

Contents

Acknowledgements	v
Abstract	vii
List of Figures	xiii
List of Tables	xxix
1	1
1.1 Fundamentals of a glass	1
1.1.1 Mechanical properties	2
1.1.2 Dielectric properties	3
1.1.3 Optical properties	3
1.2 Glass transition and Physical Aging	4
1.3 Dynamic Slowdown	6
1.4 Static and dynamic correlation functions	8
1.5 Dynamic Heterogeneities	9
1.6 Theoretical developments	11
1.6.1 Adam Gibbs Theory (AGT)	11
1.6.2 Mode coupling theory (MCT)	12
1.6.3 Random first-order transition (RFOT) theory	13
1.7 Significance of Glassy Polymers	14
1.8 Recent advances in Glassy systems	15
1.9 Motivation	16
1.10 Objectives	18
1.11 Thesis outline	18
Refernces	19

2		29
2.1	Introduction	29
2.2	Preparation of polymer films	31
2.3	Tensile testing	32
2.4	Response to mechanical perturbation	33
2.4.1	Elastic response	34
2.4.2	Plastic response	34
2.4.3	Comparison of mechanical properties	39
2.5	Raman spectroscopy	43
2.5.1	Theoretical background	43
2.5.2	Raman instrumentation	47
2.5.3	Methodology for thermal quench	48
2.5.4	Data collection and analysis	49
2.6	Effect of thermal perturbation	49
2.6.1	PPC	50
2.6.2	HDPE	55
2.6.3	LLDPE	58
2.7	Effect of change in temperature	64
2.8	Correlation between vibrational and mechanical properties	70
2.9	Effect of processing techniques	73
2.10	Summary	75
	References	76
3		87
3.1	Introduction	87
3.2	Preparation of polymer film	89
3.3	Raman spectroscopy	90
3.4	Methodology for thermal perturbation	91
3.4.1	Thermal ramp	91
3.4.2	Thermal quench	91
3.4.3	Data collection and analysis	91
3.5	Raman spectrum of unprocessed PVAc and PVAc film	92
3.6	Effect of thermal ramp	96
3.6.1	Unprocessed PVAc	96
3.6.2	PVAc film	100

3.6.3	Analysis of hysteresis in Raman modes peak parameters . . .	108
3.7	Effect of thermal quench	109
3.7.1	Unprocessed PVAc	109
3.7.2	PVAc film	116
3.8	Thermal relaxation of Raman modes	122
3.9	Summary	126
	Refernces	128
4		135
4.1	Introduction	135
4.2	Effect of thermal perturbations on unprocessed PVAc and PVAc film	137
4.3	Correlations in Raman modes	138
4.4	Dynamic heterogeneities in glassy polymer	142
4.5	Spatial and temporal correlations	148
4.6	Experimental dynamic Susceptibility	151
4.7	Summary	156
	Refernces	157
5		161
5.1	Introduction	161
5.2	Preparation of polymer solutions	163
5.3	Fluorescence recovery after photobleaching (FRAP)	164
5.3.1	Instrumental setup	165
5.3.2	Diffusion analysis using FRAP	166
5.4	Micro-scale mechanical properties from diffusion	168
5.4.1	Diffusion of fluorescent probe in PEG solution	173
5.4.2	Effect of CMC nanofibers on diffusion	174
5.4.3	Effect of bentonite nanoparticles on diffusion	176
5.4.4	Cluster analysis of diffusion coefficient	178
5.5	Micro-scale structuring in polymer solutions	181
5.5.1	Structure factor and 2D correlations from FRAP	181
5.5.2	Micro-scale structural analysis using phase contrast microscopy	184
5.5.3	Small angle X-ray scattering (SAXS)	186
5.5.4	Medium resolution small angle neutron scattering (MSANS)	189
5.6	Summary	190

References	191
6	199