What are the characteristics of the organic polymers at nanoscale?

The properties of a polymer in the bulk scale are determined by the mobility of molecular chains which are subject to entanglement and segmental motion. Glass transition temperature (Tg) is an index of this molecular chain dynamics. The deeper the molecules lie beneath the surface, the greater is the constraint on the chain mobility. For the molecules in the surface/interfacial layer, the degree of mobility is greatly influenced by the nature of interface and the consequent confinement.

- Free surfaces: These are the polymer surfaces open to air or other fluids. There is no confinement of chain dynamics on the open side. HenceTg of the surface layer in thick polymer film is significantly lower than the bulk Tg.

- Rigid interfaces: These are the interfaces where polymer surface is in contact with a rigid solid phase and there is no free or open surface. There is a confinement of the polymer chains in all directions. Hence, Tg of the layer near such an interface is higher than the bulk Tg.

This leads to the hypothesis that Tg of nanophase polymers will be substantially different than the bulk Tg depending upon the nature of confinement. If the nanophase surface is free or open, the Tg will be lower. On the contrary, if the nanophase is restricted by rigid interfaces the Tg will be higher. Indeed, this has been validated experimentally by the researchers for nanofilms by employing techniques like AFM and florescence dye labeling.

The difference in Tg between nanophase and bulk can range from 5 deg ~ 50 deg C for various polymers. It has also been found that the change in Tg, increases with the decrease in the nanofilm thickness (D). There exists a critical value, D0, where all the molecules lie on the surface/interface and the change in the Tg is the highest. (For open nanofims, the Tg is also significantly affected by the type and thickness of the underneath layers)

The chain mobility of the polymer nanostructures may be restricted in zero, one or two dimensions leading to formation of the nanoparticles, nanowires and nanofilms respectively. These nanostructures with free surfaces are sometimes called as ‘soft nano-materials’ due to their lower Tg. Rigid nanophases with the higher Tg are obtained in nano-composites.

Nanoscale polymeric matter with its property of altering the Tg has following interesting implications:

Nanophase with free surfaces:

- Nanosize polymer emulsions will exhibit lower Minimum Film Formation Temperature (MFFT) than their microscale counterparts.
- Multi-shell morphologies can help fabricate ‘High Tg–Low MFFT’ emulsion polymers.
- Nanopolymer fibers and films will show lower elastic modulus and high flexibility.

Nanophase with rigid interfaces:

- Coating films with high rigidity by creating nano confinement using nanofillers.

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