CHAPTER VII

SUMMARY

The salient features of the thesis are summarized in this chapter. The thesis deals with the investigations made by the author on the free volume changes brought about by iodine sorption, UV irradiation and isochronal annealing in the three technologically important polymers Acrylonitrile-Butadiene-Styrene (ABS), Poly(ethyleneterephthalate) (PET) and Polycarbonate (PC). These effected changes are studied using the defect tool, Positron Annihilation Lifetime technique. The thesis consists of six chapters, viz., (1). introduction, (2). theoretical resume, (3) . experimentation and data analysis. (4). diffusion of iodine in polymer matrix, (5). influence of UV irradiation on polymers and (6). isochronal annealing studies on polymers. The focus of the thesis is in understanding the microstructure of polymers when subjected to the aforesaid three external treatments as these have tremendous applicability in material science and technology, particularly in polymer technology.

Chapter I gives a general introduction to the subject. It states the importance of the knowledge on polymer microstructure and how it is affected when subjected to sorption, UV irradiation and temperature. Besides this general introduction, every chapter has its own introduction to illustrate the particular interest and the motivation for the

present studies along with a brief review of the present knowledge available in the literature concerning the particular polymer. The polymer microstructure and a brief knowledge of free volume are provided in section 1.1. The motivation for undertaking the present work is highlighted in section 1.3. of this chapter. Chapter II provides a detailed description of the theoretical models relevant to present experimental investigation. The third chapter gives the description of the positron lifetime spectrometer used in the present investigation and the sample treatment procedures.

From the iodine sorption study (chapter IV) in all the three polymers viz., ABS, PET and PC, it has been found that the iodine gets into the free volume holes and in particular, the I_3^- specie. The rate of iodine diffusion is fast as compared to the segmental relaxation in the case of ABS and PET. For PC, the segmental relaxation is fast in comparison to rate of diffusion. Usually, segmental and chain mobilities are easier in case of amorphous polymers than in crystalline polymers [2]. In agreement with this, PC is exhibiting more segmental relaxation as it is less crystalline (almost amorphous) than ABS and PET. ABS and PET exhibits swelling on iodine sorption where as PC donot show such an effect. PC is having two phenylene groups in its chain backbone and hence is more rigid. Probably, because of this it is unable to show swelling on iodine sorption. It has been observed that in all the three

polymers, CTC formation with iodine is possible and the possible CTC centers are identified as phenylene group in the case of ABS and carbonyl groups/group in the case of PET and PC respectively. The changes in o-Ps intensity upon sorption is more in the case of ABS suggesting more number of iodine species accommodated in the polymer. This may be due to the fact that the free volume hole size in ABS is bigger when if compared to PET and PC. Furthermore, ABS is a high molecular weight polymer and amenable to chain folding [292]. This makes it to allow more number of the diffusant specie. The present study has also made an attempt to correlate the diffusion type with Fujita's free volume theory. Sorption in ABS and PET show non-Fickian behaviour and do not follow Fujita's concept of free volume. On the otherhand, sorption in PC obeys both. To make meaningful conclusion, one needs more investigations of this kind especially with different diffusant species.

The results on the effects of UV irradiation on these polymers are provided in chapter V. The UV irradiation in ABS results to chain scission leading to the production of free radicals in the earlier stages. Cross-linking seems to be more predominant in the later stages of UV exposure. In the case of PC, UV exposure in the initial stages results in chain scission like in ABS. UV irradiation in later stages leads to partial-cross linking resulting in micro-gel formation. At long exposure to UV irradiation, due to Photo-Fries rearrangement,

the PC seems to attain photostability.

The annealing behaviour of these polymers is presented in chapter VI. The results show that all these three polymers are of high T_g materials. In case of PET and PC, due to the presence of phenylene groups in the main chain backbone, they show high T_g. Even though ABS do not possess a phenylene group in its chain backbone, since it exhibits high cross-linking under UV irradiation and hence results to high T_g [7]. The energies involved in the thermal activation process are estimated in the ordered and in disordered regions separately.

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LIST OF PUBLICATIONS

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