**Effect of Confinement on Phase Separation and Morphology in
Polymer/Small Molecule Composites**

by

Bindu Tuteja

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the requirements
for the degree of

Masters of Science

Carleton University
Department of Chemistry
1125 Colonel By Drive
Ottawa, Ontario, Canada

April, 2004

© Copyright
Bindu Tuteja, 2004

National Library
of Canada

Bibliothèque nationale
du Canada

Acquisitions and
Bibliographic Services

Acquisitons et
services bibliographiques

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 0-612-93991-X

Our file Notre référence

ISBN: 0-612-93991-X

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this dissertation.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de ce manuscrit.

While these forms may be included in the document page count, their removal does not represent any loss of content from the dissertation.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

PAGINATION ERROR.

TEXT COMPLETE.

ERREUR DE PAGINATION.

LE TEXTE EST COMPLET.

ABSTRACT

The effects of annealing time, temperature and film thickness on the phase separation and morphology of plasticizer/polymer composites in confined and unconfined conditions are presented. The polymer bisphenol-A polycarbonate (BPAPC) with the plasticizers diphenyl terephthalate (DPTP) and diphenyl isophthalate (DPIP) were used. For confinement, the composite film was confined between two microscopic slides.

Upon annealing, the extent of phase separation and the average area of the phase separated crystals of the plasticizers were found to be significantly different between unconfined and confined films. The melting points of DPTP and DPIP were reduced while dispersed in the polycarbonate. A significant difference in the morphologies was also observed between thick ($\sim 20\ \mu\text{m}$) and thin films ($\sim 700\ \text{nm}$) with DPTP/BPAPC. Sublimation of DPTP and DPIP occurs at higher annealing temperatures and this contributes to the differences seen between unconfined and confined conditions. FTIR and molecular modeling show molecular level interaction exists between plasticizers and polymer.

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. P. R. Sundararajan for giving me an opportunity to work in the exciting field of polymer morphology and for providing me with continuous guidance, support, numerous discussions and ideas over the duration of this project.

Thanks are also due to Xerox Research Centre of Canada (XRCC) and NSERC for providing the financial support necessary to carry out this research work.

I would also like to thank Dr. F. Khan for his overall help over the duration of this project. Thanks are also due to my other lab mates, especially Patrick Yao for his help with molecular modeling software, Dr. Shanti Singh, Dr. V. Sriram and M. Moniruzzaman for periodic discussions as well as Hong Xu and Shallu Bhalla for their friendship over the last couple of years.

Thank you to Dr. Andrew Yu for showing me how to use Alpha-Step 200 Tencor instrument to measure the thickness of thin films and to Dr. Z.Y.Wang for allowing me to use this instrument in his laboratory. In addition, I would like to thank Mr. Lewis E.C. Ling for his help with Scanning Electron Microscopy (SEM). Further, thanks are also due to Mr. Jim Logan for making the Dip coater instrument.

Last but not the least I would like to thank my husband Rohit for being patient, understanding and supportive throughout this period.

TABLE OF CONTENTS

Abstract	iii
Acknowledgements	iv
Table of Contents	v
List of Tables	viii
List of Figures	ix
List of Abbreviations	xv
Chapter 1: Introduction.....	1
1.1 Types of Confinement.....	2
1.2 Plasticizer/Polymer composites.....	10
1.3 Objective and Thesis Overview.....	15
1.4 References.....	17
Chapter 2: Materials and Methods.....	21
2.1 Materials.....	22
2.1.1 Bisphenol-A-Polycarbonate (BPAPC).....	22
2.1.2 Plasticizers.....	23
2.2 Film preparation.....	25
2.2.1 Thick Film (~20 μm thickness).....	25
2.2.2 Thin Films (~700 nm).....	25
2.3 Measurement of the thickness of the films.....	27
2.3.1 Thick Film (~20 μm thickness)	27
2.3.2 Thin Film (~700 nm).....	27

TABLE OF CONTENTS Continued

2.4	Confined and Unconfined Configurations.....	28
2.5	Evaporation Measurements.....	29
2.6	Characterization Methods.....	30
2.6.1	Thermal Analysis.....	30
2.6.2	Powder X-ray Diffraction.....	31
2.6.3	FTIR Spectroscopy.....	34
2.6.4	Optical Microscopy.....	35
2.7	Molecular Modeling.....	36
2.8	References.....	37
Chapter 3: DPTP and BPAPC Composites.....		39
3.1	Thick Film.....	40
3.1.1	Effect of DPTP on the T_g of BPAPC in as Prepared Solvent Cast Films	40
3.1.2	Effect of Temperature and Time on the Glass Transition Temperature of Solvent Cast DPTP/BPAPC Composites Films.....	47
3.1.3	Effect of Annealing Temperature and Time on the Melting point of DPTP in the Composites Films.....	54
3.1.4	Testing for Degradation of DPTP.....	57
3.1.5	Evaporation of DPTP.....	58
3.1.6	Optical Microscopy.....	63
3.2	Thin Film (~700 nm).....	71
3.3	Comparison between the Thick Film and the Thin Film.....	77
3.4	Summary and Conclusions.....	81
3.5	References.....	84

TABLE OF CONTENTS Continued

Chapter 4: DPIP and BPAPC Composites.....	86
4.1 Thick Film.....	86
4.1.1 Effect of DPIP on the T_g of BPAPC in as Prepared Solvent Cast Films	86
4.1.2 Effect of Temperature and Time on the Glass Transition Temperature of Solvent Cast DPIP/BPAPC Composites Films.....	92
4.1.3 Testing for Degradation of DPIP.....	101
4.1.4 Evaporation of DPIP.....	103
4.1.5 Optical Microscopy.....	107
4.2 Thin Film.....	107
4.3 Compatibility of DPIP with BPAPC.....	108
4.4 Summary and Conclusions.....	119
4.5 References.....	121
Chapter 5: Conclusions.....	122
Chapter 6: Recommendations for future work.....	123
Appendices	124
Appendix A:	125
Appendix B:	129

LIST OF TABLES

Table 3.1	Results of Thermal Analysis of DPTP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the confined state.....	50
Table 3.2	Results of Thermal Analysis of DPTP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the unconfined state.....	52
Table 4.1	Results of Thermal Analysis of DPIP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the confined state.....	96
Table 4.2	Results of Thermal Analysis of DPIP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the unconfined state.....	98
Table 4.3	Results of Thermal Analysis of DPIP/BPAPC: 40/60 composite films, after annealing at various temperatures and times in the confined state.....	111
Table 4.4	Results of Thermal Analysis of DPIP/BPAPC: 40/60 composite films, after annealing at various temperatures and times in the unconfined state.....	111

LIST OF FIGURES

Figure 1.1	Schematic of composite structures obtained using layered silicates. The rectangular bar represents the silicate layers. (a) Single polymer layers intercalated in the silicate galleries (intercalated hybrids); (b) composites obtained by delamination of the silicate particles and dispersion in continuous polymer matrix (delaminated hybrids).....	3
Figure 1.2	Polymer ICs formed between (a) trans-1, 4- polybutadiene and perhydrotriphenylene, (b) poly (ethylene glycol) and α - Cyclodextrin.....	5
Figure 1.3	Schematic for the principle of threading a polymer inside a host to give a polypseudorotaxane, and capping to give polyrotaxane...	6
Figure 1.4	Glass transition of n-alkyl esters of polyacrylic acid and polymethacrylic acid.....	11
Figure 1.5	Schematic of a typical photoreceptor	15
Figure 2.1	Chemical structure of bisphenol A polycarbonate.....	22
Figure 2.2	Chemical structure of diphenyl terephthalate (DPTP).....	24
Figure 2.3	Chemical structure of diphenyl isophthalate (DPIP).....	24
Figure 2.4	Dip coater.....	26
Figure 2.5	SEM micrograph showing the edge of the composite film.....	27
Figure 2.6	Schematic for the (a) Confined state, (b) Unconfined state	28
Figure 2.7	Confined device used to measure % weight loss of plasticizer from the composite film.....	29
Figure 2.8	(a) Schematic of the unit cell, lattice planes and the d spacings; (b) Bragg construction illustrating the principle of diffraction	32
Figure 2.9	An example of optical micrographs showing the effect of threshold function of a set of particles (taken from Nothern Eclipse image analysis version 6.0 software).....	36

LIST OF FIGURES Continued

Figure 3.1	(a) The variation of T_g of the polycarbonate with various concentrations of DPTP, (b) The depression of ΔT of the T_g with various concentrations of DPTP.....	41
Figure 3.2	Overlay of DSC thermograms of “as prepared” DPTP/BPAPC composite films.....	41
Figure 3.3	Schematic of two different levels: (a) The domain level, (b) The molecular level.....	43
Figure 3.4	FTIR spectra of (a), (c), (e) DPTP, BPAPC and DPTP/BPAPC: 15/85; (b), (d), (f) DPTP, BPAPC and DPTP/BPAPC:10/90.....	45
Figure 3.5	Minimum energy conformations of (a) DPTP, (b) 12- mer of BPAPC and (c) DPTP/BPAPC.....	46
Figure 3.6	Glass transition temperature (T_g) versus annealing time of composite films in the confined state: (a) DPTP/BPAPC: 5/95; (b) DPTP/BPAPC: 10/90; (c) DPTP/BPAPC: 15/85	49
Figure 3.7	Glass transition temperature (T_g) versus annealing time of composite films in the unconfined state: (a) DPTP/BPAPC: 5/95; (b) DPTP/BPAPC: 10/90; (c) DPTP/BPAPC: 15/85	51
Figure 3.8	Comparison of T_g between confined and unconfined DPTP/BPAPC composite films annealed at 130 and 140 °C.....	53
Figure 3.9	Overlay of DSC thermograms of the confined DPTP/BPAPC: 15/85 composite film annealed at 120, 130, 140 °C for 0.5h.....	56
Figure 3.10	Overlay of DSC thermograms of the unconfined DPTP/BPAPC: 15/85 composite film annealed at 140 °C for various times.....	56
Figure 3.11	TGA thermograms of DPTP, BPAPC and DPTP/BPAPC: 5/95, 10/90, 15/85 composite films.....	58
Figure 3.12	Normalized weight loss (%) versus annealing temperature of DPTP as received and DPTP/BPAPC composite films annealed for 3 h at various temperatures.....	60
Figure 3.13	X-ray diffraction traces of the evaporated DPTP from (a) DPTP as received sample and (b) DPTP/BPAPC: 15/85 composite films.....	62

LIST OF FIGURES Continued

- Figure 3.14** Optical micrographs of as prepared composite films:
(a) DPTP/BPAPC: 5/95, (b) DPTP/BPAPC: 10/90,
(c) DPTP/BPAPC: 15/85..... 64
- Figure 3.15** Optical micrographs of the composite film annealed at 130 °C for various times in the confined state: (a) DPTP/BPAPC: 10/90, 1 h; (b) DPTP/BPAPC: 10/90, 2 h; (c) DPTP/BPAPC: 10/90, 3 h; (d) DPTP/BPAPC: 15/85, 1 h; (e) DPTP/BPAPC: 15/85, 2 h; (f) DPTP/BPAPC: 15/85 3 h..... 65
- Figure 3.16** Optical micrographs of the composite film annealed at 130 °C for 2 h at various concentrations: (a) DPTP/BPAPC: 5/95, confined; (b) DPTP/BPAPC: 5/95, unconfined; (c) DPTP/BPAPC: 10/90, confined; (d) DPTP/BPAPC: 10/90, unconfined; (e) DPTP/BPAPC: 15/85, confined; (f) DPTP/BPAPC: 15/85, unconfined.....68
- Figure 3.17** Average crystal area (optical microscopy) versus annealing time: (a) DPTP/BPAPC: 5/95, confined; (b) DPTP/BPAPC: 5/95, unconfined; (c) DPTP/BPAPC: 10/90, confined; (d) DPTP/BPAPC: 10/90, unconfined; (e) DPTP/BPAPC: 15/85, confined; (f) DPTP/BPAPC: 15/85, unconfined..... 69
- Figure 3.18** Effect of Annealing for 3 h on Crystal Area Distribution: (a) DPTP/BPAPC: 10/90, confined; (b) DPTP/BPAPC: 10/90, unconfined; (c) DPTP/BPAPC: 15/85, Confined; (d) DPTP/BPAPC: 15/85, unconfined..... 70
- Figure 3.19** Optical micrographs of the thin composite film annealed at 90 °C for 2 h: (a) DPTP/BPAPC: 10/90, confined; (b) DPTP/BPAPC: 10/90, unconfined; (c) DPTP/BPAPC: 15/85, confined; (d) DPTP/BPAPC: 15/85, unconfined.....73
- Figure 3.20** Average crystal area (optical microscopy) versus annealing time in the thin composite film: (a) DPTP/BPAPC: 10/90, confined; (b) DPTP/BPAPC: 10/90, unconfined; (c) DPTP/BPAPC: 15/85, confined; (d) DPTP/BPAPC: 15/85, unconfined.....75
- Figure 3.21** Effect of annealing for 3 h on crystal area distribution in the thin composite film: (a) DPTP/BPAPC: 10/90, confined; (b) DPTP/BPAPC: 10/90, unconfined; (c) DPTP/BPAPC: 15/85, confined; (d) DPTP/BPAPC: 15/85, unconfined.....76

LIST OF FIGURES Continued

Figure 3.22	Optical micrographs for DPTP/BPAPC: 15/85 confined composite film annealed at various temperatures for 2 h: (a) Thin film annealed at 80 °C; (b) Thick Film annealed at 80 °C; (c) Thin film annealed at 90 °C; (d) Thick film annealed at 90 °C; (e) Thin film annealed at 120 °C; (f) Thick film annealed at 120 °C.....	78
Figure 3.23	Comparison of the average crystal area between the thin and the thick film, annealed at 120 °C for various times in the confined state: (a) DPTP/BPAPC: 10/90; (b) DPTP/BPAPC: 15/85.....	80
Figure 4.1	(a) The depression of T_g of the polycarbonate with various Concentrations of DPIP, (b) the depression of ΔT of T_g of the polycarbonate with various concentrations of DPIP.....	88
Figure 4.2	Overlay of DSC thermograms of “as prepared” DPIP/BPAPC composite films.....	88
Figure 4.3	FTIR spectra of (a), (c), (e) DPIP, BPAPC, and DPIP/BPAPC: 15/85; (b), (d), (f) DPIP, BPAPC and DPIP/BPAPC: 10/90.....	90
Figure 4.4	(a) Variation of the frequency with the concentration of DPIP in BPAPC, (b) correlation between the T_g depression (ΔT) and Frequency shifts.....	91
Figure 4.5	Minimum energy conformations of (a) DPIP, (b) 12 mer of BPAPC and (c) DPIP/BPAPC.....	93
Figure 4.6	Glass transition temperature (T_g) versus annealing time of composite films in the confined state: (a) DPIP/BPAPC: 5/95; (b) DPIP/BPAPC: 10/90; (c) DPIP/BPAPC: 15/85.....	95
Figure 4.7	Glass transition temperature (T_g) versus annealing time of composite films in the unconfined state: (a) DPIP/BPAPC: 5/95; (b) DPIP/BPAPC: 10/90; (c) DPIP/BPAPC: 15/85.....	97
Figure 4.8	Overlay of DSC thermograms of the confined DPIP/BPAPC: 15/85 composite film annealed at 120 °C for various times.....	99
Figure 4.9	Overlay of DSC thermograms of the unconfined DPIP/BPAPC: 10/90 composite film annealed for 2 h at various temperatures.....	99

LIST OF FIGURES Continued

Figure 4.10	Comparison of T_g between confined and unconfined DPIP/BPAPC: 5/95, 10/90, 15/85 composite films annealed at 130 and 140 °C.....	100
Figure 4.11	TGA thermograms of DPTP, BPAPC and DPTP/BPAPC: 5/95, 10/90, 15/85 composite films.....	102
Figure 4.12	Normalized weight loss (%) versus annealing temperature of DPIP as received and DPIP/BPAPC composite films annealed for 3 h at various temperature.....	104
Figure 4.13	X-ray diffraction traces of the evaporated DPIP from (a) bulk DPIP sample and (b) DPIP/BPAPC: 15/85 composite films.....	106
Figure 4.14	The depression of T_g of the polycarbonate with 20, 30, and 40 % of DPIP in BPAPC.....	109
Figure 4.15	Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed at 120 °C for various times in the confined state.....	112
Figure 4.16	Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed at 120 °C for various times in the unconfined state.....	112
Figure 4.17	Comparison of T_g between confined and unconfined DPIP/BPAPC: 40/60 composite films.....	113
Figure 4.18	Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures in the confined state.....	115
Figure 4.19	Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures in the unconfined state.....	115
Figure 4.20	X –ray diffraction pattern of the as prepared DPIP/BPAPC: 40/60 composite film, film annealed at 130 °C for 4 h in confined and unconfined states.....	116

LIST OF FIGURES Continued

Figure 4.21	Optical micrographs of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures: (a) annealed at 120 °C, confined; (b) annealed at 120 °C, unconfined; (c) annealed at 130 °C, confined; (d) annealed at 130 °C, unconfined; (e) annealed at 140 °C, confined; (f) annealed at 140 °C, unconfined.....	118
--------------------	---	-----

LIST OF APPRIEVIATIONS

BPAPC	Bisphenol-A polycarbonate
CTL	Charge transport layer
DPIP	Diphenyl isophthalate
DPTP	Diphenyl terephthalate
DSC	Differential scanning calorimetry
FTIR	Fourier Transform Infrared spectroscopy
h	hour (s)
ICs	Inclusions compounds
IR	Infrared
KBR	Potassium Bromide
nm	nanometer
PS	Polystyrene
SEM	Scanning electron microscopy
SiO _x	Silicon Oxide
Si	Silicon
TCP	tricresyl phosphate
T _g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
T _m	Melting Temperature
TPD	N,N'-diphenyl-N,N'-bis(3-methylphenyl)[1,1'-biphenyl]-4,4'-diamine
XRD	X-ray diffraction
μm	micrometers

Chapter 1

Introduction

Polymers can be modified in various ways to tailor the properties for specific applications and their processability. These modifications could be internal or external. The internal modifications include functionalization, adding side groups etc. The external modifications, however, find widespread applications in industry, since the compositions can be modified at will. Examples of such external modifications are blending two or more polymers, the addition of plasticizers or the addition of nanoscale inorganic filler or particles, such as alumina (Al_2O_3), silica (SiO_2), titania (TiO_2). These polymer composites or polymer blends are generally used in the form of a film. Polymer films play an important role in a wide range of applications, for example, coating, adhesives, optoelectronic devices etc. To retain their intended properties, these films should remain stable under varying usage environments, such as varying temperature, humidity, mechanical abuse etc. One of the ways destabilization can occur is by phase separation, which would result in deterioration of the device performance. The morphology of the composite material has a significant effect on the efficiency and functioning of the device. For example, the size of the domains in polymer blends plays a significant role in the mechanical properties of polymer. If the domain size is significantly large it results in poor mechanical property and hence affects the functional properties of a device.

The polymer film may be free standing (e.g., polyethylene bags) or the film may be cast on a substrate, which is rigid or flexible. The film then has one interface with the substrate and the other with air (e.g.; the charge transport layer (CTL) of a photoreceptor). Another possibility is that the film may be sandwiched between two soft or hard surfaces, where the film has interaction on both sides with a rigid hard or soft wall (e.g., the charge generation layer of a photoreceptor). Overcoating or cladding of devices also gives rise to such “confinement” between two surfaces.

Confinement of polymer films can be done in a different ways. The definition of “confinement” itself varies from one context to another. This chapter discusses the various types of confinement, plasticizer/polymer composites, objective and the overview of thesis.

1.1 Types of Confinement

Polymer synthesis in the pore structure such as clay

The introduction of a polymer into the interlamellar spaces of a layered material such as clay is one kind of confinement. In this case, interchain interactions are essentially eliminated and one can study the single chain structure and mobility. In general, two types of hybrid structures are possible: *intercalated*, in which a single, extended polymer chain is intercalated between the silicate layers, resulting in a well-ordered multilayer with alternating polymer/inorganic layers; and *disordered or delaminated*, in which the silicate layers (e.g., 1 nm thick) are exfoliated and dispersed in a continuous polymer matrix¹ (Figure 1.1)

Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix that is imbedded with inorganic particles, which have at least one dimension in the nanometer size range². Because of their nanometer-size dispersion, the nanocomposites exhibit markedly improved properties when compared with the pure polymers or conventional composites.

Figure 1.1 Schematic of composite structures obtained using layered silicates. The rectangular bar represents the silicate layers. (a) Single polymer layers intercalated in the silicate galleries (intercalated hybrids); (b) composites obtained by delamination of the silicate particles and dispersion in continuous polymer matrix (delaminated hybrids)³

These include increased modulus and strength, enhanced thermal stability⁴, decreased gas permeability, increased solvent and heat resistance and decreased flammability. For example, a doubling of the tensile modulus and strength is achieved for nylon-layered silicate nanocomposites with as little as 2 volume percent of inorganic content². In addition, the heat distortion temperature of the nanocomposites increases by up to 100°C, extending their use to higher-temperature environments, such as automotive under-the-hood parts².

Polymer small molecule inclusion compounds.

Several small-molecules such as urea, perhydrotriphenylene, and cyclodextrins have the ability to form the inclusion complexes with polymers, the studies with cyclodextrins being numerous. (Cyclodextrins are cyclic oligoamyloses whose shape is almost annular (i.e., has a central void) but whose outside surface is that of truncated cone with a small vertex angle. The α , β , γ , δ , cyclodextrins have 6, 7, 8, 9 saccharide units, respectively, in the macrocyclic ring). In these inclusion compounds (ICs), the guest polymer chains occupy narrow cylindrical channels ($D \sim 5\text{--}10 \text{ \AA}$) created by the crystalline host lattice. As a result, the included polymer chains are constrained to assume highly extended conformations and are generally segregated from neighboring included polymer chains by the channel walls of the host crystalline lattice. Two examples of polymer ICs are presented in Figure 1.2, in which the crystalline ICs 2,3 *trans*-1, 4-poly (butadiene)/perhydrotriphenylene, and poly (ethylene glycol)/ cyclodextrin are shown⁵. When these polymer-IC crystals are washed with a solvent for the host that does not dissolve the guest polymer, the ICs are disrupted, the host is dissolved and removed, and the guest polymer chains are forced to coalesce into a bulk solid. It has been reported that the structure, morphology, chain conformation and physical properties of this coalesced polymer are distinct from those generally observed for the bulk sample^{5,6}.

5

Another type of inclusion involves rotaxanes. Figure 1.3 shows the schematic diagram for the principle of threading a conjugated polymer inside a β -cyclodextrin to give a polypseudorotaxane, and or when capped by a sulfonated naphthyl group, to give a polyrotaxane⁷. This is an example of a molecular device: a conjugated conducting polymer covered by insulated cyclic molecule.

Figure 1.3 Schematic for the principle of threading a polymer inside a host to give a polypseudorotaxane, and capping to give polyrotaxane

Freely standing film

Although free standing films might be considered “not confined” by any surface, their properties change significantly when their thickness approaches molecular dimensions. These are extremely thin films (e.g., nm dimensions) in which the polymer is confined essentially into two dimensions i.e. confining thickness of the film⁸.

A polymer **thin** film on a rigid or a flexible substrate, (where the film is at the interface of a rigid substrate and air) is the simplest kind of confined geometry, also known as partial confinement. From the review of literature it appears that the terms “uncapped” or “unconfined” has also been used for this type of confinement by various researchers^{8,9}. In the present work the term **Unconfined** is used for this type.

Confining the polymer molecules to a thickness that is smaller than a few times the molecular size influences properties such as chain conformation and mobility, phase separation, glass transition, chain diffusion. The nature of interaction between the polymer molecule and the confining material determine the thermal stability of the confined molecule¹⁰. By reducing the thickness of the film appropriately one perturbs the conformation of the polymer molecule and these confinement restrictions may affect the mechanical properties of the polymer⁸.

The glass transition in a confined polymer film is found to increase or decrease with the thickness of the film and of the interface. Forrest et. al. established that a freestanding poly (styrene) film exhibited a reduction in T_g as the thickness of the film decreased^{8,11}. Keddie et.al. and several other researches^{12,13,14} reported the reduction in T_g with film thickness in the polystyrene(PS)- SiOx/Si system below its bulk value. The opposite trend, i.e., an increase in T_g with decreasing film thickness have been reported for poly vinylpyridine (PVP)- SiOx/Si, Poly(methyl methacrylate) (PMMA)-SiOx/Si, and Polystyrene -tetramethyl bisphenol polycarbonate (PS-TMPC)/SiOx/Si systems^{11,15,16}. In these systems, unlike the PS-SiOx/Si system, the polymer segments have a particularly strong interaction with the substrate (hydrogen bonding). Therefore in the thin polymer

film, the effective T_g is influenced by the nature of the polymer segment-segment interaction in relation to segment – wall (free surface or substrate) interaction. Sufficiently strong segment interaction –“wall” interactions contribute to an increase in the T_g of the film, provided the film is sufficiently thin.

If the polymer blend is confined to a thin film geometry such that surface area to volume ratio is large, surface effect may dominant and phase separation behavior may be different from the bulk mixture¹⁷.

Polymer films confined between two hard or soft surfaces

In this case the polymer film has been capped on both film surfaces with a solid capping layer. In the present work the term **Confined** is used for this type. In this type of confinement again the nature of interaction between the polymer molecule and confining material induces profound effect on the properties such as the glass transition. The glass transition temperature is typically lower in the confined geometry⁸, although experiments also indicate the cases where T_g increases as well^{18,19}.

A number of studies have been reported on the phase separation morphology of the polymer blends in confined geometry^{20,21}. The confinement using the solid boundary restricts the phase growth perpendicular to the film plane and modifies the thermodynamic and kinetic behaviour of thin film blends with respect to that of bulk mixtures²⁰. Veress et. al. found that as the thickness of the upper capping layer was increased, a transition from lateral to lamellar morphology occurred, in phase separated

morphology after annealing the SiO_x/PS:PMMA/ SiO_x system above the T_g of both polymer components²¹. In glass/PS:PVME(30:70)/glass system the growth of phase separated PS rich phase was found to be anisotropic, flattened along the film direction due to the constraint exerted by the rigid substrate and it was found that the course of phase separation is hindered at a later stage²⁰. Various morphologies that result when a thin film of diblock copolymer is confined between two dissimilar hard parallel surfaces have been studied²². Confinement effect of poly (styrene)- poly (methacrylate) (PS-PMMA) and poly (ethylenepropylene)-poly (ethylene) (PEP-PEE) between the similar hard walls, have also been reported^{23,24}. Besides studying the difference in phase separation morphology between bi-layer and tri-layer films it was reported that the thickness of the film plays an important role. Pan and Composto²⁰ reported that the evolution of phase separation is faster in a thin film and as the thickness of the film increases, the rate of phase separation slow down.

A review of literature shows that most of the studies on the effect of confined geometry have been reported on polymer blends. However, to our knowledge, no study on the effect of confinement on the phase separation and morphology of plasticizer/polymer composites has been reported which is the subject of the present study. This work relates to the studies on the morphological stability of multilayered films and devices as a long range goal.

1.2 Plasticizer/Polymer composites

Addition of plasticizers to the polymer matrix is a well-established technique for tailoring the polymer properties for specific applications and their processability²⁵. The plasticization process often uses small molecules, which are crystallizable organic materials. These are either molecularly dispersed, or exist in aggregate crystalline form in the composites²⁶.

A **plasticizer** is a material, which is added to another material (usually plastic, resin and elastomer) to increase its flexibility, extensibility and processibility. Adding of the plasticizer may lower the melt viscosity, glass transition temperature or the elastic modulus of the product without altering the fundamental chemical character of the plasticized material²⁷. According to theory, plasticization on the molecular level is the weakening of selective interactions between the chains, and the accompanied free volume which enables the shaping, flexing, or molding of the material²⁵.

Plasticizers are usually inert organic materials with high boiling points and low vapor pressures. Esters are commonly used due to their favorable physical interactions with high-molecular-weight polymers. This physical interaction causes the polymer and plasticizer to form a “homogenous physical unit.” In other words, they do not separate out. Plasticizers have been in common use since prehistoric time. Water for clay to make pottery and lime for easier workings of cement are but two ancient examples from inorganic chemistry²⁸.

Polymers can be plasticized in two general ways: "internally" and "externally."

Internal plasticization involves the chemical alteration of a polymer or its monomer (prior to polymerization). This can be done by two ways. One of the methods of internally plasticizing a polymer is to copolymerize a second monomer into the polymer structure, thereby making it less ordered, and therefore, more difficult for the chains to fit closely together. This softens the polymer i.e., lowers the T_g or the modulus. Usually the monomer chosen is one whose polymer has a low transition temperature. The styrene-butadiene polymer is a good example of internal plasticization. Another type of plasticization involves the introduction of side chains (either substituents or grafted branches) of various lengths on the polymer backbone. This effect is well known with polyacrylates and polymethacrylates (Figure 1.4), and causes a weakening of the intermolecular forces between the polymer chains owing to the bulkiness of the substituent group. It should be noted from Figure 1.4 that although the T_g initially decreases with the side chain length, it increases beyond a certain length. This is due to the crystallization of side chain²⁹.

Figure 1.4 Glass transition of n-alkyl esters of polyacrylic acid and polymethacrylic acid³⁰

The advantage of internally plasticized products lies in the strong chemical combination of “hard” and “soft” segments which cannot be separated from each other by extraction. This type of plasticization does suffer the disadvantage of having unsatisfactory narrow use temperature range due to relative immobility of internal plasticizer group³¹.

The second type of plasticization is external that involves the addition of a compound of low vapour pressure, which interacts with the polymer only physically. This enables a processor to adjust the flexibility of the basic polymer (PVC, rubber mixtures, coating) over a wide range. Thus the product properties are tailored to the application, e.g. for use in hot or cold climate, for normal or elevated service temperature, or for articles in contact with oil or fuels. A main disadvantage of this type is that since the plasticizer molecules are not attached to the resin by primary bonds, plasticizer can be lost by evaporation or migration^{32,33,34}. External Plasticizer is of two distinct classes: Primary and Secondary.

A **primary plasticizer** for a given polymer is one which is compatible enough with that polymer that it does not separate from the polymer into a discrete phase when used at enough concentration to achieve the desired degree of plasticization²⁸.

A **secondary plasticizer** is one that is not compatible enough to achieve the desired degree of plasticization without separation of polymer and plasticizer into more or less discrete phases, although the plasticizer might be compatible at some lower concentration. This separation may be as “exudation” which is the separation into liquid droplets or a liquid surface film and is at times called “sweat out”. It may occur as

“bloom” which is the development of tiny crystals on the surface or slightly under the surface. e.g. the combination with a primary plasticizer to achieve the needed compatibility. Sometimes they are used alone to lower the cost, but they are also used to achieve some physical or chemical property that cannot be readily developed without them. They are called extenders (e.g., chlorinated hydrocarbons). The boundary between the

primary and secondary plasticizers is not clear and depends on the concentration and ambient conditions. In PVC, phthalates such as dioctyl phthalate and butyl benzyl phthalate show satisfactory compatibility under almost all environments²⁸ aliphatic dicarboxylic acid esters. Secondary plasticizers are normally used in.

A depression of the glass transition temperature (T_g) of the polymer usually accompanies the addition of such plasticizers^{26,35,36}. Such a depression depends on the type and concentration of the plasticizer used. Pochan and coworkers³⁷ reported the effect of plasticizers on the dynamic relaxations of polycarbonate. An investigation²⁶ on roll extruded, plasticized amorphous poly(styrene-co-n-butyl methacrylate) with low glass transition temperatures showed that above a certain limit of compatibility, the excess of plasticizer was dispersed as crystallites, which act as particulate fillers. In the absence of such crystallites, the plasticizers can be viewed as a molecular dispersion. There is also a tendency towards phase separation of the plasticizer after annealing the plasticizer/polymer composites at a temperature close to the T_g of host polymer³⁵. It has been reported that the relative molecular conformations of the polymer and plasticizer molecules can affect the morphology and rheological behaviour of the composite³⁸. The relative stiffness and polarity of the polymer and the plasticizer also has profound

influence on resulting properties, if it acts as a plasticizer or an antiplasticizer e.g. there is a decrease or an increase in tensile strength and modulus. Belfiore et.al. reported that certain plasticizers e.g., di-n-butyl phthalate act as an antiplasticizer at low concentration and as a plasticizer at higher concentrations³⁹. Studies on several polycarbonates by Jackson and Caldwell^{40,41,42} showed that certain small molecules, in a definite range of concentration and temperatures, acting as antiplasticizers, have complex effect on mechanical properties of the host polymer. Whereas the glass transition temperature (T_g) of the macromolecule is depressed by the diluent, an increase in Young's modulus of elasticity is observed.

Since the polar bonding only retards molecular motion to give antiplastization rather than stopping it absolutely, antiplastization effects are subject to time-temperature superposition principle. Mascia⁴³ has shown that PVC containing 10% of tricresyl phosphate (TCP) is antiplasticized below 30 °C but is plasticized above that temperature. Below 38 °C it is rigid and does not show creep in the first hour or two. But in longer test times, it shows creep with increased compliance, as does plasticized PVC.

In addition, some plasticizers have been shown to be efficient promoters of polymer crystallization. The efficiency however depends critically on the nature and the concentration of the plasticizer. Conix and Jeurissen studied the influence of tricresyl phosphate (TCP) plasticizer on the crystallization behaviour of PC and found that 3 to 5% of TCP markedly increases the crystallization rate⁴⁴. The use of plasticizers including tritolyl phosphate, pentaerythritol tetranonanoate, and trimellitic acid –tridecyloctyl ester to aid in the crystallization of polycarbonate has been demonstrated. The use of 10%

trimellitic acid tridecyloctyl ester reduces the crystallization half time at 170 ° C to 100 min from 300 h for the unplasticized material^{45, 46}.

1.3 Objective and Thesis Overview

Organo-electronic devices such as photoreceptors, organic light emitting diodes and electrochromic devices are generally multilayered composites. Such organic devices are normally prepared as a binary solution, consisting of charge transporting or acceptor molecules dispersed in a polymer binder⁴⁷.

Figure 1.5 Schematic of a typical photoreceptor

The hole transporting molecule TPD is known to be an electron donor and is employed in organic photoreceptor in the charge transport layer (CTL). The polycarbonate is generally used as the binder polymer. It has also been found that the phase separation and crystallization of TPD occurs if the sample were annealed at temperatures close to the T_g of host polymer. The thickness of the CTL of the photoreceptor is in the range of 10-40 μm ⁴⁷. As shown in Figure 1.5 this CTL layer is confined between the two soft surfaces.

The main objective of the present work is to study the effect of annealing time, temperature and film thickness on the morphology and phase separation of plasticizer/polymer composites in confined and unconfined states.

In the present work, we have made a “model” of CTL layer of photoreceptor in which a plasticizer was used instead of TPD with polycarbonate and the plasticizer/polycarbonate composite films was confined between the two hard surfaces instead of soft surfaces.

The confinement of the composite film between the hard or soft surfaces leads to the behaviour which is different from that of the unconfined.

Chapter 2 entitled Materials and Methods presents the physical properties and application of the polymer and plasticizers used in the present study, procedure used for sample preparation and different methods used for the characterization of the polymer composite film. Chapter 3 presents the results for DPTP and BPAPC composites and discussion of the results thus obtained. Chapter 4 presents the results for DIP and BPAPC composites and discussion of the results obtained. Chapter 5 presents the main conclusions from the present work and finally, Chapter 6 lists key recommendations for the future work.

1.4 References

- 1 Binder, K.; De Gennes, P. G.; Grest, G.S. et.al. *Adv Polym. Sci*, **1999**, 138, 107-147
- 2 Wang, Qi.; Zhou, Zhiyin; Song, Lixin; Xu, Hong; Wang, J. *Poly. Sci. Part A: Poly. Chem.*, **2004**, 42, 38-43
- 3 Giannelis, E.P. *Appl. Organometal. Chem.* **1998**, 12, 675-680
- 4 Kuchta, F-D.; Lemstra, P.J.; Keller, A.; Batenburg, L.F.; Fischer, H.R.; *Mat. Res. Soc. Symp. Proc.* **2000**, 628, CC11.12.1-CC11.12.7
- 5 Tonelli, A.E. *Polym. International*, **1997**, 43, 295-309
- 6 Bullions, T.A.; Wei, F.E.; Porbeni, F.E. et. al. *J. Polym. Sci.: Part B: Polym. Phys.*, **2002**, 40, 992-1012
- 7 Cardin. D.J. *Adv. Mater.*, **2002**, 14(8), 553-563
- 8 Forrest J.A.; Veress-Dalnoki K.; Dutcher J.R.; *Phys. Rev. E*, **1997**, 56(5), 5705-5716
9. Suh, K.Y.; Hong, H.L. *J. Polym. Sci. : Part B: Polym Phys*, **2001**, 2217-2224
- 10 Veress- Dalnoki , K.; Nickel B.G.; Dutcher J.R. *Phys. Rev. Let.*, **1999**, 82(7), 1486-1489
- 11 Forrest, J.A.; Veress-Dalonki, K.; Stevens, J.R.; Dutcher, J.R. *Phys. Rev. Lett.*, **1996**, 77(10), 2002-2005
- 12 Keddie, J.L.; Jones, R.A.; Cory, R.A. *Faradays Discuss.*, **1994**, 98, 219-230.
- 13 Keddie J.L.; Jones A.L.; Cory R.A. *Europhysics Letters*, **1994**, 27(1), 59-64
- 14 Kawana, S.; Jones, R.A. *Phys. Rev. E* **2001**, 63, 021501-6
- 15 Van Zanten, J.H.; Wallace, W.E.; Wu, W.I. *Phys. Rev. E*, **1996**, 53(3), R2053-

- 16 Pham, J.Q.; Green, P.F. *Macromolecules*, **2003**, 36, 1665-1669
- 17 Dalonki- Veress, K.; Forrest, J.A.; Stevens, J.R. *Physica A*, **1997**, 239, 87-94
- 18 Fryer, D.S.; Nealey, P.F.; Pablo, J.J. *Macromolecules*, **2000**, 33, 6439
- 19 Schuller, J.; Richert, R.; Fischer, E.W. *Phys. Rev.*, **1995**, B52, 15232
- 20 Pan, Q.; Composto, R.J. *Mat. Res. Soc. Symp. Proc.*, **1995**, 366, 27-32
- 21 Veress-Dalnoki, K.; Forrest, J.A.; Dutcher, J.R.; *Physical Review E*, **1998**, 57(5), 5811-5817
- 22 Koneripalli, N.; Levicky, R.; Bates, F.S. *Langmuir*, **1996**, 12, 6681-6690
- 23 Lmbooy, P.; Russel, T.P.; Kellogg, G.J. et. al. *Phys. Rev. Lett.*, **1994**, 72, 2899
- 24 Koneripalli, N.; Singh, N. Levicky, R.; Bates, F.S.; Gallagher, P.D.; Satija, S.K. *Macromolecules*, **1995**, 28, 2897-2904
- 25 Sears J.K.; Darby, J.R. *The Technology of Plasticizers*, Wiley, New York, **1982**
- 26 Alexandru, L.; Zamin, J.; Sundararajan, P.R. *J. Appl. Polym. Sci.*, **1991**, 43, 2259-2266
- 27 Shah ,B.L.; Shertukde, V.V. *Popular Plastics & Packing*, **2001**, 65-72
- 28 Seras J.K.; Darby, J.R. Solvation and Plasticization , in *Encyclopedia of PVC*, **1986**, 2nd Edition, 435-554
- 29 Immergut, E.H.; Herman, M.F. Principles of Plasticization, in *Plasticization and Plasticizer Process*, R.F. Gould, Ed. ACS advances in chemistry series No. 48, American Chemical Society, **1965**, 1-25
- 30 Jenkins, A.D. *Polymer science: a material science handbook*, North- Holland publishing company-Amsterdam. London, **1972**

-
- 31 Gachter, R.; Muller, H. *Plastics additives Handbooks: Stabilizers, Processing aids, Plasticizers, Fillers, reinforcement, colorants of thermoplastic*, Munich, New York, **1990**
- 32 Papakonstantinou, V.; Papaspyrides, C.D. *J. Vinyl Technology*, **1994**, *16*, 192-19632
- 33 Papaspyrides, C.D.; Tingas, S.G. *J. Appl. Polym. Sci.*, **2001**, *79*, 1780-1786
- 34 Audouin, L.; Dalle, B.; Metzger, G.; Verdu, J. *J. Appl. Polym. Sci.*, **1992**, *45*, 2091-2096
- 35 Ljungberg, N.; Wesselen, B. *J. Appl. Polym. Sci.*, **2002**, *86*, 1227-1228
- 36 Onu, A.; Legras, R.; Mercier, J.P. *J. Polym. Sci.*, **1976**, *14*, 1187-1199
- 37 Pochan, J.M.; Hinman, D.F.; Turner, S.R. *J. Appl. Phys.*, **1976**, *47*, 4245-4250
- 38 Drappel, S.; Sundararajan, P.R.; Rudin, A. *Polymer*, **1997**, *38*(6), 1259-1272
- 39 Belfiore, I.A.; Henrichs, P.M.; Massa, D.J. et. al. *Macromolecules*, **1983**, *16*, 1744-1753
- 40 Jackson, W.J.; Caldwell, J.R. *Adv. Chem. Ser.*, **1965**, *48*, 185-195
- 41 Jackson, W.J.; Caldwell, J.R. *J. Appl. Polym. Sci.*, **1967**, *11*, 211-226
- 42 Jackson, W.J.; Caldwell, J.R. *J. Appl. Polym. Sci.*, **1967**, *11*, 227-244
- 43 Mascia, L. *Polymer*, **1978**, *19*, 325-329
- 44 Conix, A.; Jeurissen, L. Plasticization of bisphenol A polycarbonate, in *Plasticization and Plasticizer Process*, R.F. Gould, Ed. ACS advances in chemistry series No. 48, American Chemical Society, **1965**, 172-184
- 45 Gallez, F.; Legras, R.; Mercier, J.P. *J. Polym. Sci. B: Polym. Phys.*, **1976**, *14*, 1367- 1377

-
- 46 Legras, R.; Mercier, J.P. *J. Polym. Sci. B: Polym. Phys.*, **1977**, 15, 1283-1289
- 47 Khan, F.; Hor, Ah-Mee ; Sundararajan, P.R. *J. Phys. Chem. B*, **2004**, 108, 117-126

Chapter 2

Materials and Methods

In order to study the effect of annealing on the morphology of plasticizer/polymer composites in both the confined and unconfined states, films were prepared with varying concentrations of the plasticizers diphenyl terephthalate (DPTP) and diphenyl isophthalate (DPIP) with the polymer bisphenol A polycarbonate (BPAPC). These were annealed at different temperatures and for various times. In addition, the influence of film thickness i.e, thick and thin films on the morphology of the plasticizer/ polymer composites was also studied.

This chapter discusses the physical properties and applications of the polymer BPAPC and the plasticizers DPTP and DPIP used in the present study. Further, the methods for film preparation, the measurement of the thickness of the film, film confinement and measuring the evaporation of the plasticizer are presented. The techniques used for characterization of the polymer composites, for example, Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), Optical Microscopy and Fourier Transform Infrared Spectroscopy (FTIR) are described briefly.

2.1 Materials

2.1.1 Bisphenol-A-Polycarbonate (BPAPC)

In the present study, the polymer BPAPC was used as the host polymer because of the activities in our group using this polymer, for studies on the morphology of model optoelectronic devices. The sample of BPAPC was supplied by Xerox Research Center of Canada located in Mississauga, Ontario, Canada and had an Mw of 250,860 and a polydispersity of 1.75 (as measured by gel permeation chromatography (GPC)) The glass transition temperature (T_g) was 154 °C . The chemical structure of BPAPC is shown in Figure 2.1

Figure 2.1 Chemical structure of Bisphenol A Polycarbonate

BPAPC which is an engineering thermoplastic material, derives its name from the carbonate group in its backbone chain. It is usually synthesized from bisphenol A, and phosgene. Aromatic BPAPC usually has high impact toughness, high glass transition and high optical clarity^{1,2}. The high toughness of BPAPC allows large scale deformation compared with other polymers such as polystyrene or PMMA. BPAPC also has good dimensional stability which permits it to retain its shape in a variety of conditions, high heat resistance and excellent processability³.

The combination of these properties leads to many beneficial, and unique applications in such diverse areas as reprographics, the electronic sector, domestic appliances (e.g. crisper trays in refrigerator), office equipment (e.g. portable computers, projectors), optical storage media (e.g. compact discs and optical discs), the construction industry (e.g. in windows, bathroom stalls), automotive engineering (e.g. headlamp covers), food and beverage containers, medical devices (e.g. syringes, medical tubing's such as kidney dialysis tubing, pacemaker component) and in leisure and safety equipment³. Polycarbonate films are used as high performance decorative information carriers in many industries, for applications including cheque and service cards, keyboard covering films, packing sheets and insulating component⁴.

Several polymer blends of polycarbonate have been developed as engineering plastics, the most common being those with poly(butylene terephthalate) to create alloys that feature improved chemical resistance⁵. These products are heavily oriented towards the automotive market areas in which gasoline resistance is required. Polycarbonate- ABS (acrylonitrile –butadiene-styrene) blends are utilized to make products that have better weatherability than the polycarbonate yet better physical properties than ASA. Primary application areas are in automotive and construction industries⁵.

2.1.2 Plasticizers

The two plasticizers selected for this study are diphenyl terephthalate (DPTP) and diphenyl isophthalate (DPIP) because they are solid at the room temperature and their crystallization behaviour can be characterized. Both DPTP and DPIP plasticizers with Mw= 318.32 were received from the K & K laboratories, Ohio, USA and had melting

temperatures of 198 °C and 139 °C respectively as determined by differential scanning calorimetry (DSC). The chemical structures of these plasticizers are shown in Figures 2.2 and 2.3.

Figure 2.2 chemical structure of diphenyl terephthalate (DTPP)

Figure 2.3 Chemical structure of diphenyl isophthalate (DPIP)

Phthalate plasticizers represent by far the largest plasticizer group and have 86% share of the world plasticizer market and are produced by the reaction of phthalic anhydride with alcohol⁷. The benzene ring based structure of phthalates helps to reduce their viscosity and also make them stable against degradation.

Phenyl phthalate is used as processing aid for rigid PVC as well as in rigid PVC foams. The film forming and flexibility properties imparted by phthalates are useful in paints, inks, adhesives and insulating properties in electrical cabling and capacitors. In personal care products, phthalates provide flexibility, impart an oily” moisturizing” film, and help

dissolve and fix other cosmetic ingredients. Phthalates are widely used in children's toys, flooring, fabrics, garden hoses, food wraps, food container and other consumer items⁸.

2.2 Film Preparation

This section describes the preparation of thick and thin films. In general, films of about 20 μm thickness are referred to as thick films and those that are about 700 nm are referred to as thin films.

2.2.1 Thick Film (~20 μm thickness)

The plasticizers were incorporated in the polymer matrix by solution blending in a common solvent (e.g. dichloromethane) of laboratory grade at the concentrations of 5, 10, 15 by weight percent (wt %). This procedure assured a molecular dispersion since both the components were soluble in the solvent. Throughout this study, films were coated on glass substrate using an electrically driven film coater and were dried at a very low rate of the solvent evaporation at ambient conditions for 24 h and then in an vacuum oven at room temperature (20 – 25 °C) for 24 hours.

2.2.2 Thin Films (~700 nm)

Thin films were prepared by the dip-coating technique. A dip coater (Figure 2.4) with a controlled 115 volt direct current (V.D.C) motor with variable speed was built in-house. The V.D.C motor enables vibration free immersion of the substrates into vessels and withdrawal. Three concentrations (5%, 10% and 15% by weight) of plasticizers in polycarbonate were used. The plasticizers were incorporated in the polymer matrix by solution blending in a common solvent (e.g. dichloromethane) of laboratory grade.

Figure 2.4: Dip coater

The dip-coating procedure used was as follows:

- (a) A microscopic slide, electrically driven at a speed of 0.45 cm/sec was dipped into the solution and held in it for 1min.
- (b) The slide was raised from the solution at a speed of 0.45 cm/sec. The entire dip-coating procedure was executed by covering the system with an aluminum foil.
- (c) The films were dried at a very low rate of the solvent evaporation at ambient conditions for 24 h. The solution on one side of the glass substrate was removed by rinsing with dichloromethane and then the films were dried in an oven under vacuum for 24 hours.

2.3 Measurement of the Thickness of the Films

2.3.1 Thick Film (~20 μm thickness)

The thickness of the film was determined from scanning electron (SEM) micrographs. For the SEM method, samples were cut and then fixed for viewing edgewise on a standard SEM puck. From the digital SEM image (Figure 2.5), the thickness can be easily measured along the cut edge of the film. Usually at one film edge, 4 to 5 measurements were made by using “Northern Eclipse ver.6.0” software (see below) and the average thickness (μm) was calculated. Thickness of the dried films was calculated to be 15-20 μm .

Figure 2.5: SEM micrograph showing the edge of the composite film

2.3.2 Thin Film (~700 nm)

Thickness of the thin films was determined by using the Alpha-Step 200 Tencor instrument. The Alpha- Step 200 CPU automatically controls leveling and the

measurement. The monitor displays both the actual scan, via the high power video microscope, and graphic charts of the scan profile.

The average thickness of the film was calculated by measuring the thickness at 5 different places on the same film.

2.4 Confined and Unconfined Configurations

In order to study the morphology in the confined state, the composite films were confined between two microscope glass slides. The two slides were held together with paper clips on both sides to enhance the contact between the two slides and no other external pressure was applied. Likewise, to study the morphology in unconfined state films were placed on the top of single microscope glass slides (Figure 2.6). Films in both confined and unconfined states were annealed in an oven at predetermined temperatures (120-140 °C) and times (0.5-4.0 h).

Figure 2.6 Schematic for the (a) Confined state, (b) Unconfined state

2.5 Evaporation Measurements

To measure the extent of loss of the plasticizer by evaporation from the composite film and the bulk, an enclosure was used. The enclosure consisted of two microscopic slides separated by a hard paper with a vertical space of 1.5 cm on all sides (Figure 2.7). The sample was placed on the bottom slide and the evaporated material was collected on the top slide. All the samples were annealed for 3h at various temperatures (90°C to 140 °C) on a digital hot plate. While annealing, the hot plate was covered with aluminum foil throughout the experiment. The weight loss was calculated using the following formula:

$$\%WeightLoss(WL) = \frac{W_1 - W_2}{W_1} \times 100 \quad (2.1)$$

$$Normalized\ weight\ loss = WL \times \frac{100}{amount\ of\ DPTP\ in\ BPAPC} \quad (2.2)$$

where, W_1 is the initial weight of the sample before annealing and W_2 is the final weight of the sample after annealing.

Figure 2.7 Confined device used to measure % weight loss of plasticizer from the composite film

2.6 Characterization Methods

This section describes the various methods that were used for the characterization of the composite films. For example, DSC was used to determine the thermal properties, TGA was used to measure weight loss, XRD was used to determine the d-spacings of the crystalline material, optical microscope along with an image analysis software was used to measure the crystal area distribution, and finally the molecular modeling software (HyperChem) was used to calculate the relative energies of non-bonded interactions in the molecules.

2.6.1 Thermal Analysis

Differential scanning calorimetry (DSC) is the widely used of all thermo analytical techniques. It is used to characterize phase transitions of materials caused by thermal energy and is applicable to several types of materials such as polymers, organic materials, metals, ceramics and composites.

The DSC technique measures the amount of energy (or heat) absorbed or released by a material as it is either heated, cooled or maintained at a constant (isothermal) temperature. The DSC instrument monitors the quantitative heat flow as a direct function of the sample temperature. This heat flow/temperature data provides valuable information of physical/chemical properties of the materials, for example the glass transition temperature (T_g), the crystalline melting temperature (T_m), the crystallization temperature (T_c) and the specific heat capacities (C_p). Polymorphic transitions are also detectible⁹

Thermal analysis was carried out using a Du-Pont 910 differential scanning calorimeter (DSC) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The DSC instrument was calibrated for temperature and energy with indium and tin reference samples. DSC thermograms were recorded with about 7-10 mg of sample, under nitrogen flow (50~70 mL/min)

Thermogravimetric analysis (TGA) method measures the change in sample mass as a function of temperature and time under controlled atmosphere¹⁰.

The thermogravimetric analysis (TGA) was carried out using a Seiko 2200 TG at a heating rate of $10\text{ }^{\circ}\text{C/min}$ from $25 - 550\text{ }^{\circ}\text{C}$ under nitrogen flow (50 mL/min). The onset temperature for decomposition for all the samples was taken at 0.5% weight loss.

2.6.2 Powder X-ray Diffraction

Powder X-ray Diffraction is the primary technique used to determine the d –spacing, degree of crystallinity, area of the crystals in the crystalline polymeric materials and several other types of materials such as organic materials and minerals. Polymorphism can also be detected by this technique.

X-rays are only a small part of the electromagnetic spectrum with wavelengths (λ) ranging from 0.002 nm to 10nm. X-Rays used to study crystals have λ on the order of 0.1 nm to 0.2 nm (e.g., Copper $K\alpha = 0.15418\text{ nm}$)

Diffraction of an x-ray beam striking a crystal occurs because the λ of the x-ray beam is similar to the spacing of atoms crystalline state (0.1-10 nm). When an x-ray beam encounters the regular, 3-D arrangement of atoms in a crystal, most of the x-rays will

destructively interfere with each other and cancel each other out, but in some specific directions they constructively interfere. It is these diffracted x-rays that produce the characteristic x-ray diffraction patterns that is used for material identification¹¹.

W.L. Bragg (early 1900's) demonstrated that measurement of diffraction yielded information on the arrangement of atoms within the unit cell. Further, he treated the diffraction of X-rays by crystals as 'reflection' from planes of atoms in the lattice (Figure 2.8) which led to the formulation of Bragg's law:

$$2d \sin\theta = n\lambda \quad (2.3)$$

Figure 2.8 (a) Schematic of the unit cell, lattice planes and the d spacing;
(b) Bragg construction illustrating the principle of diffraction where d is the spacing between two atomic planes.

where λ is the wavelength of X-ray radiation, d the distance between atomic planes, θ the angle of incidence of the x-ray beam on the atomic planes and n (1,2,3 ...,n) is the order of the reflection. In real cases, higher order reflections corresponding to $n>1$ are extremely weak in intensity. Hence only those corresponding to $n=1$ are observed. Hence the above equation reduces to

$$2d \sin\theta = \lambda \quad (2.4)$$

For diffraction to occur, the path difference between the two rays should be an integral multiple of the wave length λ . For a given λ of incident x-rays and interplanar spacing (d) in a crystal, only specific θ angles will satisfy the Bragg equation^{12,13}.

Powder X-ray Diffraction (XRD) is a technique in which a collimated beam of nearly monochromatic X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. In practice, this can be applied to films as well. The sample-diffracted X-rays are then collected to reveal information about the structural present in the sample.

X-ray diffraction data were collected using a Philips automated powder diffractometer Model PW 1710. Nickel-filtered Cu K α radiation ($\lambda = 0.154$ nm) was used at 40 kV and 40 mA. The MDI Data scan 3.2 software (Materials Data Inc., Livermore, CA) was used for data collection. The d - spacings were analyzed using MDI Jade 5.0 software.

2.6.3 FTIR Spectroscopy

Infrared spectroscopy is one of the most often used spectroscopic tools for the study of characterization of polymers. FTIR can be used for the determination of crystallinity, geometric isomerism, characterization of polymer blends i.e. whether they are compatible or not, the molecular level interaction in polymer composites¹⁴, etc.

Molecules consist of atoms held together by valence forces. These atoms vibrate by thermal energy, giving every molecule a set of resonance vibrations analogous to the resonance modes of mechanical structures. Accordingly, when impinging radiation passes through the material, it is absorbed only at frequencies corresponding to molecular modes of vibration, and a plot of transmitted radiation intensity versus frequency shows the absorption bands. IR spectroscopy measures the vibrational energy level of molecules. The characteristic band parameters measured in IR spectroscopy are frequency (energy), intensity, band shape (environments of bonds), and the polarization of various modes, that is, transition- moment direction in the molecular framework¹⁴.

The position of an infrared absorption band is specified in frequency units by its wavenumber measured in reciprocal centimeter (cm^{-1}), or by wavelength measured in micrometer)

$$\bar{\nu} = \frac{1}{\lambda} \text{ (with } \lambda \text{ in cm)} \quad \text{or} \quad \bar{\nu} = \frac{10,000}{\lambda} \text{ (with } \lambda \text{ in } \mu\text{m)} \quad (2.5)$$

In IR spectra, the region from $4000 - 1400 \text{ cm}^{-1}$ gives the information about the functional group present in the structure. The region from 600 cm^{-1} – 1400 cm^{-1} is called the fingerprint region because the pattern of absorption in this region is unique to any particular compound¹⁵. The bands in this region can be used with great utility to assign the ring substitution pattern¹⁶.

FTIR spectroscopic measurements were carried out at ambient conditions using a Michelson M129 BOMEM Fourier Transform Infrared (FTIR) spectrometer. All the data were collected using BOMEM GRAMS/386 software. The spectra of DPTP and DPIP were obtained in the form of transparent KBr pellets. The FTIR spectra of the polymer and composites were taken in the film form. A background spectrum was taken for each experiment with the identical sample holder.

2.6.4 Optical Microscopy

A Zeiss Axioplan 2 imaging universal optical microscope with the Q-imaging Retiga digital camera was used to record optical micrographs. All the optical micrographs were taken in transmission mode. The average area of crystals formed as a result of annealing induced phase separation in confined and unconfined state was calculated using the image analysis “Northern Eclipse ver.6.0” software.

In order to select the crystals for the calculation of the average area of crystals, a threshold function was used. This function is used to select objects in an image by specifying ranges(s) of values (from 116 to 255 in the thick film and from 90 to 255 in the thin film) that differentiate it from rest of the image.

Figure 2.9 An example of optical micrographs showing the effect of threshold function of a set of particles (taken from Nothern Eclipse image analysis version 6.0 software)

For the purpose of averaging, the images were captured from five different areas for each sample and the average area was calculated using

$$\text{Average area} = \frac{\sum N_i X_i}{\sum N_i} \quad (2.6)$$

Where, N_i is the number of crystals in the average area X_i .

2.7 Molecular Modeling:

Simple molecular modeling was performed using Hyper Chem. software (version 6.01). Models of plasticizers, polymer (12 units) were generated using the HyperChem software. In order to determine relative energy of the structure, geometry optimization was done using MM+ force field.

2.8 References

- 1 Schnell, H. Chemistry and Physics of Polycarbonates, Interscience Publisher: A division of John Wiley & Sons, New York. London. Sydney, **1964**
- 2 Madkour, T.M. Polymer Data Handbook, Mark J.E. Ed., Oxford University Press, New York, **1999**, 363-367
- 3 Sehanobish K.; Pham H.T.; Bosnyak C.P. *Encyclopedia of Polymer Science and Engineering* ,Wiley-Interscience, New York, 2nd ed , **1996**, 5697-5708
- 4 Pakull P.; Grigo D. *Rapra Review Reports*, **1991**, 4(6), 21
- 5 Legrand D.G.; Bendler J.T. Handbook of Polycarbonate Science and Technology ,Marcel Dekkar, Inc., **2000**, 314-315
- 6 Gachter, R.; Muller, H Plastics additives Handbooks: Stabilizers, Processing aids, Plasticizers, Fillers, Reinforcement, Colorants of thermoplastic, Munich, New York, **1990**, 369
- 8 www.noharm.org/library/docs/Phthalate_Report.pdf
- 9 Edith, T. A. Thermal characterization of polymeric materials, San Diego : Academic Press, **1997**
- 10 Haines P.J. Principles of Thermal Analysis and Calorimetry, The Royal Society of Chemistry, **2002**
- 11 <http://www.csam.montclair.edu/earth/eesweb/gorring/geos443/443notes/xray.html>
- 12 Alexander, L.E. X-Ray Diffraction Methods in Polymer Science, Wiley-Interscience, New York, **1969**
- 13 Meyer, F.W. JR. Textbook of Polymer Science, Wiley- Interscience, New York, **1984**

-
- 14 Koenig, J.L. Spectroscopy of Polymers, American Chemical Society,
Washington, DC **1992**
 - 15 Kalsi P.S. Spectroscopy of organic chemistry, New Age International
LTD, **2000** , 4th Ed., 60-63.
 - 16 Pavia D.L.; Lampman G.M.; Kriz G.S. Introduction to Spectroscopy, Harcourt
College Publisher, **2001**, 3rd Ed., 41

Chapter 3

DPTP and BPAPC Composites

The effect of annealing on the morphology of the DPTP/BPAPC composites will be discussed in this chapter. The hard surface confinement leads to a behaviour different from that of the films annealed without. As mentioned before, polycarbonate was chosen as the host polymer because of the activities in our group using this polymer, which is used as a binder in optoelectronic devices. The DPTP was chosen since it is solid at room temperature and the crystallization behaviour can be characterized. In addition, it does not promote the crystallization of polycarbonate, except in rare instances as will be discussed below. Glass microscope slides were used for confinement, since it is the common practice in the study of materials using optical microscopy. The discussion below will show that the use of such a confinement by a glass surface leads to phase separation behaviour which is different from that of an unconfined film. Differences were also found between the morphologies of thick ($\sim 20\mu\text{m}$) and thinner films ($\sim 700\text{nm}$). We discuss the (1) depression of the T_g , (2) possible molecular level interactions between DPTP and BPAPC (3) the recovery of T_g upon annealing, (4) the morphology of the phase separated DPTP and (5) the sublimation of DPTP. Throughout this chapter, the composition of the films is denoted by X/Y where X is the wt % of DPTP and Y is that of BPAPC.

3.1 Thick Film

3.1.1 Effect of DPTP on the T_g of BPAPC in as Prepared Solvent Cast Films

In this case, the films were approximately 20 μm in thickness. Differential scanning calorimetry (DSC) analysis of DPTP showed an endothermic melting peak at approximately 198°C, with a heat of fusion of 38.9 cal/g. Further, DSC thermograms for the solvent cast film of BPAPC showed the glass transition temperature (T_g) at 154° C.

The variation of T_g of BPAPC, with the addition of DPTP at different concentrations is shown in Figure 3.1a for the as prepared solvent cast films. The depression in T_g i.e.

$$\Delta T_g = T_g \text{ of (polycarbonate)} - T_g \text{ (composite)} \quad (3.1)$$

is also shown in this Figure 3.1b. It is seen that the T_g of the polymer in the composite is significantly lowered with the addition of DPTP. The T_g of polycarbonate is depressed by as much as 25 °C with 5% of DPTP, and 43 °C with 10 %. With 15%, a broad melting endotherm was observed (Figure 3.2) and it was difficult to identify the T_g from the first scan. Hence the T_g shown in Figure 3.1 T_g for DPTP/BPAPC: 15/85 is from the second thermal scan. A number of studies have analyzed the dependence of T_g depression on the type and amount of the plasticizer^{1,2,3,4}. This demonstrates that the plasticization takes place in these composites. In the DSC thermograms (Figure 3.2) an endothermic peak was observed at 154.5°C for DPTP/BPAPC: 10/90 and at 151.4 °C (1st scan) for DPTP/BPAPC: 15/85 films, which is attributed to the melting of the DPTP. This indicates that the melting temperature T_m of DPTP is depressed by 44-46 °C when dispersed in BPAPC. Similar depression of T_m of the small molecule has been noted in

Figure 3.1 (a) The variation of T_g of the polycarbonate with various concentrations of DTP, (b) The depression of ΔT of the T_g with various concentrations of DTP

Figure 3.2 Overlay of DSC thermograms of “as prepared” DTP/BPAPC composite films

the case of the charge transport molecule TPD when dispersed in BPAPC⁵, diphenyl terephthalate and diphenyl isophthalate when dispersed in poly(styrene-co-n-butyl acrylate)¹, and a liquid crystalline polymer⁶. This could be attributed to the imperfection of ordering in these crystals¹. The result in Figure 3.2 suggests that DPTP phase separates. The fact that even in these cases the T_g of BPAPC is lowered can be explained by considering that only a fraction of DPTP acts as plasticizer and the rest separate into distinct phase¹. In contrast, no phase separation occurs in as-prepared films of TPD/BPAPC, upto 50% concentration of the small molecule. The absence of a melting endotherm in DPTP/BPAPC: 5/95 indicates the compatibility of plasticizer with BPAPC in this composition. Thus, the compatibility limit between DPTP and BPAPC is low. Similar was the case when DPTP was added to poly(styrene-co-n-butyl acrylate)¹

It has been shown that the depression in T_g is not only due to the increase in the free volume of polymer by addition of small molecule but also due to the molecular level interaction⁵. When a small molecule is added to a polymer, it could influence the polymer at two different levels. It could intercalate at the domain level or at the molecular level (Figure 3.3). The domain level corresponds to about 100 nm, characteristic of the amorphous domain size (that could be measured by small angle scattering techniques) whereas the molecular level involves interactions on the scale of <1 nm, the typical distance between the chains themselves. Such a molecular level interaction was indicated in the case of TPD/BPAPC composites in which significant shifts in infrared frequencies in the BPAPC spectrum were observed and these shifts increased with the concentration of TPD in the composite⁵.

Figure 3.3 Schematic of two different levels: (a) The domain level,
(b) The molecular level

Figure 3.4 shows the FTIR spectra for as prepared composite film DPTP/BPAPC: 10/90 and 15/85 along with the spectra of pure DPTP and BPAPC. The bands at 1602 and 1505 cm^{-1} in the BPAPC spectrum corresponds to the C=C aromatic ring stretch^{5,7}. No change in the absorption frequency of these bands was observed in the DPTP/BPAPC composites for all concentrations. The peaks in the region $\geq 3000 \text{ cm}^{-1}$ correspond to aromatic CH stretch, and those for the =C-O stretch of BPAPC occur at 1000-1300 cm^{-1} . No shift in the absorption frequency for the bands were observed in this region in any of the above composite film with respect to DPTP and BPAPC.

In addition, the band at 1731 cm^{-1} with DPTP arises due to the conjugation of C=O with phenyl ring stretch. With DPTP/BPAPC: 15/85 no shift in absorption frequency of this band was observed. However, with DPTP/BPAPC: 5/95 and 10/90 this band shifts to

1740 cm^{-1} which indicates an increase in the C=O bond strength. This shift in frequency can be attributed to the interaction between the C=O groups of BPAPC and of DPTP. Since the concentration of BPAPC in DPTP/BPAPC: 5/95 and 10/90, is higher than in DPTP/BPAPC: 15/85 the shift in DPTP/BPAPC: 5/95, 10/90 is more pronounced. In other words, when the concentration of DPTP is low, the interaction between DPTP and BPAPC is more significant than that between the DPTP molecules, and these molecules are influenced by the C=O dipoles of BPAPC. With an increase in concentration, each DPTP molecule is increasingly surrounded by its own kind, and the influence of BPAPC is reduced. Such a behaviour was discussed for the case of TPD/PS composites⁸. The DPTP absorption band at 719 cm^{-1} , corresponding to the out of plane vibration of the aromatic ring, shifted to 724 cm^{-1} in DPTP/BPAPC : 5/95, 10/90 while no shift in the absorption frequency for this band was observed with DPTP/BPAPC :15/85

To examine if there is a molecular level interaction, a simple molecular modeling was performed. Models of a BPAPC chain (12 units) and DPTP were generated and energy minimized using Hyperchem software (Figure 3.5). These were then placed in close proximity and energy minimized. This corresponds to a weight fraction of 10% of DPTP in BPAPC (Figure 3.5). The energy of DPTP, the 12-mer of BPAPC and DPTP/BPAPC were 12.9, 98.7 and 97 kcal mol^{-1} respectively. The energy of BPAPC was reduced by just 2 kcal/mol (i.e., <0.2 kcal/mol/monomer) . The reduction in energy is not significant as in the case TPD/BPAPC⁵. The electrostatic component of the energy decreases from -4.2 to -5.1 kcal/mol, indicating dipole -dipole interaction between the C=O groups of DPTP and BPAPC. Further, no change in the bond length was observed for DPTP and BPAPC when the two molecules placed together in close proximity. The possible reason

Figure 3.4 FTIR spectra of (a), (c), (e) DTP, BPAPC, and DTP/BPAPC: 15/85; (b), (d), (f) DTP, BPAPC and DTP/BPAPC: 10/90

Figure 3.5 Minimum energy conformations of (a) DPTP, (b) 12-mer of BPAPC and (c) DPTP/BPAPC

could be that the modeling performed here is too simple. Molecular dynamics was not used to relax the molecules.

Although the molecular modeling indicates an interaction between the C=O dipoles of the polymer and DPTP (as seen from the small shifts in the corresponding IR frequencies) it appears that there is no significant interaction such as between the phenyl groups of DPTP and BPAPC. This could be one of the reasons that a phase separation is noted with concentrations as low as 15% of DPTP, whereas no such phase separation occurs upto 50% concentration of TPD in BPAPC.

3.1.2 Effect of Temperature and Time on the Glass Transition Temperature of Solvent Cast DPTP/BPAPC Composites Films

Composite films were annealed both in confined and unconfined states at a temperature lower than the T_g of polycarbonate i.e. 120, 130 and 140 °C for times ranging from 0.5 to 4.0 h, and the results thus obtained are presented in Tables 3.1 and 3.2 (it should be noted that the T_g reported here is within the range of ± 2 °C with instrumental uncertainty in the measurement of T_g).

Annealing these films at different temperatures results in the crystallization of DPTP to varying degree, as a result of which the T_g of the BPAPC is partially recovered. The extent of recovery depends on the temperature and time of annealing and concentration of the DPTP in BPAPC.

In the confined state, it was observed that the T_g increases with an increase in annealing time up to 0.5 h for DPTP/BPAPC: 15/85 and 10/90 at 120 °C and 130 °C after which no

further significant increase is observed. In contrast, no change in the T_g is observed when the film is annealed at 140 °C (Figure 3.6 and Table 3.1). It is also interesting to note that for DPTP/BPAPC: 15/85 and 10/90 composites, the recovery of T_g decreases with increase in annealing temperature, i.e., the increase in T_g is less when the film is annealed at 140 or 130, than at 120 °C. This is attributed to the presence of the hard wall. The crystals of DPTP are not getting enough space to grow and as a result, the crystals which are a few μm in size melt with increase in annealing temperature and diffuse back into the polymer matrix resulting in the plasticization. Note that an annealing temperature of 130 or 140 °C is close to the melting temperature of DPTP in the matrix. However, with DPTP/BPAPC: 5/95 no change in T_g has been observed with annealing time and temperature (Figure 3.6).

In the unconfined state, in general, the T_g increases with an increase in either annealing time or temperature (Figure 3.7 and Table 3.2). With DPTP/BPAPC: 5/95, and 15/85 no change in T_g is observed upon annealing at 120 °C., and it is small with 10/90. It was observed that upon annealing at 140 °C there is sharp increase in T_g up to 30 min. after which there was no significant change in T_g up to 1 h. There is again a sharp increase in T_g from 2 to 4 h for all concentrations of DPTP/BPAPC. Thus, we see a distinctly different trend in T_g recovery upon annealing in the confined state versus the unconfined. Figure 3.8 shows comparison of T_g between the confined and the unconfined states. It is seen that in the former case, the recovery is less as the annealing temperature is increased, while in the unconfined state, the T_g increases with annealing temperature.

Figure 3.6 Glass transition temperature (T_g) versus annealing time of composite films in the confined state: (a) DTP/BPAPC: 5/95; (b) DTP/BPAPC: 10/90; (c) DTP/BPAPC: 15/85

Table 3.1: DPTP/BPAPC - Results of Thermal Analysis of DPTP/BPAPC: 5/95, 10/90, 15/95 composite films, after annealing at various temperatures and times in the confined state

Annealing Temperature (°C)	Annealing Time (h)	DPTP/BPAPC: 5/95		DPTP/BPAPC: 10/90		DPTP/BPAPC: 15/95	
		T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
As prepared		129.1		113.6	154.5	96.6 (2 nd Run)	151.4
120	0.5	129.3		117.3	156.3	127.5	151.3
	1	129.2		118.9	156.9	126	152.7
	2	128.6		122.8	158.7	126	152.5
	3	129.5		122.1	157.6	126.3	153.6
	4	129.2		122.3	157.8	125.3	153.1
130	0.5	129.7		117.8	157.1	114.2	156.5
	1	129.8		119.1	158.2	116.3	157.3
	2	128.7		119.6	157.8	117.6	158.5
	3	129.0		120.9	158.9	115.3	159.5
	4	129.2		120.3	155.7	117.9	162.5
140	0.5	129.7		113.7	155.2	101.2	162.2
	1	129.7		111.4	154.8	103.7	163.2
	2	129.6		113.8	155.9	100.5	161.6
	3	129.2		113.6	154.9	99.4	162.3
	4	129.2		113.6	155.2	100.5	161.9

Figure 3.7 Glass transition temperature (T_g) versus annealing time of composite films in the unconfined state: (a) DPTP/BPAPC: 5/95; (b) DPTP/BPAPC: 10/90; (c) DPTP/BPAPC: 15/85

Table 3.2: Results of Thermal Analysis of DPTP/BPAPC: 15/85, 10/90, 5/95 composite films, after annealing at various temperatures and times in unconfined state

Annealing Temperature (°C)	Annealing Time (h)	DPTP/BPAPC: 5/95		DPTP/BPAPC: 10/90		DPTP/BPAPC: 15/85	
		T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
As prepared		129.1		113.6	154.5	96.6 (2 nd Run)	151.4
120	0.5	128.8		119.8	156.2	125.3	152.2
	1	129.9		119.8	156.0	126.6	153.1
	2	129.5		122.6	154.6	125.1	152.8
	3	129.8		124.8	156.4	126.8	152.2
	4	128.6		125.6	156.2	126.3	151.8
130	0.5	131.8		119		116.6	160.7
	1	130.8		119.4		116.6	160.0
	2	133.2		121		116.1	158.8
	3	134.2		126.7		119.1	159.6
	4	136.0		128.1		121.9	156.9
140	0.5	131.5		119.1		106.0	159.9
	1	135.3		119.3		107.4	159.4
	2	137.7		126.6		122.8	
	3	140.7		134.3		132.0	
	4	144.5		134.7		131.7

Figure 3.8 Comparison of T_g between confined and unconfined DTPP/BPAPC composite films annealed at 130 and 140 °C.

In the unconfined case, due to crystallization of DPTP upon annealing, there would be depletion of the small molecule in the polymer matrix and this leads to the recovery of the T_g of the host matrix ⁵.

3.1.3 Effect of Annealing Temperature and Time on the Melting point of DPTP in the composites films

A study on the effect of annealing time and temperature on the peak position of the melting endotherm T_m was conducted using DSC. A DSC overlay (Figure 3.2), of the as-prepared films of DPTP/BPAPC: 10/90 and 15/85 shows a distinct melting peak due to DPTP. It was found that the melting point of the plasticizer remains approximately 46 °C less than that of the pure plasticizer ($T_m = 198$ °C).

In the confined state with DPTP/BPAPC: 15/85 (Figure 3.9 and Table 3.1) T_m increases with an increase in temperature. There is no significant change in T_m is observed with annealing time. In the as prepared film, the T_m was found to be 151.4 °C which increases to 163 °C with annealing temperature. With DPTP/BPAPC: 10/90 there is a modest increase in T_m with annealing temperature of upto 130 °C, and a small decrease thereafter.

The overlay plot of DPTP/BPAPC: 15/85 (Figure 3.9) shows that the transition is boarder with annealing temperatures of 120 and 130 °C than in case at 140 °C. With the later, the endotherm becomes narrower, suggesting that this temperature is the optimum for a perfect crystalline growth⁶. The broader peak and in some cases with a small shoulder suggest varying degree of order and size of DPTP crystals in the composites films⁹.

In the unconfined state with DPTP/BPAPC: 15/85 the same trend is observed at 120 to 130 °C. The T_m was found to increase with an increase in annealing temperature by as much as 10 °C. But at 140 °C (Figure 3.10) there is an absence of an endothermic peak after 1 h. No endothermic peak was observed with DPTP/BPAPC: 10/90 also, when the film was annealed at 130 and 140 °C.

However, no endothermic melting peak was observed in DSC thermograms with DPTP/BPAPC: 5/95 both in the confined and unconfined states and this is attributed to the compatibility of DPTP with BPAPC at this concentration¹.

Thus, there is a pronounced recovery of T_g (Figure 3.8) and an absence of a melting peak for DPTP/BPAPC: 15/85 when annealed at 140 °C after 1 h (Figure 3.10) and for DPTP/BPAPC: 10/90 at 130 and 140 °C in unconfined state. This is in contrast to the behaviour noted for the confined state. Note that the T_m of the plasticizer was reduced by ~ 46 °C when dispersed in the polymer. The question then arises as to the possibility that this might be due to the degradation or sublimation of the plasticizer upon prolonged heating at higher temperatures. This is discussed in the next section.

Figure 3.9 Overlay of DSC thermograms of the confined DPTP/BPAPC: 15/85 composite film annealed at 120, 130 and 140 °C for 0.5 h.

Figure 3.10 Overlay of DSC thermograms of the unconfined DPTP/BPAPC: 15/85 composite film annealed at 140 °C for various times.

3.1.4 Testing for Degradation of DPTP

To examine if there is a degradation of DPTP at the experimental temperatures, TGA analysis was done with DPTP, BPAPC and DPTP/BPAPC: 5/95, 10/90, 15/85 as-prepared composites films. The weight loss versus temperature graphs of TGA analysis is shown in Figure 3.11. This figure shows that the polycarbonate is thermally stable up to 388 °C and the as received DPTP begins to decompose at 201°C.

With the composites films the TGA weight loss occurs in two steps. The first step corresponds to the beginning of weight loss for DPTP and the second step is due to the onset of weight loss for BPAPC. As seen from Figure 3.11, in DPTP/BPAPC composite films, BPAPC begins to decompose almost at the same temperature i.e. 391 °C with all the three concentrations. In the as prepared composites, DPTP begins to decompose at 210 °C with DPTP/BPAPC: 15/85, 233 °C for DPTP/BPAPC: 10/90 and 241 °C for DPTP/BPAPC: 5/95. This tends to lead to the conclusion that the thermal stability of DPTP increases with a decrease in the concentration of DPTP in DPTP/BPAPC composite films. However, this behaviour could be attributed to the low concentrations of DPTP in the film, the degradation of which could be detected only at a temperature higher than the degradation temperature of the bulk sample of DPTP

No evidence of weight loss was observed in the TGA thermograms for DPTP/BPAPC composites at the annealing temperatures used here, i.e., from 120 °C to 140 °C. The above results suggest that the pronounced recovery of T_g and the absence of melting peak for DPTP/BPAPC: 15/85 at 140 °C after 1 h and for DPTP/BPAPC: 10/90 at 130°C

and 140 °C in the unconfined state as compared to the confined state in the composites is not due to the degradation of the plasticizer on prolonged heating at these temperatures.

Figure 3.11 TGA thermograms of DPTP, BPAPC and DPTP/BPAPC: 5/95, 10/90, 15/85 composite films

3.1.5 Evaporation of DPTP

Since the plasticizers are not attached to the polymer matrix by primary bonds, plasticizer can be lost from the polymer matrix by evaporation or migration¹⁰. Such a migration of plasticizers depends on several factors such as the temperature, the molecular size of the migrant and the compatibility of the migrant with the polymer^{11,12,13,14}. Of course, such migration would result in deterioration of the dispersion, and cause phase separation and changes in the morphology and hence the properties of the composite. A number of known plasticizers for example, dioctyl phthalate (DOP), butyl benzyl phthalate (BBP)

are liquid at room temperature and in these cases the phase separation would lead to droplet formation or evaporation. With those plasticizers which are solid at room temperature, phase separation would lead to crystallization of the plasticizer.

The absence of a melting endotherm in the case of unconfined films when annealed at 130 or 140 °C led us to believe that DPTP might be subliming from the polymer matrix at these temperatures. Therefore, the as received DPTP and DPTP/BPAPC composites films were annealed at temperatures ranging from 90 to 140 °C for 3 h in an enclosed device as described in the experimental section and the weight loss of DPTP from the film was measured. The results thus obtained are presented in Figure 3.12.

As observed from Figure 3.12, in composites films the normalized weight loss percentage increases with increase in annealing temperature. There is no weight loss at 90°C while at 140°C it reaches 33% in DPTP/BPAPC: 15/85. The same trend is observed with DPTP/BPAPC: 10/90. It is interesting that no significant change in the percentage loss is observed with a decrease in plasticizer concentration with annealing temperature. Even while annealing the samples in the vacuum oven, drops of plasticizer were found on the oven walls. Several researches have reported the migration of plasticizer from plasticized PVC by determining the weight loss of the PVC film. The weight loss kinetics was studied in the PVC-Didecyl phthalate¹⁵ in the 80-120 °C temperature range. However, Didecyl phthalate is a liquid at room temperature, with a melting point of 3 °C. In contrast, the melting point of DPTP is 198 °C.

Figure 3.12 Normalized weight loss (%) versus annealing temperature of DTPP as received and DTPP/BPAPC composite films annealed for 3 h at various temperatures

By the same method, the as received powder of DTPP was also annealed at 100 to 140 °C for 3 h in the enclosed device as described in the experimental section and the percentage weight losses of DTPP from the bulk powder and from the composites film were compared.

As seen from Figure 3.12, the percentage weight loss of DTPP evaporated from bulk is very small as compared to the composite film. This is rationalized on the basis that the cohesive energy is higher in bulk DTPP as compared to the composite film. Prior to phase separation and crystallization, the DTPP exists as a molecular dispersion or as microcrystalline domains in the composite. The cohesion between the molecules can be

expected to be less than that in the bulk DPTP. Note also that the melting temperature of DPTP in the composite is 151°C, which is about 47° less than that of DPTP in the bulk.

In order to confirm that the sublimed material is DPTP, the evaporated crystals of DPTP were collected on a glass slide, from DPTP and from the DPTP/BPAPC composite films (by the same experiment used for the weight loss described in experimental section) and the XRD were run on these microscopic slides (Optical micrographs of evaporated DPTP deposited on the top microscopic slide are shown in Figure A 1 of appendix A).

The X-ray diffraction patterns for the crystals collected from the as received sample and from the DPTP/BPAPC: 15/85 composite film on the top microscopic slide of the enclosed device are shown in Figure 3.13. The major peaks were found at $2\theta = 4.98, 9.78, 14.76, 19.52, 23.14^\circ$ for the as received DPTP. The peaks for the evaporated DPTP collected from as received sample and from the composite films were found to be in the same 2θ positions. The peaks for the evaporated samples began to appear at 120 °C.

The above experiment supports the conclusion that the pronounced recovery of T_g and the absence of a melting peak for DPTP/BPAPC: 15/85 at 140 °C after 1 h and for DPTP/BPAPC: 10/90 at 130 and 140 °C in the unconfined state is due to the evaporation of the plasticizer on prolonged heating at these temperatures.

Figure 3.13 X-ray diffraction traces of the evaporated DTP from (a) DTP as received sample and (b) DTP/BPAPC: 15/85 composite films.

3.1.6 Optical Microscopy

The optical micrographs (Figure 3.14) show the presence of very tiny crystals of less than a μm in size, suggesting that phase separation occurred in the as prepared films for DPTP/BPAPC: 15/85 and 10/90. With DPTP/BPAPC: 15/85, dendritic growth was also observed. The cloudiness in the film was also observed visually for DPTP/BPAPC: 15/85 while with DPTP/BPAPC: 10/90 slight cloudiness was observed. The film with DPTP/BPAPC: 5/95 was clear. These results corroborate the DSC data (Figure 3.2), which shows a transition corresponding to melting of DPTP for DPTP/BPAPC: 15/85 and 10/90 while no melting endotherm was observed with DPTP/BPAPC: 5/95.

Annealing these films at temperatures of 120, 130 and 140 °C for times ranging from 0.5 to 4 h results in the formation of phase separated crystals of DPTP of varying shapes and sizes in both confined and unconfined states. However, there are significant differences in the morphology corresponding to these two cases.

The optical micrographs of the composite films annealed at 130 °C for various times are shown in Figure 3.15. With DPTP/BPAPC: 15/85 large dendritic growth was observed. With DPTP/BPAPC: 10/90 the distribution of the crystals were uniform and large number of well distributed crystals were observed. With DPTP/BPAPC: 5/95 very tiny crystals were observed.

(a)

(b)

(c)

Figure 3.14 Optical micrographs of as prepared composite films: (a) DTP/BPAPC: 5/95, (b) DTP/BPAPC: 10/90, (c) DTP/BPAPC: 15/85

Figure 3.15 Optical micrographs of the composites film annealed at 130 °C for various times in the confined state:
 (a) DPTP/BPAPC: 10/90, 1 h; (b) DPTP/BPAPC: 10/90, 2 h; (c) DPTP/BPAPC: 10/90, 3 h;
 (d) DPTP/BPAPC: 15/85, 1 h; (e) DPTP/BPAPC: 15/85, 2 h; (f) DPTP/BPAPC: 15/85, 3 h

The significant differences between the confined and unconfined states are illustrated in Figure 3.16, for the composite films upon annealing at 130 °C for 2 h. The differences are pronounced with 10/90 and 15/85 compositions. In Figure 3.16c, a large number of crystals are seen when the film is confined during annealing. Most of these crystals are quite uniform in size, of about few μm . However, in Figure 3.16d, the crystals are very few and smaller than those in (c). Comparing Figures 3.16 e and f, a large dendritic growth is seen when the film is confined, while there are fewer and well defined crystals in the unconfined film.

Figure 3.17 shows the effect of annealing time and temperature on the average crystal area in the confined and unconfined states. In the confined state, with DPTP/BPAPC: 15/85 the average area of the crystal is maximum at 3 h for annealing the films at 130 and 140 °C. In addition, it was found that in the confined stage, the average area of the crystals increases with an increase in annealing temperature. The average crystal area for the film annealed at 120 °C for 3 h was found to be $62 \mu\text{m}^2$ which increases to 183 and $199 \mu\text{m}^2$, respectively at 130 and 140 °C. These results corroborate the DSC thermograms i.e., as the temperature increases, the melting endothermic peak becomes narrow suggesting that this temperature is the optimum for a more perfect crystalline structure⁶. Further, with DPTP/BPAPC: 10/90 at 140 °C average crystal area was found to decrease to $9 \mu\text{m}^2$ at 3 h. A very small and shallow endothermic peak was observed with DSC analysis at this temperature.

In the unconfined state, with DPTP/BPAPC: 15/85, the same trend was observed as in the confined stage. But at 140°C, the average crystal area increases up to 1 h, then there is a significant decrease in the average crystal area with an increase in the annealing time. It was discussed before that in the DSC thermograms no endothermic peak is observed at 140 °C for DPTP/BPAPC: 15/85 after 1 h (Figure 3.10). With DPTP/BPAPC: 10/90 the average crystal area decreases with an increase in annealing temperature and also no endothermic peak was observed at 130 and 140 °C in DSC thermogram (additional Figures are in appendix B) . The sudden decrease in the average crystal area at 130 and 140 °C with DPTP/BPAPC: 10/90 and at 140 °C after 1 h with DPTP/BPAPC: 15/85 is attributed to the evaporation of DPTP molecule as discussed in section 3.1.5. However, no significant change is observed in average crystal area with DPTP/BPAPC: 5/95 both in the confined and the unconfined state suggesting the compatibility of BPAPC and DPTP at this concentration.

Comparing the graphs in Figure 3.17, it can be seen that the average crystal area in the unconfined state is significantly smaller than corresponding confined state. Similar differences are also seen in the distribution of the average area in the confined and unconfined states (Figure 3.18). As can be seen from figure the size distribution is boarder in 15/85 when compared to 10/90 composite films.

Figure 3.16 Optical micrographs of the composite film annealed at 130 °C for 2 h at various concentrations: (a) DTP/BPAPC: 5/95, confined; (b) DTP/BPAPC: 5/95, unconfined; (c) DTP/BPAPC: 10/90, confined; (d) DTP/BPAPC: 10/90, unconfined; (e) DTP/BPAPC: 15/85, confined; (f) DTP/BPAPC: 15/85, unconfined

Figure 3.17 Average crystal area (optical microscopy) versus annealing time:
 (a) DPTP/BPAPC: 5/95, confined; (b) DPTP/BPAPC: 5/95, unconfined;
 (c) DPTP/BPAPC: 10/90, confined; (d) DPTP/BPAPC: 10/90, unconfined;
 (e) DPTP/BPAPC: 15/85, confined; (f) DPTP/BPAPC: 15/85, unconfined

Figure 3.18 Effect of Annealing for 3 h on Crystal Area Distribution: (a) DPTP/BPAPC: 10/90, confined; (b) DPTP/BPAPC: 10/90, unconfined; (c) DPTP/BPAPC: 15/85, confined; (d) DPTP/BPAPC: 15/85, unconfined.

In the case of confinement, the possible reason could be that interactions between the polymer chain and hard walls increase contacts between the chain and the walls, decrease the chain mobility and segmental motion of the molecule¹⁶. The small molecules are not getting enough space to grow, as a result small crystals join together to form large crystals size.

In contrast, in the unconfined state there could be two possible contributions (i) the molecular mobility of the polymer is not restricted which leads to fast diffusion of the small molecules, and these molecules are getting enough space to grow. (ii) Evaporation of DPTP molecule. We have shown that the latter contributes significantly to the morphology observed in the unconfined state.

3.2 Thin Film (~ 700 nm)

Thin composites films of DPTP/BPAPC: 5/95, 10/90, 15/85 both in the confined and unconfined states were annealed at the temperatures in the range of 80, 90 and 120 ° for 0.5 to 4 h. The results show the formation of phase separated crystals of DPTP of varying shapes and sizes in both the confined and unconfined states. The rationale for annealing the thin composite film at 80, 90 and 120 °C and not at 130 and 140 °C is that due to rapid evaporation of DPTP at later temperatures, no phase separated crystals were observed in the unconfined state.

The optical micrographs of the composite film annealed at 90 °C for 2 h are shown in Figure 3.19. It is observed that there is a significant difference in morphology between the confined and the unconfined states. In the confined state for DPTP/BPAPC: 15/85,

the phase separated crystals grow in a flat leaf-like structure and orientation of the crystals are parallel to the plane which implies that the phases are anisotropic in shape and the growth perpendicular to the film plane is constrained by the two hard walls¹⁷.

In the unconfined state, needle shaped crystals are seen, whose growth starts from a central nucleus. These crystals are larger than those seen in the confined case. With DPTP/BPAPC: 10/90 in the unconfined state the crystals are fewer in number as compared to the confined state. With DPTP/BPAPC: 5/95 very few crystals were observed and no change in the morphology was observed between the confined state and unconfined state.

Figure 3.20 shows the effect of annealing time and temperature on the average crystal area in the confined and unconfined states. The average area of the crystals was found to be 100 times larger than the film thickness. In the confined state, the average crystal area of the DPTP/BPAPC:15/85 was found to increase with an increase in annealing temperature with the exception at 120 °C after 3 h. Average area of the crystal for the film annealed for 1 h at 80 °C was found to be 325 μm^2 which increases to 484 μm^2 at 90 °C and 611 μm^2 at 120 °C. In addition the average area of the crystals increases with an increase in annealing time at 80 °C and 90 °C. However, at 120 °C the average area of the crystal increases upto 2 h and then there is a significant decrease with an increase in annealing time. Further, with DPTP/BPAPC: 10/90 same trend was observed as in the case of DPTP/BPAPC: 15/85; average area of the crystals increases with an increase in annealing time and temperature.

Figure 3.19 Optical micrographs of the thin composite film annealed at 90 °C for 2 h: (a) DTP/BPAPC: 10/90, confined; (b) DTP/BPAPC: 10/90, unconfined; (c) DTP/BPAPC: 15/85, confined; (d) DTP/BPAPC: 15/85, unconfined

In the unconfined state, with DPTP/BPAPC: 15/85, the average area of the crystals increases with an increase in annealing temperature. However, the average area of the crystals reaches a peak after 2 h of annealing and then there is significant decrease in size. For DPTP/BPAPC: 10/90 same trend was observed as with DPTP/BPAPC: 15/85 with exception for annealing the films at 90 °C for 4 h where average area of the crystals decreases from 187 μm^2 at 80 °C to 59 μm^2 at 90 °C.

In the unconfined state no phase separated crystals was observed at 120 °C for both DPTP/BPAPC: 15/85 and DPTP/BPAPC: 10/90 due to the evaporation of DPTP. Since with DPTP/BPAPC: 5/95 the frequency of the crystals was very small, no measurement was done at this composition.

From Figure 3.20, it is seen that the average area of the crystal in the confined state is significantly smaller than that of the unconfined state. The same trend was observed in crystal area distribution graph (Figure 3.21). The possible reason could be that the presence of the hard wall constrained the growth perpendicular to the film plane and thus hinders the development of phase separation¹⁷.

Figure 3.20 Average crystal area (optical microscopy) versus annealing time in the thin composite film: (a) DTP/BPAPC: 10/90, confined; (b) DTP/BPAPC: 10/90, unconfined; (c) DTP/BPAPC: 15/85, confined; (d) DTP/BPAPC: 15/85, unconfined

Figure 3.21 Effect of annealing for 3 h on crystal area distribution in the thin composite film: (a) DTPP/BPAPC: 10/90, confined; (b) DTPP/BPAPC: 10/90, unconfined; (c) DTPP/BPAPC: 15/85, confined; (d) DTPP/BPAPC: 15/85, unconfined.

3.3 Comparison between the Thick Film and the Thin Film

No phase separated crystals were observed on annealing the thin composite films at 120°C in the unconfined state. Therefore, for the purpose of comparison, thick films of DPTP/BPAPC: 15/85, 10/90, and 5/95 were annealed at 80 and 90 °C. With DPTP/BPAPC: 15/85 no change in the morphology was found upon annealing at these temperatures and it was impossible to measure the crystal size. With DPTP/BPAPC: 10/90, 5/95 the average area of the crystal size was found to be between 7 to 11 μm^2 and no significant change in the morphology was observed with the annealing time or the annealing temperature.

Significant differences in the morphology between the thin and the thick films are illustrated in Figure 3.22, upon annealing at 80, 90 and 120 °C for 2 h. As can be observed from the figure the phase separation in the thin film occurs at a very earlier state as compared to that of thick film.

Further, the average area of the phase separated crystal in the thin film was significantly larger when compared with the thick film with DPTP/BPAPC: 10/90 and 15/85 (Figure 3.23).

In the unconfined state, results similar to the confined state were observed for the thin and the thick film with the exception at 120 °C in the thin film, where no phase-separated crystals were observed. The later may be due to the evaporation of DPTP. This shows that since the film is only a few nanometers in thickness

Figure 3.22 Optical micrographs of the DPTP/BPAPC: 15/85 composite film annealed at various temperatures for 2 h in the confined state: (a) Thin film annealed at 80 °C; (b) Thick film annealed at 80 °C; (c) Thin film annealed at 90 °C; (d) Thick film annealed at 90 °C; (e) Thin film annealed at 120 °C; (f) Thick film annealed at 120 °C

i.e. the surface to volume ratio is too large, the evaporation of DPTP occurs at a very early stage as compared to the thick films with prolonged annealing.

Further it was observed that the average area of the crystal is large in the thin film as compared to the thick film in both the confined and the unconfined state. The possible reason could be (i) that the surface area to volume ratio is large in the thin film as compared to the thick film, so that the crystals were getting enough space to grow. (ii) The cohesive energy must be higher in thick film as compared to thin film. (iii) Diffusion and aggregation / crystallization of small molecule is not inhibited by the polymer matrix in the thin film

These results suggest that the thickness of the film plays an important role in controlling the morphology or the average area of the crystal size and thus the development of phase separation. Many researchers have reported the difference in morphology by changing the thickness of film in polymer blends^{18,19,20,21,22,23}. The fact that the phase separation evolves faster in the thin film seems to imply that the system become less stable as the film thickness decreases¹⁷.

Figure 3.23 Comparison of the average crystal area between the thin and the thick composite film, annealed at 120 °C for various times in the confined state: (a) DTPP/BPAPC: 10/90; (b) DTPP/BPAPC: 15/85.

3.4 Summary and Conclusions

This chapter described the effect of annealing temperature (120, 130, and 140 °C), annealing time (0.5- 4 h) and film thickness on the morphology of DPTP/BPAPC: 5/95, 10/90, 15/85 composites film in both confined and unconfined states.

The T_g of the polycarbonate was found to be depressed significantly with an increasing concentration of DPTP in BPAPC. The DPTP was found to be compatible with the BPAPC up to 5 % in as prepared composite films. With DPTP/BPAPC: 10/90 and 15/85, a melting endothermic peak for DPTP was observed and the T_m of DPTP was found to decrease by 44 -46°C. IR spectra show a shift in C=O absorption band of DPTP in DPTP/BPAPC: 5/95, 10/90 while no shift in absorption frequency of this band was observed with DPTP/BPAPC: 15/85. IR spectra and molecular modeling indicate an interaction between the C=O dipoles of the polymer and DPTP.

In the confined state, with DPTP/BPAPC: 15/85, 10/90 T_g generally increases with an increase in annealing time but decreases with an increase in annealing temperature. With DPTP/BPAPC: 5/95, the T_g does not change significantly with an increase in either annealing time or temperature. In the unconfined state, the T_g generally increases with an increase in both annealing time as well as annealing temperature. It was found that the recovery of T_g was more pronounced when the film is unconfined.

The T_m of DPTP in composite films was found increase by approximately 10 °C with DPTP/BPAPC: 15/85 and by 5 °C with DPTP/BPAPC: 10/90 with an increase in annealing temperature in the confined as well as in the unconfined states. In the unconfined state no melting endotherm was observed in DPTP/BPAPC: 15/85 at 140 °C after 1 h and with DPTP/BPAPC: 10/90 at 130 and 140 °C.

Significant difference in the morphology was found between the confined and unconfined states with DPTP/BPAPC: 10/90 at 130 °C and with DPTP/BPAPC: 15/85 at 130 and 140 °C. The average area of the phase separated crystals of DPTP in DPTP/BPAPC composites film is larger when the film is confined as compared to when the film is unconfined.

In thin films, a significant difference in the morphologies between confined and unconfined states was observed. The average area of the phase separated crystals is larger when the film is unconfined as compared to when the film is confined.

On comparing the thick film with the thin film, it was found that the phase separation occurs at a very early stage in the thin film and the average area of the phase separated crystal in the thin film is much larger than in the thick film. In the thick film, the average area of phase separated crystals is larger in the confined state than in the unconfined state, while the reverse trend was observed in the thin film.

Sublimation of DPTP was observed in both the composite film and the bulk DPTP at the annealing temperatures between 120 °C to 140 °C and this biases the effect of confinement. The normalized weight loss of DPTP was found to be more in the composite film as compared to the bulk DPTP.

3.5 References

- 1 Alexandru, L.; Zamin, J.; Sundararajan, P. R. *J. Appl. Polym. Sci*, **1991**, 43, 2259-2266
- 2 Ljungberg, N.; Wesselen, B. *J. Appl. Polym. Sci*, **2002**, 86, 1227-1228
- 3 Onu, A.; Legras, R.; Mercier, J.P. *J. Polym. Sci.* **1976**, 14, 1187-1199
- 4 Pizzoli, M.; Scandola, M. *Polymeric Materials Encyclopedia*, Salamone, J.C. Editor, **1996**, 7/p, 5301-5308
- 5 Khan, F.; Hor, Ah-Mee ; Sundararajan, P.R. *J. Phys. Chem. B*, **2004**, 108, 117-126
- 6 Drappel, S.; Sundararajan, P. R.; Rudin, A. *Polymer*, **1997**, 38, 1259-127
- 7 Pavia, D.P.; Lampnam, G.M; Kriz, G.S. *Introduction to spectroscopy*, 2001
- 8 Khan, F.; Hor, Ah-Mee ; Sundararajan, P.R., *Pure Appl. Chem.*, In Press
- 9 Hsu, Wen-Ping *J. Appl. Polym. Sci*, **2001**, 80, 2842-2850
- 10 Seras J.K.; Darby, J.R. *Solvation and Plasticization*, in *Encyclopedia of PVC*, **1986**, 2nd Ed., 435-554
- 11 Papakonstantinou, V.; Papaspyrides, C.D.; *J. Vinyl Technology*, **1994**, 16, 192-196
- 12 Papaspyrides, C.D.; Papakonstantinou, V. *J. Polym. Eng. ,* **1995**, 15, No 1-2, 153-159
- 13 Papaspyrides, C.D.; Tingas, S.G.; *J. Appl. Polym. Sci*, **2001**, 79, 1780-1786
- 14 Papaspyrides, C.D. *J. Appl. Polym. Sci*, **1986**, 32, 6025-6032
- 15 Audouin, L.; Dalle, B.; Metzger, G.; Verdu, J. *J. Appl. Polym. Sci*, **1992**, 45, 2091-2096

-
- 16 Forrest, J.A.; Veress, K.D.; Dutcher, J.R. *Phys. Rev E*, **1997**, 56, 5705-5715
 - 17 Pan, Q.; Composto, R. J. *Mat. Res. Soc. Symp. Proc.* **1995**, 366, 27-32.
 - 18 Mareau, V'H.; Prud'homme E.; *Macromolecules*, **2003**, 36, 675-684
 - 19 Newby, B.-M. Z.; Wakabayashi, K.; Comosto, R. J. *Polymer*, **2001**, 42, 9155-9162
 - 20 Konaripalli, N.; Levicky, R.; Bates, F. S. *Langmuir*, **1996**, 12, 6681-6690
 - 21 Dalnoki-Veress, K.; Nickel, B. G.; Dutcher, J. R. *Phys. Rev. Letters*, **1999**, 82, 1486-1489.
 - 22 Dalnoki-Veress, K.; Forrest, J. A.; Dutcher, J. R. *Phys. Rev. E*, **1998**, 57, 5811-5817.
 - 23 Dalnoki-Veress, K.; Forrest, J. A.; Stevens, J. R.; Dutcher, J. R. *Physica A*, **1997**, 239, 87-94.

Chapter 4

DPIP and BPAPC Composites

The effect of annealing temperature and time on the morphology of the DPIP/BPAPC composites in both confined and unconfined states will be discussed in this chapter. As mentioned in Chapter 2, polycarbonate was chosen as the host polymer, which is used as a binder in optoelectronic devices. The DPIP was chosen as it is a solid at room temperature and the crystallization behaviour can be characterized. Glass slides were used to study the effect of confinement. This chapter will discuss (1) the depression of the T_g , (2) possible molecular level interaction between DPIP and BPAPC, (3) the recovery of T_g upon annealing, (4) the sublimation of DPIP, (5) the phase separated morphology of DPIP and (6) crystallization of BPAPC induced by DPIP above a certain concentration. Throughout this chapter, the composition of the films is denoted by X/Y where X is the wt % of DPIP and Y is that of BPAPC.

4.1 Thick Film

4.1.1 Effect of DPIP on the T_g of BPAPC in as Prepared Solvent Cast Composites Films

The thickness of the film in this case was approximately 20 μm . Differential scanning calorimetry (DSC) of DPIP showed an endothermic peak at 139 $^{\circ}\text{C}$, with a heat of fusion of 25.8 cal/g. Further, the DSC thermogram for the solvent cast film of BPAPC showed the T_g at 154 $^{\circ}\text{C}$.

The variation of T_g of BPAPC, with the addition of DPIP at different concentrations for the as prepared solvent cast film is shown in Figure 4.1a. The depression in T_g , i.e.

$$\Delta T = T_g \text{ of (polycarbonate)} - T_g \text{ (composite)} \quad (4.1)$$

is shown in the Figure 4.1b. As seen from Figure 4.1a, the T_g of the polymer in the composite is significantly lowered with the addition of DPIP. The T_g of polycarbonate is depressed by as much as 54 °C with 12.5% of DPIP and 63 °C with 15% of DPIP. This demonstrates that the plasticization takes place in these composites. A number of studies have analyzed the dependence of T_g depression on the type and amount of the plasticizer^{1, 2, 3, 4}

Further, in the overlay of the DSC thermograms (Figure 4.2) no melting endotherm is observed for all the three concentrations of DPIP in BPAPC. This suggests that DPIP is molecularly dispersed in the polymer matrix¹. The absence of a melting endotherm in DPIP/BPAPC: 5/95, 10/90, 15/85 indicates good compatibility of the DPIP with BPAPC for the as prepared solvent cast composite films¹.

As mentioned in section 3.1.1 the depression in T_g may not only be due to the increase in the free volume of polymer by addition of small molecules but also due to the molecular level interaction⁵. Such a molecular level interaction (See Figure 3.3 in Chapter 3 showing schematic of domain level and molecular level interaction) was indicated in the case of TPD/BPAPC composites in which a significant shifts in frequencies in the infrared spectrum of BPAPC in the aromatic region were observed and these shifts

Figure 4.1 (a) The depression of T_g of the polycarbonate with various concentrations of DPIP, (b) the depression of ΔT_g of the polycarbonate with various concentrations of DPIP

Figure 4.2 Overlay of DSC thermograms of “as prepared” DPIP/BPAPC composite films

increased with the concentration of TPD in the composite⁵. Figure 4.3 shows the FTIR spectra for the as prepared composite films of DPIP/BPAPC: 10/90, 15/85 along with the spectra of pure DPIP and BPAPC, for three regions. The bands at 1602 and 1505 cm^{-1} in the BPAPC spectrum corresponds to C=C aromatic ring stretch^{5,6} and the peaks in the region of 3000 cm^{-1} corresponds to CH stretch. No shift in the absorption frequency for the bands in this region was observed in any of the above composite films with DPIP.

The bands at 1732 cm^{-1} for DPIP corresponds to the conjugation of C=O with phenyl ring stretch. The frequency of these bands shifted to 1744 cm^{-1} for DPIP/BPAPC: 5/95, and to 1742 cm^{-1} for DPIP/BPAPC: 10/90, 15/85 composite films which indicates an increase in the C=O bond strength. The DPIP absorption band at 719 cm^{-1} , which corresponds to the out of plane vibration of the aromatic ring, shifted to 724 cm^{-1} and the BPAPC absorption band at 707 cm^{-1} shifted to 712 cm^{-1} for all the above composite film. In addition, the peaks in the region 1000-1300 cm^{-1} correspond to =C-O stretch of BPAPC. With BPAPC the peaks corresponding to =C-O stretch appear at 1225 cm^{-1} and 1290 cm^{-1} . With DPIP/BPAPC: 5/95 a peak is observed at 1291 cm^{-1} almost at same frequency as with BPAPC. However with DPIP/BPAPC: 10/90 and 15/85, this band shifted to 1294 cm^{-1} and 1297 cm^{-1} , respectively. The shift in frequency for these bands were also observed with the higher concentration of DPIP in BPAPC i.e., DPIP/BPAPC: 20/80, 30/70, 40/60. Figure 4.4 shows the frequency shift of the 1290 cm^{-1} peak with the concentration of DPIP. Also shown in this figure is the frequency shift as a function of the ΔT , the extent of depression of T_g with concentration of DPIP.

Figure 4.3 FTIR spectra of (a), (c), (e) DPIP, BPAPC, and DPIP/BPAPC: 15/85; (b), (d), (f) DPIP, BPAPC and DPIP/BPAPC: 10/90

Figure 4.4 (a) Variation of the frequency with the concentration of DPIP in BPAPC, (b) correlation between the T_g depression (ΔT) and frequency shifts.

Although the depression of the T_g would be due to a combination of factors such as molecular interaction, change in the free volume of the polymer, etc. it is interesting that IR frequency shift follow the same trend with the concentration of the DPIP. The above shift in frequency for the bands of DPIP at 1731 cm^{-1} and for the bands of BPAPC at 1290 cm^{-1} in the composite film indicates an interaction between the carbonyl groups of BPAPC and of DPIP. It should be noted that no such shift was observed in the case of DPTP/BPAPC composites. This suggests that the presence of the carbonyl group in the meta position in DPIP is more favourable for interactions with the carbonyl group of BPAPC than in para position, as in DPTP.

Shifts in the absorption frequency of the carbonyl group of plasticizer ester to lower wave number, indicative of the reduction in polarity (i.e. some interaction between functionality and the polymer) have also been reported ^{7,8}.

To examine if this molecular level interaction could be detected by modeling, a simple molecular modeling was performed. Models of the BPAPC chain (12 units) and DPIP were generated and energy minimized using Hyperchem software (Figure 4.5). This corresponds to a weight fraction of 10% of DPIP in BPAPC. These were then placed in close proximity and energy minimized. The energy of DPIP, the 12-mer of BPAPC and DPIP/BPAPC were 12.7, 98.7 and 96.7 Kcal mol⁻¹ respectively. The energy of BPAPC was reduced by just 2 Kcal/mol (i.e. <0.2 Kcal/mol/monomer). This reduction in the energy is not significant as in the case of TPD/BPAPC. The electrostatic component of the energy decreased from -4.2 to -5.4 Kcal/mol⁻¹, which indicates a dipole-dipole interaction between the C=O groups of DPIP and BPAPC. However, no change in the bond length was observed for DPIP and BPAPC when the two molecules placed together in close proximity. The possible reason could be that the modeling performed here is too simple. Molecular dynamics was not used to relax the molecules. However significant shift in the frequency was observed for C=O bands of DPIP which indicates an interaction between the carbonyl group of DPIP and BPAPC. The shift in the frequency for =C-O bands of BPAPC was also observed. This could be the possible reason that no phase separation occurs up to 15% concentration of DPIP in BPAPC. It appears that there is no significant interaction between the phenyl groups of DPIP and BPAPC.

4.1.2 Effect of Temperature and Time on the Glass Transition Temperature of Solvent Cast DPIP/BPAPC composites films

Composite films were annealed both in confined and unconfined states at a temperature lower than the T_g of polycarbonate i.e. 120, 130 and 140 °C for times ranging between

Figure 4.5 Minimum energy conformations of (a) DPIP, (b) 12 mer of BPAPC and (c) DPIP/BPAPC

0.5 to 4.0 h, and the results thus obtained are presented in Tables 4.1 and 4.2 (it should be noted that the T_g reported here is within the range of ± 2 °C with instrumental uncertainty in the measurement of T_g).

In the confined state, no significant change in the T_g is observed with either annealing time or annealing temperature (Figure 4.6 and Table 4.1) This suggests that no phase separation occurs after annealing the film at different temperatures and times used for this study.

In the unconfined state, with DPIP/BPAPC: 10/90 and 15/85 the T_g was found to increase gradually with an increase in either annealing temperature or annealing time (Figure 4.7 and Table 4.2). With DPIP/BPAPC: 15/85, annealing at 120 °C for 4 h increases the T_g from 91 °C to 98 °C which increases to 102 °C at 140 °C. Further, no significant change in the T_g was observed for DPIP/BPAPC: 5/95 with annealing time or temperature.

No melting endothermic peak was observed in both confined and unconfined states either with annealing time or annealing temperature with DPIP/BPAPC: 5/95, 10/90, 15/85 suggesting no phase separation occurs in these composites either with annealing time or temperature (Figure 4.8 and 4.9). The absence of a melting endotherm indicates the compatibility of the DPIP with the BPAPC even after annealing the composite film at different temperatures for various times.

As is observed from Figure 4.10, the recovery of T_g is more pronounced in the unconfined state than in the confined state. In the confined state, with DPIP/BPAPC: 10/90 annealed at 130 °C for 3 h, no change in the T_g was observed when compared to

Figure 4.6 Glass transition (T_g) versus annealing time of composite films in the confined state. (a) DPIP/BPAPC: 5/95; (b) DPIP/BPAPC: 10/90; (c) DPIP/BPAPC: 15/85

TABLE 4.1: Results of Thermal Analysis of DPIP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the confined state

Annealing Temperature (°C)	Annealing Time (h)	DPIP/BPAPC: 5/95	DPIP/BPAPC: 10/90	DPIP/BPAPC: 15/85
		T_g (°C)	T_g (°C)	T_g (°C)
As prepared		126.2	106.2	90.6
Ann 120	0.5	124.3	106.2	90.1
	1	125.4	106.0	90.1
	2	126.7	106.0	91.7
	3	126.1	106.4	91.5
	4	126.5	106.8	91.7
Ann 130	0.5	126.1	106.7	91.0
	1	126.7	106.5	89.1
	2	127.2	106.2	90.6
	3	126.7	106.2	91.0
	4	127.0	106.0	92.4
Ann 140	0.5	126.3	106.5	91.2
	1	127.9	106.0	90.8
	2	127.6	106.5	91.5
	3	127.4	106.9	91.2
	4	127	106.5	91.2

Figure 4.7 Glass transition temperature (T_g) versus annealing time of composite films in the unconfined state. (a) DPIP/BPAPC: 5/95; (b) DPIP/BPAPC: 10/90; (c) DPIP/BPAPC: 15/85

TABLE 4.2: Results of Thermal Analysis of DPIP/BPAPC: 5/95, 10/90, 15/85 composite films, after annealing at various temperatures and times in the unconfined state

Annealing Temperature (°C)	Annealing Time (h)	DPIP/BPAPC: 5/95 T_g (°C)	DPIP/BPAPC: 10/90 T_g (°C)	DPIP/BPAPC: 15/85 T_g (°C)
As prepared		126.2	106.2	90.6
Ann 120	0.5	126.1	108.0	93.1
	1	126.3	109.1	95.5
	2	126.3	109.7	96.5
	3	126.5	109.9	96.5
	4	126.1	109.5	98.0
Ann 130	0.5	127.5	108.5	95.2
	1	127.5	109.6	96.3
	2	127.3	109.4	98.8
	3	127.8	110.6	100.2
	4	127.8	111.4	100.7
Ann 140	0.5	127.7	110.1	95.5
	1	127.8	111.2	97.5
	2	128.5	112.7	101.0
	3	127.6	115.7	101.2
	4	128.3	117.6	102.4

Figure 4.8 Overlay of DSC thermograms of the confined DPIP/BPAPC: 15/85 composite film annealed at 120 °C for various times.

Figure 4.9 Overlay of DSC thermograms of the unconfined DPIP/BPAPC: 10/90 composite film annealed for 2 h at various temperatures

Figure 4.10 Comparison of T_g between confined and unconfined DPIP/BPAPC: 5/95, 10/90, 15/85 composite films annealed at 130 and 140 °C

the as prepared film. However in the unconfined state the T_g increases up to 110 °C. The difference is more pronounced in the case of DPIP/BPAPC: 15/85. The recovery of T_g is significant in the unconfined state. Thus we see a distinctly different trend in T_g recovery upon annealing in the confined state versus the unconfined state.

It is to be noted here that no melting endotherm of DPIP was observed in the DSC thermogram, which indicates that no phase separation of DPIP occurred both in the confined and the unconfined films. Since no crystallization of DPIP was observed in the unconfined state, the question arises if the pronounced recovery of T_g might be due to the degradation or sublimation of the plasticizer upon prolonged heating at these temperatures.

4.1.3 Testing for Degradation of DPIP

To examine if there is a degradation of DPIP at the experimental temperatures, TGA analysis was done with DPIP, BPAPC and DPIP/BPAPC: 5/95, 10/90, 15/85 as prepared composites films. The results thus obtained are shown in Figure 4.11. This figure shows that the polycarbonate is thermally stable up to 388 °C and DPIP begins to decompose at 213 °C. With the composites films the TGA weight loss occurs in two steps. The first step corresponds to the beginning of weight loss for DPIP and the second step is due to the onset of the weight loss for BPAPC. It is seen from this figure that in the as prepared DPIP/BPAPC composites films, DPIP begins to decompose at 224 °C for DPIP/BPAPC: 5/95, 228 °C for DPIP/BPAPC: 10/90 and 213 °C for DPIP/BPAPC: 15/85 while BPAPC begins to decompose almost at same temperature i.e. 405 °C with all the three concentrations. This trend leads to the conclusion that the thermal stability of DPIP

increases with a decrease in the concentration of DPIP in DPIP/BPAPC composite films. This was the case with DPTP also (refer to chapter 3, Section 3.1.4).

No evidence of weight loss was observed in the TGA thermograms for DPIP/BPAPC composites at the annealing temperature used here, i.e. from 120 °C to 140 °C. The above results suggest that the recovery of T_g in the unconfined state as compared to the confined state was not due to the degradation of the plasticizer on prolonged heating at these temperatures.

Figure 4.11 TGA thermograms of DPIP, BPAPC and DPIP/BPAPC: 5/95, 10/90, 15/85 composite films

4.1.4 Evaporation of DPIP

Since the plasticizers are not chemically bonded to the polymer matrix, the migration of the plasticizer in polymer composites is well known. Such a migration of the plasticizer depends on several factors such as temperature, the molecular size of the migrant, and the compatibility of the migrant with the polymer^{9,10, 11,12}. For details refer to section 3.1.5.

Although no phase separation was observed in the unconfined state, the recovery of T_g was still observed. This led us to believe that DPIP might be subliming from the polymer matrix at the experimental temperatures. Therefore, the as received DPIP and DPIP/BPAPC composite films were annealed at temperatures ranging from 90 to 140 °C for 3 h in the enclosed device as described in experimental section. The normalized weight loss % of DPIP from the film was measured. Note that the “weight loss” here refers to the DPIP material that evaporated from the polymer matrix. The weight loss thus obtained is presented in Figure 4.12.

As is observed from Figure 4.12, in the composites films, the normalized weight loss % increases with an increase in annealing temperature. There is no weight loss at 90 °C while at 140 °C it reaches 30% in DPIP/BPAPC: 15/85. The same trend is observed with DPIP/BPAPC: 10/90. Several researches have reported the migration of plasticizer from plasticized PVC by measuring the weight loss of the PVC film^{9,10,11,12,13}.

By the same method, the as received powder of DPIP was also annealed at 90 to 140 °C for 3 h in the enclosed device as described in the experimental section and the normalized

weight loss % of DPIP from the bulk powder and from the composite film were compared.

As seen from Figure 4.12, the normalized weight loss % of DPIP evaporated from the bulk is small as compared to the composite film. This is rationalized on the basis that the cohesive energy is higher in bulk DPIP as compared to the composite film. The cohesion between the molecules of DPIP in the composite films can be expected to be less than in the bulk DPIP since DPIP in the composite film exists as a molecular dispersion or as microcrystalline domains. The melting temperature of DPIP is 139 °C in the bulk, which is close to or same as the experimental temperatures used. This could be the possible reason that the sublimation of DPIP was observed both in the composite film as well in bulk powder.

Figure 4.12: Normalized weight loss (%) versus annealing temperature of the DPIP as received and DPIP/BPAPC composite films annealed for 3 h at various temperatures

In order to confirm that the sublimed material is DPIP, the evaporated crystals of DPIP from the bulk DPIP and from DPIP/BPAPC composite films were collected on the glass slide (Optical micrographs of evaporated DPIP deposited on the top microscopic slide are shown in Figure A 1 of appendix A).

The XRD patterns for the material collected from the bulk DPIP and from DPIP/BPAPC: 15/85 composite films on the top microscopic slide of the enclosed device are shown in Figure 4.13. The major peaks were found at $2\theta = 5.4^\circ$ and 21.5° for the bulk as-received DPIP. The peaks for the evaporated DPIP collected from the bulk DPIP and from the composite films were found to be in the same 2θ positions. The peaks for the evaporated samples began to appear at 120°C . Of note are (i) the splitting of peaks at these 2θ positions from the evaporated samples, both from the bulk and from the film when compared to peaks of bulk DPIP itself; (ii) the significant difference in the relative intensities of the peaks, at $2\theta = 5.4^\circ$ and 21.5° . The former is significantly dominant in all the diffraction traces from the evaporated samples. The possible reason could be that in the powder, the crystals are randomly oriented while in the case of the sublimed DPIP in the form of a thin film, preferred orientation of DPIP crystals might exist. This is further verified by running the XRD on the same sample by changing the angle by 90°C . The splitting of the peak was observed again which suggest that the splitting is due to the preferred orientation of the crystal. The above experiment supports the conclusion that the pronounced recovery of T_g in the unconfined state is due to evaporation of the DPIP upon prolonged heating at higher temperature.

Figure 4.13 X-ray diffraction traces of the evaporated DPIP from (a) bulk DPIP sample and (b) DPIP/BPAPC: 15/85 composite films.

4.1.5 Optical Microscopy

In the optical micrograph or the SEM, it was not possible to detect any phase separated crystal of DPIP in the as prepared film for DPIP/BPAPC: 5/95, 10/90, 15/85 suggesting the compatibility of DPIP with BPAPC with all the three compositions. Also the films were visually clear for DPIP/BPAPC: 5/95, 10/90, 15/85. These results corroborate the DSC data (Figure 4.2) showing no melting endothermic peak for DPIP in DPIP/BPAPC: 5/95, 10/90, 15/85.

The presence of phase separated crystals could not be detected after annealing these films at temperatures of 120, 130 and 140 °C for times ranging from 0.5 to 4 h. No phase separation (or recovery of T_g) was noted in the case of confined films. In the case of unconfined films, sublimation occurred which led to the recovery of T_g but not the formation of phase separated crystals on the surface of the film. Therefore, no calculation was done to calculate the average crystal area and average crystal area distribution.

4.2 Thin Film

Thin composite films with DPIP/BPAPC: 5/95, 10/90, 15/85 both in confined and unconfined states were annealed at temperatures in the range of 120, 130 and 140 °C. Optical micrographs showed similar results as was observed with the thick films i.e. the presence of the phase separated crystal was not observed. To check whether the phase separation occurred at 80 and 90 °C as was observed in case of DPTP/BPAPC composite film, the DPIP/BPAPC: 5/95, 10/90, 15/85 samples were annealed at 80 and 90° C. The results thus obtained showed no phase-separated crystals of DPIP both in thick as well as in thin film.

4.3 Compatibility of DPIP with BPAPC

As discussed above, no phase separation of DPIP in BPAPC was observed with DPIP/BPAPC: 5/95, 10/90, 15/85 composite films suggesting that DPIP is compatible with BPAPC. In order to check the limiting concentration of DPIP for compatibility with BPAPC, the DSC analysis was done on DPIP/BPAPC: 20/80, 30/70, 40/60 composite films and results thus obtained are shown in Figure 4.14.

It is seen from the figure that the T_g of the polycarbonate (154 °C) is depressed by as much as 78 °C with 20%, 97 °C with 30% and 107.8 °C with 40 % DPIP. No melting endotherm was observed with 20% and 30% DPIP indicating the compatibility of plasticizer with BPAPC at these compositions. However with DPIP/BPAPC: 40/60 a melting endothermic peak was observed at 127.5 °C, which is attributed to the melting of the DPIP. This indicates that the melting temperature T_m of DPIP (139 °C) is depressed by 11.5 °C when dispersed in BPAPC. Similar depression of T_m of the small molecule has been noted in the case of TPD when dispersed in BPAPC⁵, diphenyl terephthalate and diphenyl isophthalate when dispersed in poly (styrene-co-n-butyl acrylate)¹, and a liquid crystalline polymer¹⁴. This could be attributed to the imperfection of ordering in these crystals¹. The DSC thermogram in Figure 4.14 suggests that DPIP phase separates at this composition.

Figure 4.14 The depression of T_g of the polycarbonate with 20, 30, and 40 % of DPIP in BPAPC

The samples of DPIP/BPAPC: 40/60 were annealed both in confined and unconfined states at a temperature lower than the T_g of the polycarbonate i.e. at 120, 130, 140 °C for 2 h and 4 h and the results thus obtained are presented in Table 4.3 and 4.4. (it should be noted that the T_g reported here is within the range of ± 2 °C with instrumental uncertainty in the measurement of T_g).

As seen in Figure 4.15, in the confined state, by annealing the film at 120 °C, no clear T_g was observed. Further, no significant change in T_g was observed after annealing the film at 130 °C for 2 h (Table 4.3). However, significant decrease in T_g was observed after 4 h. In addition, a significant decrease in T_g was observed at 140 °C after annealing the film

for 2 h after which no change in T_g was observed with an increase in annealing time. Thus the T_g decreases with an increase in annealing temperature.

In the unconfined state trends similar to that seen with the confined state were observed. At 120 °C (Figure 4.16), no clear T_g was observed while at 130 °C, T_g decreases with an increase in annealing time (Table 4.4). However at 140 °C no significant change in the T_g was observed.

The reason that there was no clear T_g observed at 120 °C in both confined and unconfined states may be due to the high concentration of DPIP in BPAPC resulting in a swelling of BPAPC. A possible reason for the decrease in T_g with annealing temperature could be that the experimental temperatures i.e. 120, 130, 140 °C used for annealing the composite film is near or above the T_m (127.5 °C) of DPIP observed in composites film and as a result the crystals of DPIP melt with an increase in annealing temperature and diffuse back into polymer matrix resulting in plasticization.

Figure 4.17 shows the comparison of T_g between the confined and unconfined states. As is seen from this figure, the T_g decreases significantly in the confined state when compared to the unconfined state at 130 °C and 140 °C. A possible reason for the higher T_g in the unconfined state as compared to the confined state may be due to the sublimation of DPIP at these temperatures.

Table 4.3 Results of Thermal Analysis of DPIP/BPAPC: 40/60 films, after annealing at various temperatures and times in the confined state

Annealing Temperature(°C)	Annealing time (h)	$T_g(^{\circ}C)$	$T_m (^{\circ}C)$	
		BPAPC	DPIP	BPAPC
As prepared		46.1	127.5	
120	2		128.5	
	4		129.9	179
130	2	43.7	129.5	181.8
	4	36.07	132.7	180.7
140	2	36.7	126	182.6
	4	36.6	132.4	186.4

Table 4.4 Results of Thermal Analysis of DPIP/BPAPC: 40/60 films, after annealing at various temperatures and times in the unconfined state

Annealing Temperature (°C)	Annealing time (h)	$T_g (^{\circ}C)$	$T_m (^{\circ}C)$	
		BPAPC	DPIP	BPAPC
As prepared		46.1	127.5	
120	2		128.5	
	4		135.0	177.4
130	2	46.2	127.7	182.6
	4	38.6	130.7	185.6
140	2	47.7	126.07	
	4	46	127.8	189.5

Figure 4.15 Overlay of DSC thermograms of the DP/PP: 40/60 composite film annealed at 120 °C for various times in the confined state.

Figure 4.16 Overlay of DSC thermograms of the DP/PP: 40/60 composite film annealed at 120 °C for various times in the unconfined state.

Figure 4.17 Comparison of T_g between confined and unconfined DPIP/BPAPC: 40/60 composite films

The DSC thermograms of DPIP/BPAPC: 40/60 annealed for 4 h at various experimental temperatures in the confined and the unconfined states are shown in Figures 4.18 and 4.19. A DSC overlay shows a distinct melting endotherm due to DPIP at 128.5 °C for the film annealed at 120 °C in the confined state. A similar peak was observed with annealing at 130 and 140 °C in both confined and unconfined states. However, it is worth noting that the depth of the peak decreases i.e. become shallow with an increase in annealing temperature. This may be due to annealing temperature, which is above the T_m of DPIP (127.5 °C) in DPIP/BPAPC composites and as a result the crystals of DPIP melt. Further, it is interesting to note that both in confined and unconfined states at 120 °C a shallow endothermic peak at 177 °C along with the T_m of DPIP (128.5 °C) appears. This peak becomes more intense with an increase in annealing temperature i.e., at 130 °C and 140 °C. The appearance of shallow endothermic peak at 120, 130 and 140 °C is attributed to the melting peak of BPAPC which suggests that the DPIP in DPIP/BPAPC: 40/60 acts as nucleating agent for BPAPC and promotes the crystallization of BPAPC.

To confirm the crystallization of BPAPC, XRD were run on DPIP/BPAPC: 40/60 composite film annealed at 130 °C for 4 h in both confined and unconfined states and the results thus obtained are shown in Figure 4.20. The X-ray diffraction pattern shows a broad hump in the as prepared composite film suggesting the composite is in amorphous phase, while after annealing the film at 130 °C, a broad crystalline peak was observed at d-spacing (d) = 5.1 Å in both confined and unconfined states.

Figure 4.18 Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures in the confined state.

Figure 4.19 Overlay of DSC thermograms of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures in the unconfined state.

It has been reported^{15,16} that the addition of plasticizer in BPAPC accelerates the crystallization of BPAPC. For example the use of 10% trimellitic acid- tridecyloctyl ester reduces the crystallization time at 170 °C to 100 min from 300 h for unplasticized material¹¹. It is also interesting to note that the T_g of BPAPC is decreased below the T_g observed in as prepared DPIP/BPAPC: 40/60 composite film.

Figure 4.20 X –ray diffraction pattern of the as prepared DPIP/BPAPC: 40/60 composite film, film annealed at 130 °C for 4 h in confined and unconfined states

Optical Microscopy

The optical micrographs of the DPIP/BPAPC: 40/60 composite films annealed for 4 h at various temperature is shown in Figure 4.21. At 120 °C in the confined state, a network of fibrillar crystals are seen. However, with annealing at 130 and 140 °C, tiny crystals of a few μm in size are observed. In addition, a meniscus formation (seen as a band) is also seen in Figures 4.21 c and e. This is attributed to the fact that the annealing temperatures are above the T_m (127°C) of DPIP in the DPIP/BPAPC films, and that the molten DPIP forms a flow pattern in the confined state.

In the unconfined state, at 120 °C, crystals similar to those in Figure 4.21a are seen. However, they are less abundant than in the case of the confined state, due to the partial evaporation of DPIP. At 130 and 140 °C, similar to the confined state, tiny crystals of a few μm in size were observed with an increase in annealing temperature. However, the flow pattern as in Figures 4.21 (c) and (e) is not observed, since the DPIP is “free to sublime”.

The significant change in the morphology i.e. the appearance of tiny crystals at 130 and 140 °C could be due the annealing temperature being above the T_m (127 °C) of DPIP in DPIP/BPAPC composite film. This result corroborates the DSC thermogram (Figure 4.18 and 4.19) where, the depth of the melting endothermic peak of DPIP decreases with an increase in temperature, and second melting endothermic peak which could be the melting endotherm of BPAPC became intense with an increase in temperature.

Figure 4.21 Optical micrographs of the DPIP/BPAPC: 40/60 composite film annealed for 4 h at various temperatures: (a) annealed at 120 °C, confined; (b) annealed at 120 °C, unconfined; (c) annealed at 130 °C, confined; (d) annealed at 130 °C, unconfined; (e) annealed at 140 °C, confined; (f) annealed at 140 °C, unconfined state

4.4 Summary and Conclusions

This chapter described the effect of annealing temperature (120, 130, and 140 °C) and annealing time (0.5- 4 h) on the morphology of DPIP/BPAPC: 5/95, 10/90, 15/85, 40/60 composites films in both confined and unconfined states.

The T_g of the polycarbonate was found to be depressed significantly with an increasing concentration of DPIP in BPAPC. The DPIP was found to be compatible with BPAPC up to 30 % in as prepared composite films. With DPIP/BPAPC: 40/60, a melting endothermic peak was observed and the T_m of DPIP was found to decrease by 11.5 °C. IR spectra show a shift of =C-O absorption band of BPAPC to higher frequency and the shift in C=O absorption of DPIP was also observed in DPIP/BPAPC composite films indicating a molecular level interaction between the carbonyl groups of BPAPC and DPIP. Molecular modeling indicates an interaction between the C=O dipoles of the polymer and DPIP.

In the confined state, with DPIP/BPAPC: 5/95, 10/90, 15/85 the T_g does not change significantly with an increase in either annealing time or temperature. In the unconfined state, the T_g generally increases with an increase in both annealing time as well as annealing temperature. The recovery of T_g with DPIP/BPAPC: 10/90, 15/85 was found to be more pronounced when the film is unconfined. No change in the T_g was observed with DPIP/BPAPC: 5/95 in both confined and unconfined states. With DPIP/BPAPC: 40/60 at 130 and 140 °C the recovery of T_g decreases with an increase in annealing temperature in the confined state while no significant change was observed in the unconfined state. In

addition, the crystallization of BPAPC occurs in both confined and unconfined states with DPIP/BPAPC: 40/60.

No phase separated crystal of DPIP was observed in optical microscopy with DPIP/BPAPC: 5/95, 10/90, 15/85 in both confined and unconfined states in thick as well as in thin film with annealing time and temperature. With DPIP/BPAPC: 40/60 annealing the films in both confined and unconfined states at different time and temperature induces the phase separation of DPIP. Significant differences in the morphology were found between the confined and the unconfined states. Sublimation of DPIP was observed in both the composite film and the bulk DPIP at annealing temperatures between 120 °C to 140 °C and this biases the effect of confinement.

4.5 References

- 1 Alexandru, L.; Zamin, J.; Sundararajan, P. R. *J. Appl. Polym. Sci*, **1991**, 43, 2259-2266
- 2 Ljungberg, N.; Wesselen, B. *J. Appl. Polym. Sci*, **2002**, 86, 1227-1228
- 3 Onu, A.; Legras, R.; Mercier, J.P. *J. Polym. Sci.* **1976**, 14, 1187-1199
- 4 Pizzoli, M.; Scandola, M. *Polymeric Materials Encyclopedia*, **1996**, 7/p, 5301-5308
- 5 Khan, F.; Horr A.M.; Sundrarajan P.R. *J. Phy Chem B*, **2003**, 108 (1), 117-126
- 6 Pavia, D.P.; Lampnam, G.M; Kriz, G.S. *Introduction to spectroscopy*, **2001**
- 7 Tabb, D.L.; Koenig, J.L. *Macromolecules*, **1975**, 8 (6), 929-934
- 8 Theodorou, M.; Jasse, B. *J. Polym. Sci: Polym Phy Edition*, **1983**, 21, 2263-2274
- 9 Papakonstantinou, V.; Papaspyrides, C.D. *J. VinylTechnology*, **1994**, 16, 192-196
- 10 Papaspyrides, C.D.; Papakonstantinou, V. *J. Polym. Eng. ,* **1995**, 15, No 1-2, 153-159
- 11 Papaspyrides, C.D.; Tingas, S.G.; *J. Appl. Polym. Sci*, **2001**, 79, 1780-1786
- 12 Papaspyrides, C.D. *J. Appl. Polym. Sci.*, **1986**, 32, 6025-6032
- 13 Audouin, L.; Dalle, B. et. al. *J. Appl. Polym. Sci.*, 1992, 45, 2091-1096
- 14 Drappel, S.; Sundararajan, P. R.; Rudin, A. *Polymer*, **1997**, 38, 1259-127
- 15 Conix A.; Jeurissen L. Plasticization of bisphenol A polycarbonate, in *Plasticization and Plasticizer Process*, R.F. Gould, Ed. ACS advances in chemistry series No. 48, American Chemical Society, **1965**, 172-184
- 16 Gallez F.; Legras R.; Mercier J.P. *J. Polym. Sci. B: Polym. Phy*, **1976**, 14, 1367-1377

Chapter 5

Conclusions

The effects of confinement on the phase separation and morphology of plasticizer/polymer (DPTP/BPAPC and DPIP/BPAPC) composites was studied. The effect of confinement was apparent from changes in the T_g of polycarbonate, average area of phase separated crystals and melting point of plasticizers in thick films.

It was found that confinement induces significant changes on the phase separation and morphology of plasticizer/polymer composites. The recovery of T_g of BPAPC was found to be more pronounced when the film was unconfined. In thick films the average area of the phase separated crystals in DPTP/BPAPC composites film is larger when films were confined as compared to when the films were unconfined. However in thin films the average area of the crystals was found to be larger when the films were unconfined.

The significant effect of the confinement occurred due to the sublimation of DPTP and DPIP from the composites films in the unconfined state at the experimental temperatures used here i.e. 120, 130 and 140 °C. The sublimation of DPTP and DPIP in composites films occurred due to the depression of the melting temperature of DPTP and DPIP when dispersed in BPAPC. The melting temperature of DPTP is reduced by approximately 46 °C with DPTP/BPAPC: 10/90, 15/85 and by approximately 12 °C with DPIP/BPAPC: 40/60 when dispersed in the BPAPC.

Chapter 6

Recommendations for Future Work

Ours is one of the very few groups in the world studying the effect of confinement on the morphology and phase separation of polymer/small molecule composites. This has important applications relevant to the functional performance of multi-layered optoelectronic devices. This thesis is the first step in this direction. Some of the recommendations for future work include:

1. To study the effect of following parameters on the morphology of plasticizer/polymer composites in confined and unconfined states:
 - Soft surfaces, which are interacting and non-interacting with the composite film.
 - Varying the thickness of the composite films.
 - Varying the pressure between two microscopic slides
2. Further investigation should be undertaken to validate the conclusion of this thesis using different polymer composites such as TPD/BPAPC composites that are in used commercially as CTL layer of photoreceptors.
3. A more in depth study should be undertaken to understand the functional group interaction between the polymer and the plasticizer using molecular modeling. Molecular dynamics simulations could be used to study the diffusion rates of the plasticizer in the polymer under unconfined and confined conditions.
4. An investigation should be undertaken to study the effect of various parameters on T_g in thin films in both confined and unconfined states.

APPENDICES

Appendix A: Optical Micrographs

Figure A 1 Optical micrographs of evaporated plasticizers: (a) DPTP from bulk, (b) DPTP from DPTP/BPAPC: 15/85 composite film, (c) DPIP from bulk, (d) DPIP from DPIP/BPAPC: 10/90 composite film

Figure A 3 Optical micrographs of the DPTP/BPAPC: 15/85 composite film annealed at 140 °C for 0.5 h (a) Confined state; (b) Unconfined state

Figure A 3 Optical micrographs of the DPTP/BPAPC: 10/90 composite film annealed at 120 °C for 3 h (a) Confined state; (b) Unconfined state

(a)

(b)

(c)

Figure A 4 Optical micrographs of the unconfined DTP/BPAPC: 15/85 composite film annealed for 1 h at various temperatures: (a) 120 °C, (b) 130 °C, (c) 140 °C

Figure A 5 Optical micrographs of the confined DPTP/BPAPC: 15/85 thin composite film annealed at 120 °C for various times: (a) 1 h, (b) 2 h, (c) 3 h

Appendix B: DSC Thermograms

Figure B 1 Overlay of DSC thermograms of the confined DPTP/BPAPC: 10/90 composite film annealed at 130 °C for various times.

Figure B 2 Overlay of DSC thermograms of the unconfined DPTP/BPAPC: 10/90 composite film annealed at 130 °C for various times

Figure B 3 Overlay of DSC thermograms of the confined DPTP/BPAPC: 5/95 composite film annealed at 130 °C for various times

Figure B 4 Overlay of DSC thermograms of the unconfined DPTP/BPAPC: 5/95 composite film annealed at 130 °C for various times