

## Polymer alloys: science and practice\*

VIKAS M NADKARNI

Polymer Science and Engineering Group, National Chemical Laboratory, Pune 411 008, India

MS received 30 March 1983

**Abstract.** The diversity of applications, versatility of property modifications, motivations for development and commercial significance of polymer alloys are reviewed with reference to commercially available materials. The key steps and scientific considerations central to the development of thermoplastic blend systems are discussed. The scientific considerations in developing the technology, such as thermodynamics of polymer-polymer miscibility, thermal and mechanical compatibility, phase diagram/morphology, interphase adhesion, and kinetics of solidification are highlighted with the help of specific examples from practice. Specific areas for research and development in polymer alloys in India are indicated emphasizing the need for an applied research bias.

**Keywords.** Polymer alloys.

### 1. Introduction

The technique of compounding polymers with other polymers, chemical additives, inorganic fillers and reinforcing fibres has given the polymer scientist and engineer an effective tool to tailor-make materials for achieving specific balanced combinations of physical properties, processing characteristics and cost. It is this flexibility of property manipulation that is mainly responsible for the diversity of applications of polymeric materials.

Polymer alloys form one class of such multicomponent polymer systems. The development of polymer alloys signifies the role of polymer engineering as a link in translating science into practice. The broad definition of polymeric alloys includes both physical and chemical modifications as illustrated in figure 1. In contrast to copolymers, where the constituents are linked by strong covalent bonds, the components in physical blends adhere through weaker secondary intermolecular forces such as van der Waals forces, dipole interaction or hydrogen bonding. Grafting represents a way to improve compatibility between the components of a polyblend. It involves chemical linking of a short side chain, that is compatible in terms of intermolecular attraction with one of the components, on to the main chain of the other component. The intermolecular linkages between the constituents of a multicomponent system can also be improved by producing network copolymers, which involves cross-linking one linear polymer with another by generating free radical sites on preformed polymers in the presence of a monomer. The different types of copolymers are schematically illustrated in figure 2. It is interesting to note that the random and alternating copolymers, wherein the scale of segregation (or separation) between the two types of chemical moieties (monomer units) is small, are generally not considered to be part of the alloy family. This is because these

\* Presented at the Symposium on 'Polymer Science and Engineering' during Annual Meeting of the Academy, Nainital October 1982.

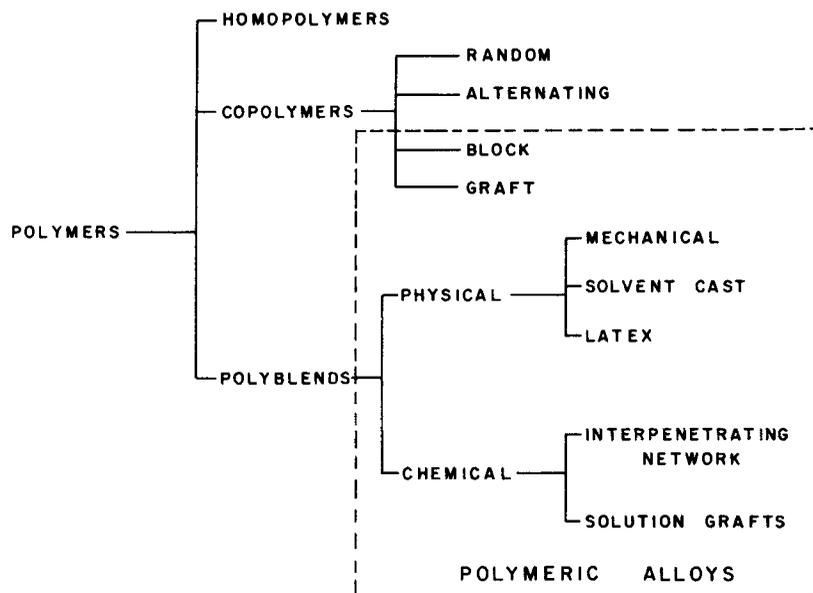


Figure 1. Broad definition of polymer alloys.

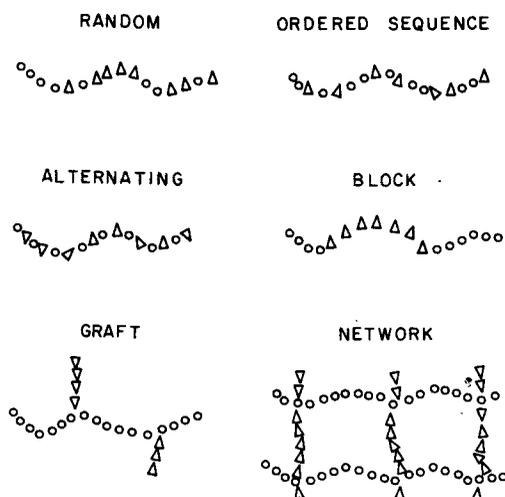


Figure 2. Types of copolymers.

copolymers form a homogeneous solid phase in which distinct morphological domains are not identifiable even on the scale of molecular dimensions of about a thousand angstroms.

Thus the scope of polymer alloy systems is quite broad and the alloys can be developed by both chemical and physical means.

However, physical blending of different polymers represents a more cost effective way of modifying properties of materials than the chemical modification routes. Hence,

recently the major thrust of the materials development efforts has been in the area of thermoplastic blends. The focus of this article would therefore be on the development of alloys by physical blending.

## 2. Polymer alloys: practice

The practice of blending two or more polymers has been employed in the coating and rubber industries for over fifty years as exemplified by the use of nitrocellulose and polyvinyl acetate in coatings, and the use of styrene-butadiene rubber with butyl rubber in tire treads for wear resistance. There are three types of blends, namely, elastomer-elastomer, thermoplastic-elastomer, and thermoplastic-thermoplastic. The blend of polyvinyl chloride with nitrile rubber is an example of the thermoplastic-elastomer systems. Thermoplastic blends are the latest entrants in the field and represent the fastest growing segment because of the fact that alloying by physical blending allows product lines to be extended with new price/performance materials without the added high capital expenditure associated with new polymer development and manufacture.

The principal thermoplastic (TP) alloy products are summarized in table 1. The most popular TP blend families include polyphenylene oxide (PPO)/polystyrene (PS), acrylonitrile-butadiene-styrene copolymer (ABS)/polyvinyl chloride (PVC), polyvinyl chloride/polymethyl methacrylate (PMMA), and acrylonitrile-butadiene-styrene copolymer/polycarbonate (PC). The versatility and flexibility of property modifications possible with alloying is indicated by the fact that General Electric Co. markets 29 grades of PPO/PS blends under the tradename Noryl<sup>(R)</sup> for extrusion, injection molding and structural foam molding.

Table 1. Principal polymer alloy products on the market [R-1].

Base Resin	Alloy Component
Acrylonitrile-butadiene-styrene	Polyvinyl chloride
	Polycarbonate
	Polysulfone
	Polyurethane
Polyvinyl chloride	Acrylics
	Ethylene-vinyl acetate
	Chlorinated polyethylene
Polyphenylene oxide	Impact polystyrene
	Polystyrene
	Styrene block copolymer
	Acrylonitrile-butadiene-styrene
Nylon	Polyethylene
	Ethylene-propylene copolymer
	Ionomers
	Polybutylene terephthalate
	Polyethylene terephthalate
Polycarbonate	Polyethylene
	Acrylics
	Acrylonitrile-butadiene-styrene
	Polyesters

Polymer alloys are increasingly being used in engineering applications, such as bearings, pump impeller, valves, electrical components, gears etc., which traditionally have been the domain of metals.

A few of the commercially important thermoplastic alloys are summarized in table 2. Economics has been the main driving force for the development of new materials through alloying to achieve balanced combinations of physical properties, processing characteristics and cost. The properties that have been found to be most responsive to improvement include impact strength, warp resistance, processibility, heat deflection temperature and of course, cost dilution. The commercial alloy system, Noryl<sup>(R)</sup>, of PPO and PS is a good example, where the mechanical properties and thermal resistance of PPO have been successfully complemented by the low cost and processibility of PS.

Alloying of ABS with PVC significantly improves the impact strength with marginal drop in the tensile strength (table 3). The PVC and PMMA alloy offers an outstanding balance of toughness, impact resistance and durability over a broad range of temperatures. It can be easily thermoformed, unlike its constituent polymers, and deep draws can be accomplished without tearing the sheet. Development of such thermoformable materials is quite relevant to Indian conditions. Thermoforming of extruded sheets represents a less capital intensive processing technique, well suited for the Indian polymer processing industry, which is decentralized and mainly falls in the small scale sector. Thermoformed plastic products such as seats, window panes, wall panels can be easily manufactured on existing metal stamping equipment with minor modifications for use in the large volume transportation industry. Because of its low cost and

**Table 2.** Thermoplastic blends: Commercial examples.

Trade name	Company	Components
Noryl	General Electric	PPO/PS
Cycovin	Borg-Warner	ABS/PVC
Bayblend	Mobay	ABS/PC
DKE-450	Du Pont	PVC/PMMA
Ropet	Rohm and Hass	PET/Acrylic
Vistaflex	Exxon	PP/E-PP
Fluorex	Rexham	PVDF/PEMA
Alton	International Polymer Corp.	PTFE/PPS
Tribolon XT	Upjohn	PPS/Polyimide

**Table 3.** Property comparison of ABS/PVC alloys

Property	Standard ABS	ABS/PVC (rigid)	ABS/PVC (flexible)
Notched Izod Impact (ft. lb/in)	6.5	12.5	15
Yield strength, psi	6000	5450	3000
Tensile Modulus, psi	$3.4 \times 10^5$	$3.2 \times 10^5$	$1 \times 10^5$
Hardness, Rockwell R	103	102	50
HDT at 264 psi	210°F	147°C	—
Sp. gravity	1.04	1.21	1.13

**Table 4.** Alloys of poly (vinyl chloride).

Polymer	Property improvement	Miscibility
Nitrile rubber	Oil resistance	M
ABS	Impact for PVC/FR for ABS	I
E/VA copolymer	Impact strength	I
E/VA/CO terpolymer	Impact strength	I
$\alpha$ -MS/AN SAN	Heat distortion temperature	M
PMMA	Thermoformability, dimensional stability, surface characteristics	PM
PU	Abrasion resistance, impact strength	I
TPU/ABS	Cost/performance tailored materials	—
Hytrel <sup>(R)</sup> TPE	Acoustical damping	M
E/N,N-Dimethyl acrylamide copolymer	Improved toughness and flexibility	—

M—Miscible; I—Immiscible; PM—Partially miscible.

compatibility with a variety of polymers and chemical additives, a number of alloy systems have been developed with PVC (table 4).

A majority of the commercial alloys are based on polar polymers (table 2). This is related to the chemical compatibility considerations that play a major role in governing the properties of the alloy systems. Recently a number of alloys have been introduced that are based on engineering polymers such as polyethylene terephthalate (PET), nylons, polycarbonate, polyphenylene sulfide (PPS) and polytetrafluoroethylene (PTFE). There are a number of instances, wherein alloying of a high cost, high performance engineering polymer with a low cost, bulk polymer has led to a material with a unique combination of properties in a *cost-effective* manner.

Exceptional toughness can be achieved by alloying high density polyethylene (HDPE) with nylon 66 without adversely affecting the inherent high filler acceptability of nylons; compounds of HDPE/nylon alloys with molybdenum sulfide are used in bearing applications. The cost effectiveness of molding grade PPS can be further enhanced by alloying it with HDPE without significantly affecting its exceptional chemical and thermal resistance. The combination of PET with acrylic has resulted in alloys with better warp resistance and faster moldability. The PET/acrylic alloys represent a classic example of modification of the crystallization behaviour through blending of crystalline and amorphous polymers.

Alloying of two engineering or speciality polymers is normally done for achieving a specific combination of properties not attainable by the use of the constituent polymers. For example, PTFE/PPS alloys have been developed for use in self-lubricating bearings and in gears, where a combination of thermal resistance, chemical resistance, lubricity, moldability and mechanical strength is required.

The potential for development of polymer alloys is virtually untapped in India, although a number of the constituent polymers of the alloys cited above are indigenously available. The relatively low-cost bulk polymers like HDPE, PVC, PS and PMMA are produced commercially in India. Engineering polymers like ABS, PET, polybutylene terephthalate (PBT) and nylon have been recently introduced based on

indigenous production. Commercial production of polycarbonate and PTFE should start in the near future. The technology for the production of polyphenylene sulfide is being developed at the National Chemical Laboratory. Thus the scope for indigenous development of polymer alloys is considerable. It is therefore pertinent to review the methodology for engineering these materials in a scientific fashion.

### **3. Scientific engineering of materials through alloying**

The critical steps in developing polymer alloys are summarized below: (i) Definition of the property improvement targets and hence the desired morphology. (ii) Selection of the constituent polymers and their composition in the alloy. (iii) Proper choice of the method and conditions of compounding. (iv) Specification of the techniques and conditions of processing the alloy.

It is important to define the property modification that is desired through alloying, since it determines whether the constituent polymers should form a miscible or immiscible blend. For example, if an improvement in heat deflection temperature of a polymer is desired, then the alloy constituents must be miscible at the molecular scale, forming a single homogeneous amorphous phase. Additionally the softening temperature of the modifier must be higher than that of the base polymer, and it should have flow characteristics equivalent to the base polymer under conditions of temperature and shear rate encountered in the compounding process. The alloy of PPO and PS is an example of such a miscible system. On the other hand, for achieving improvement in impact strength, a two-phase morphology is essential. The constituent polymers should therefore be immiscible, yet chemically compatible for good interfacial adhesion and effective stress transfer at the interface. The shape, scale and uniformity of dispersion are important factors influencing the alloy properties in such immiscible systems. Consequently a proper choice of the method and conditions of compounding becomes more critical than in the case of a homogeneous alloy. Thus the key scientific considerations involved in the development of polymer alloys include: (i) Polymer-polymer miscibility (ii) Thermal compatibility (iii) Mechanical compatibility/rheology (iv) Phase morphology (v) Domain structure (vi) Level of dispersion (vii) Interfacial adhesion/stress transfer (viii) Kinetics of solidification.

Depending on the type of property improvement sought, the importance and weightage given to one or more of the above factors would vary. Polymer-polymer miscibility has a bearing on the choice of constituent polymers as per the desired morphology, and it also influences the selection of the compounding process. The aspects of thermal and rheological compatibility are important in defining the compounding process technology in terms of both the hardware design details and the processing parameters (temperature, shear rate etc.). Phase morphology considerations are critical in immiscible system and greatly influence the extent of property improvements achieved through alloying. All these factors are discussed in detail in the subsequent sections as we sequentially trace through the steps involved in alloy materials development.

### **4. Selection of alloy constituents and composition**

Polymer-polymer miscibility is an important consideration in selection of the alloy constituents, since it governs the phase morphology obtained and hence the property

modifications possible by alloying. The miscibility of polymers has the same meaning as in low molecular weight chemicals. It is distinct from compatibility. For example, alcohol and water are miscible and asphalt and water are immiscible, but asphalt can be made compatible with water as in asphalt emulsions.

Miscibility in polymers is not as uncommon as conventionally believed. Olabisi *et al* (1979) have given a comprehensive survey of miscible polymer systems. A miscible polymer blend has a single homogeneous amorphous phase as indicated by a single composition dependent glass transition temperature. The glass transition temperature,  $T_g$ , while not a thermodynamic property, represents a change in the mobility of the polymer chain segments in the amorphous phase.

The observation of a single  $T_g$  does not imply that the homogeneous amorphous phase is the thermodynamic equilibrium state. For example, homogeneous solutions of polymethyl methacrylate and polyvinyl acetate can be rapidly freeze-dried to produce a homogeneous blend with a single  $T_g$ . This homogeneous phase will persist indefinitely unless heated to just over the  $T_g$  where demixing occurs because of the increased segmental mobility. It is therefore more appropriate to state that the single  $T_g$  ought to be reversible in repeated heating and cooling if the two polymers are miscible (Paul and Barlow 1979).

Another very useful test for miscibility which is easier to employ and simpler to interpret than  $T_g$  behaviour is the appearance of lower critical solution temperature (LCST). It is observed that a clear blend phase separates at a certain temperature on heating and becomes cloudy. For many systems, this process reverses itself on cooling. Such behaviour is excellent thermodynamic proof that the original clear blend consisted of a single, equilibrium, homogeneous phase.

In a miscible polymer alloy, interphase stress transfer is not an issue since each phase is continuously interconnected throughout the bulk. Just as miscibility of polymers is not an uncommon observation, immiscibility does not preclude blending. As a matter of fact, there are certain property improvements that require the existence of a two phase morphology. Improvements in impact strength, and coefficient of friction (antislip and antiblock agents) require a two-phase behaviour.

Once the property improvement target is defined it becomes clear as to whether the constituent polymers should form a miscible or immiscible system. One of the research goals in the field of polymer alloys has been to develop a strategy for determining *a priori* from the knowledge of the chemical structures of a given polymer pair whether the pair is miscible or not. A discussion concerning the thermodynamics of mixing of macromolecules is pertinent in this connection. The free energy of mixing is given by the following equation

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

where  $F$ ,  $H$  and  $S$  are free energy, enthalpy and entropy respectively.

In polymer-polymer mixtures, the change in entropy on mixing is small. This is schematically illustrated in figure 3. In small molecules, the square represents a mixture of 50 molecules of  $A$  (open circles) and 50 molecules of  $B$  (filled circles). There are about  $10^{30}$  ways of arranging these 100 molecules in the given square. As soon as ten molecules of each type are connected forming an oligomer (polymer of very low molecular weight), the number of ways in which the five macromolecules of type  $A$  can be accommodated with five macromolecules of type  $B$  in the same square reduces to  $10^3$ . Thus the contribution of the entropy change to the free energy of mixing is

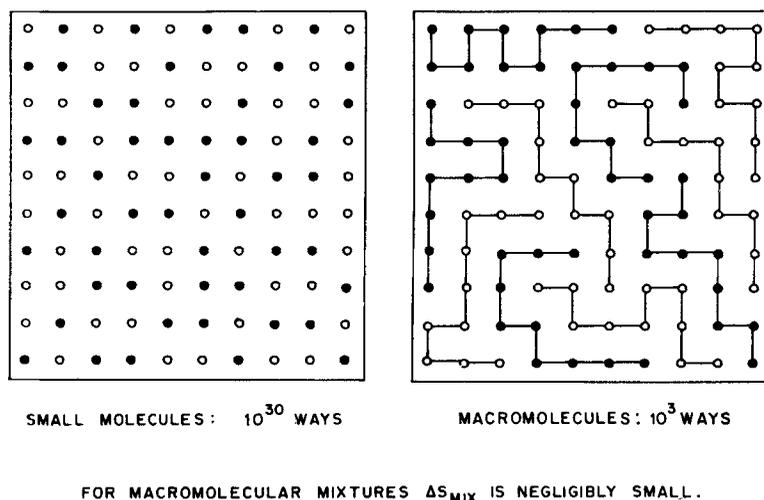


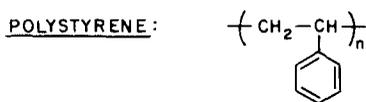
Figure 3. Entropy of mixing.

insignificant and, the enthalpy change is the controlling factor in mixing of polymers. Therefore, to have a negative free energy of mixing, an exothermic heat of mixing is required. It is then obvious that miscibility would result when polymer pairs interact together to give an exothermic heat of mixing. The enthalpy of mixing is associated with the nearest neighbour interactions. Hence, polymer systems, wherein the intermolecular attraction forces between molecules of different types are stronger than those between polymer molecules of the same type, would exhibit an exothermic heat of mixing.

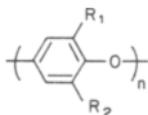
The above discussion helps us define the strategy for seeking structural guidelines for alloy constituents to find miscibility or vice-versa. It also means that the chemical structure of the two polymers need not be similar, but they should be complimentary with regard to favourable energetic interactions. For example, high density polyethylene and low density polyethylene, although similar in chemical structure, do not form a miscible alloy. Whereas, polyphenylene oxide and polystyrene form miscible blends, inspite of being structurally different as illustrated by their chemical formulae shown in figure 4. This is because of the favourable energetic coupling between the aromatic rings of PPO and PS. It is interesting to note here that the benzene rings in PPO are part of the main chain, whereas benzene rings in PS appear as pendant groups on the main chain. This difference may facilitate coupling between them. The types of interactions that could lead to favourable energetics between molecules of different polymers include acid-base type, donor-acceptor type, dipole-dipole, hydrogen bonding, phenyl group coupling, complex formation etc.

A number of new techniques such as pulsed NMR, small angle neutron scattering, non-radiative energy transfer, and excimer fluorescence have been developed for elucidating the molecular interactions.

Once the constituent polymers have been identified based on the property improvement target for achieving the desired morphology, the composition of the alloy must be defined. A detailed investigation of the effect of composition on the property of



POLYPHENYLENE OXIDE:



WHERE,  $R_1 = R_2 = -\text{CH}_3$   
 $R_1 = -\text{CH}_3, R_2 = -\text{CH}_2\text{CH}_3$   
 $R_1 = -\text{CH}_3, R_2 = -\text{CH}_2\text{CH}_2\text{CH}_3$   
 $R_1 = R_2 = -\text{CH}_2\text{CH}_3$   
 $R_1 = -\text{CH}_2\text{CH}_3, R_2 = -\text{CH}_2\text{CH}_2\text{CH}_3$   
 $R_1 = R_2 = -\text{CH}_2\text{CH}_2\text{CH}_3$

Figure 4. Chemical structures of PPO and PS.

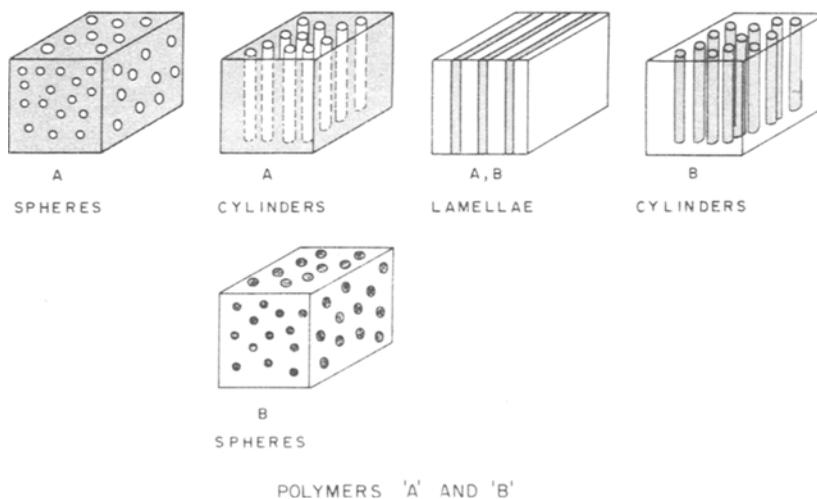


Figure 5. Schematics of domain structure.

interest is warranted. In some cases, the miscibility is also dependent on composition. For example, polymethyl methacrylate and polyvinyl chloride are completely miscible at compositions of PVC greater than 40%. However, the alloy is heterogeneous at PVC concentrations less than 40%. In immiscible systems, the composition also influences the equilibrium domain structure. The various types of domain structures possible in a two phase system are schematically illustrated in figure 5. The equilibrium domain shape as a function of the weight fraction of the dispersed phase polymer is illustrated in figure 6. Thus if the preferred domain shape is a sphere, then the composition of the

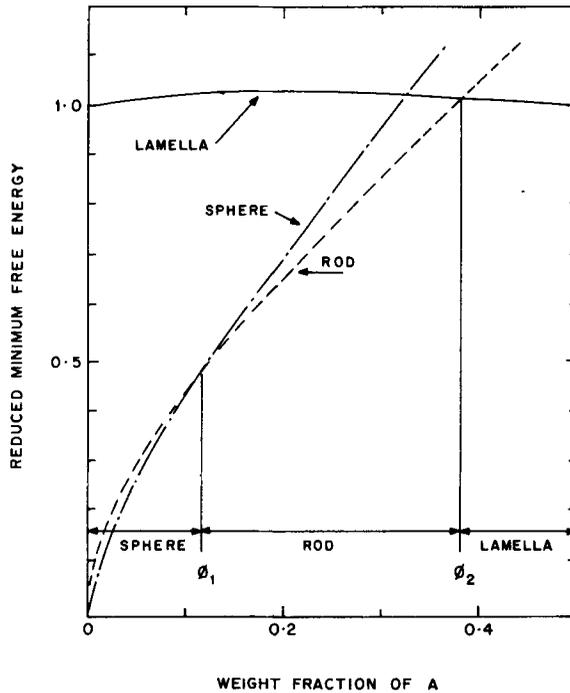


Figure 6. Equilibrium domain structure.

dispersed component has to be less than about 12% in order to obtain an equilibrium phase. Besides affecting the phase morphology, the alloy composition also governs the solid-liquid phase diagram and mechanical compatibility, thereby influencing the selection of the compounding process. These factors are discussed in detail in the next section.

### 5. Compounding of polymers for alloying

The compounding of polymers whether miscible or immiscible is done either in the molten state or in solutions. Two polymers may be thermodynamically miscible but mechanically incompatible due to large differences in the melt viscosities at conditions of compounding. In such case, solution blending is the automatic choice. Also, in cases where the constituent polymers are immiscible in the molten state yet could form miscible phases in the solid state, single phase alloys can be produced only by rapid precipitation from homogeneous solutions. Sometimes lack of thermal compatibility precludes melt blending. A pertinent example of considerable research interest would be the possibility of producing alloys of rigid chain aromatic polyamides like poly-*p*-phenyl terephthalamide (Kevlar<sup>®</sup>) or PPD-T with flexible aliphatic nylons.

The melting point of PPD-T polymer is above its degradation temperature and, therefore, melt processing is not possible.

The various compounding processes are (i) Single screw extruder/static mixer (ii) twin screw extruder (iii) Banbury (iv) Mill (v) Farrel (vi) Latex blending (*e.g.* ABS) (vii) Solution grafting (*e.g.* HIPS).

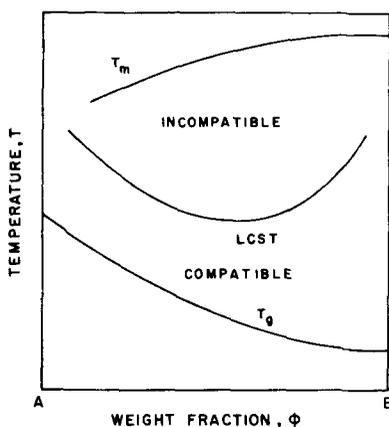


Figure 7. Phase diagram considerations in blending process selection.

The data on lower critical solution temperatures are very useful in the proper selection of compounding techniques. Figure 7 represents a superposition of the LCST curve on the melting point and glass transition behaviour of a polymer pair as a function of composition. The two polymers are incompatible in the molten phase (figure 7). It is therefore not possible to produce a homogeneous blend by melt compounding. However, it is possible to solvent blend the two polymers at a temperature below the LCST and produce a single phase alloy. In such a case where the LCST curve lies at a temperature below the melting point, it is important to ensure that the alloy is not used in applications where the material would be exposed to temperatures above the LCST curve. This is critical because as soon as the material sees a temperature above the boundary of compatibility, slow phase separation may take place even in the solid state, thereby adversely affecting properties such as thermal fatigue, warp resistance, environmental stress crack resistance (ESCR) etc.

The scientific considerations of miscibility, mechanical compatibility and thermal compatibility are important in developing the compounding process technology the requirements of which are summarized below:

(i) Blending without exceeding degradation temperatures (ii) generation of sufficient shear stresses for dispersion (iii) homogenization without producing stratified/layered blend (iv) optimum particle size by control of shear, molecular weight, composition and viscosity.

The thermal degradation considerations determine the temperature and environment (air or nitrogen atmosphere) for melt blending. The temperature of melt blending has to be above the melting point of the higher melting constituent and below the degradation temperature of the more degradable constituent. Such thermal compatibility factors often preclude alloying of polymer pairs, deemed attractive from property modification and cost dilution considerations.

For example, alloying of polypropylene with polycarbonate by melt compounding is not possible, since polypropylene is easily degraded at temperatures above 250°C which is normally required for melt processing of polycarbonate. The necessary data for thermal compatibility evaluation can be generated by using Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA).

The level of dispersion greatly influences the properties of two phase polymer alloys as a result of interfacial adhesion affecting stress transfer between phases. A fine dispersion is normally desired and can be obtained by proper hardware design to give adequate mixing patterns and by specification of temperature and shear rate at which the two melts have comparable viscosities. The size of the dispersed phase depends upon the viscous and elastic behaviour of the two components. In general, the following relationships provide valid guidelines for evaluating mechanical compatibility of a polymer pair vis-a-vis the morphology requirements. Polymer *B* forms a continuous phase,

when  $C_B > C_A$  and  $\eta_A = \eta_B$

or when  $C_B = C_A$  and  $\eta_A > \eta_B$

where *C* is the concentration,  $\eta$  the shear viscosity and *A*, *B* are the components.

It is generally advisable to superimpose the viscosity vs shear rate curves for the constituent polymers at the desired temperatures of melt blending (temperature range determined by thermal compatibility) and specify shear rates at which the viscosities of the two components are comparable. The shear rates of compounding should be in the shear-thinning or non-Newtonian portion of the rheograms for ease of mixing. Alternatively, if the major component (in terms of volume fraction) is desired to be in the dispersed phase, then the compounding process conditions and the polymer grades should be so chosen as to give a sufficiently lower melt viscosity of the major component relative to the other component.

Extensive rheological characterization of various grades of the constituent polymers and their blends at various compositions is required before the optimum compounding conditions can be specified. These data are generated by using sensitive instruments such as Weissenberg Rheogonimeter, Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer etc. over a range of temperatures and shear rates.

In specifying conditions for a solution blending process, data on solubility of the constituent polymers in common solvents are required. The effect of rate of precipitation on the alloy morphology is also an important consideration. In general, a solution blending process is not preferred because of the high cost, high energy requirements and safety hazards in handling toxic and flammable solvents.

## 6. Processing of polyblends

The major processing methods used in converting polymer alloys into useful products include extrusion, injection molding, compression molding and thermoforming. In all these processes, the molten alloy is subjected to shearing flows. The range of shear rates encountered is quite wide (table 5), and the temperature of flow/deformation also varies with the process. In specifying the process conditions, a knowledge of the melt viscosity of the alloy over a range of shear rates at temperatures relevant to processing is essential. Shenoy *et al* (communicated) have reviewed the rheology of polymer blends and proposed a method for estimating the rheograms from the melt flow index with the use of a master curve. However, in addition to the rheological data, mechanical compatibility considerations vis-a-vis phase separation, coalescence and migration become more critical in processing of blends, which is not the case in processing single component systems.

**Table 5.** Shear rates in processing of polymer alloys.

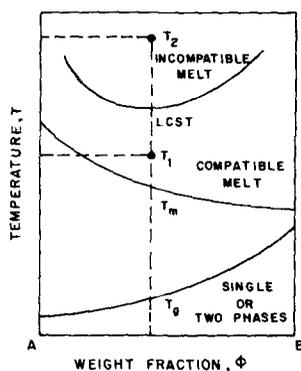
Process	Shear rate (sec <sup>-1</sup> )
Compression molding and thermoforming	1-10
Mixing and calendaring	10-100
Extrusion	100-1000
Injection molding	1000-10000

If differences exist between the viscosities of the matrix and the dispersed phase polymers, then local differences in shear rate can produce translation of low viscosity material to regions of higher shear rate. In capillaries, if the viscosity of the dispersed phase is low, it is sometimes transported to regions near the wall resulting in enlargement of the average particle dimensions. This change in the scale and shape of the domain structure could adversely affect the solid state properties. Thus, a high viscosity matrix with a low viscosity dispersed phase (minor component) though desirable for achieving fine dispersion in blending, may spoil the blending result during the processing which may follow. If during the processing the shearing forces are lower than in the compounding operation, increase in particle dimensions by coalescence can be expected.

The problem of particle coalescence can be overcome by additives which reduce surface tension and/or by processing under higher shear than during compounding. Investigation of the chemical and thermal compatibility of various additives, and definition of a shear rate range for processing are therefore additional considerations in specifying the technique and conditions of processing. These factors are of greater significance in processing of immiscible polymer alloys.

In alloys based on thermodynamically miscible polymers also, kinetic considerations play an important role. Figure 8 depicts the superposition of the LCST curve of a polymer pair on the melting and glass transition curves. The morphology of the product made from the alloy can be affected by the processing technique and also by the conditions of processing. If the alloy melt temperature in processing is  $T_1$  at which the constituents are miscible, both injection and compression molding would lead to a homogeneous single phase product. However, if the melt temperature has to be maintained at  $T_2$  where the constituents are immiscible, then injection molding of the alloy could result in a two phase solid state, because of the normally high quench rate (short mold cycle) involved in injection molding. Compression molding may yet produce a homogeneous solid state since the cooling is relatively more gradual. In such cases, it may still be possible to obtain a homogeneous solid state in injection molding by proper specification of the mold temperature, thereby controlling the quench rate. Pertinent data required for such manipulation of molding conditions can be generated by the technique of DSC.

In alloys where one or both the constituents are crystalline, the implications of phase segregation by crystallization need to be investigated with reference to the processing conditions. Even if the polymers are thermodynamically miscible, crystallization results in separation of polymer molecules unless the polymers can form isomorphous blends. In an isomorphous polymer alloy, the constituent polymer molecules are miscible in the crystal lattice and therefore the alloy would manifest a sharp single melting point. There



TEMPERATURE	MOLDING PROCESS	MORPHOLOGY
$T_1$	IM OR CM	SINGLE PHASE
$T_2$	INJECTION (FAST QUENCH)	TWO PHASES
$T_2$	COMPRESSION (SLOW QUENCH)	SINGLE PHASE

Figure 8. Effect of phase diagram/processing on morphology.

are only a few known examples of isomorphous polymer blends. These include polyvinyl fluoride and polyvinylidene fluoride, poly(isopropyl vinyl ether) and poly(sec-butyl vinyl ether), and poly(4-methyl pentene) with poly(4-methyl hexene).

It is interesting to note that similarity in chemical structures of the constituent polymers is a requirement for forming isomorphous alloys, although it is not a requirement for polymer-polymer miscibility. This is to be expected since molecular arrangement in the crystalline phase is tighter than in the amorphous phase necessitating equivalence in lattice type and dimensions of the constituent polymers.

## 7. Research and development areas

The development of commercially viable polymer alloys involves close interaction between polymer chemists, physicists and engineers. A fair amount of basic research has already been done concerning polymer-polymer miscibility and solid mechanical aspects of rubber toughened systems. The key to successful materials development is in analysing the available scientific information to provide guidelines for technology development, and generate scientific information pertinent to specific systems of high applications potential. The various research areas in the field of polymer alloys are summarised below:

- (i) Chemical structure guidelines for scientific selection of polymer pairs to tailor-make materials.
- (ii) Rheology/Composition investigations of commercially relevant polyblends.
- (iii) Structure-property relationships in alloys.
- (iv) Stress transfer/toughening mechanisms in micro-heterogeneous systems.
- (v) Effect of compounding conditions on the phase morphology (domain size, shape

**Table 6.** Characterization techniques for research and development.

<i>Molecular interactions</i>	<i>Quantitative composition analysis</i>
Pulsed NMR	Infra-red
Small angle neutron scattering	X-ray fluorescence
Non-radiative energy transfer	
Excimer Fluorescence	
<i>Miscibility</i>	<i>Thermal Compatibility</i>
Differential scanning calorimetry	Thermogravimetric analysis
Dynamic mechanical analysis (solids)	Differential thermal analysis
Lower critical solution temperature	
<i>Rheology/mechanical compatibility</i>	<i>Morphology</i>
Weissenberg Rheogoniometer	Electron microscopy
Instron rheometer	Phase contrast microscopy
Mechanical spectrometer	Small angle x-ray scattering
	Light scattering

and dispersion) and properties of alloys.

- (vi) Development of interpenetrating polymer networks.
- (vii) Modification of crystallization behaviour by alloying.
- (viii) Development of alloys of flexible and rigid chain macromolecules.
- (ix) Investigations in interfacial adhesion *via* grafting.

A number of sophisticated analytical tools are available to the polymer scientist/engineer for generating the necessary scientific data and for translating these into commercially viable materials technology. These are summarized in table 6.

The scope for scientific investigations focussed on industrially relevant material systems is considerable in polymer alloys. An interdisciplinary approach is essential in the materials engineering efforts. The technique of alloying polymers could then be effectively used to tailor-make materials in a cost effective manner to specific application needs.

## References

- \*Alfrey T Jr and Schrenk W J 1980 Multipolymer Systems *Science* **208** 813
- \*Krause S 1972 Polymer Compatibility *J. Macromol. Sci. Rev. Macromol. Chem.* **C7** 251
- Olabisi O, Robeson L M and Shaw M T 1979 Polymer-Polymer miscibility (New York: Academic Press)
- Paul D R and Barlow J W 1979 High performance polymer blends and grafts, Course notes, Plastics Institute of America
- \*Platzer N 1976 Multicomponent Polymer Systems *Chem. Tech.* Vol. **6** p. 56
- \*Senelon P J 1981 Multicomponent polymer systems could be industry bellwether *Plast. Eng.* **37**
- Shenoy A V, Saini D R, and Nadkarni V M 1983 Melt Rheology of polymer blends from melt flow index (communicated)

\* Not referred in text.