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Introduction to Polymer Blends and Alloys*

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SCOPE

From 1970 to 1980, the demand for plastics in the United States increased from 20 to 50 billion pounds. The success of plastics is due to the broad spectrum of applications, attributable to a wide range of properties which made plastic replace metals, glass, ceramics, paper, natural fibers, packaging, consumer products, piping, furniture, etc...

The important properties of plastics are light weight, breakage resistance, ability to consolidate functional parts, relatively inexpensive, easy automated production, lower costs of manu/facturing,..

With the accomplishment of substituting all possible traditional materials, slower economic and population growth in the developed regions of the word and polymer down grading (due to environ/mental protection, reinstitution of older values) becoming a significant trend, the polymer growth rates slowed down. Intercompetition among polymers in addition has increased and the development risk of new polymers often outweighs the potential commercial reward.

These factors favored the relative inexpensive route of combining two or more commercial available polymers through alloying or blending in order to create product differentiation for new applications.

The blending technology turned out to be an excellent tool for tailoring a polymer compound for specific applications requirements, often at much lower production costs then the current available material. Alloys and blends developments are market driven and demand an on going dialogue between supplier and customer. The continuous modification and adjustment of blends and alloys for new applications requires an extensive understanding of the relation of material structure, processing and end-use performance. Material testing instruments including Rheometers, dynamic mechanical ana/lyzers, etc...are a fundamental need o insure this development

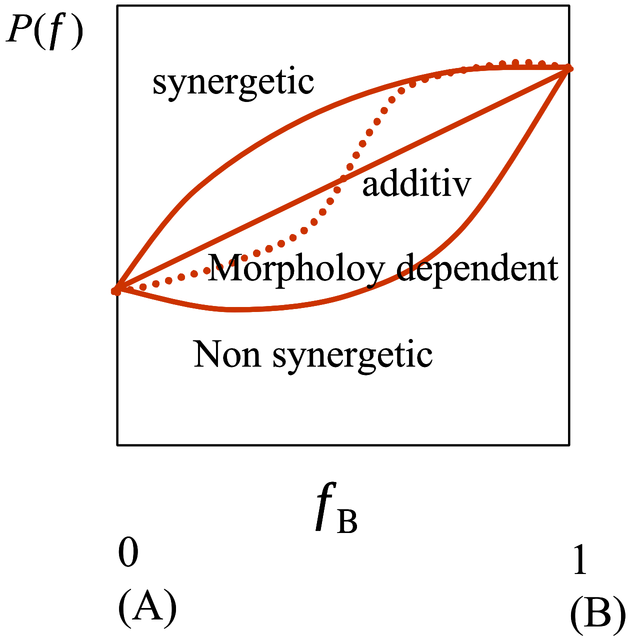

Figure 1: Concentration diagramm of blend & alloys.

ALLOYS AND BLEND TECHNOLOGY

In order to mix two components and obtain a product, which doesn't undergo complete phase separation during processing or end use, a minimum thermodynamic compatibility is necessary. Beyond this level of compatibility, greater attractive forces

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* Reference: Advances in Polymer blends and Alloys Technology Volume 1; Chapter 1 by S.Y. Kienzle

between the constituents serve to enhance the properties of the final product.

In general for two component mixture, any property can be described by the following equation:

$$P=P_1c_1+P_2c_2+IP_1P_2$$

P_i is the property value, c_i the concentration and I the interaction coefficient. For I>0, the resultant polymer has better properties then the arithmetic average of the property.

For I=0, the properties are additive

For I<=, the resultant polymer has properties, worse than the arithmetic average of the components.

Alloys are synergistic polymer combinations (I>0), if the components are thermodynamically compatible, or strong intermolecular forces make the mixture behave as a single phase material with one single transition (TG). f.ex: PS modified PEO (Noryl) or PS modified PPE (Prevex). For these blends, PS reduces the melt viscosity sufficiently to allow easy processing and largely retaining strength(modulus), impact resistance, hydrolytic stability of the PEO or PPE.

Blends show less intense thermodynamic compatibility and therefore exhibit discrete polymer phases with multiple glass transitions. In general, the properties of blends reflect the weighted arithmetic average of the properties of the consti/ tuents (I=0). f.ex: PC/ABS blends. Specific gravity, coefficient of thermal expansion, flexural modulus, etc... are arithmetic averages.

BLEND/ALLOY PREPARATION

There are different ways to mix polymers, melt blending, solution blending, latex or dispersion blending.

The melt blending using an extruder is predominately used method to prepare blends. Compatibilizing agents may be incorporated in the same time in order to enhance the synergism (compounds with functional groups that mate with the dissimilar polymers) to prevent phase separation and to enhance the physical and mechanical properties; for example: block co-polymers.

SELECTING POLYMER COMBINATIONS

Polymer components, which make the blend, are generally selected to complement each other in one or more of the following properties, costs, processability, mechanical properties, warpage, chemical resistance, thermal performance

Blends are typically viewed as cost savings: - the more expensive polymer is combined with the less expensive product to provide adequate performance at a significant reduced price (ABS/ PC, ABS/Polysulfone, PES/PEEK). In addition, the development of a synergistic property profile (I>0) is the goal.

Very often crystalline and amorphous polymers are blended to achieve a specific property range. Crystalline polymers have excellent chemical resistance, good mechanical properties (especially with reinforcements), low viscosity whereas amorphous polymers provide good dimensional stability (no warpage) and excellent impact strength.

	Crystallinepolymers	Amorphous polymers
properties	• chemical resistance • sharp melting point • low viscosity melt • good flexural and heat distorsion properties with reinforcements	• dimensional stability and warpage resistance • clarity • good impact strength • No property changes at high temperatures • melting range
polymers	PP Nylon PBT	ABS PC poly sulfone poly acrylate

Tabel 1: Crystalline and amorphous properties and polymers

Typical blends/alloys

Amoco	PSO/ABS; PSO/Polyester
Borg Warner	PPE/PS; ABS/PC; ABS/Nylpn;
Celanese, Hoechst	PBT/PET; Nylon/Elastomers; PBT/Elastomers
DOW	PC/ABS
Dupont	Nylon/Elastomer; PET/Elastomer; PBT/PET
GE	PPO/PS; PC/ABS; PPO/Nylon; PBT/PET; PC/Polyester
ICI	PEEK/PES
BAYER	ABS/Nylo

Tabel 2: Typical blends/Alloys

The combination typically results in a product of good dimensional stability, easy processing, chemical resistance and mechanical properties tailored to the specific need. f.ex: Nylon/PPO, PBT/polyacrylate, PBT/PC. Typical applicationsare automotive body panels.

The combination of elastomers with a polymer represents another important group of alloys/blends. The application is for impact resistance performance parts. The polymer gives the necessary stiffness, thermal resistance and strength. The rubber provides the impact modification. f.ex: PP/EPDM. An important application is in car bumpers.

PHASE BEHAVIOR*

A prime consideration in any polymer mixture is the degree of homogeneity of the blend. Immiscible blends form multiple phases for all ratios of composition, the composition of each phase being essentially those of the individual component. Miscible materials mix completely at all blend ratios forming a single phase. Partially miscible systems are very frequent. These blends are miscible at a selective composition and phase separation occurs at other compositions.

The thermodynamic driving force for mixing is minimization of the free energy of the system $\Delta G_{mix} = \Delta H_{mix} - T\Delta S$. Thus if the free energy is positive, the system will be immiscible. If the free energy of mixing is negative at any composition, some degree of dissolution will occur and the system will be at least partially miscible. For the system to be miscible, the second partial derivative on composition of the free energy must be positive. That means, that the plot of the free energy vs. composition must be negative for all compositions and concave upward at all compositions (Figure 2). Blends, which are miscible at one set of conditions, may undergo phase separation if conditions are changing. As such, variations in temperature, pressure and/or shear stress can induce phase separation.

Partially miscible systems exhibit local maxims and minims at constant temperature and pressure. The overall composition and the exact shape of the free energy diagram determines whether such a system is present as a single phase or multiple mixed phases.

The kinetics of the phase separation and the morphology of the resulting blend depends upon the stability of the homogeneous mixture at the given condition. If the mixing composition is near a local minimum in the free energy of mixing, the compo-

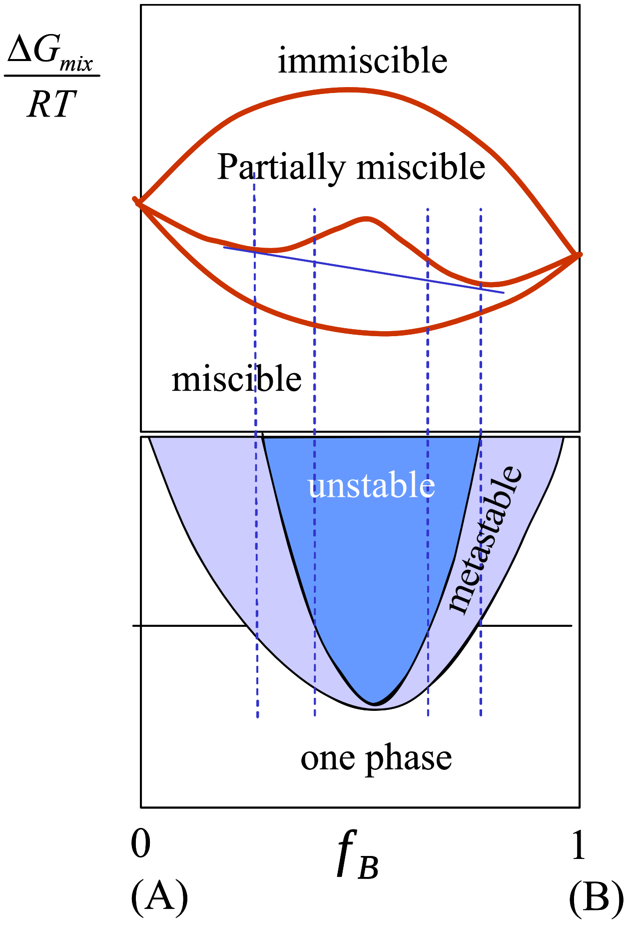

Figure 2.: Free energy of mixing

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*M.E. Stewart, Eastman Kodak, Kingsport, Tennesee & D.R. Paul University of Texas, Austin sition is metastable and will separate by a nucleation and growth mechanism. When the new composition condition is near a local maximum in the free energy diagram, then the blend is unstable and will spontaneously phase separate. The equilibrium compositions of the phases at equilibrium are given by the points of tangency of the free energy diagram.

The relative contribution of the combinatorial entropy of mixing for polymers, due to the much larger size of the molecules, is small - thus the driving force for mixing is only the enthalpy ΔH_{mix}. As such even relatively weak repulsion forces (non-polar molecules) ($\Delta H_{mix}>0$) are sufficient to oppose mixing.

The glass transition of polymer blends is strongly affected by the degree of phase separation at segmental level. The determination of the glass transition temperature(s) of a blend is a straightforward method to access the degree of mixing of a blend. (Figure 3) Generally, the presence of a single, composition- dependent Tg at a temperature between the Tg's of the component polymers is accepted as evidence of miscibility. Conversely, two-phase blends exhibit two Tg's. If the polymers are completely immiscible, the Tg's of the blend will equal the Tg's of the component polymers. If there is partial miscibility, however, the exact positions of the Tg's in a two-phase blend will depend upon the relative amount of each component in each phase.

MORPHOLOGY AND COMPATIBILIZATION

Miscibility refers to mixing in the amorphous phase and doesn't preclude crystallization of the blend components. In the absence of crystallinity, miscible blends consist of a single amorphous phase. Because of the lack of structure, miscible amorphous blends are transparent. Transparency therefore is often used as evidence of miscibility. However this is not a proof, as immiscible blends can also be transparent if the dispersed phase refractive index matches that of the matrix.

Immiscible and partially miscible blends are more common, than miscible blends. The properties of these blends are highly dependent upon its phase behavior and morphology. When separate phases are present and the proper morphology is obtained, it is possible to combine the desirable attributes of each polymer into a single material. Phase separated blends, thus offer the potential to retain the desirable properties of both components. However the properties related to ductility and toughness, are often less attractive in the blend than in either of the components. This is due to a large extent to the extreme dependence of these properties on the morphology. Toughness requires a homogeneously dispersed phase of spherical particles. High interfacial tension opposes particle breakdown, during melt mixing for example, and causes coalescence. Consequently, the dispersion of the components in many immiscible blends is very poor. Large interfacial energies produce sharp phase boundaries, which results in poor adhesion between phases. This reduces stress transfer between phases.

In order to overcome these problems, production of block or graft copolymers has become an important technique to increase adhesion between phases and to control (stabilize) the dispersion of the dispersed phase. The general term for this process is compatibilization and the production of copolymers

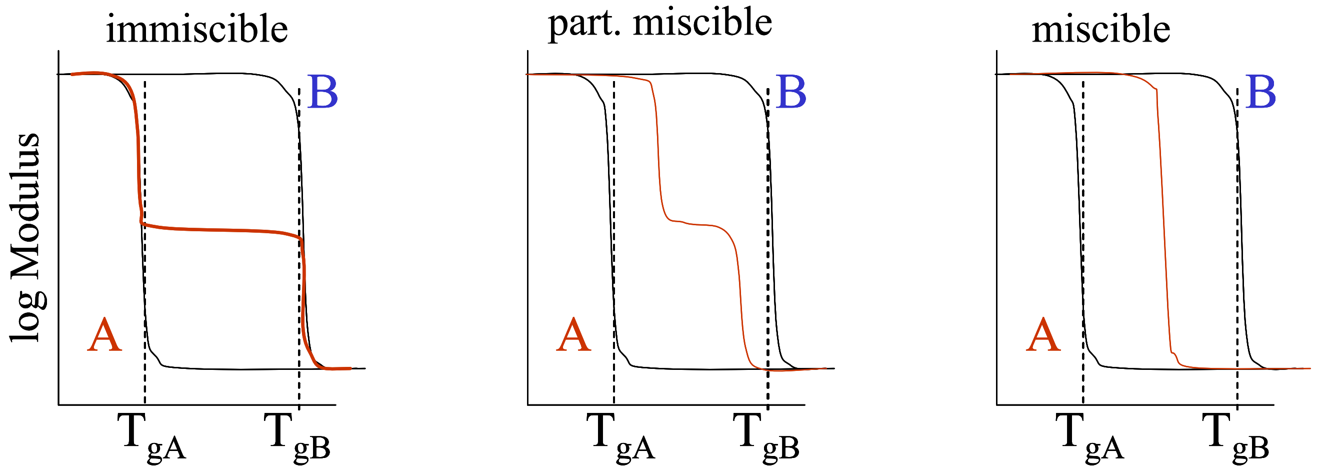

Figure 3: Tg's of binary inniscible, partially, and miscible blendsr.

in situ during the melt mixing process is known as reactive compatibilization. The goal of most compatibilization schemes is to increase the properties of the blends while retaining the two-phase nature and not to promote miscibility of the blend.

MARKET FOR BLENDS AND ALLOYS - LOOKOUT IN THE FUTURE

Increased inter-polymer competition with resultant losses in market share and margins force the polymer suppliers to focus their attention on providing polymer systems that offer unique competitive advantage to their customers. With the development and commercialization of -8 years (compared to 15 to 20 years for new polymers) the blend market is very dynamic. Suppliers are continually developing new alloys and blend to satisfy the changing applications and needs with better engineered products and lower cost products.

Alloys and blends represent inexpensive routes to satisfy both end use material requirements and suppliers desires for competitive product differentiation. Despite the recession in polymers, the continuous development effort of thesuppliers in a growing market for blends creates a need for advanced material testing instruments to characterize the specific mechanical and other physical properties of blends in the product development environment.