standard texts.

Miscible systems can be treated as homopolymers. Immiscible systems can present much more complicated problems because of the effect of processing an ultimate morphology and hence end use properties.

Phase separation is an overriding occurrence, and can be overcome or controlled by a number of methods and choice of correct processing technologies.

The processing of filled (particulate, fiber) thermoplastics is a very important industrial process. Rheologically these systems can be treated as fluids with suspended particles (isotropic or anisotropic). The theoretical

treatments using as starting points the properties of pure polymer fluids - themselves complex - are extensive and complicated and deal with such phenomena as normal stress, die swell, orientation, etc. An obvious practical consideration is the possibility of barrel abrasion caused by the presence of the fibers.

The processed article made from filled polymers also has variables more extensive than those of the pure polymer. These include non-homogeneous placement of the reinforcing agent (e.g. in injection molding operations) the orientation (possibly non-uniform) of the filler, degradation of the filler, effects of differential thermal expansion coefficients, etc. These effects are manifested in the usual properties: modulus, tensile and compressive, strength and failure, impact strength, fatigue.

Reaction injection molding (RIM) is a modern process in which two monomeric components are injected (after mixing) into a mold cavity where polymerization takes place. This process is typically used for polyurethane systems though other chemistries (e.g. nylon) are being developed. Reinforced RIM (RRIM) using glass-filled (or other fibers) RIM systems are just entering commercial application. Special considerations regarding the filler (size, pretreatment, abrasion) are necessary. Mat-reinforced RIM are very high strength materials under development.

VII. REFERENCES

A few selected books for further reading are listed. All of these contain extensive bibliographies.

1. Polymer Processing, D.H. Morton-Jones (Chapman and Hall, London, 1989)

2. Mechanical Properties of Reinforced Thermoplastics, D.W. Clegg and A.A. Collyer, eds. (Elsevier, London, 1986)
3. Polymer Alloys and Blends, L.A. Utracki (Hanser, New York, 1989)
4. Composite Material Handbook, M.M. Schwartz (McGraw-Hill, N.Y., 1984)