

Lec-1

Introduction to Polymer Blend

Polymer blend (PB): Mixture of at least two macromolecular substances, polymers or copolymers, in which the ingredient content is above 2 wt%.

Types of polymer blends:

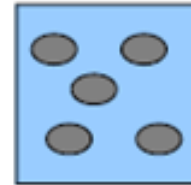
1- Miscible polymer blend: Polymer blend, homogenous down to the molecular level, associated with the negative value of the free energy of mixing: $\Delta G_m \approx \Delta H_m \leq 0$, and a positive value of the second derivative: $\partial^2 \Delta G_m / \partial \phi^2 > 0$. It is a single –phase structure , has properties of average values between the values of properties of its components and has one T_g .

2-Immiscible polymer blend: A blend exhibits more than two phases. It is a blend whose free energy of mixing; $\Delta G_m \approx \Delta H_m > 0$

Usually, has two T_g 's , since the two components are phase separated.



Miscible PB



Immiscible PB

Scientists often measure the T_g of a blend to find out if it is miscible or immiscible. If two T_g s are found, then the blend is immiscible. If only one T_g is observed , then the blend is likely to be miscible.

3-Homologous polymer blend: Mixture of two or more fractions of the same polymer each of which has different molecular weight distribution.

4-Isomorphic polymer blend: Polymer blend of two or more different semi-crystalline polymers are miscible in the crystalline state as well as in the molten state.

5-Compatible polymer blend: An immiscible blend is called compatible if it is useful blend wherein the inhomogeneity (caused by different phases) is on a small enough scale not to be apparent in use.

OR:

Blends that miscible in a certain useful range of composition and temperature, but immiscible in others.

Most compatible blends are immiscible and can be made compatible only by a variety of compatibilization techniques. When the interface

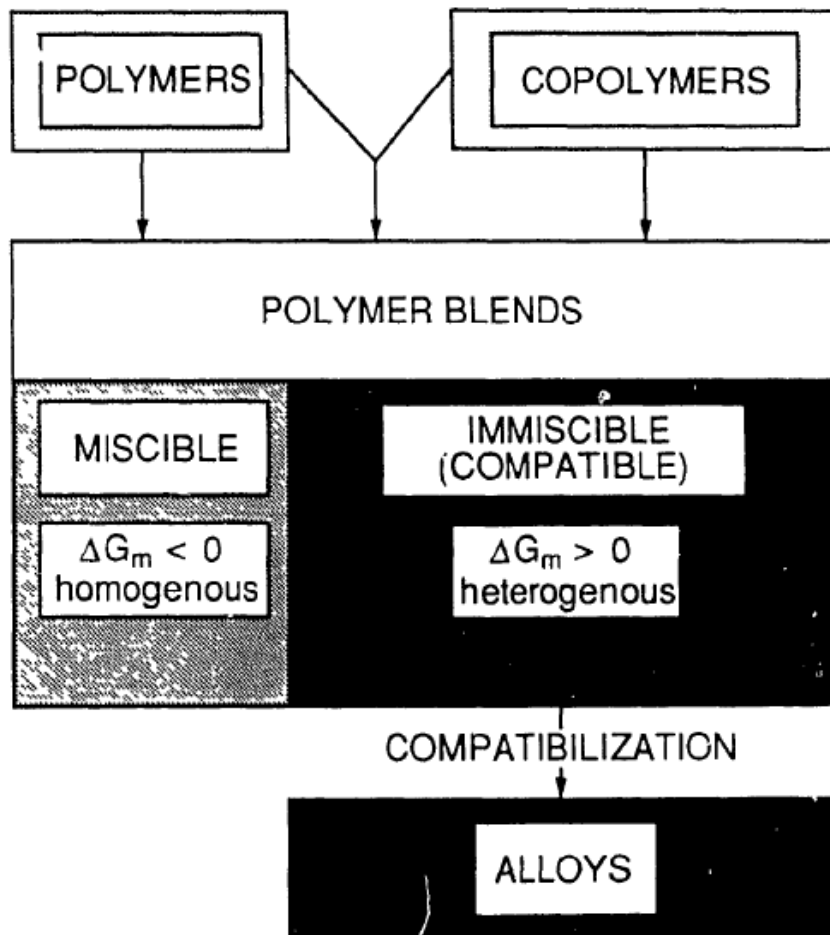
and/or the morphology of an immiscible blend is modified a polymer *alloy* is obtained .

6-Polymer alloy: Immiscible, compatibilized polymer blend with modified interface and morphology.

Polymer Blend Vs. Polymer Alloy:

The properties of many plastics can be greatly modified by blending or alloying two or more polymers. These terms are often used interchangeably, but technically , blends are mixtures that are not fully compatible and alloys are mixtures that are fully compatible .

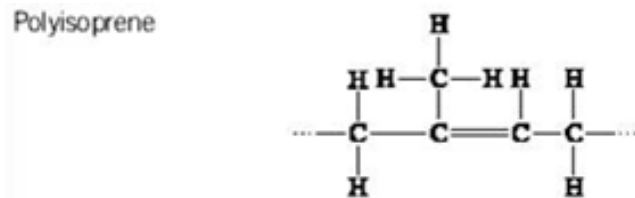
Polymer alloy constitutes a specific sub-class of polymer blend; virtually all high performance engineering blends are alloys.



The Beginnings

The polymer industry traces its beginning to the early modifications of shellac, natural rubber (NR -an amorphous *cis*-1,4-polyisoprene), gutta-percha (GP- a semi-crystalline *trans*-1,4-polyisoprene), and cellulose.

In 1846, Parkes patented **the first polymer blend**: NR with GP partially co-dissolved in CS₂. Blending these two isomers resulted in partially crosslinked (co-vulcanized) materials whose rigidity was controllable by composition. The blends had many applications ranging from picture frames, table-ware, ear-trumpets, to sheathing the first submarine cables.



The first compatibilization of polyvinylchloride (PVC) by blending with polyvinylacetate (PVAc) and their copolymers date from 1928. PVC was commercialized in 1931 while its blends with nitrile rubber (NBR) were patented in 1936 — two years after the NBR patent was issued.

The modern **era of polymer blending** began in 1960, after Alan Hay discovered the oxidative polymerization of 2,4-xylenols that led to polyphenyleneether (PPE). Its blends with styrenics, *Noryl*□, were commercialized in 1965.

Today:

At present, polymer alloys, blends, and composites consume over 80 wt% of all plastics.

Today the market pressure forces the resin manufacturers to provide better, more economic materials with superior combinations of properties, not as a replacement for wood or steel, but rather to replace the more traditional polymers. This has resulted in:

- Increased scale of production.
- Use of multicomponent and multiphase materials.
- New processing methods.

For example:

- 1- **Twin-screw extruders** with 80 tons/hr throughput and injection (100,000 kN) molding presses with shot size of 100 liters of polymer are available.
- 2- Composites where the matrix is a polymer blend that comprises **six different polymers** have been introduced.
- 3-6-Gas and multiple injection processes, melt-core technology, solid-state forming, microcellular foams all lead to new products with advanced performance.

Evolution of Polymer Alloys and Blends:

The historical evolution of the polymer blend technology is presented in the following order:

1. Commodity resins:

The commodity resins represent 71% of all consumed plastics. (Styrenics, PVC, Acrylics, PE's, PP).

2. Engineering resins:

The term engineering polymer is applied to a processable resin, capable of being formed to precise and stable dimensions, having high performance at $T \geq 100^\circ\text{C}$, and the tensile strength of $\sigma \geq 40 \text{ MPa}$.

Five polymer families belong to this category: PA (Polyamide or Nylon), PEST (Thermoplastic polyester), PC (Polycarbonate of bisphenol-A), POM (Polyoxymethylene or Acetal), and PPE (Polyphenylene ether).

3. Specialty resins :

The *specialty* resins are expensive, produced in relatively small volumes either for a specific application or looking for a market niche. Their $T_g > 200^\circ\text{C}$ and modulus $> 3 \text{ GPa}$

(PSF, PAE, PARA, PAR, PPS, LCP, PEI, PEA, etc.).

Methods of Blending

Most polymer pairs are immiscible, and therefore, their blends are not formed spontaneously. Moreover, the phase structure of polymer blends is not equilibrium and depends on the process of their preparation. Five different methods are used for the preparation of polymer blends : melt mixing, solution blending, latex mixing, partial block or graft copolymerization, and preparation of interpenetrating polymer networks (IPN).

An IPN is defined as a blend of two or more polymers in a network form, at least one of which is synthesized and /or cross-linked in the immediate presence of the other(s). An IPN can be distinguished from polymer blends, blocks, or grafts in two ways: (1) an IPN swells, but does not dissolve in solvents, and (2) creep and flow are suppressed.

Melt mixing is the most widespread method of polymer blend preparation in practice. The blend components are mixed in the molten state in extruders or batch mixers.

Solution blending is frequently used for preparation of polymer blends on a laboratory scale. The blend components are dissolved in a common solvent and intensively stirred. The blend is separated by precipitation or evaporation of the solvent. Advantages of the process are rapid mixing of the system without large energy consumption and the potential to avoid unfavorable chemical reactions.

During several past years, novel solid state processing methods, such as shear pulverization or cryogenic mechanical alloying, have been developed to provide efficient mixing of polymer blends . The polymers are disintegrated in pulverizes at cryogenic temperatures, and nanoscale blend morphologies are achieved.

Generally, blending methods are:

- 1- Mechanical mixing-cheapest
- 2- Dissolution in co-solvent, then film casting, freeze or spray drying
- 3- Latex blending
- 4- Fine powder mixing
- 5- Use of monomer(s) as solvent for another component, then polymerization(interpenetrating network)

The advantages of blending fall into two categories:

A. Blending may improve resin or product performance by:

1. Producing materials having a full set of the desired properties at lowest cost.
2. Extending the engineering resins' performance by incorporation of less expensive polymers.
3. Improvement of specific properties.
 - ◆ **Brittleness** : Toughening brittle polymers, thus eliminating the need to use low molecular weight additives
(*e.g.*, plasticizer in the flexible PVC formulations)
 - ◆ **Modulus & Dimensional Stability**: Blending with more rigid and more heat resistant resin

- ◆ **Improve Solvent and Chemical Resistance:** Incorporation of semicrystalline polymer into an amorphous resin (*e.g.*, blends of PC with PEST)
- ◆ **Improve Flame Resistance :** Incorporation of non-flammable resin into a flammable one (*e.g.*, styrenics or acrylics with PVC)
- ◆ **Permanently Anti-Static blends :** Blends with polymers having either –OH or –SH functionality (*e.g.*, ethylene oxide-coepichlorohydrin with ABS/PC blend).

Where S-H: Thiols (FTIR= 2550-2600 cm^{-1})

- ◆ **Biodegradability:** Incorporation of a biodegradable resin
- ◆ Blending makes it possible to produce integrated **multi-layer** structures

4. Providing means for recycling of industrial and/or municipal plastics waste.
5. The blending technology makes it possible to rebuild high molecular weights of partially degraded polymers, thus to produce high performance articles from the plastics waste.

B. Blending may lead to improved processability:

- 1. Process the high T_g resin at temperatures well below the thermal degradation limit:** Incorporation of a miscible resin with a lower glass transition temperature (T_g) (*e.g.*, PS/PPE blends).
- 2. Reduce pressure drop across dies or runners, thereby increasing productivity:** Incorporation of an immiscible, low viscosity resin (*e.g.*, LCP/PEEK blends).
- 3. Blends having a controllable degree of strain hardening (SH):** Blending with resin that either by itself shows high (SH) (*e.g.*, LDPE in blends with another PO), or when reactively blended forms long chain branches (*e.g.*, PS in blends with PO). These materials show better processability in technologies where the extensional flow field is important, viz., film blowing, blow molding, wire coating, foaming, etc.
- 4. Stabilize the Foaming Process:** Incorporation of elastomeric particles improves nucleation of gas bubbles, hence it stabilizes the foaming process, reduces bubble size and the final foam density.
- 5. Provides the means for generation of a controllable amount of the foaming gas during the ensuing stages of processing, viz., injection molding :** Incorporation of a degradable resin into an engineering or specialty one.
- 6. Easier, More Stable Processing:** Blending different grades of the same resin broadens the molecular weight distribution, which in turn results in easier, more stable processing (as well as better mechanical performance).

7. Blending **improves product uniformity** (scrap reduction) and plant economy.
8. Blending **ascertains quick formulation changes**, thus plant flexibility and productivity
9. Blending **reduces the number of grades** that need to be manufactured and stored.
10. Blending technology offers methods for **producing higher esthetic value materials**, *e.g.*, **films or coatings without gel particles** (or “fish eyes”), moldings with streak-free surface finish, etc.