

**STUDIES ON THE EFFECT OF NUCLEATING
AGENTS ON THE CRYSTALLISATION
BEHAVIOUR OF POLYESTERS**

by

DEBAPRASAD MITRA

Centre for Materials Science & Technology

A thesis submitted
in fulfilments of the requirements
of the degree of
DOCTOR OF PHILOSOPHY



to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

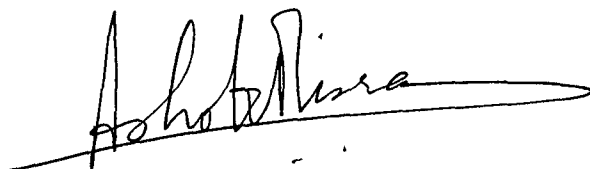
May 1987

Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled "Studies on the Effect of Nucleating Agents on the Crystallisation Behaviour of Polyesters" being submitted by Mr. Debaprasad Mitra to the Indian Institute of Technology, New Delhi for the award of the degree of Doctor of Philosophy in the Centre for Materials Science and Technology, is a record of bonafide research work carried out by him. Mr. Debaprasad Mitra has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.



(ASHOK MISRA)

Thesis Supervisor
Centre for Materials Science
and Technology,
Indian Institute of Technology, Delhi
New Delhi-110016

ACKNOWLEDGEMENTS

It is impossible to do proper justice to one's own sense of gratitude and indebtedness if it has to be expressed in few common and formal lines. However, it is a great pleasure for me on this occasion to express my sincerest thanks to Professor Ashok Misra, Centre for Materials Science and Technology, Indian Institute of Technology, Delhi. It is due to his outstanding guidance, constant encouragements and constructive criticisms that this work could be completed satisfactorily within stipulated time.

I am thankful to Professor (Mrs.) I.K.Verma, Head, Centre for Materials Science and Technology, I.I.T. Delhi for providing all the facilities in the centre. I also wish to thank Dr.A.K.Gupta for his whole hearted cooperation throughout my research work.

I am much thankful to Dr.B.L.Deopura, Assistant Professor, Dept. of Textile Technology, I.I.T. Delhi, for his fruitful discussions and for providing instrumental facilities in the Department.

My special thanks are due to my group mates Dr.S.K.Bhattacharya, Dr.A.Tendolkar, Mr.R.S.Halder, and Dr.S.K.Sharma whose contributions towards my work during our frequently held group meetings helped me gain theoretical as well as practical knowledge.

I wish to express my thanks to Mr.D.C.Sharma for the excellent quality of photographic work.

Last but not the least, I am thankful to M/s.SOFTPRO ASSOCIATED for wordprocessing of this thesis.

Debaprasad Mitra
(Debaprasad Mitra)

ABSTRACT

The effect of different nucleating agents on the crystallisation of polyesters, e.g. polyethylene terephthalate (PET) polybutylene terephthalate (PBT) has been studied. The major portion of the work has been devoted to the study of the effect of organic nucleating agent, namely dibenzylidene sorbitol (DBS) on the crystallisation of PET. This nucleating agent was mixed with PET using different blending techniques, solution blending and melt blending. The former process gave slightly better uniformity in dispersion of the nucleating agent. The effect of DBS on the crystallisation of PET was studied by differential scanning calorimetry (DSC), density measurements, wide angle X-ray diffraction (WAXD). The optical and morphological properties were studied using spectrophotometer and small Angle light scattering (SALS). The effect of potassium monophthalate, (KPH) plasticiser neo-pentyl dibenzoate on the crystallisation and morphology of PET was also studied.

Thermal analysis by DSC showed that the temperature (T_{ch}) of crystallisation from glassy state markedly decreased in presence of DBS. The effect was maximum when

DBS was used in the range of 0.5 - 1%. Beyond this level, the effect was slightly reduced. The temperature of crystallisation from melt (T_{cc}) was also increased indicating the nucleating effect of DBS.

The overall rate of crystallisation of pure PET and PET nucleated by DBS was measured by density and WAXD. The half time of crystallisation of PET was found to be considerably reduced by DBS. The induction period was also observed to be reduced significantly in presence of DBS. The effect was slightly reduced when DBS was added beyond 1 weight%. Study of crystallisation by WAXD showed the same kind of effect of DBS.

The morphology and optical property were studied by SALS and spectrophotometry. Study by SALS showed that the sizes of the spherulites were significantly reduced in presence of DBS. The optical clarity of PET increased thereby due to formation of smaller spherulites. In these studies also, it was observed that the effect of DBS on the morphology increased with the increase in the level of the same but beyond a certain level, there was no additional effect; rather the excess amount of DBS might form agglomerates which decreased the rate of crystallisation slightly and also gave scattering of visible light which was harmful for optical clarity.

The phenomenon of agglomeration was conclusively proved by the study of V_v scattering of the films. Some amorphous polymers e.g., polystyrene (PS) and polycarbonate (PC) were selected as these would provide the ideal matrix for the study of density fluctuation taking place on incorporation of the foreign ingredients and these density fluctuations are related to the agglomeration size. Using the theory of Debye and Bueche, the sizes of the agglomerations, where DBS was used in these polymers in certain higher levels, were determined.

The effect of DBS on the crystallisation and morphology of polybutylene terephthalate (PBT) and polycarbonate (PC) was also studied. Thermal study showed that the effect of DBS on the crystallisation rate of PBT was not very significant. DBS also did not change considerably the spherulite size of PBT crystallised at different temperatures. At higher temperatures, the little change in spherulitic size was observed. PC ^{in presence of DBS} was found to develop fully identifiable crystalline morphology when crystallised ^S at higher temperature for a time which is considerably lower than that required for pure PC. The crystal morphology of PC was confirmed both by SALS and WAXD studies.

The effect of KPH on PET was not as remarkable as that in case of DBS. The main disadvantage of KPH was observed to be poor uniformity in mixing. This was manifested in both thermal and morphological studies. The plasticizer neo-pentyl dibenzoate was observed to have little effect on crystallisation rate of PET. But when used alongwith DBS, the increased rate was comparable to PET containing DBS only. Another remarkable difference observed, was that the ultimate spherulitic radius for PET containing both DBS and plasticiser was slightly higher than that for PET containing DBS only, It might be due to the less effectiveness of DBS in presence of plasticiser. In presence of plasticiser, the chance of nucleation become less which might be due to dilution effect.

CONTENTS

Page No.

ABSTRACT

CHAPTER I

1.1	General Introduction	1
1.2	Literature Review	5
1.2.1	Crystallisation of polyethylene terephthalate (PET) without nucleating agent	5
1.2.2	Crystallisation of PET with nucleating agents	9
1.2.3	Crystallisation of Bis-phenol-A polycarbonate (PC)	13
1.2.4	Crystallisation of polybutylene terephthalate (PBT)	15
1.2.5	The study on the crystallisation of polyolefines with nucleating agents	17
1.3	Objective of the present work	19

CHAPTER II EXPERIMENTAL

2.1	Materials	22
2.2	Mixing of the nucleating agents with Polymers	24
2.3	Sample Preparation	26

CHAPTER III THERMAL ANALYSIS

3.1	Qualitative Analysis	36
3.1.1	Results	36
3.2	Study on the Kinetics of non-isothermal crystallisation of PET by DSC	41

3.2.1	Introduction	41
3.2.2	Characteristics of the Kinetics of non-isothermal crystallisation	42
3.2.3	Methods of determining analytical quantities on the non-isothermal Kinetic study on the crystallisation of polyethylene terephthalate	45
3.2.4	Results and Discussions	47

CHAPTER IV CRYSTALLISATION KINETICS

4.1	Introduction	53
4.2	Kinetics of Crystallisation: The Avrami Equation	55
4.3	Results and Discussion	63
4.4	Crystallisation Rates By X-Ray Method	70

CHAPTER V MORPHOLOGY AND OPTICAL PROPERTIES

5.1	Morphological study by small angle light scattering (SALS)	
5.1(a)	Introduction	72
5.1(b)	The basic concept of the theory of light scattering	74
5.2	Study on the clarity by the method of optical transmittance measurements	82
5.3	Results	83

CHAPTER VI KINETICS OF SPHERULITIC GROWTH

6.1	Introduction	90
6.2	Nucleation	
6.2.1	Homogeneous Nucleation	91
6.2.2	Heterogeneous Nucleation	93
6.3	Growth in Polymer Crystals	97
6.3.1	Growth rate	98
6.4	Results and Discussion	100

CHAPTER VII	DISPERSION OF NUCLEATING AGENT	
7.1	Introduction	105
7.2	Theoretical Background	107
7.3	Results and Discussion	109
CHAPTER VIII	PBT AND PC MORPHOLOGY	
8.1	Crystallisation and Morphology	116
8.1.1	Introduction	117
8.1.2	Results and Discussion	
8.2	Crystallisation of PC	120
8.2.1	Introduction	120
8.2.2	Results and Discussion	121
8.2.2(a)	Thermal Study by DSC	121
8.2.2(b)	WAXD	122
8.2.2(c)	Morphological Study by SALS	122
CHAPTER IX	SEMIORGANIC NUCLEATING AGENT AND PLASTICISER	
9.1	Introduction	124
9.2	Effect of KPH	125
9.3	Effect of Plasticiser And Plasticiser & DBS on PET	126
9.3.1	Thermal Studies	126
CHAPTER X	SUMMARY, CONCLUSIONS AND SCOPE OF FUTURE WORK	
	Summary	128
	General Conclusions	134
	Suggestions for Future Work	136
	Reference	137