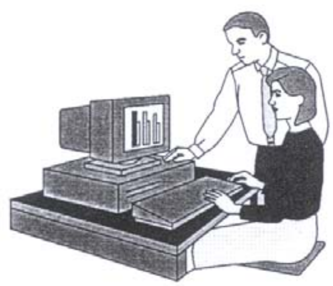
CHAPTER VII



SUMMARY

The salient features of the thesis are summarized in this chapter. The thesis deals with the free volume changes brought about by compression, elongation, physical aging and isochronal annealing (both in the unstrained and in strained conditions) in a technologically important polymer Poly(chlorotrifluoroethylene)-PCTFE. Further, to study the effect of Vinylidene fluoride (VF_2) on the microstructure of PCTFE, the author has selected three types of PCTFE with varying VF_2 content viz., (i). 22A (with 3% VF_2), TVS (with 0.5% VF2) and HP (0% VF_2). The effected changes are studied using the defect tool, Positron Annihilation Lifetime technique. The thesis comprises of six chapters viz., (1). Introduction, (2). Experimental technique and data processing, (3). Effect of stress on the microstructure of PCTFE, (4). Physical aging of PCTFE, (5). Influence of Vinylidene fluoride on the annealing behavior of PCTFE, (6). Effect of pressure on the annealing behavior of PCTFE and (7). Summary. The focus of this thesis is to understand the effect of VF_2 comonomer on the microstructure of PCTFE when subjected to aforesaid external treatments.

Chapter I gives a general introduction to the importance of copolymers and their effect on the physical and mechanical properties of polymers. Further, Positron Lifetime Technique applied to polymer studies is also discussed. A detailed description of the theoretical models relevant to the present experimental investigation in terms of free volume leading to WLF theory is also provided in this chapter. The motivation for undertaking the present work is highlighted in section 1.13. of this chapter. Besides this general introduction, every chapter has its own introduction to illustrate the particular interest and the motivation for the present studies. The second chapter gives the description of the positron lifetime spectrometer used in the present investigation and the sample treatment procedures.

From the tensile study in 22A and HP (chapter III(a)), it has been found that the addition of 3% VF_2 alters the elongation behavior of PCTFE. The chain straightening process precedes the chain orientation in these two polymers. Further, the absence of VF_2

in HP reduces the amorphous content and thus found to offer restriction to the rotation of chain segments beyond the critical strain. Due to the increased amorphous content in 22A, the yield point and the ultimate yield strength is found to be lesser than that of HP.

The compression study on 22A and HP (chapter III(b)), reveals that the compression can be divided into two parts; molecular compression and free volume compression and the molecular compression precedes the free volume compression in agreement with the literature reporting [1]. The addition of VF_2 results in increased amorphous content [2] which inturn leads to more flexibility. The free volume compression of 22A occurs at a lesser pressure than HP whereas, the molecular compression for both the samples occurs at the same pressure (around 4 kbar). These results points to the fact that VF_2 influences mainly the amorphous region. The minor difference in the variations of second lifetime and intensity in these samples shows VF_2 has a little influence on crystalline regions as well as in c-a boundary regions. The present results also support the observation that certain crystalline materials do transform to amorphous phase on compression [3] which occurs at a lesser stress in 22A and HP.

Physical aging effects of PCTFE (types 22A and HP) are explained based on the changes in o-Ps intensity which has been well resolved into two additive exponentials is described chapter IV. As per literature [4,5], only the o-Ps intensity shows variation whereas in PCTFE (both 22A and HP) both the o-Ps lifetime and its intensity show considerable changes as a function of aging time. From this, the relaxation times are evaluated. The free volume behavior exhibits Doolittle type of free volume relaxation. The results also show that the Narayanaswamy model can be extended to study the relaxation behavior of polymeric glasses above T_g with a little modification. In agreement with the results of the tensile and elongation study on this polymer, the aging results also show that addition of VF_2 increases the amorphous content and thus reduces the relaxation time. From the values of the non-exponential parameter in Kolrausch- Williams-Watts function, it is found that only fewer segments are involved in the relaxation process in 22A than in HP. Since 22A has more amorphous content (more of VF_2 content) than HP, the additional free volume in 22A allows the molecular segments to reach their equilibrium state faster than in HP at a given thermal state. Naturally, one expects that 22A to relax quickly than HP and the present results are in agreement with this.

The results on the effect of VF_2 on the annealing behavior of three types of PCTFE viz., 22A (with VF_2 3%), TVS (with VF_2 0.5%) and HP (with VF_2 0%) is provided in chapter V. The results show that with the increase in VF_2, there is a decrease in the glass transition temperature. In all the three samples, below T_g the segmental motion is very small and this is in conformity with the WLF theory [6].

The results on the effect of pressure (both elongation and compression) on the annealing behavior of PCTFE is discussed in chapter VI. In the elongated PCTFE (HP), at lower annealing temperatures, the stretched polymer chains begin to shrink. The presence of residual stresses both in elongated HP and compressed 22A induces negative thermal expansion. As a result, there is a decrease in free volume in the rubbery region with an increase in T_g. It is observed that there is an increase in the rate of crystallization in elongated HP, incontrast with a decrease in the rate of crystallization in compressed 22A compared to their undeformed state.

REFERENCES

[1]. R.N. Haward; J. Polym. Sci., A-2, **7**, (1969) 219.

[2]. G. Moggi and P. Bonardelli; J. Polym. Sci., Polym. Phys., **22**, (1984) 357.

[3]. S.M. Sharma; Ind. J. of Pure and AppI. Phys., **33**, (1995) 562.

[4]. AJ. Hill, P.L. Jones, J.H. Lind and G.W. Pearsall; J. Polym. Sci., Polym. Chern., **26**, (1988) 1541.

[5]. Y. Kobayashi, W. Zheng, E.F. Meyer, J.D. McGervy, A.M. Jamieson and R. Simha; Macromolecules, **22**, (1989) 2302.

[6]. M.L. Williams, R.F. Landel and J.D. Ferry; J. Am. Chern. Soc., **77**, (1955) 3701.

LIST OF PUBLICATIONS OF THE AUTHOR

A. IN REFEREED JOURNALS

1. Free volume study of poly(chlorotrifluoroethylene) using positron annihilation spectroscopy as a microanalytical tool.
   P. Ramachandra, R. Ramani, TSG. Ravichandran, G. Ramgopal, S. Gopal, C. Ranganathaiah and N.S. Murthy; Polymer, **37**, (1996) 3233.

2. Physical aging of poly(chlorotrifluoroethylene): A positron annihilation study.
   P. Ramachandra, R. Ramani, G. Ramgopal and C. Ranganathaiah;
   European Polymer Journal, **33**, (1997) 1707.

3. Effect of Stress on the free volume content of Poly(chlorotrifluoroethylene).
   P. Ramachandra, R. Ramani, G. Ramgopal and C. Ranganathaiah and N.S. Murthy;
   Polymer, **39**, (1998) 2987.

4. Infuence of Strain on the Thermal behaviour of Poly(chlorotrifuoroethylene).
   P. Ramachandra, R. Ramani, G. Ramgopal, Gani Shariff, M.C. Thimmegowda, P.M. Sathyanarayana and C. Ranganathaiah; Polymer International [In press].

5. Microstructure of polycarbonate seen by positron as an in-situ probe.
   R. Ramani, P. Ramachandra, TSG. Ravichandran, G. Ramgopal, S. Gopal and C. Ranganathaiah; Applied Physics A, **60**, (1995) 481.

6. Correlation between electron density and momentum in free volume holes of some semicrystalline polymers.
   R. Ramani, P. Ramachandra, G. Ramgopal, TSG. Ravichandran, C. Ranganathaiah and S. Gopal; Physica Status Solidi (a), **158**, (1996) 3.

7. Structural modifications in Bivoltine silk fiber under thermal treatment.
G. Ramgopal, R. Ramani, P. Ramachandra and C. Ranganathaiah;
Journal of Applied Polymer Science, **63**, (1997) 395.

8. Transport of iodine in Poly(ethyleneterephthalate)
R. Ramani, P. Ramachandra, G. Ramgopal and C. Ranganathaiah;
European Polymer Journal, **33**, (1997) 1753.

9. A Positron Annihilation study of iodine sorption in Acrylonitrile-Butadiene-Styrene.
R. Ramani, P. Ramachandra, G. Ramgopal and C. Ranganathaiah;
Journal of Applied Polymer Science **68**, (1998) 2077.

10. UV degradation of silk fiber: A Positron Anihilation study.
G. Ramgopal, R. Ramani, P. Ramachandra and C. Ranganathaiah;
European Polymer Journal, [In press].

11. A Positron Annihilation study on the tensile behavior of bivoltine silk fibers.
G. Ramgopal, R. Ramani, P. Ramachandra and C. Ranganathaiah;
European Polymer Journal [In press].

12. A Free volume microprobe study of Diffusion kinetics in Polymers.
R. Ramani, P. Ramachandra, G. Ramgopal, Gani Shariff, M.C. Thimmegowda,
P.M. Sathyanarayana and C. Ranganathaiah.
Physical Review B., [Communicated].

B. IN SYMPOSIA

1. Thermal behaviour of Nitrile Butadiene Rubber probed by positron annihilation spectroscopy.
   TSG. Ravichandran, R. Ramani, P. Ramachandra, G. Ramgopal, Blaise Lobo, S. Gopal, C. Ranganathaiah, M.R. Ranganath and S.N. Chintalapudi;
   National Seminar on Defects in condensed media, IGCAR, Kalpakkam, September 20-22, (1995).

2. Influence of iodine sorption on the positronium trapping sites in polycarbonate.
   R. Ramani, P. Ramachandra, G. Ramgopal, Blaise Lobo, M.R. Ranganath, C. Ranganathaiah and S. Gopal;
   Solid State Physics Symposium, Jadavpur University,
   Calcutta, December 27-31, 1995.

3. Microstructural changes in Nitrile Butadiene Rubber by positron annihilation spectroscopy.
   TSG. Ravichandran, R. Ramani, P. Ramachandra, G. Ramgopal, Blaise Lobo. S. Gopal, V. Sreeramalu, C. Ranganathaiah, M.R. Ranganath and S.N. Chintalapudi;
   Solid State Physics Symposium, Jadavpur University,
   Calcutta, December 27-31, 1995.

4. Sorption of iodine in Acrylonitrile-Butadiene-Styrene.
   R. Ramani, P. Ramachandra, G. Ramgopal and C. Ranganathaiah;
   Solid State Physics Symposium, B .A.R.C., Mumbai, December 27-31, 1996.

5. A positron annihilation study on the degradation of polycarbonate by UV irradiation.
   R. Ramani, P. Ramachandra, G. Ramgopal, Gani Shariff, M.C. Thimme Gowda,
   P.M. Sathyanarayana and C. Ranganathaiah;
   Solid State Physics Symposium, Cochin University, Kochi, December 27-31, 1997.