

## ABSTRACT

From the beginning, to tune the physical properties of polymer, blending of two or more polymers have been a common practice. It is well-known that the crystallization behaviour of a polymer blend is much more complex as compared with the constituting homopolymers due to influence of different factors like interaction in between the blend components, physical properties and crystallization kinetics of individual blend components etc. The complexity in the crystallization behavior reaches to a much higher level in case both the constituting polymers of the blends are miscible and crystallizable. In this case, the interplay between the crystallization of two components makes the analysis as well as understanding of the morphology and crystallization of the binary blend system very difficult. Here, the difference in the melting temperatures of the two crystallizable polymers plays a significant role in governing the final crystalline morphology of the blend system.

Moreover, recently, with the advent of nanotechnology, the importance of crystallization behavior in nanosized domains, formed in practical systems, have gained more attention. This is driven by the fact that any perturbation of crystallization behaviour in confinement may significantly alter the properties of the materials. Hence, an understanding of the polymer crystallization under nano-confinement is necessary for tailoring of the polymer properties when used in nanotechnology related applications. The electrospun fibres processed from polymer blends, where a crystalline polymer is present as a dispersed phase, depicts a nice example of such non-equilibrium systems where the radial dimensions of the fibres restrict the size of the dispersed phase domains. The confined crystallization behavior of polymers in electrospun nanofiber, hence, has received lot of interest in last few years. In the present study, the crystallization and morphological behavior of different crystalline/crystalline melt miscible polymer blends have been investigated in bulk state as well as under confinement in the electrospun fibres in order to gain vital fundamental understanding of crystallization in crystalline/crystalline (C/C) polymer mixtures.

For a more comprehensive understanding of the crystallization behaviour of C/C polymer blends under confinement, the present research focussed on investigating two classically different C/C blends in bulk as well as in confined state. The first blend system was composed of poly(ethylene oxide) (PEO) and poly(1,4-butylene adipate) (PBA) where the constituent polymers had almost similar melting temperatures. The crystallization behaviour as well as

blend morphology of PBA/PEO blend was thoroughly studied. The crystalline structure and morphology of the PEO/PBA blends were found to be governed by a strong competition between the faster crystallization kinetics of PEO and relatively much higher nucleation density of PBA. Furthermore, the crystallization behaviour of PBA/PEO blend confined by surrounded PS matrix, in electrospun fibres of polystyrene (PS)/PBA/PEO ternary blends, was investigated systematically. The results obtained in electrospun fibre system has been compared with their corresponding as-casted film as well as homopolymers under similar confined environment. A promotion of the heterogenous nucleation of both PEO and PBA was observe in the ternary blend fibres. Also, the chain orientation memory favoured the formation of  $\alpha$ -crystals of PBA in the PEO/PBA as well as PS/PEO/PBA blend fibres. The second C/C blend system studied consisted of PEO and poly (L-lactide) (PLLA) where the constituting polymers had a wide difference in their melting temperatures. Due to broad difference in melting temperature, on cooling from melt state, the PLLA/PEO blends underwent sequential crystallization. Hence, PLLA crystallized first and subsequently PEO crystallized within the existing template formed by PLLA crystals. Furthermore, under confinement, in electrospun fibres from the ternary blend of PS/PLLA/PEO, the geometrical confinement restricted the phase separation of PLLA and PEO during crystallization due to which, during crystallization of PLLA, a large fraction of PEO were trapped into the interlamellar region of PLLA which resulted in the formation of very defective PLLA crystals. Such defective crystals were found to melt at significantly low temperatures. Moreover, during crystallization, the PEO experienced a very high degree of confinement by the pre-existing PLLA crystals and surrounding hard glassy matrix of PS. This resulted in the formation of thin and defective PEO crystal lamellae which melted at a very low temperature.

The present study also focussed on understanding the role of spinning solvent in the morphology and, hence, the confined crystallization behavior of polymer in electrospun fibres from amorphous/crystalline blend. The investigated PS/PEO blend fibres formed phase separated structure in the fibres, where the minority PEO component was present as the dispersed phase in the PS matrix. It was found that the dielectric constant and volatility of the spinning solvent may profoundly affect the morphology of the electrospun blend fibres and, hence, the crystallization behavior of the minority component. The research reported in the thesis highlights the complex crystallization behaviour of crystalline polymer mixtures under confinement especially in electrospun fibres and will catalyse further research in this direction.