Module 16: Thin Polymer Blend films – 2
Lecture 22: Thin Polymer Blend films – 2
22.1 Phase-Separation of Polymer Blend Thin Film:
The physics of Phase-separation in thin film (Thickness less than 100 nm or less than twice the radius of gyration of unperturbed chain) is different from bulk due to film-substrate and film-air Interfacial Interactions. Initiation of phase separation of the spin-cast blend thin film occurs due to solvent-evaporation. Another important aspect is preferential surface enrichment by one particular component of the binary blend is rapid increase in viscosity due to fast solvent evaporation. Factors affecting the phase-separated structure are concentration, polymer-substrate interaction, surface tension of polymers and interfacial tension of polymer-substrate, Flory-Huggins interaction parameter, molecular-weight of polymer, blend composition, rate of evaporation etc. Further, in an ultra thin film, a long chain polymer molecule is in a nonequilibrium state, as the conformational entropy of an individual chain is reduced in comparison to that in an three-dimensional unconfined bulk. Since, polymeric chains at the interface, in general, are thermally unstable due to vigorous thermal molecular motion and different surface free energy, the molecular aggregation structure in the two-dimensional ultrathin film of a binary polymeric is greatly different from that in a thick film. In the subsequent section, we present a brief discussion on the influence of each parameter on the phase segregation of a thin polymer blend.

22.1.1. Solvent Effect:
Typically, the two constituents are dissolved in a common solvent and spin or dip coated on a substrate. Solvent evaporation leads to increase in viscosity as well as decrease in diffusivity. As a result, demixing of the blend components out of the smooth surface occurs during spin-coating itself due to different relative solubility of one component (less soluble in the common solvent) than the other. The less soluble component depletes into solid earlier. However, the solvent effect is substrate-dependent, too. Phase Separation can be mostly explained by Hildebrand Solubility Parameter. For a common system like PS/PMMA blend, different indicatevive morphologies can be seen in the AFM images shown in figure 39.4. Table 39.1 gives a brief idea
of solubility of PS and PMMA in different solvents. The solubility of the polymer increases when its Solubility Parameter is closer to that of the solvent.

Table 22.1: Comparison of Hildebrand Solubility Parameters for Various Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Hildebrand Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(Styrene) [PS]</td>
<td>9.13</td>
</tr>
<tr>
<td>Polymethylemethacrylate [PMMA]</td>
<td>9.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.9 (PS more soluble)</td>
</tr>
<tr>
<td>MEK</td>
<td>19.0 (PMMA more soluble)</td>
</tr>
<tr>
<td>THF</td>
<td>9.3 (PS more soluble)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>9.3 (PS more soluble)</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>9.5 (PMMA more soluble)</td>
</tr>
</tbody>
</table>

From the values of Hildebrand Solubility Parameters, it can be concluded that Toluene and THF are better solvent for PS. PS collapses earlier into solidification, forming the surface-covering layer while PMMA forms islands-like structures in PS/PMMA blends into these two particular solvents. Sharp-edge of PMMA domain, as shown in Figure 39.4 can be observed. On the other hand, MEK shows just a reverse result as it is a better solvent for PMMA. A typical round shape of PMMA domain.

22.1.2. Concentration:

Concentration of polymer solution is the main parameter of varying thickness of the polymer film. Concentration of the blend solution strongly influences the thickness of the film. As we have already understood that a lower thickness will lead to higher number of surface molecules, the concentration vis – a – vis the film thickness significantly influence the blend film morphology. Study of solution-concentration has shown that a critically high concentration leads to a stable thick film, while a very low concentration eventually shows Dewetting on the thin film formed.
Fig.22.1: Typical indicative morphological variation of PS/PMMA blend thin films spin coated on a Silicon Substrate from Toluene. The blend compositions are (PS:PMMA) (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1, (g) 4:1. In all cases the concentration of the polymer was maintained at 2.0%.

22.1.3 Surface Tension:

An exposed surface having low surface energy is always thermodynamically favorable. Some blends are miscible in bulk, but phase separation is observed when its dimension becomes ~ 100 nm, when the thickness of the film becomes less than $2R_G$ of the unperturbed chain. Lower surface-free energy component of blend preferentially enriches the air-polymer interface in order to minimize the surface free-energy.

Another important aspect in this regard is the difference of surface energy between the chain-end ($Y_e$) and main-chain group ($Y_m$). If $Y_e < Y_m$, the chain-end groups are preferentially localized at the surface. Moreover, lower molecular weight increases the miscibility. The effect of surface tension of the groups present at the main-chain and the end-chain becomes significant as decrease of Molecular weight due to increase in no. density at the chain-end.

22.1.4 Interfacial Tension:

Though the major issue of preferential surface enrichment with one component of a blend can be highly explained by the surface tension and solubility parameters, the interfacial tension between the polymer and the substrate can never be ignored. If the one component shows a better affinity to the substrate and it would move towards the polymer-substrate interface. Spreading
coefficients of the components of a blend system with respect to the substrate has an important contribution in phase segregation. The other important aspect is variation of surface tension with temperature and molecular weight. Surface tension decreases linearly with temperature, but increases with Molecular weight. Equation (39.4) and (39.5) give the variation of surface tension of Polystyrene with temperature and molecular weight.

\[ \gamma = \gamma_{\infty} - \frac{K}{M_n} \]  

\[ \gamma = A - Bt \text{ (t in } ^\circ C) \]  

Where, K, A, B are the empirical constants and \( \gamma_{\infty} \) is the surface tension of infinite Number Average Molecular Weight.

In case of a PS – PMMA blend, no preferential wetting of one component over the other possible. Hence the only possible reason for preferential surface enrichment is the effect of substrate used. For a component having greater affinity to the substrate used to migrate towards the substrate and enriches the polymer-substrate interface. However, a lateral phase-segregation occurs for a blend thin film on a neutral substrate (like PS/PMMA on glass).

22.1.5 Influence of the Substrate

We have already discussed earlier that the preferential surface enrichment due to phase segregation must satisfy the essential criteria of minimization of the polymer-air interfacial area. Study of spreading coefficients and interfacial tension explain that the wetting behaviour of one component at the polymer-substrate interface depends on the substrate utilized. For hydrophilic surface (clean native Si oxide or mica) the more polar PMMA is strongly attracted to the substrate interface forming a wetting layer after annealing. PS droplet formation occurs on top of a PMMA substrate-wetting layer at the substrate-polymer interface. Concentration of PMMA at the air-polymer interface decreases with increasing substrate hydrophilicity. Thermodynamic equilibrium of this kind of morphology is attained on annealing at a particular condition. Substrate and solubility are related to each other to explain the preferential morphology. If the common solvent is a better solvent for the polymer that has the lower surface tension as the
topographical surface structure exhibits sharp, well-defined edges. In the opposite case, rather round surface structures are observed. With variation of substrate surfaces, a homogeneous layer of either polymer phase next to the substrate is formed.

22.1.6 Flory-Huggins Interaction Parameter:
Flory-Huggins Parameter is an important Segment-Segment Interaction Parameter useful for explaining the preferential surface enrichment due to phase separation of polymer blends. It’s expression is already given in equation 39.3. As already discussed, for $K$ positive and $\Sigma$ negative $f$ increases with decreasing temperature, generating an UCST, which is a limiting value of temperature, above which the system is completely miscible and no phase segregation possible at all. Phase-separation is not at all possible due to chain immobility at low temperature. Thus we can see that temperature dependent Flory-Huggins parameter plays a leading role in Phase Separation. For a Ternary system of polymer A, B and C, i.e., for three different polymer-polymer interfaces, if $f_{A-B}$ is much greater than $f_{A-C}$ and $f_{B-C}$, then the free energy can be minimized by wetting of A-B interface by C.

22.1.7 Composition of the Blend:
Variation of blend-compositions (x:y, say) create a drastic change in the whole surface morphology. Formation of columnar to island-like structures by one component over the substrate-covering layer of the other component can be done by varying compositional ratio. If the y component has such a surface tension as well as solubility parameter that surface enrichment is thermodynamically preferred by it, then surface enrichment by y will increase with increasing proportion of y in the blend. This can be clearly understood from figure 22.1.

22.1.8. Rate of Evaporation:
This is a critical parameter that significantly influences the morphology of the system. Immiscible polymer blends undergo phase separation even during preparation of film due to a very fast evaporation speed of the solvent. Phase Separation strongly depends on Evaporation Speed or Volatility of Solvent. More volatile solvent leads to a rapid evaporation. A faster
evaporation rate gives a greater viscosity, simultaneously lower diffusivity of the blend. If volatility is not compatible with polymer-chain mobility, phase-separated structure freezes before attainment of Thermodynamic Equilibrium. Phase Separated structure can be differed significantly by forcefully increasing/decreasing evaporation speed. Thus the evaporation speed may lead to the formation of a thermodynamically unstable but kinematically stable film.

22.2 Possibility of Ordered pattern formation with polymer blend thin films

In general, the typical final morphology of a phase-separated blend thin film is an isotropic disordered phase structure with a characteristic length scale. Though the pattern has a specific structure, which depends on all the previously discussed parameters, it is far from an ordered structure. A chemically patterned substrate can initiate and guide the phase separation in polymer blend film transferring the designed pattern on the substrate into the polymer film. Well arranged sea-islands, holes or porous structures may be obtained in a polymer film in one step by controlling the convection inside the film or exposing the film to a humid environment during the solidification process. The pattern structure and size can be tuned through several parameters. More complex patterns like multiscaled/ multi-component patterns, patterns with different geometries or stimuli-responsive patterns can be controlled by controlling the preparation conditions or exposing the sample to different environments.