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

by

DEBAPRASAD MITRA

Centre for Materials Science & Technology

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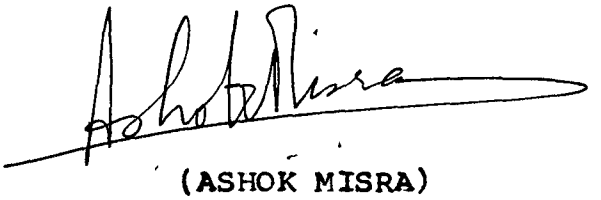
Dedicated to my parents

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

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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 beter 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 (Tch) 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 (Tcc) 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 differenct 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 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.

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