Polymer Blends and Alloys

[Note: contents of these notes are compiled from various sources to cover the course syllabus, made for self study purpose. It is for fast reference, & hence for detailed information, the textbooks shall be referred. Suggestions are welcome. Apart from this typed notes, even the class discussions which are noted by students are equally important, some of which are not covered in this due to shortage of time. While answering, please understand & write to the point without much of extra information which is given in notes below. Answer question number wise & use statistical approach to be precise.]

Course outcomes: Upon successful completion of this course, the student will be able to understand-

CO1- the fundamentals of polymers blends and blending equipments;

CO2- thermodynamic aspects, phase diagram and morphology of blends;

CO3- miscibility and characterization of blends;

CO4- the mechanism and approaches of compatibilization and toughening;

CO5- interpenetrating polymeric networks, and Design polymer blends/alloys system to meet the requirements.

[Percentage of POs & CLs covered & mapping with COs.]

Course material: Unit-1 (foundation Unit, important one- because the basics covered in this unit will be utilized directly in other units, So, while answering any question of other 4 units, students shall mention information from this unit accordingly)

Definitions:

- Polymer Blend: Mixture of two or more polymers. (The second polymer added will be of significant quantity i.e. > 2% by weight).
- Polymer Alloy: compatibilized polymer blend.

Some distinctions for clarity:

- Copolymer (Cop): Polymer formed by two or more types of- repeating units or co-monomers.
- Polymer Compound: Mixture of polymer and additives/ingredients (from any material class).
- Polymer Composite: Any combination of polymer and filler in any form (from any material class).
- Solid state Material classification: Polymers, Metal, Ceramics.

- Polymer Crosslinking/ curing/ vulcanization: process of getting 3 dimensional networks of polymeric chains. (by chemical bonds)

- Physical cross links results out of localized crystallization/ interactions due to secondary forces / entanglements.

- Interpenetrating Polymeric Networks (IPNs) can be of both types (i.e. resulting from physical/chemical crosslinks).

- Thermoplastic Elastomers (TPEs) - polymeric materials behaving like rubbers & having processibility of thermoplastics. [could be achieved via blends/ cop/ chemical or physical cross linking]

- Polyelectrolytes/ ionomers/ ionic polymers: polymer backbone with 1 kind of charge (an/cation) & pendant/side groups with another kind of charge.

- Miscible - Homogeneous mixture in any proportion [will be homogeneous at molecular level].

- Soluble- Homogeneous mixture in limited proportion (up to saturation level).

- Homogeneous- just means same, & can be wrt morphology/ orientation/ distribution.

- Compatible: to work harmoniously (so they can be heterogeneous or immiscible but yet perform harmoniously without losing original properties).

- State: usually 3 states of matter- solid, liquid & gas (just based on molecular packing at physical level).

- Phase: sometimes used as synonymous to state but here the phase difference arises due to chemical and/or physical differences, any material or combination of materials exhibit distinct phases. For example in the liquid state mixture of water & oil, we can observe two phases. Semi-crystalline polymers show phases of crystalline region & amorphous region. Immiscible polymers shows phase separation.

- Compatibilization: Incompatible/ Immiscible blend + compatibilizer → to get → Alloy (this can still possess phases).

- Interphase: a third phase [of about 2-60nm] between the two phases of immiscible polymer blend (or binary system).

- Binary=2, ternary=3.

- Toughened polymer: brittle polymer with increased toughness [mixing with rubber (for

low temp. application)/ with engineering plastics (for high temp. application)/ with little **plasticizer/process aid/ toughener** (is a compounding approach)].

- Morphology: study of micro structure. Microscope assists the study of various phases.

- Physical compatibilization: achieved by changing temperature, pressure, rate of mixing, radiation, δH, δS, co- dissolution. [$\delta G = \delta H - T\delta S$]

- Specialty polymers – stable up to 500^0C.

- Aromatic/ Engineering polymer's properties can be 500 times more than that of aliphatic/ (Polymers [e.g. mechanical property of aliphatic polyester is 70 Mpa & that of aromatic polyes

- E.g. of blends: PC/ABS (mobile panel), PS/BR (HIPS), PS/ PPO, PMMA/SAN, NR/GP (gutta purcha), PE/PP. Blends are represented using "/" symbol between the polymers and it should not be read as "or" as we do in other case! The second polymer is referred to as second component, & denoted as: X_2 or X_b or φ_2 or φ_b.

Need for blending (the driving force): instead of carrying out research in developing new monomers/ polymers/ copolymers with required set of properties as per requirement, and to establish it across the market, which consumes lot of time, money & energy; it is worth developing a blend with existing materials with known properties.
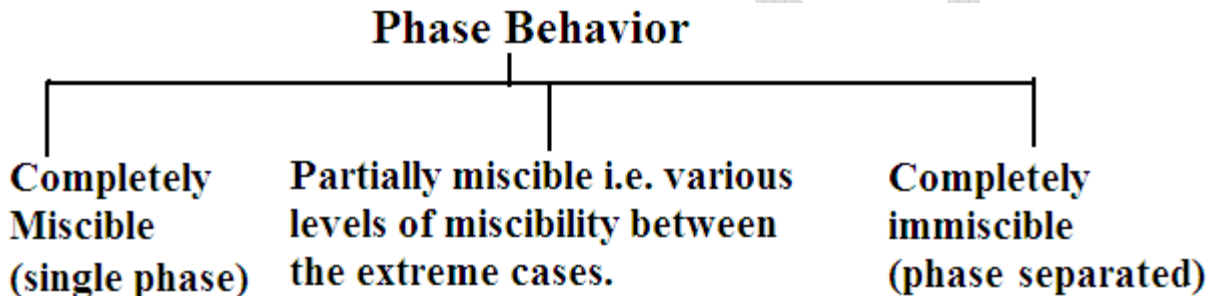
Classification of polymer blends: on various basis-

- Based on polymer type:
    o Thermoplastic/thermoplastic
    o Thermoplastic/rubber
    o Rubber/rubber
    o Rubber/thermoset
    o Engineering plastic/rubber, etc

- Based on component interaction:
    o Miscible/ immiscible
    o Compatible/ incompatible

- Based on application (i.e. performance at high temperature & high load) :
    o Commodity blend
    o Engineering blend

- Homologous polymer blends: Blend of polymers in order of molecular weight.

- 3 Types of mixtures based on performance (i.e. components interaction leading to property changes):
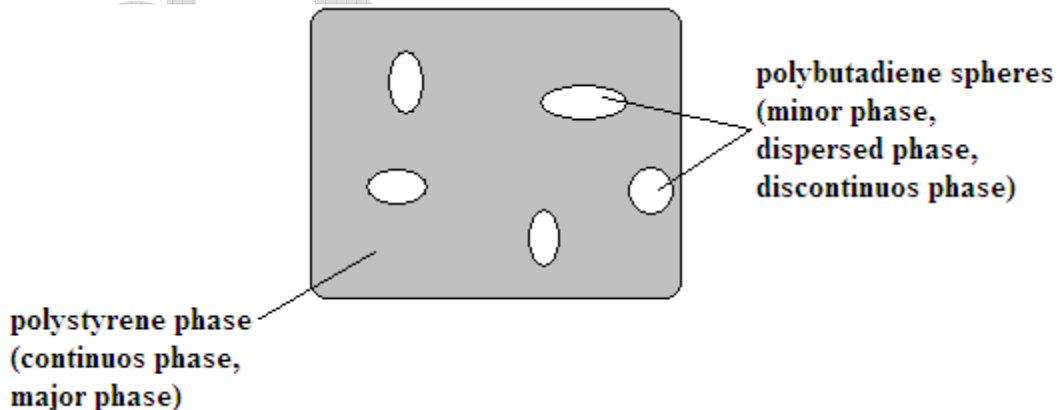
Mixture type	Effect
Additive	A+B = (A+B)
Synergistic	A+B > (A+B)
Antagonistic	A+B < (A+B)

Blends can also be classified as above.

Important Characteristic of blend is "Phase behavior". That is, the 2 or more polymers when mixed may show following phase behavior:

Phase Behavior

Completely Miscible (single phase) — **Partially miscible i.e. various levels of miscibility between the extreme cases.** — **Completely immiscible (phase separated)**

Whether a blend should be miscible or not depends on application requirements, for example, HIPS is immiscible blend of PS & BR where 2 phases are separated as shown below, & is used in market for some applications:

polybutadiene spheres (minor phase, dispersed phase, discontinuos phase)

polystyrene phase (continuos phase, major phase)

And, if compatibility is required then it is compatibilized addingg SB block copolymer as compatibiliser. It helps distribution of load, and also propagation of load takes place gradually. Therefore better tensile properties are achieved than unmodified HIPS as required for some applications.

Advantages/ Reasons for blending:

- To extend engineering resin performance by diluting it with low cost (commodity/ tonnage) polymer.
- To develop materials with a full set of desired properties.
- To utilize the scrap generated at various steps. [sometimes blending is also done to develop a recyclable material, e.g. using starch as second component]
- To get a high performance blend from synergistically interacting polymers.
- To achieve customer specifications in a product.
- Reduced R&D expenses & the time consumed in developing new monomers & polymers to yield a similar property profile.
- Lower capital expense involved with scale-up &commercialization.

How to Design a Polymer Blend? Steps:

1. Define the physical and chemical properties the ideal blend should have.
2. From a list of resin properties, select those polymers which may provide some of the required behavior (usually a wider range of desired properties requires several types of potential candidates).
3. Tabulate the advantages and disadvantages of the selected resins. There must be alternating candidates capable of providing each of the required properties.
4. From the list of candidates, select a set of resins which assures most suitable complementarily properties.
5. Determine the miscibility of selected resins and method of making them compatible if needed.
6. Examine the economics, compatibilization, compounding, as well as the effect of forming, maintenance, longevity, etc.
7. Define the ideal morphology which will assure the optimum performance of the finished product.
8. Select the rheological properties of the blend components, concentration of ingredients, amount of compatibiliser, type and intensity of deformation field needed for generating the pre-cursor morphology.
9. Determine the method of stabilizing the morphology e.g. by controlled cooling rate, crystallization, chemical reaction, irradiation, etc.

10. Select the optimum fabrication method which will assure formation of the final morphology (if not achieved go back to step 8.)

Limitations of blending:

- Recycling is complex in some cases.
- No specific test methods and standards are available. (used that of plastic/rubber)

Criteria for selecting the blend components:

- ➢ Principle advantages of 1st polymer (base polymer or component one) should compensate for deficiencies of the 2nd polymer; and vice versa.

  E.g.: Disadvantage of PPE (processibility & impact strength are compensated by advantageous properties of HIPS.

- ➢ Complex balance of property is usually achieved by multi-component blending with some unavoidable compromises {such blends can play multiple roles- mechanical properties, chemical resistance, dimensional stability, paint ability, etc., e.g.: PC/TPE/Latex System.}

Methods of blending: Solutions mixing/ melt mixing/ mixing above T_g/ mix one polymer in another monomer & polymerize/ mix two monomers & polymerize simultaneously/ latex mixing/ powder mixing & processing.

- Mechanical mixing: mechanical mixing of polymers includes such methods as roll milling and melt mixing.
    - o In roll milling, the mixing of polymers can be accomplished by squeezing the stock between the rolls.
    - o In melt mixing the polymers are mixed in the molten state. E.g. in extruder.
- Dissolution in co-solvent (followed by film casting, freeze/spray drying)
- Latex blending: Emulsion polymerization is employed for the preparation of rubber toughened plastic blends. The polymers should be in the latex or emulsion form. The mixing process of these micro-sized latexes and the subsequent removal of water produce excellent dispersion.
- Fine powder mixing: In this method components are taken in powder form and mixed. Followed by suitable processing technique.

- Use of monomers as solvents for another blend component, followed by polymerization as in interpenetrating networks.

Mixers for blending polymers: Mixers can be used either batch or continuous types.

Under batch mixers there are of three types namely:

- Roll mills (exposed)
- Sigma blade mixer (internal mixers)
- Kinetic energy mixers.
- ❖ Sigma blade mixers: Sigma Blade batch systems provide complete, homogeneous mixing, even in small quantities. The vessel and moving parts inside are designed to ensure consistent granulation action, and a predictable homogeneous blend in a broad range of products. A special breaker ensures movement of elements to eliminate dead spots and ensure all material are blended thoroughly and granulated consistently.
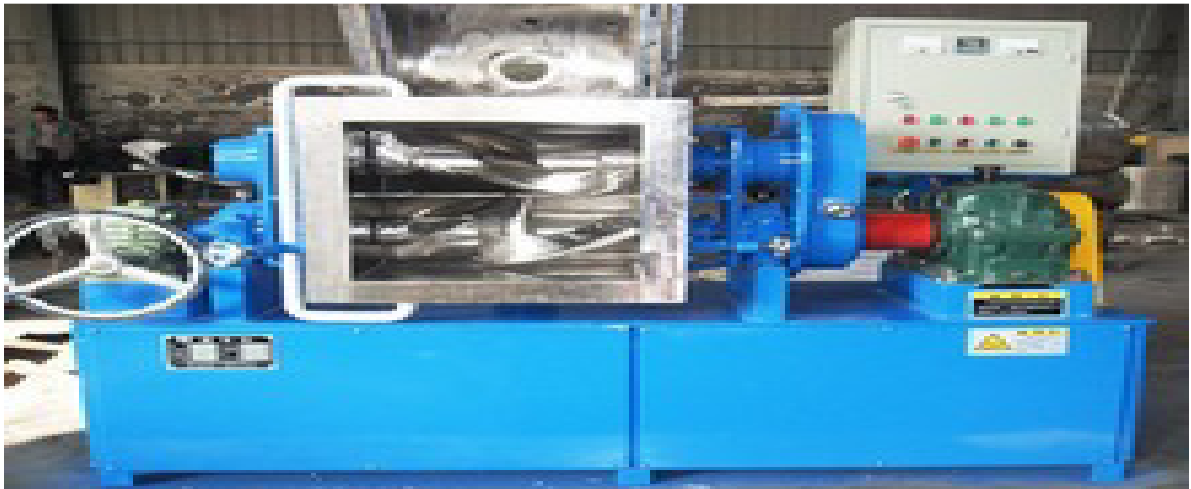
Sigma blade Mixer Operation: the tangential action of mixing and kneading is thoroughly obtained by 'Z' (SIGMA) shaped kneading blades, which rotates very accurately at different speed towards each other causing product to be transferred from blade to blade. Discharge of the mixed product is achieved by tilting the container or through the valves at the bottom or by means of an extrusion screw below the container if provided.

Continuous mixers:

- ❖ Single or twin screw extruder.
- ❖ Dynamic melt mixer.
- ❖ Disc extruder.
- ❖ Twin shaft intensive mixer/single-shaft.

- ❖ Motionless mixer also called static mixer.
- ❖ Repro CTM mixer.

Special machines:

- • Plastificator patfoort.
- • Reverser.
- • Multistage systems.

Reactive extrusion: process where the reactive site incorporation and melt extrusion of blends is carried in a single pass extrusion operation. The reactive extrusion compatabilization has been one of the most practical methods employed for achieving mechanical compatibility for many diverse polymer blends. Commercial example includes EPR toughened PA called as "super-tough nylon", Polyolefin/PVA_{OH} [an extreme example of incompatibility because of hydrophobic & hydrophilic (hygroscopic) or non-polar & polar natures polymers respectively].
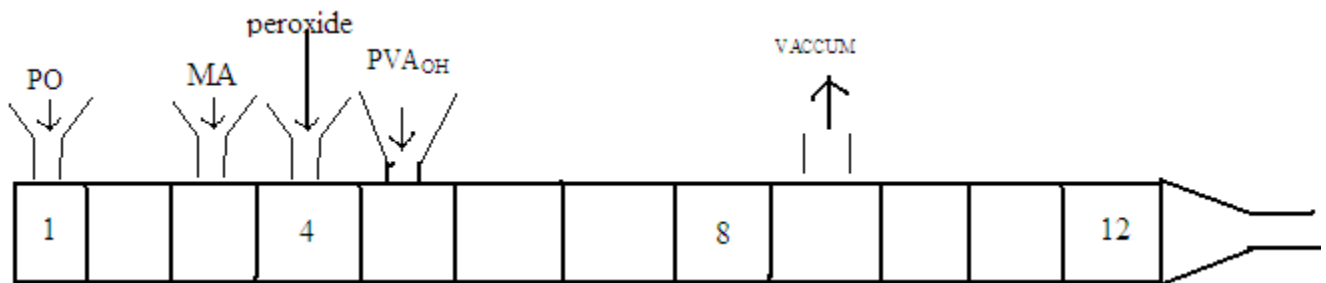

Fig. Reactive extrusion of PO/PVA_{OH} blends using twin screw extruder with 12sections

The design & operation of extruders as reactors for conducting single pass operation allowing for economic advantage has been noted in several book chapters.

Examples of some commercial blends & its applications:

- • < Elastomer blends- Tyre application >
- • <Emulsion blends – Adhesion & coating application >
- • PVC/Nitrile rubber → To overcome migration of plasticizers in PPVC
- • There are various parameters which contribute to miscibility or immiscibility of any blend. Viz. type of polymers, composition, molecular weight, crystallinity, polarity, temperature, H-bonding/ secondary forces of interactions, mode of blending, solubility parameter difference, Gibbs free energy, etc. [it needs deep study to know 'what influences how much' in each case of blend system using knowledge & analytical techniques].

- Here is an example which sounds irrational: PMMA is incompatible with PS, & PMMA is also incompatible PAN, but PMMA is compatible with SAN, which is a copolymer of repeating units of previous 2 polymers with which it was incompatible!

- Para (hexa fluro 2-hydroxy isopropyl) styrene & polystyrene co-polymer is compatible with PC, PMMA, PVAc, etc. this is an example to show how functionalization of a polymer can bring in compatibility with many polymers.

- HDPE & PP forms immiscible blends, though polarity, solubility parameter & secondary interactions matches; here, the crystallinity difference overtakes leading to immiscibility of these two polyolefins. [by nature, any system tends to be more random, but in above case, as blending forces them to be more crystalline, they oppose to be miscible and continue in their randomness]

- PPO/PS is a miscible blend due to overlapping of aromatic rings of both polymers. This is developed for easier processing of PPO. Because, PPO's Tg is 210^0C & processing temperature would be still high plus melt viscosity is also high, where as PS's Tg is100^0C & helps easy processing of PPO.

- Blends of crystalline thermoplastics and amorphous rubbers are developed to achieve a combination of low temperature flexibility &high temperature resistance; e.g. the TPOs [thermoplastic polyolefines class of TPE] used for automobile part applications.

Unit-2

Morphology:

- Even the phase morphology do change depending on various parameters as mentioned above plus the processing, post treatments, way of cooling, etc for e.g. In HIPS, phase inversion is observed if BR composition is increased, then BR becomes a co-continuous phase, & still further becomes a major continuous phase and then PS becomes discontinuous or minor phase, if same is extruded then the spherical morphology becomes rod like cylindrical **[recall all those morphology structures studied in analysis subject & use them over here]**; which increases tensile properties of HIPS, as it acts like Composites. [I.e. fiber like structure inside the matrix]. In case of PBT/PVA$_{OH}$→ Lamellae (sheet) morphology is achieved when it is biaxially oriented <using stretch blow molding /blow film extrusion or via cross head extrusion>, this is used in container application like bottles to have 2 layers of polymers with different properties as required for application like- the one used to contain carbonated beverages because, carbondioxide cannot pass through Poly Vinyl Alchol, so, soda remains fizz. [note: in Mackintosh (rain coat) outer layer is of rubber to protect from water & inner from (cellulose) cotton to feel comfort by absorbing sweat, this arrangement is not blend, this is an example of composite.]

**Miscibility depends on temperature and composition also:**
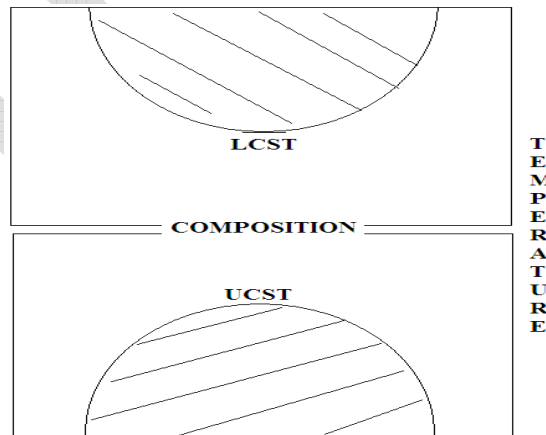
Phase diagram (to show temperature dependency on miscibility)

In the above figure of temperature versus composition [phase diagram for blends or solutions or any mixtures], the shaded region represents phase separation & outer

boundary the single phase (miscible region). It says that, depending on type of material, the temperature at which a mixture is miscible varies with composition.

LCST: Lower critical solution temperature- the lowest temperature below which all compositions are miscible.

UCST: Upper critical solution temperature- the highest temperature above which all compositions are miscible.
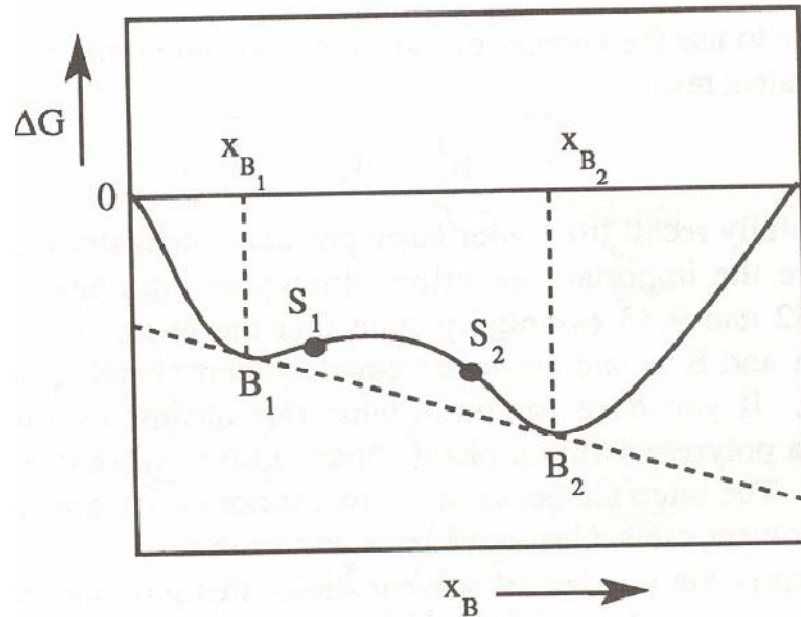
Schematic of free energy vs composition for systems of limited solubility: Phase diagram (to show composition dependency on miscibility)

At any composition less than B1 and greater than B2 a single phase (given by the solid curve) as lower free energy then any 2 phase system with the same overall composition. i.e. at these compositions only one phase will exist. For compositions in between, the system will consist of two phases of composition B1 and B2.Figure shows miscibility variation of blend A/B, where B's composition at 30 & 70 % are favorable in getting a more miscible blend (because low Gibbs free energy) than that between 30 and 70% composition. [Note: the y-axis is delta G_{mix}].

Note: In a blend which is immiscible, additives reside usually in the softer region (softer polymer).

Phase diagrams of composition vs Temperatures (ɸ-T) **observed with various polymer blends**

- The phase diagrams of polymer mixtures can take many forms as shown in figure below where the single phase and phase separated regions exists in the composition temperature range depicted. Many miscible systems i.e. (a), exhibit miscibility over the entire composition temperature range where both polymer exhibit thermal stability. Miscible system where the level of miscibility is border line will often show phase separation within the experimentally determined ɸ-T space LCST and UCST i.e (c) and (d), have been observed in many polymer blends; and both were observed in rare cases i.e (e). The hour glass diagram depicts overlapping LCST and UCST behavior i.e (f), (e.g. a study involving PS and poly pentyl methacrylate showed this behavior). The most common case is as in (b), where the phase separated regions comprises the majority of the T-ɸ phase.

  With all immiscible blends, each phase will contain both polymers. However, with highly immiscible blends, the concentration of the second polymer in a polymer rich phase will be extremely low and have an undetectable influence on the properties of that phase. Double LCST and double UCST i.e (g) and (h), behavior can be obtained via the equation of state theory predictions. All of the diagrams shown in figure below have been experimentally observed and also can be predicted from various theories. [usually got by varying components, composition, T, P, MW, etc]
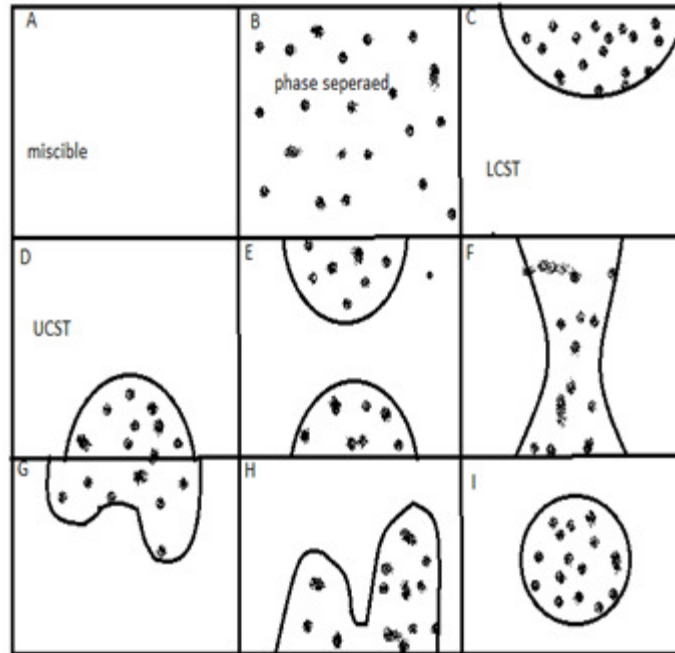
Phase diagrams observed with polymer blends <shaded area= phase separated region>

Resultant property after mixing two polymers:

[**Case:** miscible blend]

The property value of blend will be in between that of the two polymers' property values, depending on composition. But, depending on interaction, this trend may slightly vary too! Consider the example of T_g variation of blends as shown in typical plot. Polymer A has low Tg, & polymer B has high Tg, so, with increase in composition B, this miscible blend surely shows increase in Tg, but if blend components have i) strong interaction- then the property increase will have higher profile; & if blend components have ii) weaker interaction- the property increase will have lower profile .
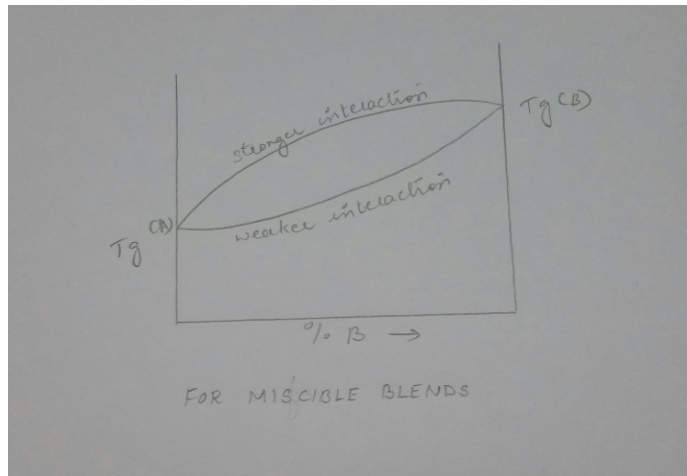
Property variance in miscible blend & its dependency on interaction

[Case: all types]

Property - composition relationship
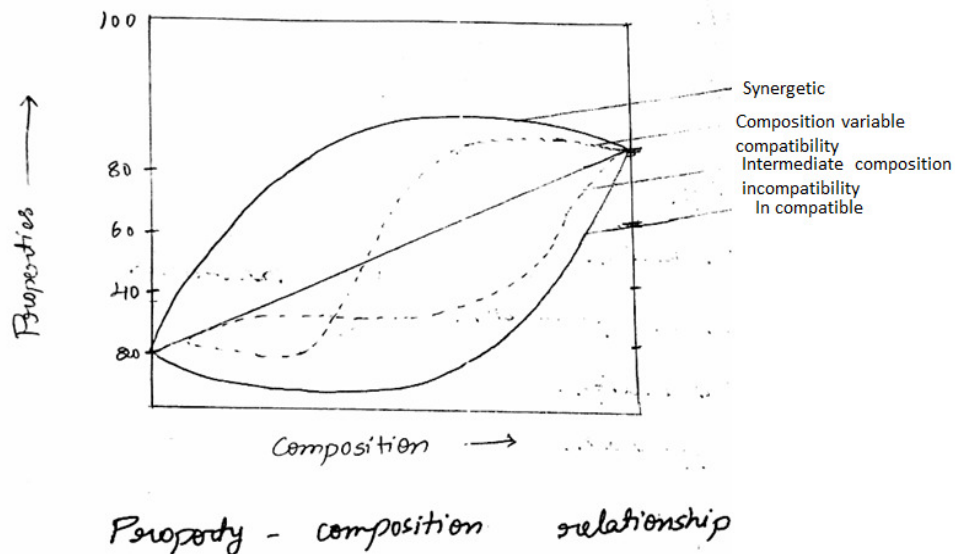
  If the straight line joining the 100% composition point of A at left to the 100% composition point of B at right is considered as median, then the curves above and below this shows the way in which property varies for differently interacting blends. For synergistic blends the properties will increase than that of 2 components & for antagonistic blends the properties will be lower than that of two, and for others it will be varying in between depending on miscibility, interaction & composition (at a given temperature).

Approaches for achieving miscibility & compatibility:

Hydrogen-bonding

Dipole –dipole interaction

Matched solubility parameter   Parameters for Miscibility

Ion –dipole interaction

~~Mean field approach~~

~~Association model~~

Ternary non-reactive component addition

Block &graft co polymer addition

Reactive compatibilization   Approaches to get alloy

                                    (Compatibility of phase separated blends)

Co-crosslinking

Interpenetrating networks

In-situ polymerization

Nano particle addition/ additives

Thermodynamic relationships for polymer blends

Thermodynamic conditions for miscibility are:

$$1. \; (\Delta G_{mix} < 0)$$

$$2. \; \frac{(\partial^2 \Delta G_m)}{(\partial \Phi B^2)_{T,P}} > 0$$

Note: both the conditions should be satisfied for miscibility, else phase separation will predominate.

Two mechanisms of phase separation:

   i.   Nucleation and growth

  ii.   Spinodal decomposition

For nucleation, the new phase must initiate with a composition which is not near to that of parent phase. Nucleation is a phase transition, which is large in degree i.e. composition change but small in extent i.e. size; whereas spinodal decomposition is small in degree but large in extent.

Comparison between Spinodal Decomposition and Nucleation and Growth

- An initially homogeneous solution develops fluctuations of chemical composition when super cooled into the spinodal region. These fluctuations are at first small in amplitude but grow with time until there are identifiable precipitates of equilibrium composition.
- In contrast, during nucleation and growth, there is a sharp interface between the parent and product crystals; furthermore, the precipitate at all stages of its existence has the required equilibrium composition.

Spinodal decomposition involves uphill diffusion, whereas diffusion is always down a concentration gradient for nucleation and growth of the type illustrated below. Spinodal decomposition refers to a mechanism of phase transformation inside a miscibility gap. It is characterized by the occurrence of diffusion up against a concentration gradient, often referred as "uphill" diffusion, leading to formation of a uniform-sized, periodic fine microstructure.
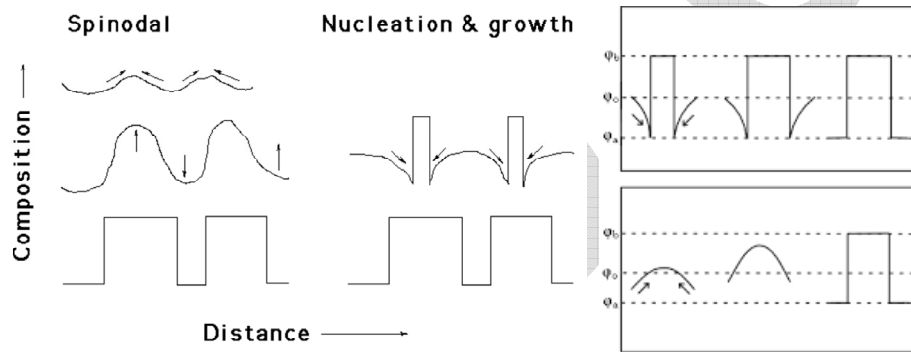

Figure: Direction of diffusion depicted by arrows in spinodal decomposition (top) and nucleation and growth (bottom).

Figure shows interconnected bicontinuous morphology of A rich and B rich phases. Nucleation and growth results in the formation of spherical particles dispersed in a matrix. Those particles, having a size greater than the critical nucleus would grow with time, at the expense of the smaller particles due to Ostwald ripening (info).

Fig. _____ Schematic of structures observed in the early stage of phase separation in a polymer blend by (a) spinodal decomposition and (b) nucleation and growth

(a) Spinodal decomposition
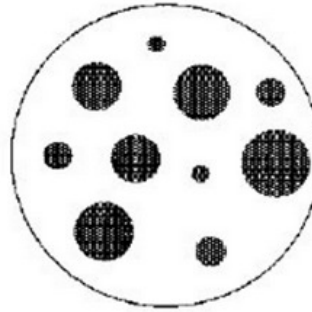
(b) Nucleation and growth

At the critical solution temperature, the two sides of the spinodal curve meet a binodal point. The critical temperature is then defined by the conditions

$$(2.31) \quad \frac{\partial \Delta G_m}{\partial \phi} = \frac{\partial^2 \Delta G_m}{\partial \phi^2} = \frac{\partial^3 \Delta G_m}{\partial \phi^3} = 0$$

In the phase diagram the spinodal and binodal curves meet at a common maximum, which is called an *upper critical solution temperature* (UCST)

| Table: Comparison of Phase Separation Processes.		
Property	**Nucleation and Growth**	**Spinodal Decomposition**
Size of phase separated region	increases with time	size constant
Concentration of phase separated region	constant with time	increases with time
Diffusion coefficient	positive	negative
Phase structure	separated	interconnected
Activation energy	required	not required
Region of phase diagram	metastable or unstable region	only unstable region

Nucleation and Growth Regime
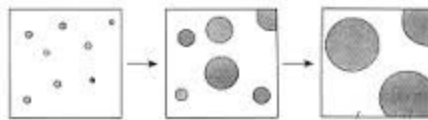
Spinodal Decomposition Regime

<u>Fig. a) Nucleation and Growth with spherical particles dispersed in a matrix, b) Spinodal</u>
<u>decomposition with an interconnected bicontinuous morphology.</u>

Reasons why classical diffusion equation fails to describe the spinodal decomposition process can also be understood by looking at free energy reduction. The driving force for any process is the free energy reduction. In the case of mass flow, this driving force manifests itself as equalizing chemical potential. [i.e. As Energy flows till temperature becomes equal, and as volume changes till pressure becomes equal, so is this mass flow till chemical potentials become equal] . Even though in classical cases such free energy reduction is also accompanied by decay of decompositional heterogeneities, in the case of spinodal it is not so. In the case of SD, 'the homogenization of chemical potentials leads to the heterogeneities in composition', therefore Fick's law is modified for this case.
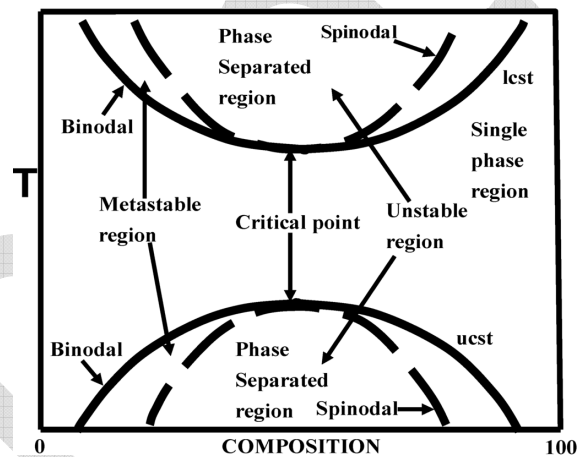
[Note: recall the sketch drawn in class with two frames, which is important]

- The spinodal cure is related to position where

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_i^2}\right)_{T,P} = 0$$

- A spinode is a cusp where 2 curves meet or a stationary point of curve. The limit of stability of a solution to decomposition into multiple phases is referred to as spinodal.
- Binodal or co- existence curve or binodal curve is the condition of miscibility for a binary system i.e. it is a boundary between mixed & separated phase therefore it is a condition at

which 2 distinct phases may co–exist & can determined at a given temperature by drawing a tangent line to free energy.

- The critical point where the binodal & spinodal intersect is determined from the expression

$$\left(\frac{\partial^3 \Delta G_m}{\partial \phi^3} \right)_{T,P} = 0$$

- The knowledge of extent of P-P miscibility is not only important to produce miscible but rather to rather device for methods for blend modification to enhance properties like modulus, HDT IS, etc.
- The miscibility provides a simpler means of accomplishing this than other types of compatibilization method.
- In a system store phase separation occurs within accessible range of variables [i.e. temperature (T), Pressure (P), Concentration of components], the processes with a particular attention to miscibility may lead to highly successful product.
- Miscibility defines flow behavior & orientation effect i.e. performance of finished product.
- Self-diffusion co-efficient of macro molecules is of low value, thus equilibrium thermodynamic conditions are difficult to achieve.
- Even though near equilibrium conditions are obtained in processing equipment [I/M &extrusion] they are not necessarily preserved in the finished product.
- P-P miscibility is determined by a delicate balance of enthalpic & entropic forces, significantly smaller than those observed in small molecules solution.
- Whenever a process goes from one state to another state say for e.g. mixing, the change in properties like H, G, S, X_b, μ, etc do change and are given by:

$$\Delta G = G - G_0$$
$$\Delta H = H - H_0$$
$$\Delta S = S - S_0$$

Thermodynamic relationship for mixtures (i.e. for miscibility of polymer blends):

The most important relationship governing mixtures of dissimilar components say 'A & B' is-

$$\Delta G_m = \Delta H_m - T.\Delta S_m \text{ ------------ (3)}$$

Where, ΔG_m = free energy of mixing

ΔH_m = enthalpy/heat of mixing

ΔS_m = entropy of mixing

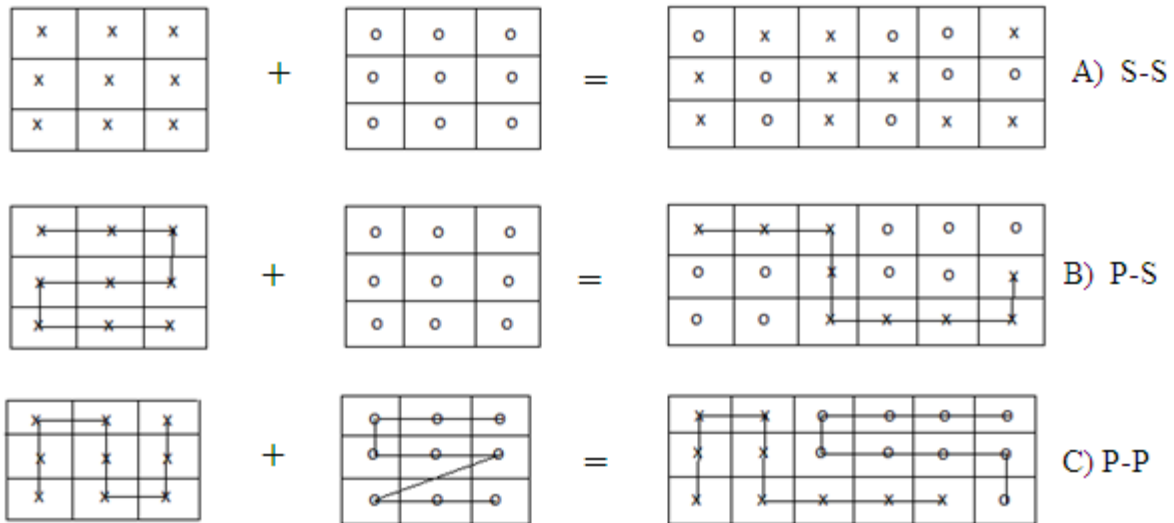T = temperature (any fixed or considered temperature)

I.   Entropy of mixing:

To understand the extent of combinatorial entropy contributions for miscibility of polymer blends, let us consider interactions between following 3 cases:

A. Solvent - Solvent

B. Polymer – Solvent

C. Polymer – Polymer

In low molecular weight components i.e. case-A, combinatorial entropy is major contribution for miscibility Therefore, solvents show broad range of miscibility; whereas it is less between polymer & solvent i.e. case-B; and still less for polymer & polymer, i.e. case-C. So, contribution of combinatorial entropy is very less for miscibility of polymer blends.

For low molecular weight materials, generally increase in temperature leads to miscibility, as TΔS increases and ΔG decreases; but, for higher MW components i.e. for polymers TΔS is small and other factors like non–combinational entropy combinations and temperature dependent ΔH values can dominate and lead to the reverse behavior namely, decrease in miscibility with increase in temperature. Thus, for case-A & case-B, UCST exists and for case-C, LCST exists!

Hence there is a need for modifying the equation 3, which is the Gibbs free energy of mixing, to suit the case of polymer blends. Also the first two equations mentioned (earlier) need to be satisfied for achieving miscibility. So, by suitable modifications of Boltzmann relationship, the combinatorial entropy of mixing for polymers is given by,

$$\Delta S_m = -k [N1\ln\Phi_1 + N_2\ln\Phi_2] \text{-----------(4a)}$$

$$\text{Or } \Delta S_m = -kV [(\Phi_1/v_1)\ln\Phi_1 + (\Phi_2/v_2)\ln\Phi_2]\text{----------(4b)}$$

$$\text{Or } \Delta S_m = -RV [(\Phi_1/v_1)\ln\Phi_1 + (\Phi_2/v_2)\ln\Phi_2]\text{----------(4c)}$$

[(4a) & (4b) is for molecular volume; & (4c) is for molar volume.]

Where,

R= Gas constant,

k= Boltzmann constant,

R & k are related as $R=Nk_b$ {here N is Avogadro constant or no. of atoms or molecules or particles},

$V = V_1 + V_2$ {V=Total volume}

$N = N_1 + N_2$ {N=Total no. of lattice cells}

Φ_1 & Φ_2 are the volume fractions of 2 polymers.

As the $\ln\Phi_i$ [i.e, $\ln\Phi_1$ or $\ln\Phi_2$] value is negative, ΔS_m is +ve, & $-T\Delta S_m$ in eq^n(3) leads to negative contribution to ΔG_m thus improving the potential for miscibility.

II. **Enthalpy of mixing:**

The expression for this is evolved from basic relationships and is given by,

$$\Delta H_m = \Phi_1\Phi_2 RTV\chi_{12}/V_r \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where, V_r is the interacting segments' volume i.e. molecular or molar volume of specific segments.

χ_{12} is Florry – Huggin interaction parameter.

$$\chi_{12}=ZW/kT\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where, Z is coordination number ranging between 6 and 12 and usually taken as 8.

W is exchange energy of interacting segments.

Also, $(\delta_1-\delta_2)^2=\Delta H_m/V\Phi_1\Phi_2 = ZW/V_r = \chi_{12}RT/V_r$

$$(\delta_1-\delta_2)^2 = Z (\sqrt{\epsilon_{11}}-\sqrt{\epsilon_{12}})^2/ (2Vr)\ldots\ldots\ldots\ldots\ldots. (7)$$

Where, δ= solubility parameter

ϵ_{12}=energy of contacts between components (1) and (2).

Flory-Huggins theory for developing an expression for free energy of binary polymer mixture: [independently derived by these two scientists, leads to key equation nos. 8/ 9/ 11/12]

From equations 3 to 7, $\Delta Gm = \Delta Hm - T\Delta Sm$

$$= [\Phi_1\Phi_2 RTV\chi_{12}/V_r] - T[-kV(\Phi_1/V_1 \ln\Phi_1 + \Phi_2/V_2 \ln\Phi_2)]$$

$\Delta Gm = [\Phi_1\Phi_2 RTV\chi_{12}/V_r] + TkV[\Phi_1/V_1 \ln\Phi_1 + \Phi_2/V_2 \ln\Phi_2]\ldots$ **(8)** (Molecular basis)

$\Delta Gm = [\Phi_1\Phi_2 RTVZW/kTV_r] + TRV[(\Phi_1/V_1)\ln\Phi_1 + (\Phi_2/V_2)\ln\Phi_2]\ldots\ldots$ **(9)** (Molar basis)

$V_r = \sqrt{V_1 V_2}\ldots\ldots\ldots\ldots$ **(10)**

$$\Delta Gm = RTV[(\rho_1\Phi_1/M_1)\ln\Phi_1 + (\rho_2\Phi_2/M_2)\ln\Phi_2] + B_{12}\Phi_1\Phi_2 V\ldots\text{ (11)}$$

OR

$$\Delta Gm = RTV\{[\Phi_1.\Phi_2.\chi_{1,2}/V_r] + [\Phi_1.\ln\Phi_1/V_1] + [\Phi_2.\ln\Phi_2/V_2]\}\ldots\text{ (12)}$$

Where,

M= molecular weight of component

ρ= density of component

B= $RT\chi_{12}/V_r$ i.e a binary interaction density parameter.

[Note: while answering the question related to FH equation without derivation, only eqn 3, & the last one have to be written with expansion of symbols/terms used]

HIGH LIGHTS OF FLORY-HUGGINS THEORY

❖ With high molecular weight polymers, the enthalpy of mixing term ($B_{12}.\varphi_1.\varphi_2.v = \Delta H_m$) determines the phase behavior of blend.

❖ $B_{1,2}$ is related to w_{12} and E_{12} so, a specific interaction must exist between the components.

❖ Though the combinatorial entropy term is multiplied by temperature, the increase in temperature has no significant effect for high molecular weight polymers.

❖ The usual convection employed for polymer blends is that a negative heat mixing is exothermic and positive heat of mixing is endothermic.

❖ Specific interaction is directly temperature dependent and experiments have shown that the negative value of H_m, X_{12}, B_{12} for blends invariably lead to single phase miscible blends. [As entropy contribution for Flory–Huggins equation is always negative]

❖ Other factor including non-combinatorial entropy of mixing terms is not covered by Flory-Huggins equation, but plays a significant factor in phase behavior and is explained in "equation of state theories".

❖ Flory-Huggins approach is not directly capable of predicting LCST.

Unit-3

Various parameters that contribute for Miscibility of polymer blends

After the thermodynamic approach of free energy determination for knowing miscibility of blends, let us see how other parameters contribute for miscibility: (in earlier Units, the list is mentioned)

Solubility parameter concept for miscibility

For liquids, solubility parameter S_p was defined as square root of cohesive energy density

$$S_p = (\Delta Ev/V)^{(1/2)}$$

Here, Ev = energy of vaporization.

[S_p values ranges from $12(MPa)^{(1/2)}$ for fluorocarbon gases to $30(MPa)^{(1/2)}$ for Hg]

While for polymers, many techniques are employed to determine S_p, one example is swelling parameter i,e. the S_p the solvent at the position which shows highest swelling of lightly x-linked polymer is considered as S_p of that polymer.

Values of S_p for some polymers:

Polymer	S_p $(MPa)^{(1/2)}$
PTFE	12.7
BR	16.7
PS	18.7
PVC	20.7
PAN	26.7 to 30.7

❖ Small (scientist) observed that the S_p of polymers could also be calculated using group combination approaches as:

$$S_p = \rho . [\sum F_i/M]$$

as, $\rho = M/V$ it can be written as $S_p = \sum F_i/V$

Here, F=molar attraction constant

M=Molecular Weight of repeat unit

V=molar volume

❖ Solubility parameter calculated by such approaches showed that values of PPO and PS are matching, i.e. 19 (MPa) ^ (½) and says that, with minor contribution of specific interactions and entropy, this blend is miscible due to matching S_p. If there is difference in S_p then specific interactions are must for miscibility. The experiments have come up with practical guide for predicting miscibility based on specific interactions and critical solubility parameter difference :

ΔS_p (MPa)$^{(1/2)}$	Specific Interactions
If <0.2	Then, dispersive force are sufficient for miscibility
If <1.0	Then, polar forces are required for miscibility
Similarly,	
<2.0	weak specific interactions
<4.0	moderate specific interactions
<6.0	strong specific interactions

❖ Also, the heat of mixing is proposed to be the sum of dispersive and specific interactions contributions.

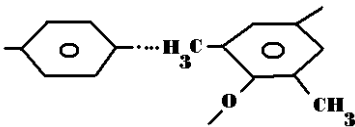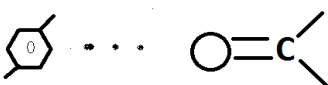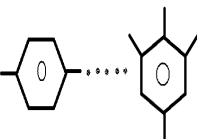$$\Delta H_m = H_{m(specific)} + H_{m(dispersive)}$$
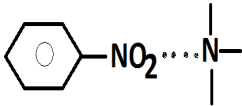
❖ Though the S_p can be used as a guide, it lacks the ability to predict specific interactions.

SPECIFIC INTERACTIONS that play one of the important roles in achieving miscibility:
In order to achieve the 'negative' heat of mixing as required by high molecular weight polymers, specific interactions play a key role. Purely dispersive interactions would not be sufficient, and hence interactions like hydrogen bonding, acid-base [Laury-Bronsted or Lewis charge transfer], dipole-dipole, ion-dipole, dipole-induced dipole, ion-induced dipole, π-hydrogen bonding, n-π complex, π-π complex formation, or etc; are also necessary to achieve miscibility. The relative

strength of these interactions range from 0.4 KJ/mole [London dispersive force/ Wander Waals force] to 25KJ/mole [hydrogen bonding]. [info: covalent bond's strength is 100KJ/mole]. The examples of polymer miscibility attributed to these interactions are as shown below:

Interaction	Contributing Groups	Examples of polymer pairs
acid-base	$-SO_3^-$ $^+N<$	Anionic polymer with Cationic polymer
	$>C=O\cdots H-O-$	Polyester or carbonyl polymer with Phenoxy or Polyvinyl phenol
	$>C=O\cdots H-C-Cl$ (with vertical bonds on C)	Aliphatic Polyester with PVC
	$>O\cdots H-O-$	PEO, PVHE with Phenoxy
	$>O\cdots H-O-\overset{O}{\overset{\|}{C}}-$	PEO, PVME with PAA, PMAA [PVME= POLY VINYL METHYL ETHER]
dipole-dipole	$>C=O\cdots \overset{F}{\underset{F}{C}}<$	PVF$_2$ with Variuos Poly acrylates, PVAc
ion-dipole	$-SO_3Li\cdots O=\overset{H-N-}{C}-$	Styrene Sulphuric acid (metal salts) containing Polymers with PA
π–hydrogen bonding		PS with PPO
n- π complex		PC with PMMA, PC with Polyester
π - π complex		PS with TMPC

charge transfer	$\langle\bigcirc\rangle - NO_2 \cdots N-$	aromatic nitro polymers with tertiary amine containing polymers

Characterization of Polymer Blends

[Note: student while answering this unit's question shall not explain the instrumentation/ procedure/ principle etc as was learnt in analysis subject previous semester! Only the technique or approach of analyzing blend for its phase, miscibility, performance, reaction with compatibilizer, and such things shall be highlighted, preferably with help of sketch, like we did in class. The Idea or basis for using certain techniques for blend analysis is mentioned below]

- Morphology using microscopy (OM, TEM, SEM, and AFM) various morphologies saying about blends' phase behavior has been discussed initially.
- Spectroscopy: UV-Vis, IR and x-rays < idea about change in crystallinity, formation of new groups, etc can be realized>
- Determination of Tg by DSC or DMA:

- **DSC:** is another research tool to investigate the polyblends. The most unambigious criterian of polymer miscibility is single Tg, where temperature is intermediate between those corresponding to the two component polymer.

Influences of various structural changes are usually associated with changes with heat adsorption or emission etc and are measured using colorimetry. The sudden change in the specific heat capacity at Tg is manifested as a step on the temperature v/s differential temperature curve. The temperature at which this transition occurs is different for different materials. In physical blend of two polymers, each polymer retains its own transition temperature and both are observed. On the other hand, the pressure of single Tg for a blend is indicator of homogeneity on a molecular level and thus mechanical integer. Hence, measurement of Tg assists determination of compatibility of amorphous or semi crystalline polymer blends.

NOTE: *The additives also influence Tg

*For highly crystalline polymer this technique is not suitable.

*Relaxation of built-in stress due to mixing/ forming/ cutting/ other process can occur at Tg and can distort shape of transition; hence preforming or premelting is required.

*For small concentration like less than 10%, the small peak is difficult to resolve and shift of the major peak is negligible.

*The combination of various techniques is also a necessary for blend analysis.

DMA: Because of excellent resolution of the Tg provided by the DMA through the measurement of E'·E'' and tan delta (loss tangent); this analysis technique offers a better means for examining poly blends. Transitions in semi miscible blends that may be difficult to resolve by DSC are readily determined by DMA. Generally, for an immiscible blend, the loss modulus (E'') curve show the presence of 2damping peaks corresponding to Tg of individual components .

For a highly miscible blend the curve shows only a single peak where as broadening of transition occurs in case of partially miscible system. [Peak or onset of increase in tan delta; peak or onset of increase in E'';]

Spectroscopy helps in study of blends: UV-visible, X-ray and IR:

Electromagnetic (EM) radiation and the interaction with the specific groups of polymer blend as a function of wavelength (frequency) is an important method to ascertain specific interactions between interacting species.

The spectroscopic techniques based on molecular vibrations can measure molecular interactions, such as hydrogen bonds or chemical reactions (with FTIR, Raman, and NMR). However, these techniques are not very sensitive to the phase separation or dispersion; and are mostly non-qualitative; therefore, they must be used in conjunction of other techniques.

X-ray photoelectric spectroscopy (XPS): Is commonly employed to determine the surface composition of polymeric materials, upon X-ray irradiations, the inner-shell electrons can be emitted & measurement of its kinetic energy can help identify the source material of electron emission & thus determine the atomic composition of surface.

For e.g. 'C' (carbon) of -CH2-; -CF3; -CF2-; -CHF-; etc all show difference in binding energy. Measurement of diffusion of one polymer into another can be found using thin film. In case of strong specific interactions, the shift in binding energy can be observed, In case of immiscible blend, the low surface energy component and can be a check to study miscibility by this technique.

IR-Spectroscopy: Most important spectroscopic method for determining specific structural groups in polymeric materials. If the blend has some interactions/reactions; there will be appearance/disappearance/shift of some peaks in spectrum of blend accordingly.

Transition between vibrational or rotational states of a molecule can be detected by IRS. H-bonding can be detected by observing the shift in frequency of absorption peak for the H-bonded unit. Specific group capable of H-bonding includes OH stretching transition around $3600cm^{-1}$; C=O absorbance around $1730cm^{-1}$; amide group exhibiting N-H & C=O stretching at $3300cm^{-1}$ & $1640cm^{-1}$ respectively. E.g. PC/PBT blend analysis showed ester exchange reaction.

UV-Visible spectroscopy: In the UV-visible frequency range [180-380-780nm], valance electrons can be excited & observed. For blends that exhibit electrons transfer complexion involving electron acceptor & electron donor polymer blends; e.g. Polymer with ester & polymer with amine group, when blended. These techniques measures optical properties of blends over the full range.

With the interactions of various polymers, there exists change in energy levels or transition bands or energy gap etc, that reflects in spectrum. e.g……. π-π* UV band of phenyl groups can be perturbed by electron donating or withdraw ability of substituent group & data shows changes in conjugation or conformation of phenyl group. UV-visible spectrum is important for evaluation of electroluminescent/photo luminescent polymer blend (the one used in LED) to determine overlap of respective adsorption spectrum & to design material with specific emission as required for electroluminescent condition.

[Information: though, Tg is the most commonly used property to check miscibility, the Tg is not a thermodynamic property!]

Unit-4

COMPATIBILIZATION

Compatibilization Methods: Many polymer mixtures are not only immiscible but also mechanically incompatible. In order to achieve desired property balance, compatibilization is employed in many commercial polymer blends. Generally, the compatibilization methods involve an interfacial agent that lowers the interfacial tension between the components leading to a more uniform blend with smaller particle dimension, as shown below:
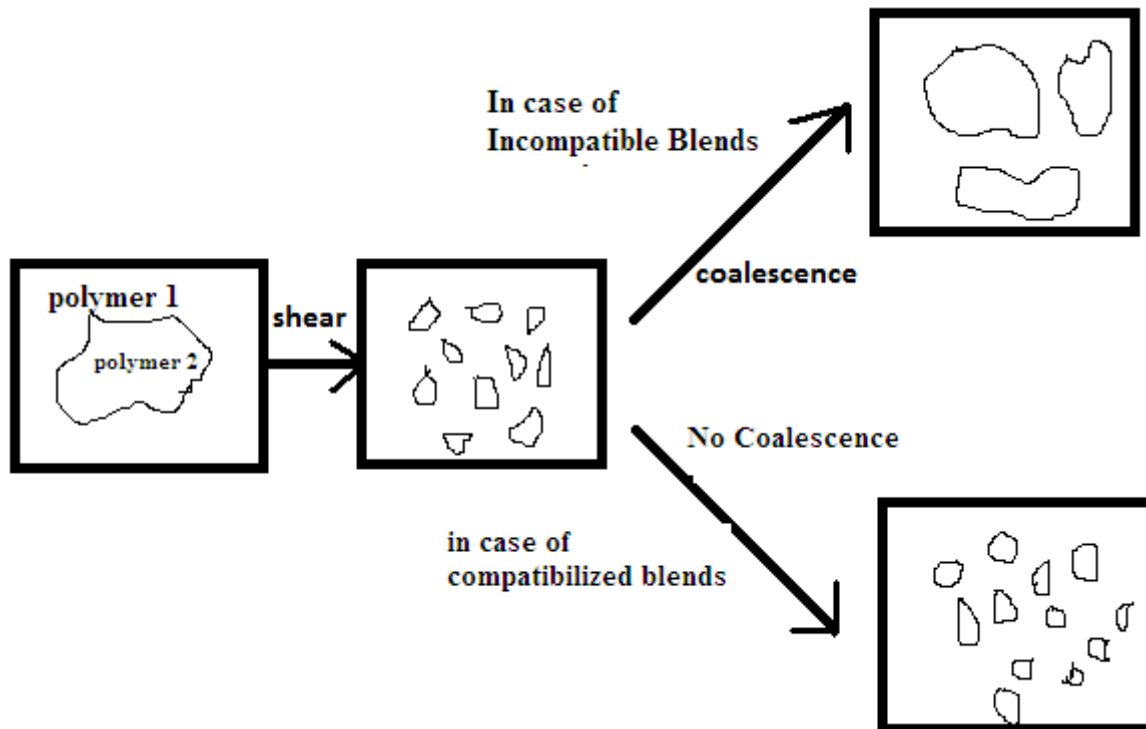
The interfacial agent allows for improved mechanical compatibility by achieving improved interfacial adhesion between phases. The agent can be considered as "polymeric surfactants" that concentrates at the interface & stabilizes the morphology, by preventing the coalescence which is one of the major problems in achieving small particle size dispersions got by shearing the incompatible blends.

Compatibilization Approaches include:

1. Introduction of specific interacting groups.
2. Insitu polymersiation grafting.
3. Addition of non-reactive ternary homo-polymer that adheres to both phases and concentrates at interface.

4. Adding non-reactive ternary block co-polymer comprised of units as that blend polymers or blocks that adhere to both phase.

5. IPNS of X-linked systems.

6. Reactive compatibilization (effective, widely used both for commercial and research purposes).

Some Specific examples-

1. **Introduction of specific interaction groups:** Rather than increasing the micibility to greater extent, this technique improves dispersion and mechanical properties. Example to this approach could be to attach small amount of proton acceptor to one component and a proton donor to another component of the blend. Examples-

    a) Less than 0.5 wt% of acidic or basic monomers grafted to PE/PP to yield improved mechanical compatibility.

    b) PS-co-4-Vinyl benzoic acid and poly butyl methacrylate-co-4-vinyl pyridine.

    c) PVOH/PE is immiscible, by introducing vinyl amine and acrylic acid respectively, properties were improved with transparency.

    d) Sulphonation of PEEK yielded miscibility with PA6 due to H-Bonding.

    e) PS with para substituted hexa fluoro iso propanol (expanded PS), its miscibility range include series of polymers: Poly Acrylates , PMA , PEO, PC, PVAc, PVMK, etc
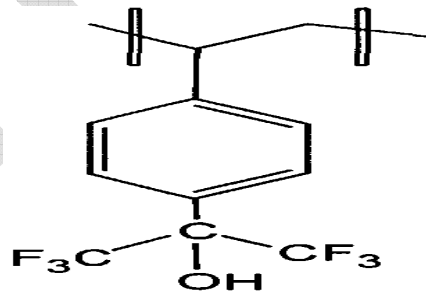
[Note: the required property improvement, Tg values, FTIR peak shift, etc were evidence for compatibilization]

2. **Addition of non-reactive ternary homo polymer:** The poly hydroxy ether of BPA (phenoxy or PHE) has been noted in various studies which have provided improved interfacial adhesion between immiscible or marginally compatible blends. E.g.-

a) The above polymer with PSF/ABS improved dispersion, increased impact strength and uniformity of injection molded surface.

b) and with PBT/PC showed 2 T_g but improved transparency

c) PCL with SAN/PC

d) PC with PPO/PBT

e) Chlorinated PE with PVC/LLDPE

f) CPE with SAN/EPDM

3. **Addition of non-reactive ternary co-polymer:** Non-reactive ternary systems include random, graft or block copolymers offering miscibility or good interfacial adhesion in blends.

a) Poly (styrene- hydrogenated diene - styrene) block copolymer with PS/Polyolefin blends. [Not only block but also sometimes random copolymer addition to binary blends involving copolymer with structural units equal to or similar to the blend components, or with specific interactive groups capable of non-reactive interaction with one or both of the blend components comprise another ternary polymer addition approach.]

b) EPR with HDPE/PP gave synergistic impact strength.

c) Graft copolymer addition with the graft copolymer comprised of a main chain of one component and the graft of other component of blend provided an effective ternary addition method. NR grafted with Styrene compatibilised the NR/PS blend showing decreased domain size and increased melt viscosity.

d) EVA grafted MMA with PVC/EVA

e) Block copolymer will concentrate at the interface and allow for improved adhesion between phases as shown below:
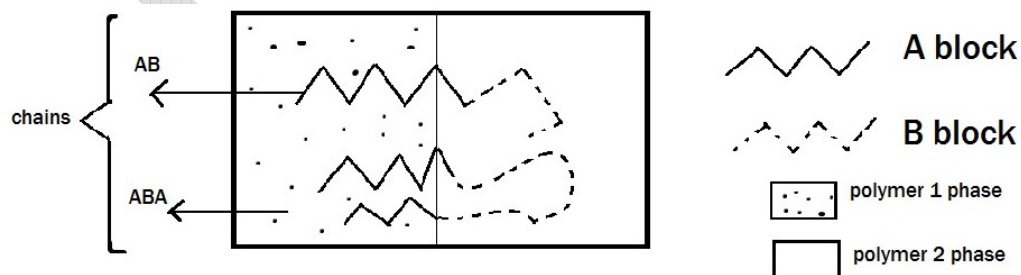

Figure: Concept of compatibilisation using AB or ABA block copolymer

SEBS (styrene ethylene butylene styrene) block copolymer with the atactic polybutylene/PE blend (i.e. at.PB/PE) or with at. PB/PP blend shows great increase in mechanical properties like impact strength and elongation at break. (SEBS with syn. PS/HDPE blend showed no improvement because crystallization of syn. PS at interface segregates SEBS out of blend domain.) SBS, SIS, SBR (random) were all good compatibilizers with PP/PS but properties vary with each type.

1. **In-situ Polymerization:** involves covalent bonding between the constituents resulting in graft or block copolymerization allowing for interfacial stabilization. Impact PS is a specific commercial example where this concept has been very important

   a) Polymerization of styrene in presence of butadiene rubber allows for graft copolymerization formation along with rubber x-linking. The resultant phase separated rubber particles yield toughening of the brittle PS matrix.

   b) Emulsion particle of BR are used in emulsion polymerization of SAN copolymerization to get ABS.

   A compatibilisation technique specifically suitable for emulsion polymerization involves the in-situ polymerization of polymer in the presence of previously polymerized polymer. As applied to the emulsion polymerization, this is typically referred to as core-shell polymerization. The procedure involves the initial polymerization of seed particles; the addition of other monomers can result two distinct results:

   i.   One result involves swelling of monomer in the particles followed by phase separation once a critical molecular weight is achieved due to immiscibility of polymers.

   ii. The other result would involve the formation of 2nd polymer as a shell around the seed core particles.

The 2nd process would be expected if the initial polymerization occurs in the aqueous phase, followed by adsorption on the core particle surface once the oligomeric molecular weight reaches limiting water phase solubility or limiting water phase water phase stability values. In practice, both process can occur and often do so simultaneously, yielding a resultant morphology ranging from true core shell to particles with both phases equally distributed in a inter-penetrating morphology. If x-linking is provided for both polymers, then this procedure would be a sub set of IPNs. Variations in morphology are illustrated below:

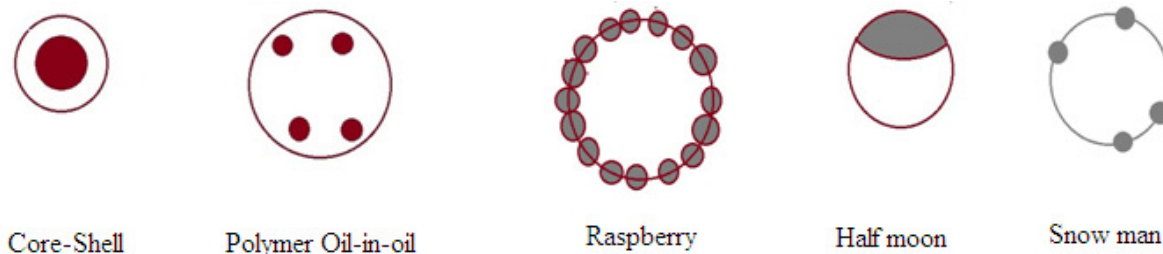Core-Shell   Polymer Oil-in-oil   Raspberry   Half moon   Snow man

Fig. core shell polymerization morphologies

Variation is due to change in- component type, composition ratio, core particle size, particle surface polarity, mode of monomer addition, staged ratio, saturation of polymer formed, chemistry of polymerization and cross linking of both polymers, inter facial energy, etc;

5. **Reactive compatibilization:** This approach is used in case of highly immiscible blends to get a good mechanical compatibility. It involves introduction of a reactive site onto a polymer chain identical or similar to one blend component capable of reacting with the other polymeric component. The resultant graft co-polymer will as usual concentrate at the interface and reduce to interfacial tension, yielding improved dispersion, domain size reduction and improved mechanical properties over the binary blend. A variation of this method can involve addition of polymer miscible with first component capable of reacting with the other component to form a graft co-polymer.

a) PS-co-(minor amount of) MA blended with PPO/PA6 and resultant PS-g-PA6 copolymer will be at interface as PS prefers PPO.

b) PA6/VLDPE-g-MA showed elongation at break more than 120% of the previous binary blend.

Following table gives examples of groups used and reactive sites for achieving reactive compatibilization of blends- (remarks: all of the below systems form graft copolymers)

Group	Method of usage	Sites and Polymer e.g.
MA	Grafted onto poly olefins or monomer with styrene copolymer or ter polymer.	* amine of PA *hydroxyl of polyester

Acrylic acid	Graft or copolymer	*amine of PA *hydroxyl of polyester
Oxazoline	Functionalization with polymer	*amine of PA *acids of polyester
NCO	Graft or copolymer	*amine of PA *hydroxyl of polyester *acid of polyester
Epoxy	Incorporation via glycidyl methacrylate containing copolymer or as grafted side group.	*amine of PA *hydroxyl of polyester *acid of polyester

Note: each of these systems can be grafted to poly olefins or unsaturated polymer by free-radical grafting techniques employing a peroxides.

Descriptions of chemical reactions are as follows:
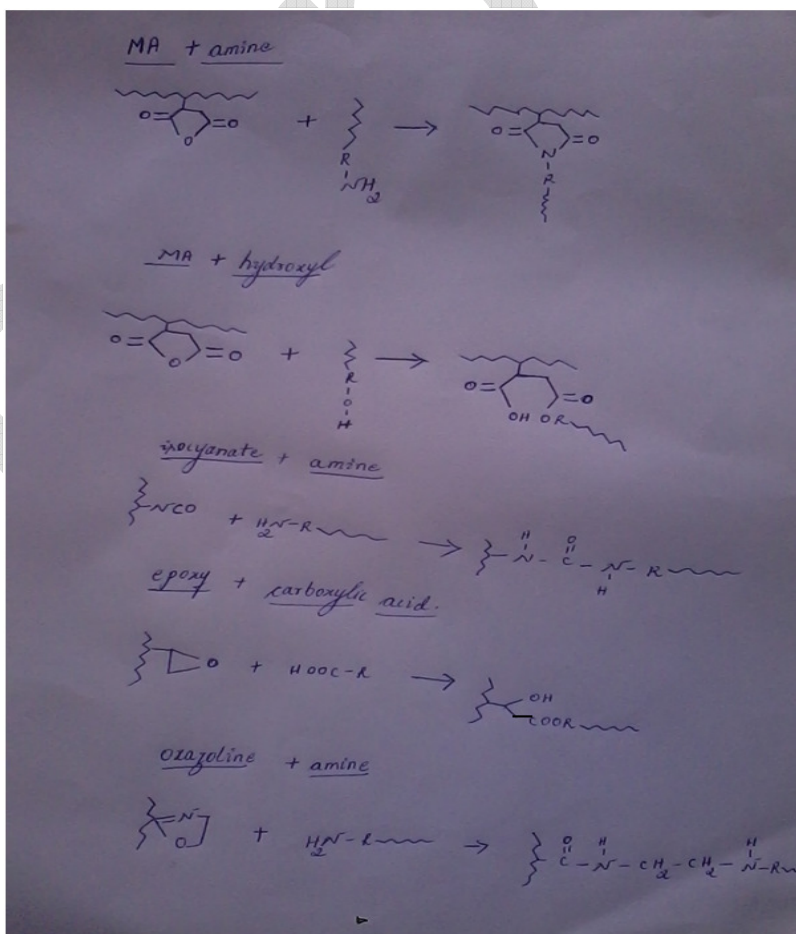
A specific subset of this method involves reactive extrusion (discussed under blending equipments)

6. **Inter-Penetrating Polymeric Networks (IPN):** this method involves compatibilizing the diverse polymers by sequential or simultaneous polymerization of polymer networks. The interlocking rings of polymers, which are referred to as catenane structure, would make the two polymers stay together (i.e. compatible). The system consist single phase behavior of monomer–monomer or monomer–polymer mixtures with appropriate x-linking additives being used. Upon polymerization of monomer/s, the incompatibility leads to phase separation but the network prevents complete localization. It's not essential that the two polymers should have covalent bond between each other but essentially the chain should get interlocked leading to mechanical adhesion as shown below:

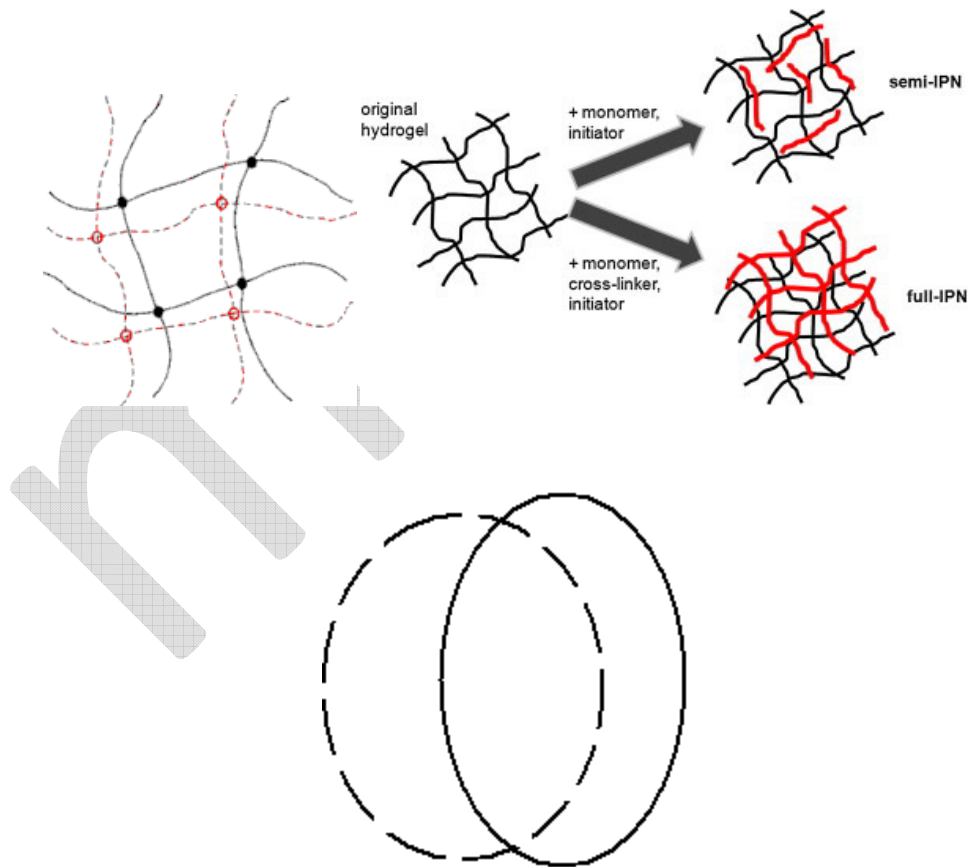Fig. interpenetrating network of flexible and rigid polymers

Fig. Catenane structure: interlocking polymeric rings

Methods of producing such IPNs include:

I.   Sequential IPN- e.g. PDMS/PMAA

II.   Simultaneous IPN- e.g. PU/PMMA

III.   Semi IPN- e.g. PU/PDMS

Note: the TP IPNs comprised of interpenetrating phases such as- block copolymers, ionomers, crystalline polymers etc. are formed by physical x-linking (specific interactions) and not by covalent bonding or chemical x-linking and hence sometimes may not be discussed here instead under other types or under specific interactions or under cross-linking phases.

7. **Other types:**

I.   X-linking between phases: It is used mostly with phase separated elastomeric systems (for tyre related applications) using sulphur or peroxide X-linking which leads to covalent bridging between two phases and thus assuring proper translation of stresses from one component to other. E.g. Co-X-linked compatabilized elastomeric blends i.e, co-vulcanized blends of EPDM/NR.

II.   Polymer-Polymer reaction: the interchange reactions between different polymer can lead to compatibilization with or without catalyst and often to miscibility between polymers that are typically phase separated. E.g.-

   a) Ester interchange between polyester like PC/PET, PET/PBT, polyarylate/PC, PC/PTT etc.

   b) Trans esterification between PHE/PBT, EVOH/PLA.

   c) Trans amidation between polyamide like PA4,6 / PA.

   d) Ester-amide interchange reaction between polyester and polyamide like PET/PA66.

   e) Acid-amide interchange reaction between SAA/PA6 (SAA=styrene acrylic acid).

III. Additional method of compatilization:

   a. Solid state shear pulverization– involves application of high shear or extrusion below the Tm or Tg to yield a fine powder. Chain scission resulting in free radicals at the chain ends allows for potential of block co-polymer formation at the inter-phase when a polymer blend is employed. E.g. PP/PS; PS/PMMA.

   b. Use of coupling agents– zirconate and titanates with PC/PET and recycled polyolefins/LCP. Silane coupling agent with PP/PET.

   c. Inorganic fibres and fillers: nano fillers, functionalized clay particles, etc have compatibilized many blends. E.g. PC/PMMA, PA6/ABS, PMMA/PVAc, etc.

Toughened Polymers (via blending)

Toughened thermoset:

Background: Most of the thermosetting resins develope dover the last decade are largely used as matrices in fiber-reinforced composite for aerospace industries. As aircrafts are pushing towards greater speed, composites with high strength to weight ratio would be preferred. Also these resins are capable of withstanding elevated temperature applications via increased rigidity & increased x-linking to form networks. However, in almost every case the same network which provides the high temperature property & strength would also inhibit molecular flow. Thus, making the material possess low toughness.

Following fig. shows example of some TS resins relating their Tg with toughness.
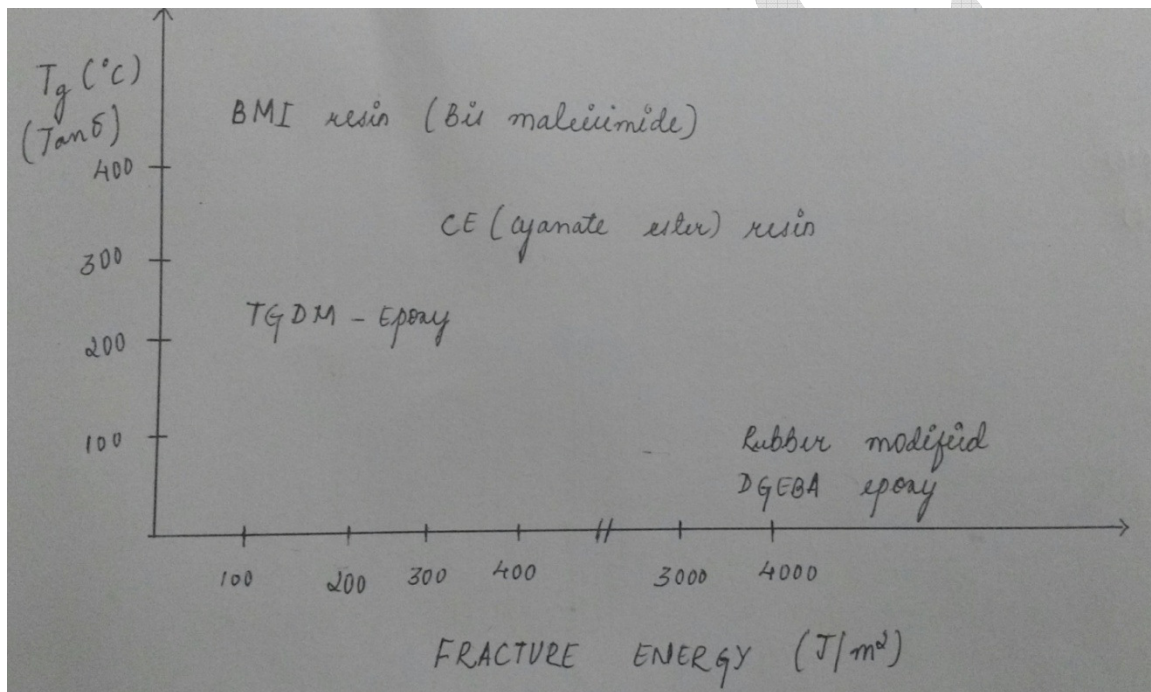
Despite their brittleness, TS resins are important for use in fiber composites because with the current system of its manufacturing, the equipments suit TS resins for processing and fabrication which does not suit TP; and also toughening the existing thermosets would be more attractive and economical than developing a new system.

The fracture toughness of TS resins of 50 to 300 J/m² is marginally higher than inorganic glass. However, by incorporating toughener into resins such as epoxy the toughness level can be brought into the line with some TPs.

Though, most of the work w.r.t. toughening a TS resins involve incorporation of soft elastomeric substances into resin matrix; but as the high temperature requirement becomes more critical, incorporation engg. TPs as toughening agents has become more popular.

CE and BMI resins have similar processing characteristics like epoxy but posses better mechanical properties with max. service temperature between 150˚-250˚C (i,e between the epoxy and poly imide respectively).

The compatibility requirement of blending the elastomer with TS resins is different from TP blending. The elastomers are usually low mol.wt. liquids and are capable enough to dissole & disperse in the resin monomer or lacquer on storage, but phase separate out during curing of the resins. Whereas, in blend of TP with TS, the significance of entropy factor is greatly diminished; consequently the miscibility influenced by the difference in value of solubility parameter.

Most of the TPs used are usually high temperature enng. TPs like PES, PI , PAS; which are either incorporated by hot melt blending or by solution blending. A small degree of chemical reaction between the TS resin and modifier (I,e with end group of engg. TP) is often desirable for effective toughening, sustaining the side effect of solvent on overall properties.

[Note: For fiber composite applications, the particle size of finely dispersed modifier must be below 8micron, which is equivalent to average fiber spacing.]

Toughening of TS resins with soft inclusions:

It is mainly for low temperature applications that elastomeric particles are used for toughening TS. One of the majorly used toughener is CTBN rubber <Carboxy terminated butadiene acrylonitrile >.

Ex 2: usage of phase separated acrylic elastomers suspended in uncured epoxy via mechanism of stearic stabilisation showed a much higher toughness (peel strength).

Ex 3: PMMA-g-NR copolymer usage showed increase in fracture toughness of both low and high cross-linked density epoxies.

Ex 4: Copolymerisation & chain extension reaction also gave tougher networks < in most cases reduction in Tg was observed >.

Ex 5: Developing SIPNs (i.e. Semi IPNs) using TPs resulted in phase separation yielding good toughness & processability along with other physico mechanical properties.

Toughened TP's: Commodity plastics such as PE, PP, PS, PVC, etc. Make up a large portion of total tonnage plastics being used mainly for non load bearing applications i.e., many of consumer

products. However efforts are made to improve their toughness, wide range of temperature applications, stiffness with retaining its lightness via blending instead of developing new polymers or using various ingredients in compounding.

The efforts are in developing heterogeneous polymer i.e., 2 phase systems which are referred as toughened TPs. Literature reveals usage of engineering plastics like PPE, PPS, PC, PEK, PEEK, LCP & their copolymers; & rubbers like EPDM, BR, NR, & their copolymers in majority, for increasing the toughness of commodity plastics.

Majority of such toughened TPs forms immiscible blends with increase in impact properties but there exist a need of compatibility at interface via copolymer technique or reactive melt processing- REX & RIM.

1. MMA-g-rubber with PMMA, PS, HIPS, ABS, etc.
2. EPDM with PP/HDPE
3. PS-Co-MA with PA6/SAN
4. PC/PS, PEEK/PS, PC/PMMA, etc
5. PP/NR with slight cross linking.

Note: Usage of thermotropic LCP's with many engineering plastics not only enhanced toughness but also ease of processing & also stiffness in flexible polymers because of their unique melt viscosity of blends that lubricates polymer melt and lowers viscosity of blends.

Ex: LCP/PC, LCP/PA6

Mechanism of toughening:

Most of TS's & few of TP's fail in brittle manner under tensile loading but some polymers will exhibit ductile behaviour under compression (even some of the highly cross linked epoxy system). The inherent ductility of a polymer matrix depends on its ability to undergo plastic deformation during stress (of course influenced by test conditions & geometry).

Incorporation of toughness can increase the fracture resistance of base polymers by:

I.   Enabling plastic deformation to occur in the matrix.
II. Increasing the plastic deformation which is occurring in the matrix.
III. Undergoing fracture themselves.

Depending on nature of base polymer & toughening polymer.

Toughening mechanism in TP's:

It is well established that rubber particles with low modulus act as stress concentrators in both TP & TS resins enhancing shear yielding and/or crazing, depending on the matrix nature.

Shear yielding in a polymer matrix involves macroscopic drawing of material without change in volume at 45° to tensile axis. Depending on polymer, the yielding may be localized into shear bands or diffused throughout the stress region. It is initiated by a region of high stress concentration due to flaws or polymeric inclusions such as rubber particles.

Crazing, on the other hand, is a more localized form of yielding and occurs in planes normal to tensile stress. These are wide at crack tip that are interconnected by highly drawn fibrils which also form the craze walls and contain approximately 50% of voids photo 200A°.
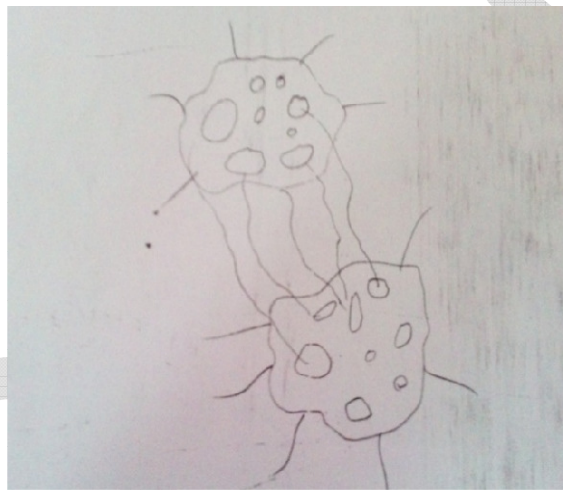
TEM micrograph showing crazes of tensile fractured specimen.

Nucleation happens at interface of high stress concentration caused by in-homogenity such as flaws and polymer inclusions. Theory of multiple crazing in rubber toughened TP systems: Crazes are initiated @ points of maximum principle strain which are usually near the equator of the rubber particles and then propagates outwards along the plane of maximum principle strain. It is terminated when stress concentration falls below the critical level for propagation, or when a large particle/ other obstacles is encountered. Thus the rubber particles are able to control craze growth by initiating and terminating crazes a shown in the figure.

Later it was proposed (by Bucknall and Smith) that shear yielding and massive crazing are the 2 energy absorbing mechanism in rubber modified plastics. According to that, areas of stress concentration produced by the rubber particles are initiation sites for shear band formation as

well as for crazes and that shear yielding is not simply an additional deformation mechanism, but an integral part of the toughening mechanism. Since the molecular orientation of shear band is normal to craze growth. Therefore as the number of shear bands increases, the length of newly formed crazes will be low and consequently a large number of short crazes are generated.

Note: The process of "voiding" as one of the toughening mechanism has been reported as successful approach from many researchers for different materials.

Toughing Mechanisms in TS Resins:

Due to range of x-link density and matrix ductility (with different TS_s) there is no one generalized mechanism that can be used to describe toughening of TS_s and hence it is a combination of number process as mentioned below:

1. Tearing and ductile drawing of dispersed phase- a crack in rubber toughened epoxy propagates through the brittle epoxy matrix and leaves the particles bridging the crack. This deformation is also applicable to TP toughened TS in which particles are well bonded to the matrices.

2. Crack tip blunting of resin matrices- the hydrostatic tension generated in well bond rubber particles due to curing & cooling, along with load on specimen, develops tri-axial stress @ crack tip leading to cavitations in particles or @ particle matrix interface. This increases the stress concentration of particles and also allows shear band to grow promoting yielding as a consequence of it. The whole process creates plastic yield zone containing distorted and voided particles that produce a crack tip blunting effect releasing the stress @tip and delaying crack propagation which eventually end up in voided plane.

3. Crack pinning mechanism of impenetrable and semi penetrable particles- usually in the filled systems.

[Note: particle size and processing also influence toughness]

Unit-5

Interpenetrating Polymeric Networks (IPNs)

These are unique type of polymer blends, usually synthesized by swelling a cross-linked polymer with a second monomer together with cross-linking and activating agents and polymerizing the monomer in-situ. The term was so adopted because both networks were being interpenetrating and continuous throughout the entire macroscopic sample (analog to worms eating out independent tunnels in an apple). Even though in some cases the two components are incompatible, they remain intimately held, and shows phase domain sizes in the order of hundreds of angstrom.

If one polymer is elastomeric and other plastic, at temperature under consideration, then the combination tends to behave either as reinforced rubber or as impact resistant plastic.

Types include:

    a. Sequential IPN.

    b. Simultaneous IPN (SINs).

    c. Semi IPN

    d. (TP) Elastomeric networks (IENs).

    e. Latex IPN.

    f. AB cross-linked copolymer.

Brief description of all 6 types:

    a. Sequential IPNs involve synthesis of a polymer network followed by addition of monomer+ X-linker which dissolves and swells the 1st polymer network. Then the 2nd monomer polymerizes and phase separates but the chains get interlocked due to X-linking.

    b. In SINs, both the networks are formed simultaneously, like- addition polymerization of one component along with condensation polymerization of other component i.e. it needs independent, non- interfering polymerization reactions that can be run at same time under same overall conditions. It involves monomers or reactive systems.

    c. Semi IPNs involves one X-linked polymer and another non X-linked polymer. Two variations of this class involve;

        ➢ Addition of monomer/s to X-linked network followed by polymerization.

> ➤ Addition of monomer/s and X-linking moieties to a non X-linked polymer.

d. IENs are prepared by mixing and coagulating two different kinds of polymeric emulsions followed by single X-linking reactions (using single X-linking agent) resulting in 3D mosaic structure.

e. Latex IPN is prepared through emulsion polymerization by taking a cross-linker and activator and polymerizing monomer on the original particles.

f. AB cross-linked copolymer: In this special kind of graft copolymer, both ends of polymer-2 are grafted to different polymer-1 molecules, causing one cross-linked grafted network to arise.

Detailed discussion of the 6 types mentioned above consists- synthesis, morphology, properties & behavior:

Sequential IPNs: The synthesis of IPN requires a cross-linked polymer-1 which may be rubber or plastic. This network-1 may be synthesized and cross-linked at same time by using chemicals like- ethyl acrylate (EA) and tetra ethylene glycol di-methacrylate (TEGDM), using UV-photo polymerization and benzoin activator. (When plastic is used, the term inverse IPNs is employed is some cases because initially rubbers were used.)

Alternatively, the linear polymer may be prepared first and cross-linked by subsequent reaction like subjecting BR films containing di-cumyl peroxide to heat and pressure.

The second network was synthesized in all cases by swelling in a controlled amount of monomer, allowing ample time for diffusion so that swelling was uniform, followed by photo-polymerization or thermally initiating peroxide species. Example: styrene +0.5%TEGDM +0.3%benzoin swelled into PEA to equivalent weight resulting in 50/50 PEA/ PS (being opaque, white and leathery).

Although both networks may be visualized as continuous, their milky appearance hints at a more complex morphology. In-order to characterize the morphology, the elastomeric portion of the IPNs was stained selectively using osmium tetroxide. IPNs exhibit a characteristic cellular structure, where the first component makes up the cell wall and the second forms cell content. E.g. cis-PB/PS and PEAB/PS. Though the cellular structure have already been observed with graft polymerization, here in IPNs the cellular structure pervades entire macroscopic sample rather than just discrete regions.

Since the chains are cross-linked to each other, the opportunity exists to form a continuous network throughout the cell walls, which connects the cell contents. The props structure of the fine dispersed phase within the cell wall is as shown schematically below:
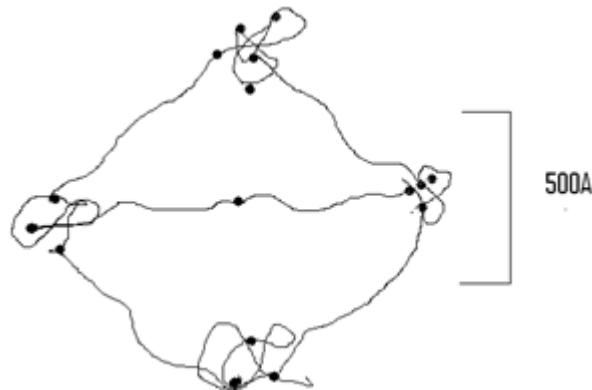
Fine structure within domains for an IPN

The solid black circles represent cross-links. Distance between phase domains is less than half the chain contour length between cross-links in the network, thus permitting phase separation to occur; at the same time some network segments provide the requisite inter connection between phase domains.

Simple homo polymers and random co-polymers exhibit single sharp glass transitions, but polymer blends and in particular IPNs show two such transitions for each phase. The intensity is related to composition and phase continuity, while shifts and broadening of transition indicate extent of molecular mixing [in contrast, EM (electron microscopy) shows phase size and shape in major, and gives only slight indication of extent of true molecular mixing].

Dynamic mechanical spectroscopy (DMS) techniques yields loss modulus compared to static mechanical tests which just gives storage modulus. DMS and EM techniques provide complementary info on two phase materials: the former is a sensitive indicator of the extent of molecular mixing, while the latter shows the size and shapes of phase domain.

The ultimate utility of any material lies in its performance. The reinforcement obtained by IPNs exhibit its good ultimate mechanical behavior. Example: The ultimate elongation and stress at break in case of random (cis-trans mixture) PBD homo-polymer is increased by three to five times with addition of PS network.

IEN: It is a special term used to designate the formation of IPN from 2 distinguishable lattices subsequently mixed, coagulated and X- linked. Except for X-linking reactions, the IENs are topologically very similar to the mixed lattices.

Lattices of urethane-urea (U) and poly-acrylate (A) over the composition range 10/90 to 90/10 by weight were initially studied extensively. The lattices of the A component were X-linked together by reacting with double bonds using Sulfur; The U polymer being self cross-linking with temperature because of free hydroxy groups; the IEN case was achieved.

As polymers were synthesized separately, the inter-molecular grafting may be entirely absent in many cases, and as a result of X-linking reactions, each phase consist of only a single molecule of infinite molecular weight.

Morphological studies says that only very limited true molecular interpenetration takes place with IENs and that too limited to the phase boundaries; Therefore the main interpretation is of the phases rather than the molecules and shows 2 transitions when characterized.

Semi IPN: Materials having one linear and one X-linked polymer. Specifically it is a graft co polymer in which one of the polymers is X-linked and other essentially is linear. The 2 semi IPNs being inverse of each other may be distinguished as:

   a) A semi IPN of first kind, with polymer-1 in network form and polymer-2 linear.

   b) A semi IPN of second kind, with polymer-1 linear and polymer-2 X-linked.

The mechanical property of first kind is better than second kind. Further, increasing the X-link density of polymer-1 produces finer phase domains. It is also possible to obtain domains that are too small to impart maximum toughness.

If both the phases are X-linked, then there will be 2 Continuous phases with better properties than the 2 types discussed before.

AB X-linked co-polymer: Also called as joined IPN, got by grafting different polymer-1 at the ends of polymer-2 leading to one X-linked grafted network. Thus ideally, one molecule is generated for AB X-linked copolymer compared to the 2 molecules that are ideally generated for the IPNs and IENs. Note that polymer-1 is grafted primarily to polymer-2 and it is not cross-linked to itself.

e.g.1: Castable polyester resin synthesized by polymerizing styrene monomer in an unsaturated polyester solution are AB crosslinked copolymer characterized by short chains of length upto 10mers between grafts. E.g.2: Epoxy resin cured by reaction with a polyamide.

A new technique for making AB cross linked copolymer involves crosslinking of suitable polymer-1 with chains vinyl polymer-2 by reaction of halogen containing groups in

polymer-1 with an organo metallic derivative (e.g. $MO(CO)_6$) in the presence of monomer-2. The reaction scheme is as shown below:
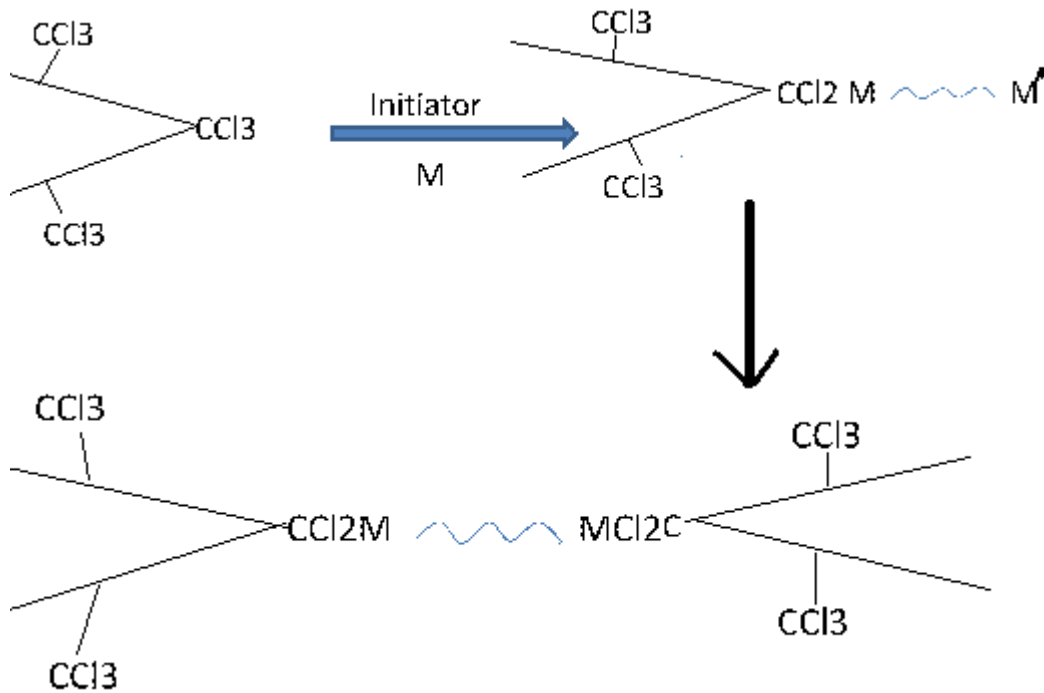
The crosslinked networks so produced shows 2 Tg when analyzed by dilatometric technique indicating phase separation.

SINs: the art of simultaneously synthesizing 2 polymers has already received attention and also shows excellent mechanical properties. A simple example includes an epoxy resin (step growth mechanism) with an ethyl acrylate formulation (free radical chain addition). When a tertiary amine was used to cure the epoxy, minimal interference occurred between the 2 reactions.

If the above reaction was photo chemically initiated and the condensation reaction was thermally controlled , the 2 reaction rates could be adjusted at will over a wide range. Starting with a mixture of the 2 monomers, application of both heat and light resulted in both networks forming together.

The SINs reacted together, had a controlled degree of phase separation as indicated by intermediate turbidity levels and were apparently superior in tensile strength to those reacted sequentially (i.e. 2050 lb/inch^2 v/s 940 lb/in^2).

Latex IPNs: Both the networks formed will be on each particle of emulsion system forming an array of micro IPNs. Due to the thermosetting nature of sequential (bulk) IPNs, they have one important drawback i.e, lack of processibility. Whereas, IPNs prepared by means of emulsion polymerization techniques may offer considerable processing advantages because the thermosetting characteristics are limited to individual microscopic particles {therefore I/M, film formation by casting/ painting, etc could be used}.

Only few latex IPNs have been developed successfully. Latex IPNs of methacrylics & acrylics display high values of tanδ over a broad temperature range.

Latex IPNs include many variables like: overall composition, x-link density, order/preparation, size of final latex particle, etc. Latex semi IPNs of both kinds have been developed & investigated. Recall the core-shell morphology discussed before.

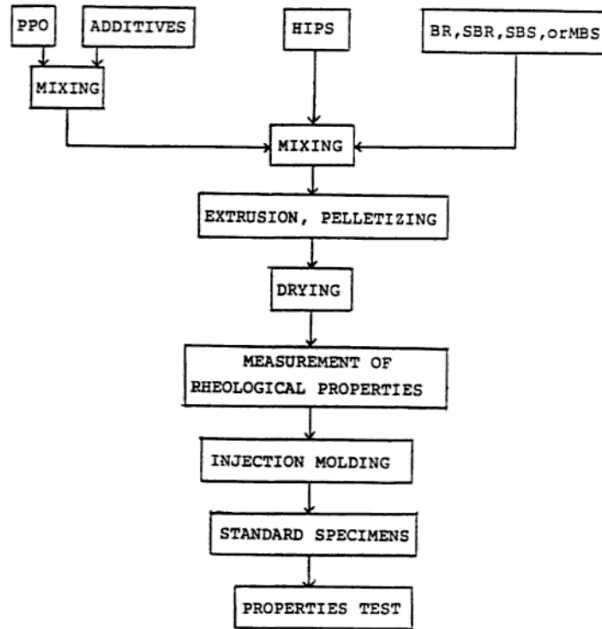## Blends case studies:

1. PPO/HIPS:

Blend system of Poly (2, 6-Dimethyl-1, 4-Phenelyne oxide) and High Impact Polystyrene. The engineering Plastic PPO's properties was extended along with cost reduction & ease of processing by using the commodity PS, however it lacked toughness in some cases. Hence, the HIPS was opted to offer excellent toughness. Blend system is compatible across the entire range of compositions and temperatures; characterized by single Tg. The combination maintained high tensile modulus and good impact resistance over a wide temperature range. It has good electrical properties but not flame retardant (can be improved by compounding). Typical compositions of PPO/HIPS blends are 40-85% w/w for achieving a complex balance of properties. Commercial applications that were widely seen are heat resistant electrical connectors, exterior automobile parts, etc. The best method for productions of PPO/HIPS parts was either by vacuum thermoforming or injection moulding.

[Rubber types used in one of the component HIPS include high cis and low cis polybutadiene, EPDM rubber and SBS block copolymers. Optimum impact properties occurred at with an average rubber particle size of approximate 2µm or less. A Core-shell morphology and the addition of very small rubber particles (0.3µm) improve the properties.]

Usually melt blended, as developed by GE! Even till the present day, these blends are prepared continuously using twin screw extruders. The flow chart shown in figure below signifies the

preparation of PPO/HIPS/MBS blend system for improved mechanical properties [the use of ternary component, i.e. MBS enhances properties].

```
┌─────┐ ┌──────────┐      ┌──────┐        ┌───────────────┐
│ PPO │ │ ADDITIVES│      │ HIPS │        │BR,SBR,SBS,orMBS│
└──┬──┘ └────┬─────┘      └──┬───┘        └───────┬───────┘
   │         │               │                    │
   └────┬────┘               │                    │
     ┌──▼─────┐              │                    │
     │ MIXING │              │                    │
     └──┬─────┘              │                    │
        │              ┌─────▼──────┐             │
        └─────────────►│   MIXING   │◄────────────┘
                       └─────┬──────┘
                   ┌─────────▼──────────┐
                   │EXTRUSION, PELLETIZING│
                   └─────────┬──────────┘
                        ┌────▼────┐
                        │ DRYING  │
                        └────┬────┘
                   ┌─────────▼──────────┐
                   │   MEASUREMENT OF    │
                   │RHEOLOGICAL PROPERTIES│
                   └─────────┬──────────┘
                   ┌─────────▼──────────┐
                   │  INJECTION MOLDING  │
                   └─────────┬──────────┘
                   ┌─────────▼──────────┐
                   │ STANDARD SPECIMENS  │
                   └─────────┬──────────┘
                        ┌────▼─────────┐
                        │PROPERTIES TEST│
                        └──────────────┘
```

The twin screw extruders used had respective zone temperatures from 1-3 as, 265°C, 270°C, 280°C and 275°C at the die. The injection moulding machine used the following temperature profile: 110°C at the hopper, 255°C at all zones of the barrel and 90°C at the mould.

Some commercial grades:

Noryl	Gen. grade	GE Plastics
Luranyl	IM grade	BASF

Applications:

Computer housings, TV components, Keyboard frames, Electrical component frames and chassis, Headlight housing, Pump housings and impellers, Valves and pipes.

2. PC/ABS:

Blend of Bisphenol-A Polycarbonate & Acrylonitrile-Butadiene-Styrene terpolymer. PC is characterized for its high modulus, high toughness, high impact strength and difficult processability, due to its high melt viscosity. (ABS) is a rubber toughened thermoplastic, characterized by its notch insensitivity and low cost. On the other hand, the limitations of ABS are: poor flame and chemical resistance, and low thermal stability. So, in order to compensate the limitations of each polymer i.e. PC and ABS and according to the need of properties, PC/ABS blends are made.

The production of the PC/ABS blends started on 1977. The addition of ABS to PC minimizes its drawbacks without affecting its superior mechanical properties, and also generates other useful characteristics, such as glossiness and low temperature toughness.

Both polymers are dried in vacuum for 24 h before processing. Dry PC/ABS mixtures with 10-90/90-10 weight compositions are prepared in a two roller mixer & pelletized. 80:20 is commercially available. PC and ABS are not completely miscible; many researchers use a variety of compatibilizers to improve the compatibility. Ordinarily, three types are considered to reduce the interfacial tension between PC and ABS resin, including block or graft copolymers, nonreactive polymers containing polar groups and reactive functional polymers. Many researchers have used: SBS, ABS-g-MA, methyl methacrylate-butadiene-styrene (MBS) and styrene-maleic anhydride (SMA.

Properties

- ABS gives the material excellent processing properties and PC gives it good mechanical properties, such as good ductility and high maximum use temperature.
- Both components of blend are amorphous.
- As with most amorphous polymers, the chemical resistance is not so good.
- Easily injection moldable, but also processable using extrusion, blow molding and thermoforming.
- PC/ABS blend offers good flow and excellent impact. Low temperature ductility.

Applications

- Automotive application: Instrument panels, grills, interior and exterior trim.
- Telecommunication: mobile phones.
- Medical: housing for (electronic) medical equipment.
- Electrical: Housing for electronic devices, electricity meter housing, switches, plugs and sockets. housings for microwave ovens and components for washing machines and dryer.
- Office equipment: housings for computers, monitors, copiers and printers.
- Middle console, lower instrument panel, pillars, knee bolster, overhead console, blow molded seatbacks in automotive applications.
- TV frames, laptop monitor enclosures, potable hand held devices, LCD panels, keypads, adapters and chargers, mobile phone bodies in electronics application.