Ministero dell'Università e della Ricerca

Università degli studi di Palermo

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali

Influence of plasticizers (or excess free volume) on semi-crystalline polyester blend solidification under processing conditions

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2008-2010

DECLARATION

I hereby declare that the dissertation entitled '**Influence of plasticizers (or excess free volume) on semi-crystalline polyester blend solidification under processing conditions**' is my own work and to the best of my knowledge and belief, it contains novel works, not previously published or written by another person nor materials which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgement has been made in the text and within the appendices.

Signed:

…….

Dedication

I dedicate this work to my parents and to my brother whose support and confidence in my capability has been unflinching throughout this academic sojourn.

Acknowledgements

I would like to sincerely thank **Prof. Stefano Piccarolo**, for serving as my advisor and giving me opportunities and ample resources to perform this research over the past few years. I would like to thank **Prof. Dr. H.J. Radusch,** for giving an opportunity to perform experiments in the research group of Polymer Engineering Center of Engineering Science Halle Germany and my gratitude towards the other members of the group Dr. Ing. R. Androsch, Daniela Mileva, Qamar Zia should be mentioned. I would like to thank **Dr. Concetto Puglisi**, the director of ICTP Catania for the instrumental availability and help from Ing. Domenico Carbone should be acknowledged. I owe my sincere gratitude to **Prof. Filardo Giuseppe**, Director of DICPM and I extend my thanks to all other professors and technicians for their help rendered throughout my research. I take this opportunity to thank **Dr. C. Ramesh**, Scientist (National Chemical Laboratory, Pune, India) and all other colleagues from the University of Palermo, especially Prof. Zebene Kiflie, Prof. Valerio Brucato, Prof. Giuseppe Spadaro, Asst.Prof. Enzo Lacarruba, Dr. Francesco Carfi, Alessandro Luzio, Vincenzo Palermo, Antonio falsone, and Nicolo' Montalbano. I find it difficult for me to write something in short to acknowledge my close friends like Sinto Jacob, Sabu Varghese, Jinto M.A., Lijo Francis, Sanosh K.P, Davis Puthussery, Fr. Martin Ponnittuseriyil, Fr. Francis Adappoor, James Lopez, Smitha Nair, Renjitha R., Dhanya P.R., Vincy V. and Mini Mary who all made my life much easier in Palermo. I extend my profound heartfelt sentiments of gratitude to my former teachers, colleagues and friends in the Star Jesus High School Karukutty, Christ College Irinjalakkuda, St.Thomas College Thrissur and Cochin University of Science and Technology. It gives great pleasure to me to express my deep sense of affection to my parents **Mr. M.J. Poulose** and **Mrs. Rosy Poulose** and to my brother **Manu**. They have been my constant source of strength and determination, and have brought a great deal of happiness to my life. I take this unique opportunity to thank all those, who contributed in some way or the other in my research odyssey, but whose names could not be included. Last but not least I would like to express

my profound sense of infinite gratitude to **Almighty Lord** whose grace and enormous blessings showered through the intercession of Santa Rosalia.

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1. INTRODUCTION

Polymer is the technical name for what is more generally known as plastic. New properties, lower prices and reuse of polymers are needed to meet the demands of today's society. For the plastics designer and processor, alloys and blends of dissimilar polymers provide new materials that are tailored to specific application requirements with performances that could not be duplicated by an existing single polymer. The science and technology of polymer blends has now acquired an important position in the area of development of new polymeric materials. Polymer blends constitute ~30% of the total polymer consumption and their pertinence continuous to grow. Annually about 5000 patents are published in world wide. The polymer blending has been accepted as an efficient and inexpensive method of property diversification and to improve the processability of the existing polymers without having to synthesise novel structures [L.A. Utracki 1998].

The blending technique applied has significant effect on the miscibility and on the resulting properties. Hobbs *et al.* [S.Y Hobbs 1987] clarified the influence of the technique of blend preparation; melt-mixed Vs solution blended, demonstrating that the former procedure may lead to a partially miscible blend and good mechanical properties [C. P. Papadopoulou 1997] whereas solution casting generally leads to a phase separated system. This is due to the combined effect of liquid-liquid phase separation and the crystallization of both polymers produces complete separation of the polymers in the cast films. In polyester blends the ester exchange reactions take place in the melt can affect their miscibility and final properties, which is discussed in detail in the literature section.

There are only few polymer blend systems of two individually crystallisable components with complete miscibility in the melt. One of such systems is PBT/PET being more widely studied because of their commercial importance [A. Escala 1979; Avramova 1995; Y. Yishan 1997; S. N. Garg 1981; S. P. Mishra 1985; J. Font 1999; B. Wunderlich 1953; M. Chen 2002; G. Aravinthan 2005]. PET is known as one of the most commercially relevant synthetic engineering thermoplastic polymer with

desirable physical properties like strength, stiffness, toughness, heat resistance etc. and find applications in daily life such as soft-drink bottles, photographic films, recording audio and video tapes, films for food packaging, or even as an electrical insulating material for capacitors. On the other hand PET, is a slow crystallizing material and blending with PBT will give the processing advantages of PBT (low melt and mold temperatures, rapid crystallization, and faster cycles), retaining basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance [K. Dangayach 1997] i.e. This system (PBT/PET) shows a synergistic effects in crystallization and in mechanical properties. PBT/PET blends have been commercialised by 'DSM engineering plastic' in the name of 'Arnite' due to its excellent combinational properties like

- Extremely low moisture absorption
- Exceptional dimensional stability
- Excellent electrical insulation properties, even at elevated temperature or in humid environment
- Excellent chemical resistance
- Good thermal resistance and heat aging properties
- High strength and stiffness of reinforced grades
- Easy moldability
- Good wear resistance properties
- Very good colour stability

As a result, such blends are well suited for a broad range of automotive, electrical/electronic, appliance and industrial equipment applications. [http://www.dsm.com/en_US/html/dep/arnite.htm]. The miscible blends of PET/PBT maintain transparency (but not PET alone) in almost all cases regardless of the blending ratio and finds application in packaging [Yoshitsugu Maruhashi 2001].

Studies related to the polymer crystallization are of great importance in polymer processing as the resulting physical properties are strongly dependent on the morphological structure (size, shape, perfection, volume fraction, and orientation of crystallites) formed by crystallization occurring during processing [S.W. Lee 1999].

Due to experimental difficulties, the study of polymer structure developed under processing conditions has been mainly performed using conventional techniques like dilatometry [Zoller Paul 1978; Jing He 1992; V. La Carruba 2002] and differential scanning calorimetry [D.M. Fann 1998; L. Liangbin 2000]. In such techniques often involve experiments under isothermal conditions or non-isothermal conditions but at cooling rates several orders of magnitude lower than those experienced in industrial processes, which often leads to quite different structures and properties. Thus, for crystallisable polymers, the crystallization behaviour especially conditions which are closest to real industrial processing is an interesting research subject to control morphological structure and for optimizing their processes and understanding properties of the processed products. In this work a continuous cooling transformation approach is applied in order to mimic the real conditions which generally met during processing [V. Brucato 2002].

2. GENERAL INTRODUCTION ON POLYMER BLENDS FOCUSED ON POLYESTERS AND THEIR CRYSTALLIZATION BEHAVIOUR

Literature survey on polymer blends: What has been done in earlier work?

2.1 Super molecular structures shown by crystalline/crystalline blends:

Binary polymer blends exhibit wide variety of super molecular structures and phase morphologies which depend on the miscibility of the components, their crystallization in particular as well as the resulting morphologies. The resulting crystalline structures have consequently been subject of continuing interest for researchers from both academia and industry. Most of the studies are focused on the polymeric mixture containing two amorphous components or amorphous and semi-crystalline components [W.B. Wu 1997]. On the other hand, polymer blends containing two crystalline components are less frequently discussed. There are only few polymer blend systems of two individually crystallisable components which form homogeneously mixed melt in the whole composition range and at all accessible temperatures. Examples are the systems of poly (vinylidene fluoride) /polyhydroxybutyrate (PVDF/PHB), poly (carbonate of biphenyl A/poly-ε-caprolactone) (PC/PCL), poly (ethylene terephthalate)/poly (butylene terephthalate) (PET/PBT) and PHB/poly (ethylene oxide) (PHB/PEO). Jungnickel and co-workers investigated in detail the blend system of Poly (vinylidene fluoride)/Poly (hydroxybutyrate) [PVDF/PHB] which shows wide variety of morphological super structures depending on the thermal treatment and blend partners which grow in their own lamellar stacks [Jieping Liu 2007].

a) Spherulitic crystallization of the components side by side.
b) Interpenetrating crystallization where spherulites of the one component intrude in those of the other.

c) Interlocking spherulitic crystallization may be observed in which one component nucleates its spherulites in the internal of the other and then grows.

d) Finally, interfilling crystallization may happen where the second component that is included in the amorphous regions of the spherulites of the first and crystallizes.

Since various morphologies that might be encountered in blends of two crystallisable components, the crystallization studies in such systems are highly interesting and show a significant degree of complexity. It can proceed along a large number of solidification paths, which in turn depends on miscibility issues, trans-esterification reactions, along with separate crystallization of individual components, which are discussed in detail in the following sections.

2.2 PBT/PET blends: various crystallization features and different techniques applied for the studies:

PBT and PET are well-known semi-crystalline polymers. The crystal form of PET is triclinic [T. Asano 1999; D. Raabe 2004] and controversies in the interpretation of WAXD of PBT are reported, both monoclinic and triclinic form is assigned [J. Liu 1997; M. L. Di Lorenzo 2003]. First report on the crystallization kinetics and the morphology of crystalline/crystalline polymer blends with homogeneous melt was from the late 1970s by Stein *et al*. [Stein 1978] whose work is one of the few studies on melt blended PET/PBT. WAXD scans on melt blended PET/PBT shows diffraction pattern which is characteristic of pure homo polymer with no appreciable shift in the peak positions. The spectra of the blends by Infra Red (IR) were essentially a superposition of contribution from the individual components. DSC studies on such blends showed separate melting peaks for the two crystalline components and on fast heating scans revealed single T_g, which is an evidence for the amorphous compatibility. The glass transition temperature obtained were closely matches with those predicted by fox equation [$1/T_g = W_a/T_ga + W_b/T_gb$], W_a, W_b and T_ga, T_gb are the weight fractions and the glass transition temperature of

the individual components respectively. By WAXD, IR and DSC techniques, the authors excluded the possibility of co-crystallization due to the mis-matching of the crystallographic parameters and also to the fact that larger co-crystallized crystals are not stable due to steric reasons.

Avramova **[**Nadka Avramova 1995] studied amorphous PET/PBT blends [xPET/ (1-x) PBT; x=1, 0.9, 0.8, 0.6, 0.5, 0.4, 0.2, 0.1, or 0] characterised by amorphous structure were prepared by ultra quenching of the melt between two metal rolls rotating in a liquid nitrogen bath. Both NMR and IR spectra indicates that the mixing procedure is not accompanied by any chemical interactions. Such blends were studied by WAXS, DSC and mechanical testing. The blends thus prepared are at highly non-equilibrium state and undergoes low temperature relaxation during storage at low temperature well below their T_g. DSC studies shows single T_g which is in between those of the individual ones, is an evidence for the amorphous miscibility. The theoretical predictions of compatibility of PBT/PET blends are based on the calculation of interaction parameter, and free energy [S.P Mishra 1985]. Among the various thermodynamic properties, such as Gibbs free energy of mixing, entropy of mixing; quantitative information about the polymer–polymer interactions are the most important element for controlling phase behaviour of blends and morphology. In PBT/PET blends the miscibility is due to the intermolecular interaction between the terephthalate residues of the individual components and the tetra-methylene glycol units of PBT provide more flexibility in order to facilitate such interactions. Such interactions can overcome the dispersion forces and can contribute to mixing. In spite of the composition, all blends show one crystallization exotherm and exhibit usual melting endotherms of the two individual components. Thus both PET and PBT crystallize simultaneously and the polymer does not form isomorphic crystals except for the compositions 10PET/90PBT and 10PBT/90PET. This system shows only one melting endotherm as 10% of the dispersed component in the matrix of the other, is not enough to form its own crystals even though it is sufficient to affect T_g and crystallization behaviour. The blends containing 60% PET starts to crystallize at a lower T_c than pure PBT which

shows that addition of PET to PBT does not suppress but is even favourable for the crystallization. In PBT/PET blends synergistic effects in the crystallization as well as in the mechanical properties were observed. i. e. both components are miscible in the amorphous phase, crystallize simultaneously and each one enhances the crystallization of the other. There are two reasons behind this a) fast crystallized PBT can act as thermal nuclei for the crystallization of PET and b) addition of PBT decreases T_g and improves the crystallization. Mishra *et al.* [Siba P. Mishra 1985] investigated the crystallization behaviour of PET/PBT blends at low % of the second component (2, 4, 6, 8, 10 wt %). The non-isothermal melt crystallization studies (5 and 10 K/min) of PET/PBT blends with lower wt % of PBT indicates that the crystallization rate is lower than that of pure PET. Thus during crystallization, PBT may remain uniformly distributed in the amorphous part of the PET and hinders the crystallization rate.

The processing operations can affect the kinetics of phase transitions and determines the morphology and properties of the final product. The methodologies applied have an important role in the characterization and even in the definition of the scale of miscibility of these complex polymer systems. So the solidification behaviour of PBT/PET (60/40 w/w) blend is studied in a wide range of cooling conditions, according to a 'Continuous Cooling Transformation' (CCT) procedure, aiming to emulate the typical conditions generally come across during polymer processing. Several samples characterized by a homogeneous structure were solidified from the melt at various cooling rates and the resulting structure and properties were subsequently evaluated by analyzing the density, Micro Hardness (MH), and Wide Angle X-ray Diffraction (WAXD). The resulting crystallization behaviour then compared to that of pure components. It was found that PBT crystallizes up until dT/dt of ~300K/s, PET of ~2K/s, and the blend crystallizes up to an intermediate cooling rate of around 50K/s. The density of the amorphous samples of the blend (at high cooling rates) is significantly lower than predicted by the rule of mixtures and assumed that this limit is related to the demixing of the two moieties before crystallization [La Carrubba 2007].

The melting, crystallization behaviour and non-isothermal crystallization kinetics of the ternary blends composed of poly (ethylene terephthalate), poly (trimethylene terephthalate) (PTT) and poly (buthylene terephthalate) (PBT) studied by DSC where PET/PTT content varied and the weight ratio of PBT kept constant. DSC thermo gram shows single and composition dependent glass transition temperature, i.e. PET, PTT, and PBT components are miscible in amorphous state. There is two melting peaks for each ternary blend, in which peak I at higher temperature is corresponds to the crystals of PET, and peak II at lower temperature is those of PBT and PTT or mixed crystals of PTT/PBT. Only one melt crystallization exotherm peak is shown in DSC curve where the weight ratio of PET/PTT/PBT are 10/50/30 and 50/10/30 which is an evidence for simultaneous crystallization [Mingtao Run 2007].

2.3 Block copolymers of PET/PBT:

Block copolymers of PET/PBT were synthesised by using antimony trioxide as a poly condensation catalyst and small amounts of PBT have much larger effect on the crystallization rate in block copolymers than in physical polyester blends [A. Escala 1979; A. Misra 1986]. Small Angle Light Scattering (SALS) studies on block copolymers of poly (ethylene terephthalate) (PET) and poly (buty1ene terephthalate) (PBT) revealed that PBT, which is the faster crystallizing component crystallizes first and provides nucleation sites for the crystallization of PET. It is found that with an increase in PBT content in the block copolymer, the spherulite size is decreased and an increase in nucleation density is observed [A. Misra 1986].

2.4 PEN/PET blends: Trans-esterification and phase behaviour:

Another polyester system widely studied is PEN/PET blend. Due to low permeability towards oxygen (PEN), this is an excellent material especially for beverage bottles. But this system shows phase separation due to partial miscibility [Z. Denchev 2002]. When these two polymers are melt blended, the end groups can react with each other, create block copolymer by trans-esterification reaction, often

acts as compatibilizer between these two phases improving miscibility. This in turn influences the gross structure through their phase behaviour and ultimately the final properties of the blends. Stewart *et al*. reported that the primary factors controlling the trans-esterification were the blending time, temperature, and the composition of the blend and the residual polyester catalysts had little or no effect on such reactions [M.E Stewart 1993]. Thus to obtain well-designed materials one has to be able to control these competitive processes of domain growth and homogenization induced by the trans-esterification occurring simultaneously in the blend during the melt extrusion processes. Okamoto *et al*. [Masami Okamoto 1997] investigated competitive domain-structure development and homogenization under annealing via time-resolved light scattering and ^{1}H NMR, in melt-quenched blends of partially miscible poly (ethylene naphthalene-2, 6-dicarboxylate) (PEN) and poly (ethylene terephthalate) (PET). NMR studies showed that the phase separation in this system occurs by the demixing of individual components by spinodal decomposition and on annealing trans-esterification starts to occur through the domain interface, and gradually leads to a homogeneous system due to the miscibility enhancement by PEN-PET multi block copolymer species. Some researchers [Dylan Dae Bong Jung 2007] did the spectroscopic analyses of PEN/PBT blends, which provide no direct evidence for the occurrence of trans-esterification reactions during melt-processing of the blends within the temperature range 250-280^{0}C.

2.5 Cold crystallization studies in PTT/PEN, PTT/PET and PTT/PBT systems:

Although the cold crystallization of PET has been used in industry to obtain larger stiffness and resistance in injection moulded parts, very few studies have been developed to investigate the kinetics and mechanisms of cold crystallization. The evaluation of the kinetics of cold crystallization has much importance in processing techniques like injection blow moulding and thermoforming, where the premature crystallization hinders the forming stage and is one of the main consequences of processing faults. The PTT/PEN blend system [Pongpipat Krutphun 2005; Mingtao Run 2006] shows single T_g, apparently related to amorphous miscibility decreases

monotonically with increasing PTT content and is being successfully described by the Gordon–Taylor equation.

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_1}$$

Where W_1 and W_2 are the weight fractions in the amorphous phase of the components, T_{g1} and T_{g2} are the T_g values of the pure components 1 and 2 respectively, and k is an adjustable parameter, ~0.57. The cold crystallization peak decreases with increasing the amount of highly crystallizing constituent (PTT) in the blend. PTT/PBT [Nujalee Dangseeyun 2004] and PTT/PET [Hao Liang 2008] systems found to be miscible at all compositions. As expected the cold crystallization temperature is found to increase with the PTT content.

2.6 Trans-esterification reactions: its significance on crystallization:

Further complications in the solidification of PBT/PET blends arise by the interchange reaction taking place between the two constituents and thus affecting the final structure of the blends. Yishan [Yishan Yu 1997] showed that the behaviour of crystallization from glassy state is influenced by entanglement and trans-esterification of chains. In the case of blends prepared by high speed melt mixing (i.e. high entanglement between the chains of PET and PBT in the amorphous phase) show two crystallization peaks and those by low mixing speed yields a single crystallization peak. Kim and Kang [H.K. Kim. 2006] showed the evidence of trans-esterification reaction between PEN and PBT by thermal annealing at 270^0C for 30 min, by Differential Scanning Calorimetry (DSC) and NMR. Dae Woo *et al*. [Dae Woo Ihm 1996] studied the influence of trans-esterification on the miscibility of poly (ethy1ene terephthalate)/poly (ethy1ene 2, 6-naphthalate) system. DSC thermo-grams in the region of glass transition of 50/50 PET/PEN blend, after the annealing at 270, 280, and 290°C for 5-80 min showed that as the annealing time increases, the two T_g's related to PET and PEN components start to merge. The melting peaks disappear for the samples, which were annealed for 80 min and have a single T_g. It is understood that the length of homo-segments in polymer chain decreases and the

crystal formation is disturbed due to the irregularity of the structure with the progress of such reactions.

Trans-esterification reactions in the condensation polymers have been extensively studied [L. Alexandrova 2002; M .Guo 1998]. The miscibility in these polymers could be improved via formation of copolymers resulting from intermolecular exchange reactions but there is negative effect on crystallization. As interchange reactions proceed, blends convert initially to block copolymers and finally to a random copolymers. ^{13}C NMR [S. C. E. Backson 1995; B. Jacques 1996], ^{1}H NMR [H. Matsuda 2002] and SANS (Small Angle Neutron Scattering) studies [S.C.E. Backson 1999] gives the evidence for such randomization processes although such evidences show up only when the extent of randomization is significant. Recently, it is shown that crystallization itself is a very sensitive probe of such randomization processes such that they become relevant even when NMR methods do not have enough sensitivity for their probing.

To control trans-esterification in polyester processing, many experiments have been conducted. Phosphite addition (Triphenyl phosphite, TPP) [S. M. Aharoni 1986; B. Jacques 1996], $BaSO_4$ [Sang Soo Lee 2001] and Silica nanoparticles [Feng Wang 2008] are presumed to reduce such ester interchange reactions. The suppression of the trans-esterification reaction is by the anchoring of polymer chains on the $BaSO_4$ surfaces and the corresponding formation of a block copolymer-like structure supposed to cause the facilitation of crystallization and an increase in the mechanical properties. High active surface hydroxyl groups of SiO_2 can react with end groups of PET and PBT leading to the inhibition of trans-esterification reactions.

Available literature on blends shows that crystallization in polymer blends can proceed along a large number of solidification paths which results in a huge variety of super molecular structures depends on the miscibility of the components, i.e., whether they are completely miscible in the whole accessible composition and temperature range, whether they exhibit a miscibility gap or forms separated phases.

These features are interesting from the underlying thermodynamics, from the rheology which governs the crystallization kinetics, as well as from their impact on the material properties.

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3. STATE OF ART ON IMPROVING CRYSTALLIZATION BEHAVIOUR OF POLYESTERS WITH FOCUS ON PET

3.1. PET as an engineering thermoplastic material and its processing difficulties:

In comparison with poly (butylene terephthalate) (PBT), PET exhibits better physical properties such as higher dimensional stability, larger modulus, yield stress and it is comparatively cheaper. However for the application of PET as an engineering plastic, the polymer must be easily processable by common processing techniques like injection moulding, blow moulding etc. For the success of this process, it is important that the polymer crystallizes rapidly so as to complete the crystallization. This is the most important shortcoming of PET since its crystallization rate is too low to permit reasonable cycle times for injection moulding.

3.2. Different methods reported in literature to improve PET crystallizability:

A number of physical methods have been applied to enhance the crystallization rate of PET. The following are some of the methods cited in the literature and are briefly summarized. PET crystallized from the melt under high pressure (400 MPa) in the temperature range 295-320°C results a material with 90% degree of crystallinity [F.J. Balta´ Calleja 1994; U. Kolncke 1996] (high pressure induced crystallization). Roland has investigated the annealing of PET at higher temperature [C. M. Roland 1991] and the crystallinity of PET was found to increase from 45% to 60% for samples annealed at 260^0C for 700 hours. But both high pressure and high temperature crystallization resulted in substantial reduction in the toughness and even in the molecular weight. Other methods were also reported such as heterogeneous nucleation by talc [Krista Bouma 2001], homogeneous nucleation by incorporating di-amide segments [Krista Bouma 2001], and Co-diols [Krista Bouma 2001] in the chain. Small quantities of such nucleating agents are able to improve

the nucleation of PET by lowering the interfacial surface free energy. However nucleated PET crystallizes much more slowly than PBT.

Another important method, widely applied in order to transform amorphous to semi-crystalline state is by solvent treatment. Solvent Induced Crystallization (SINC) has been the subject of increasing interest for both amorphous and semi-crystalline polymers. One reason for this interest is the recognition that the physical structure and morphology of SINC polymers may be significantly different from that produced by thermal and stress induced crystallization. Extensive research on solvent-induced crystallization of PET has been conducted [Ajit B. Desai1974; P.J. Makarewicz 1978; A.H. Khan 1981; Hasan Jameel 1982; Shaow Burn Lin 1983; C.J**.** Durning 1986; C.J. Durning 1986; Hao Ouyang 2002; D. Chidambaram 2003; Wen Hao Lee 2003; Beatriz Veleirinho 2008]. The solvents widely used are dimethyl formamide (DMF) [Hasan Jameel 1982], Dioxane [Ajit B. Desai 1974], methylene chloride ($MeCl_2$) vapour [C.J**.** Durning 1986], trichloroacetic acid–chloroform (TCAC) mixture [D. Chidambaram 2003], Acetone **[**Hao Ouyang 2002], and trifluoroacetic acid/dichloromethane (TFA/DCM) mixture [Beatriz Veleirinho 2008]. Spectroscopic studies (IR) [A.H. Khan 1981; Shaow Burn Lin 1983; D. Chidambaram 2003] were reported in literature in order to get information on molecular orientation and trans-gauche conformation of drawn PET. Polymer-solvent interaction studies by Atomic Force Microscopy (AFM) were carried out [Christopher Freure1999] to get better understanding of the effects of solvent interaction at the surface of PET films and to study the stress cracking phenomenon.

In addition to the changes in the crystalline structure, SINC has been shown to cause (a) local spherulite deformation, (b) stress cracking, (c) cavitation caused by the diffusion front of the solvent being evaporated out of the bulk material, d) internal void structure etc. The onset of such features, depend on the solvent interaction coefficient, treatment temperature, draw ratio, and the method of solvent removal. Such treatment often leads to deterioration of mechanical properties such as lower

values of moduls (E) and yield stress ($\sigma_{y)}$ [Ajit B. Desai1974; P. J Makarewicz 1978].

3.3. Melt blending technique: advantages:

Avramova [Nadka Avramova 1995] reported one of such method for enhancing the crystallizability of PET, by blending with highly crystallizing polymers; where each constituent enhances the crystallization of the other. Isothermal crystallisation studies on PET/PBT blend showed that the crystallization behaviour of the blend is governed by the mobility of PBT. When isothermal crystallization (T_C) is performed below 200^0C, Misra *et al.* [S.P Mishra 1985**]** observed a decrease in average melting temperature T_m and ΔH_m, with increasing fraction of PBT, and when crystallization is done above 200^0C (Tc > 200) an increase in T_m and ΔH_m were observed. Hence below 200^0C, it restricts the crystallization of PET, by the incorporation of PBT in the spherulites of PET while at higher temperature PBT may be excluded from the spherulites and PET crystals grow larger.

Misra *et al*. [A. MISRA 1986] studied the block copolymers of two crystallizable compounds, poly (ethylene terephthalate) (PET) and poly (buty1ene terephthalate) (PBT). The Rates of crystallization were determined by measuring density as a function of time for isothermal crystallization. It was carried out at 95°C and reported that incorporated PBT increased the overall crystallization rate, considerably over that of PET. The results were explained on the basis that the faster crystallizing PBT blocks crystallized first and provided built-in nucleation sites for the subsequent crystallization of PET, thus resulting in relatively fast crystallizing co-polyester. The crystallization behaviour of PET blended with Co [poly (butylene terephthalate-p-oxybenzoate)] was also reported [Cheng Fang 2000]. From non-isothermal crystallization studies by DSC, the overall crystallization rate (heat of crystallization in a unit time (ΔH_c /time) were determined from the crystallization peak width (ΔT_c) and the heat of crystallization (ΔH_c) values. They shown that the crystallization rates for the blends are greater than that of PET (0.114 J/g s^{-1}). From

the above reports, it is clear that the blending of PET with PBT highly enhances the crystallization rate of PET.

3.4 Addition of plasticizers: (diols and phthalates):

The influence of a rigid diol incorporated into PBT via SSP (Solid State Polymerisation) has been studied and it was reported that the dianol [2, 2-bis [4-(2-hydroxyethoxy) phenyl] propane] has a dual role; as a reactant for trans-esterification and as a swelling agent for the rigid amorphous PBT chain segments. When it is below 15mol%, one observes that crystal thickening predominantly occurs while when it exceeds 15mol %, rigid amorphous chain segments are so small that only trans-esterification occurs [M.A.G. Jansen 2008]. Xue *et al.* [Gi Xue 1998] noticed that the PET prepared from PET/PEG gel is highly crystalline with fewer intermolecular segmental interactions. The intrinsic viscosity measurements show that the molecular weight remains unchanged during such process. In PEG solution, PET inter-chain entanglements were partially replaced by PET/PEG interpenetration and PEG imposes only a weak constraint and allows the long chain to move in a rapidly renewed tube. On cooling phase separation occurs and PET molecules continuously diffused into the polymer rich domains. The crystallization behaviour of PEG end capped linear PET, synthesised via melt polymerization technique [Quin Lin 2003] showed a dramatic decrease in the crystallization temperature of PET, and the copolymers with high level, i.e. larger than 17.6 wt% PEG, crystallize even at room temperature. Ramesh *et al*. [E Bhoje Gowd 2006] explored the use of small amounts (2.5–10 %) of poly (ethylene glycol) (PEG) and end-capped poly (ethylene glycol) [i.e. poly (ethylene glycol) dimethyl ether (PEGDME)] of number average molecular weight 1000 $gmol^{-1}$ as plasticizers to understand the effect of plasticizer on the Solid State Polymerisation (SSP) of PET. Glass transition temperature and crystallization rate were strongly affected by both PEG and PEGDME. The PEG incorporated samples can form copolymers with PET shows improved SSP rate than the one without plasticizer. But in PEGDME incorporated PET, since the end groups are protected, it cannot form a copolymer, and hence retards the SSP rate.

The study of PEG and PPG, poly (propylene glycol) as plasticizer has been extended to other biodegradable polymers such as PLA, Poly (L-lactide) [Z. Kulinski 2006; E. Piorkowska 2006; Isabelle Pillin 2006; Z. Kulinski 2005]. The advantage of using PPG is that it does not crystallize, has low glass transition temperature, and it is miscible with PLA [Z. Kulinski 2006; E. Piorkowska 2006]. Thermal analysis data for PLA plasticized with PPG clearly shows a decrease of T_g due to enhanced segmental mobility of PLA chains by the presence of plasticizer, which increases with the plasticizer content. The plasticized PLA shows decrease of yield stress and an increase of elongation at break. These results show that the incorporated plasticizer increases the ability of PLA to undergo plastic deformation. Poly (ethylene glycol) (PEG) and acetyl triethyl citrate (ATC) were shown to be efficient plasticizers for PLA [Hongbo Li 2007]. Non-isothermal DSC experiments, were performed in order to study the crystallinity developed upon cooling at different cooling rates (10, 20, 40 or 80^0C/min) and showed that the combination of nucleant (talc) and plasticizer is necessary in order to develop significant crystallinity especially at high cooling rates.

In recent years, great efforts have been taken to develop biodegradable polymers for the industrial or academic purpose due to serious environmental problems. There are many kinds of biodegradable polymers, including aliphatic polyesters such as, poly (α-amino acids), poly (ortho esters), and poly anhydrides. Unfortunately, their wider industrial application is restricted due to their higher cost. Recently, poly (ethylene glycol) incorporated into aromatic polyester backbone in order to increase the hydrophilicity and biodegradability of these raw materials. Poly (ethylene terephthalate)/poly (ethylene glycol) (PET/PEG) copolymers and poly (butylene terephthalate)/poly (ethylene glycol) (PBT/PEG) copolymers were studied more extensively. Due to its low cost and good biodegradability, these materials find potential application in biomedical and ecological fields [A.A. Deschamps 2001; Z. Y. Qian 2004; Y. Wang 2005].

Phthalates are one of the most widely used plasticisers, primarily to make soft and flexible polyvinyl chloride (PVC) [Wayne D. Cook 2007] for the applications in the industry of automotive, building & construction material, cable, flooring, medical device and toys. PET blends modified with dioctylphthalate (DOP), a miscible plasticizer, have shown a significant reduction in the glass transition temperature [L.Woo 1990]. Dioctyl phthalate (DOP) plasticizer made Poly (3-hydroxybutyrate) (PHB), more flexible, causing 54% increase of tensile strength at break, decreases T_g, but at high DOP concentrations of ~30%, the polymer matrix became fragile [Rodrigo Cirillo Baltieri 2003].

In conclusion, there are different methods such as high pressure induced crystallization, annealing at high temperature, nucleating agents such as salts, poly-olefins, aliphatic polyamides etc. and solvent induced crystallization (DMF, dioxane, $MeCl_2$, trichloroacetic acid–chloroform mixture, TFA/DCM, acetone etc), are reported in literature in order to enhance the crystallization rate of polyesters. Such treatments have positive effects on crystallization but often lead to deterioration of physical properties such as modulus, yield stress etc. So in search for new methods, it is found that when blending is done with highly crystallizing polymer, the above mentioned disadvantages can be eliminated and gives better combination properties along with good processability. Addition of plasticizers such as diols and phthalates further improves the processability of such polyesters by decreasing the melt viscosity, glass transition and there by increases the over all crystallization rate.

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4. PATENT SEARCH AND INDUSTRIAL RELEVANCE

Poly (ethylene terephthalate) (PET) is particularly suitable for the manufacture of fibers, filaments and sheets, but it is hardly suitable for injection molding because of high molding temperatures and relatively long molding times. Thus, wider use of this polymer is restricted not only because of its long processing cycle but also by the inability of many potential end users to process the resin. Poly (butylene terephthalate) (PBT) require shorter molding times and lower molding temperatures owing to their higher rate of crystallization, but they are inferior to poly (ethylene terephthalate) in physical properties, particularly in heat distortion temperature. Other disadvantage of the poly (butylene terephthalate) resin resides in their significantly higher cost of manufacture in comparison with poly(ethylene terephthalate) mainly due to the higher cost of the raw materials employed in its manufacture. Much research has been conducted to find out PET compositions which have a higher crystallization velocity and higher crystallinity.

Prior art methods to increase the rate of crystallization of PET have been directed towards incorporation of inorganic compounds, salts, polyolefin's, and aliphatic polyamides into PET to act as nucleation aids **[**Coleman *et al*., United States Patent 4,448,913 and WO2005/116106A1**]**. The use of the nucleating agents, often have a desired effect on the crystallization rate, sometimes have adverse consequences, such as lowering mechanical properties or its molecular weight. There exists a need in the art for a method to accelerate the rate of crystallization of PET in compositions without the limitations of the prior art. When poly (ethylene terephthalate) and poly (butylene terephthalate) resins are physically blended, a number of the above problems can be eliminated. When high levels of poly (butylene terephthalate) are utilized in the blend, it is not necessary to use a nucleating agent. Avramova **[**United States Patent 4915885**]** provided a high modulus thermoplastic polymer material based on commercial PET and PBT, which is a homogeneous mixture or blend of commercial PET and PBT in ratio between 10:90 and 90:10 parts by weight, characterized by an amorphous structure. Isothermal treatment (120°-180° C), for about 60 min. gives a material which has a

tensile strength 3-4 times higher and an elasticity modulus 2-5 times higher than that of commercial PET and PBT. Thus poly (ethylene terephthalate)/poly (butylene terephthalate) (PET/PBT) molding compositions are characterized by a rapid rate of crystallization and the capacity to be molded into high quality articles at low molding temperatures. The advantage of such process is that, it requires very less energy consumption. Many of the additives consisting of reinforcing fillers like glass fibres, mineral fillers and nucleating agents (such as calcium carbonate, average particle size, 0.07 micron) etc., can be further utilized to improve the final properties of the poly (alkylene terephthalate) compositions which are disclosed in the following patents. [U.S Patent 4351758; WO/1985/003717; U.S Patent 4203887; US Patent 4257937; US Patent 4220735**]**.

The use of a plasticizer is well known to the art to enhance crystallization rate. A plasticizer typically decreases the melt viscosity and lowers the glass transition temperature of the thermoplastic, which in turn increases crystallization rate at a lower temperature. Bier, *et al*. reported a rapidly crystallizing thermoplastic compound comprising a high molecular weight poly (alkylene terephthalate) and an aromatic acid ester, which helps the polyester to crystallize rapidly [United States Patent 4,223,125]. The composition comprising of a linear saturated polyester and ester of an ethoxylated aromatic alcohol (ethoxylated bisphenol A) has been found to improve the mold release properties and the appearance of such articles [WO 88/03155]. It has been found that neopentyl dibenzoate is an effective promoter of the crystallization rate of poly(ethylene terephthalate) [Coleman, United States Patent 4,368,285] and phthalate esters, which are widely used to produce plasticized PVC [US2007/0179229A1].

Low molecular weight organic esters are known plasticizers for polyesters, but they tend to be volatile in the dryers. Prior to melt processing, especially in the case of polyesters, it is important to minimise or eliminate the moisture to prevent the hydrolytic degradation, which results a diminished molecular weight and unacceptable mechanical properties. Poly(alkylene ether)'s such as poly(ethylene

glycol) (PEG), poly(tetramethylene glycol) (PTMG), and poly(propylene glycol) (PPG), and end-capped poly(alkylene ether)'s, have been reported to be non-volatile processing aid plasticizers for polyesters like poly (ethylene terephthalate) (PET), poly (propylene terephthalate) (PPT), poly (butylene terephthalate) (PBT), poly (ethylene naphthalate) (PEN), and poly (1,4-cyclohexanedimethylene terephthalate) (PCT). End-capped poly (alkylene ethers), such as the organic esters of poly (alkylene ether)'s, are preferred because they improve the thermal stability of the poly (alkylene ether) and reduces reaction between the polyester and poly (alkylene ether) which is important to preserve the semi-crystalline character of the polyester blend [Brink, *et al*. United States Patent H1,987]. Other ways to reduce such reaction include addition of a catalyst deactivating agent (such as a phosphorous compound), [WO2004/065487A1] and processing the blend under mild conditions.

5. EXPERIMENTAL PART

5.1. Melt blending: Brabender mixer:

All the blends melt mixed in a Brabender mixer under nitrogen blanket at a temperature of 260^0C, for a mixing time of 4 min., at 50 rpm. The melt blending is done under inert atmosphere to avoid chemical interactions like oxidation. The mixing time carefully chosen so that the trans-esterification reactions are minimised and ensure that there exists well mixing of the components.

5.2. Continuous Cooling Transformation (CCT approach) – State of art:

Since the solidification during polymer processing often involves high velocity gradient, high thermal gradient and high pressures, and the development of a model to describe the polymer behaviour turns out to be highly complex. Due to experimental difficulties the studies often carried out by conventional techniques like DSC and dilatometry [Zoller Paul 1978; Jing He 1992; V. LaCarruba 2002; D.M Fann 1998; L. Liangbin 2000]. The investigations by these techniques often involve experiments under isothermal or non-isothermal conditions where the latitude of cooling rates available are nowhere near to those experienced in industrial processes, which often leads to quite different structures and properties [V. Brucato 2002]. Thus the solidification behaviour of polymers were investigated under conditions emulating polymer processing by a CCT approach very similar to that adopted in metallurgy to investigate the morphology developed in steels [S. Piccarolo 2002].

5.2.1 Description of the experimental route:

Piccarolo *et al.* developed a new experimental set up in order to study non-isothermal crystallization at high cooling rates. A schematic representation of the apparatus and the sample in the sample holder is shown in **figure 5.2(a) and figure 5.2 (b).** The sample is wrapped in aluminium film to prevent leakage of the hot melt and placed between two Cu-Be slabs and heated to the desired temperature by means of electric heaters under nitrogen atmosphere. After the necessary holding

time in order to erase the memory effects, the sample assembly moved to the lower part of the container where it is quenched by a coolant symmetrically sprayed through two opposite identical nozzles. The temperature is measured by a fast response thermo couple embedded in one of the metal slab. The slabs are slightly pressed on to the sample by means of metal springs in order to compensate the shrinkage during solidification and to guarantee thermal conductivity. The cooling rate can be varied by changing the coolant, its flow rate and temperature, as well as by changing the slab thickness. The exact cooling rates are determined after quenching, from the temperature-time curves by taking the first derivation at a temperature, which shows the maximum crystallization rate **[Figure 5.2(c) and figure 5.2(d)]**. After cooling, the sample is taken out of the assembly, placed into plastic bags and stored at -10^0C to prevent thermodynamically caused phase changes.

The solidified samples obtained are structurally homogeneous both across their thickness (~100-200 micron) and surface, which can be analysed by macroscopic methods like Wide Angle X-ray Diffraction (WAXD) and density measurements.

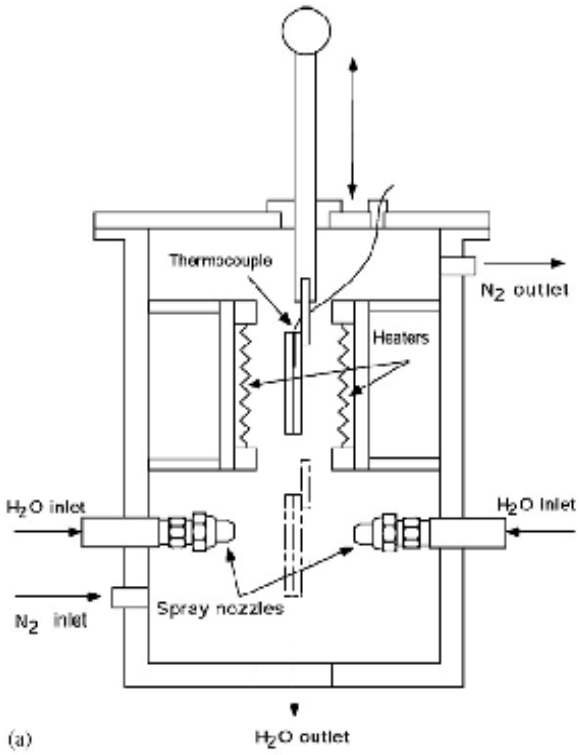

Fig: 5.2 (a): *Quenching Apparatus*

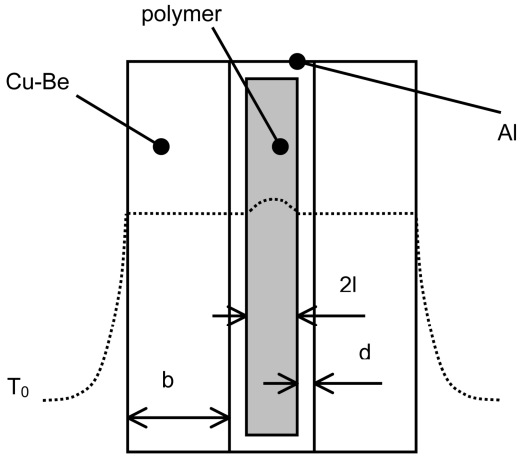

Fig: 5.2 (b): *Sample holder*

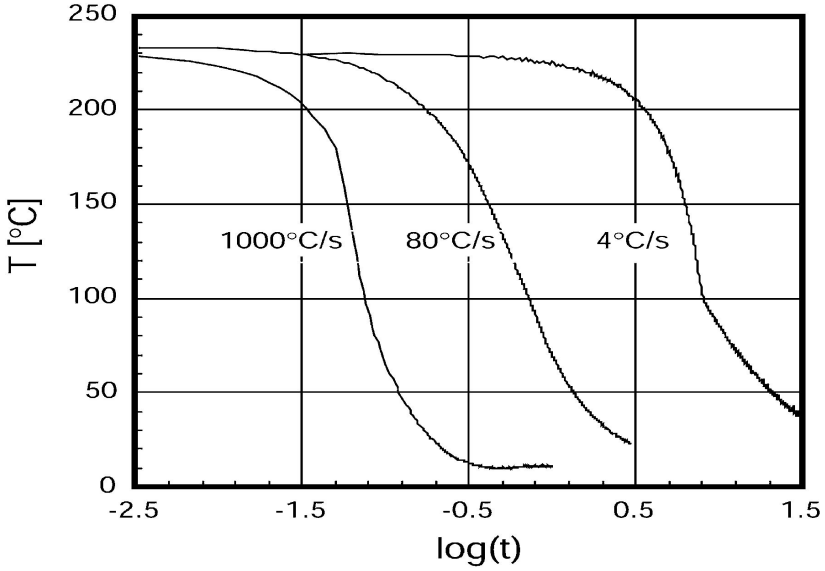

Fig: 5.2 (c): *Temperature Vs time (log scale)*

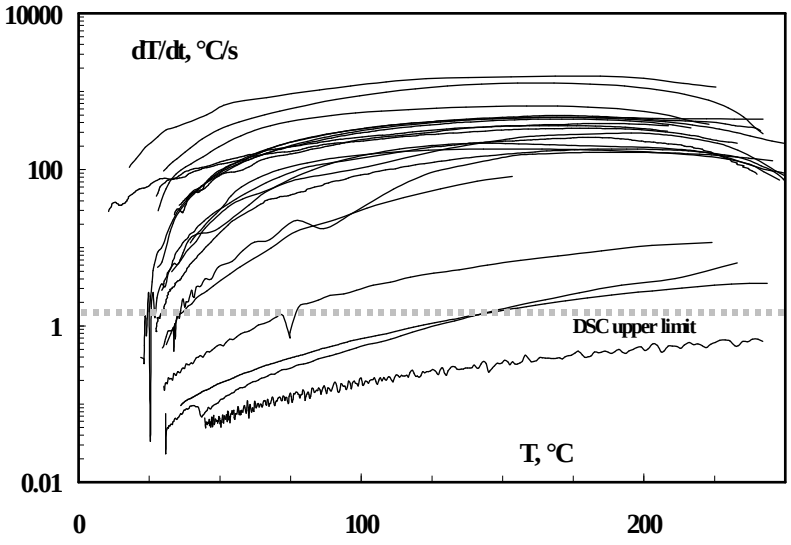

Fig: 5.2(d): *dT/dt*

5.3 Wide Angle X-ray Scattering (WAXS):

WAXS profiles of the samples were obtained by a Brucker advance D8 X-ray instrument with CuKα-Ni filtered radiation having a wavelength of 0.154nm. The scanning is done in the 2Θ range from 12 to 30" in the step scanning mode with resolution 0.1^0 and step time 20s.

5.4 Density measurements by Density Gradient Column:

Density and its reciprocal specific volume are sensitive to the state of aggregation of a material i.e. density increases and specific volume decreases from polymer melt to the solid sate. As move from lower to higher cooling rate the density decreases significantly depending on the crystallizing rate of the polymer. Density measurements were carried out with a gradient column filled with a mixture of carbon tetra-chloride and n-heptane according to ASTM D 1505 standard test method. The column is calibrated by means of glass beads of known density. The reliability of the results depends on the column preparation and gradient should be constant through out the column.

The samples were cut into small pieces which were checked against air bubbles by microscope and degassed under vacuum before being introduced into the gradient column**.** For each cooling rate at least three samples were introduced into the column in order to avoid the error propagation. Meas**u**rements were done at 6°C**.** The resolution of the density column was 0.0001 kg/L and repeatability within ± 0.0002 kg/L was obtained.

5.5. Differential Scanning Calorimetry (DSC):

Differential Scanning Calorimetry (DSC) data collected with a power compensation type DSC 7 from Perkin-Elmer. The instrument is operated in conjunction with the cryogenic cooling accessory CCA 7, using liquid nitrogen as coolant. The sample and reference furnaces were purged with gaseous nitrogen at a flow rate of 35 mL min^{-1}. We used 20 µL aluminium pans from Mettler-Toledo for

encapsulation of the samples. The sample weight was approximately 6-8 mg and scanning was performed using rates of temperature-change of 20 K min^{-1} on heating, and 10 K min^{-1} on cooling.

5.6. Dynamic Mechanical Thermal Analysis (DMTA):

DMTA experiments were done in Rheometric Scientific Instruments @ 10 Hz. The heating program was carried out from -10 to 150^0C under constant strain rate.

5.7. Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) was performed using a Microscope Philips 505 on sample cross section fractured in liquid nitrogen, gold stained and mild etching is done in order to get good image.

5.7.1 Etching Procedure:

The sequence of operations is: (1) grind the appropriate amount (1% wt/vol., i.e., 10 mg per mL of acid mixture) of potassium permanganate add to the swirling acid mixture, 3:2 vol. Con.H_2SO_4 and dist. H_2O (12 ml sulphuric acid+8ml distilled water) [etching solution] and keep stirring until dissolved.

(2) Shake the specimen in the mixture for the desired time (10 min.)

5.7 1 (a) Quenching solution:

Mixture of (2 vol. conc. sulphuric acid and 7 vol. water), already prepared and having been allowed to cool to room temperature, add 1 vol. of 30% hydrogen peroxide. Cool the total mixture to near freezing.

After 10 min. take out the sample from the etching solution (use platinum wire to avoid any mark on the sample) and put it in the quenching solution to stop the reaction. The sample is then washes with distilled water and finally with pure alcohol [M. M. Shahin 1999].

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6. PBT/PET BLENDS SOLIDIFICATION UNDER CONDITIONS EMULATING POLYMER PROCESSING STUDIED BY CCT

6.1 Introduction:

Binary polymer blends may be made of pairs of polymers in which one or both components are crystalline. Nowadays the crystalline/crystalline polymer blends received much attention not only because of their commercial importance; blending of such polymers offer an effective route to wide range of morphological patterns [L.Z Liu 1997] and novel structure-property relationships.

The crystallization behavior and the properties of binary crystalline polymer blends are influenced by the relative amount of the individual components, their chemical compatibility, miscibility and the level of dispersion, the latter in turn affected by the techniques and the conditions of compounding. From recent studies it is found that crystallization behavior (i.e. rate of crystallization and degree of crystallinity) and the heat stability of cryomilled PET is better than those of non grinded sample [Y.G. Zhu 2006]. To study the influence of grinding on the crystallization of polyester blends, two blends prepared, one melt blended with pellets and the other with pulverized components and the solidification curves (density g/cm^3 Vs cooling rate K/s) for the pure and plasticized samples were compared [i.e. GROO Vs RWOO and GR5P Vs RW5P].

When two polymers are mixed, the most frequent result is a system that exhibits complete phase separation due to the repulsive interaction between the components (i.e. the chemical incompatibility between the polymers). Thus majority of polymer species are often immiscible and the blended mixture shows phase separation due to the inhomogeneous nature. This can have a negative effect on the macroscopic properties of the resulting polymeric material [L.H. Sperling 1997]. Attention must be given while selecting the individual components so that the mixture of two polymers satisfies the following condition.

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

Where ΔG_m, ΔH_m and ΔS_m are change in Gibb's free energy, enthalpy and entropy of mixing at temperature T, respectively.

Thus the miscible polymer blend is the one which is homogeneous down to the molecular level and associated with negative value of free energy of mixing. For low molecular weight materials increasing temperature generally leads to increase in miscibility as $T\Delta S_m$ term increases thus driving ΔG_m to more negative values. But for higher molecular weight components $T\Delta S_m$ term is small and ΔH_m term dominates and lead to the reverse behavior i.e. miscibility decreases with increasing temperature. Therefore, for polymers the sign of ΔG_m always depends on the value of the enthalpy of mixing ΔH_m and polymer pairs mix to form a single phase only if free energy exceeds the enthalpy contribution, $\Delta H_m < T\Delta S_m$ [Di Lloyd M. Robeson 2007]. The miscibility behaviour of the blend is crucial for understanding and tailoring the properties relevant for practical application. The molecular origin of polymer blend miscibility is a fascinating topic because, with small entropy of mixing, extremely delicate interactions can play a decisive role. PBT/PET blend system is a good example where inter-molecular interactions play major role in amorphous phase miscibility. The solidification studies of such blends are complex because of miscibility issues, trans-esterification and degradation reactions, along with separate crystallizations of the blend constituents which are discussed in the following section.

6.2 Materials:

PET01:

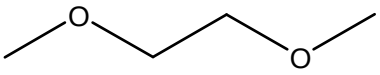
PET, supplied by DSM Engineering plastics, (Netherlands) having an intrinsic viscosity of 0.62dl/g (phenol/tetrachloro ethane (60/40) solution at 30^0C).

PBT02:

Supplied by DSM Engineering plastics, (Netherlands) having an intrinsic viscosity 0.85dl/g (phenol/tetrachloro ethane (60/40) solution at 30^0C).

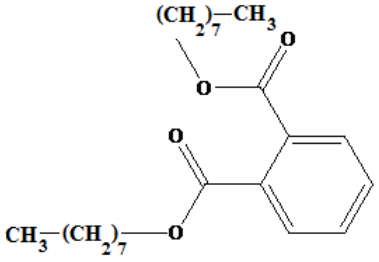
Poly (ethylene glycol) di-methyl ether (PEGDME): [P]

Supplied by Aldrich, Number average Molecular weight Mn ~1,000



Dioctyl phthalate (DOP): [D]

Supplied by Aldrich & has a Molecular Weight of 390.56g.



6.3 Experimental:

6.3(a). Melt blending: Brabender Mixer:

All blends have melt mixed in Brabender mixer under nitrogen blanket at a temperature of 260^{0}C [except for PEN (280^{0}C)]; for a mixing time of 4 min. and at 50 rpm.

Table 6(a): *Samples prepared for the study*

Sample notations	Materials
RW00	PBT/PET(60/40 wt/wt), pellets
GR00	PBT/PET(60/40 wt/wt), grinded
RW5P	PBT/PET(60/40wt/wt), pellets+5wt% PEGDME plasticizer
GR5P	PBT/PET(60/40wt/wt), grinded+5wt% PEGDME plasticizer

6.3(b) Controlled rapid quenching technique:

The apparatus set up is described in chapter 2. Thin films (150-200micron thickness) for the quenching experiments were prepared with the help of hydraulic press by taking appropriate sample weight and by applying suitable pressure. The temperature and holding time have chosen properly to minimise trans-esterification reactions. From these films, samples of approximately 20x20mm were cut and wrapped carefully inside aluminium foil. The sample assembly is then introduced into the heating zone and heated up to 260^{0}C [for PEN (280^{0}C)], for 3 min. (holding time) in order to remove the thermal history and quenched immediately. The effective cooling rate is taken at 150^{0}C [for blends and PBT], [for PTT at 160^{0}C], [for PEN and PET at 170^{0}C] and the sample stored at -10^{0}C to prevent ageing.

6.3(c) Wide Angle X-ray Scattering and density:

WAXS measurements were done within the 2θ range 12 to 27^0 with a step of 20s and the density measured in a density gradient column as explained in chapter2.

6.3(d) Differential Scanning Calorimetry (DSC):

Approximately 6-8 mg sample was taken in an aluminum pan and scanning was performed at a rate of 20 K min^{-1} on heating, and 10 K min^{-1} on cooling. The heating was done from -40 to 280^0C.

6.3(e) Dynamic Mechanical Testing Analysis (DMTA):

The heating was performed from -20 to 130^0C at a rate of 2 K/min @ 10Hz under constant strain rate (0.1%).

6.4 Influence of grinding on crystallization of blends:

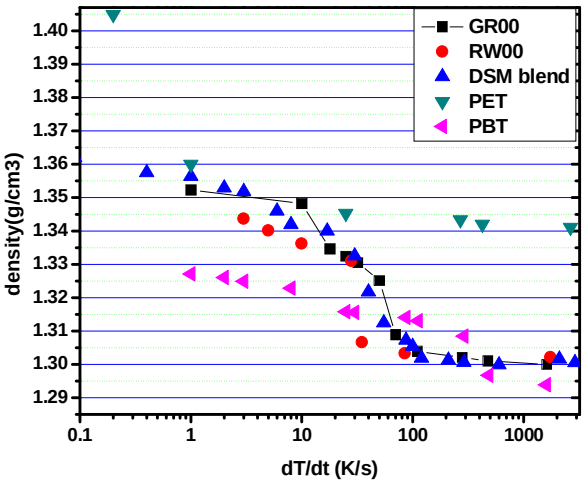


Fig: 6.4(a): *Solidification curves: GR00, RW00, DSM (60/40) blend, PET and PBT*

From the **figure 6.4(a)**, one can observe sharp density drop for RW00 especially in the intermediate cooling rate with respect to the grinded ones (GR00) and in GR00 the density drop occurs at a cooling rate higher than that of the non grinded one i.e. the crystallization more favored in blends where grinding is accompanied before blending. Small particle size improves the homogeneity of the feed and provides better contact among the individual components [R. Schexnaydre 2008; J. Mano. 2003]. This yields stronger intermolecular interaction among the individual polymer chains and better temperature distribution during melt blending. All such factors favor the miscibility rate and the mixing quality.

In GR00, one can clearly observe two density plateaus, one in the low cooling rate region (1-10K/s) and latter in the amorphous region (100-1000K/s). PET is a less crystallizing material and is amorphous above ~2K/s. In GR00, upon comparison with the solidification curve of PET, the crystallization of PET can be clearly observed up to a cooling rate ~10K/s and followed by a drop in density (10-18K/s) due to significant decrease in PET crystallites. The second drop in density is observed ~50K/s and above this cooling rate, the percentage of PBT crystallization is less and the amorphous blend behaves as amorphous PBT. Such a clear cut, i.e. the separate density drop which arises due to significant decrease in the amount of PET and PBT crystallites could not be seen in non grinded sample. In RW00, only one density drop exists around 50K/s.

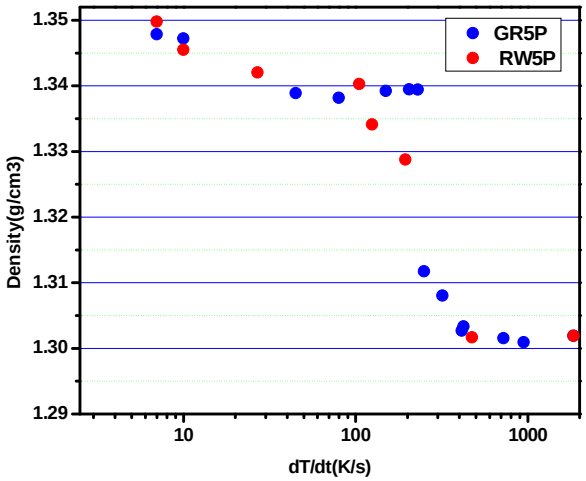


Fig: 6.4(b): *Solidification curves: GR5P and RW5P*

In the case of blends with plasticizers where grinding is done before blending, density drop shifted to higher cooling rate as shown in **figure 6.4(b)**. Since the pulverization process increases the specific surface area [E. Bilgili 2001] and the degree of dispersion of the plasticizers; thus the plasticizing action will be more effective in blends with grinded components [**Figure 6.4 (b)]**.

6.5 Density comparison with ideal behavior:

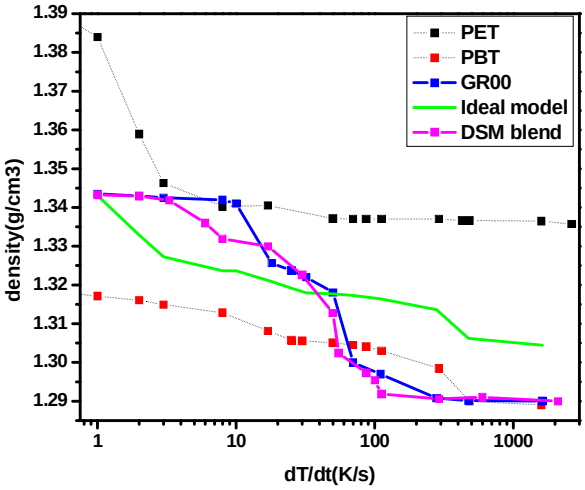


Fig: 6.5(a): *Solidification curve PET, PBT, GR00 and ideal model.*

Figure 6.5(a) shows the solidification curve i.e. the density dependence on cooling rate for the blend were compared with those of the individual components. The PBT/PET (60/40 w/w) blend shows a density of 1.350 g/cm^3 in the low cooling rate region and a density of 1.290 g/cm^3 in the higher cooling rate region; which is in between those of the pure polymers. PET [larger density span, 1.405 g/cm^3 to 1.335g/cm^3, Piccarolo 2000] and PBT [1.32 g/cm^3 to 1.285 g/cm^3, a smaller span]. It exhibits a density drop in an intermediate position between the two homo polymers, located around 50 K/s and in intermediate cooling rates, the blends shows unique density behavior, does not bear any resemblance to that of PET and PBT.

[If the blend behave as an 'ideal' model where additivity of specific volumes of the two components at each temperature can be hypothesized, at each cooling rate the blend specific volume would be given by the following equation.

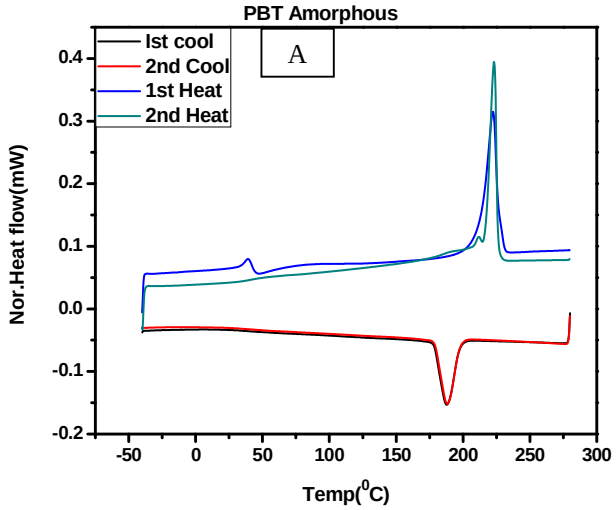
$$V_{blend} = \varphi_{PBT} V_{PBT} + \varphi_{PET} V_{PET}$$

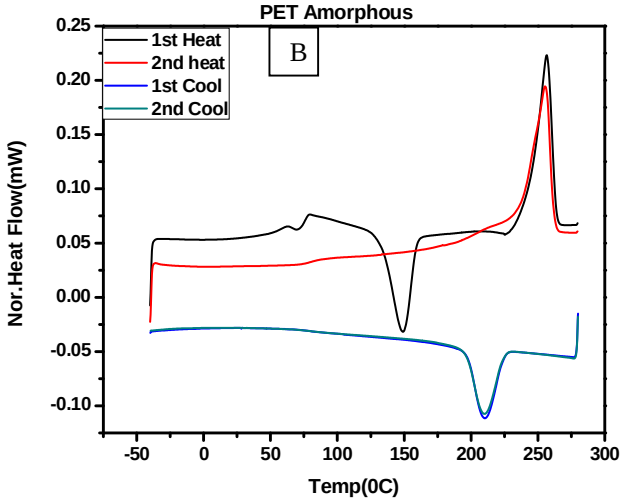
Here, φ_i are the volume fractions and V_i (=1/ρ_i) the specific volumes at each cooling rate].

For cooling rates below 1 K/s the model supplies a good fit of the experimental data and in the low density region the experimentally calculated density is significantly lower than those predicted by the ideal model. This points out that the amorphous phase of the blend (being the amorphous phases of PET and PBT are miscible) exhibits PBT like behavior with a density comparable to those of PBT even though it contains 40%PET. DSC and DMTA analysis on such blends confirm the amorphous miscibility as it shows single T_g which lies in between those of PET and PBT [**Figure 6.5 (b), Figure 6.5 (c), Table 6(b) & 6(c)].** Apart from those of the components; no new peaks were observed in the diffraction patterns of PBT/PET blend, [**Figure 6.5 (d)]** indicates that PBT and PET components in the blends crystallized separately in their own lattices. DSC studies confirms such observation as it shows individual melting peaks and the presence of single melt crystallization temperature presumes both PET and PBT crystallizes at the same time (simultaneous crystallization) and the miscibility in the crystalline phase could be ruled out.

Melt crystallization studies on PBT/PET blends by DSC at cooling rates below $1Ks^{-1}$ shows the onset of two independent crystalline entities related to those of PET and PBT moieties [Antonio Stocco 2009]. These observations confirm that a preliminary step must take place before crystallization if the two components do not co-crystallize. From the above results, one can propose a 'complete' demixing of the PET and PBT moieties, at least those giving rise to the crystalline phases, had taken place from the homogeneous equilibrium melt to satisfy the requirement for the onset of two independent non-miscible crystalline phases. In other words there exists a demixing process and follows the crystallization from a completely miscible phase in the molten state.

In the intermediate cooling rate the density of the blend is higher than the ideal behavior; hence one can presume that the PET crystallizes even at a cooling rate more than one order of magnitude than PET alone (i.e. in non blended state).





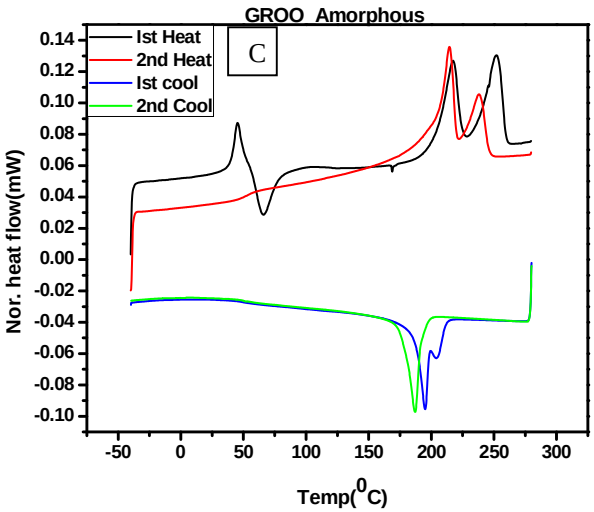
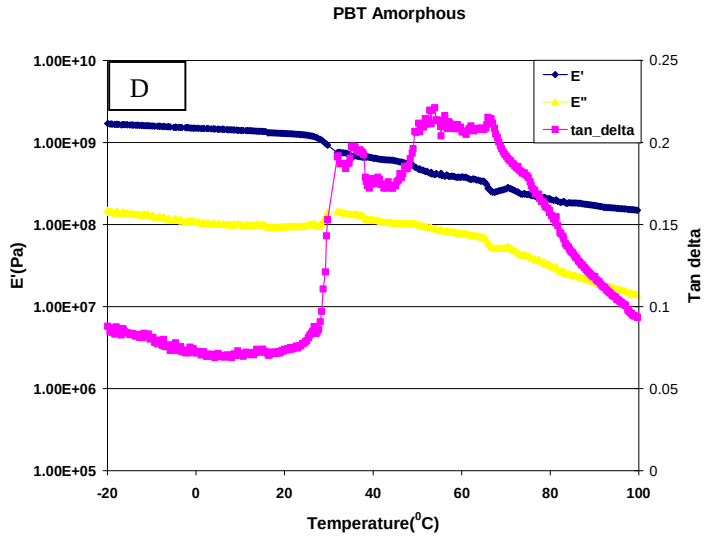
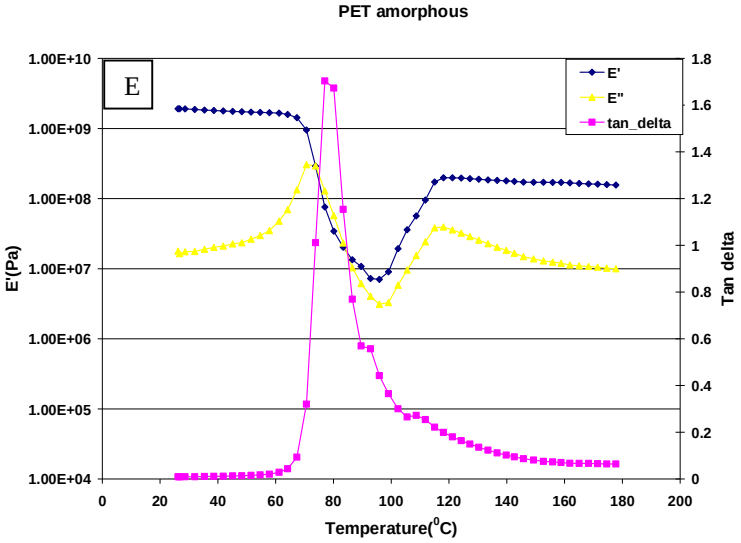


Fig: 6.5(b): *DSC scan on PBT (A), PET (B) and GR00 (C)*

Table 6(b): *DSC data: T_g, T_c and T_m*

Sample (Amorphous)	**T_g Ist Heat**	**T_c(cold crystallization) (^{0}C)**	**T_c(melt crystallization) (^{0}C)**	**T_m(^{0}C)**
PBT	35	NA	188	222
PET	76	149	210	257
GR00	45	NA	195	217PBT, 252 PET


PBT Amorphous
D
E'
E"
tan_delta
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
E'(Pa)
0.25
0.2
0.15
0.1
0.05
0
Tan delta
-20
0
20
40
60
80
100
Temperature(0C)


PET amorphous
E
E'
E"
tan_delta
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
E'(Pa)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Tan delta
0
20
40
60
80
100
120
140
160
180
200
Temperature(0C)

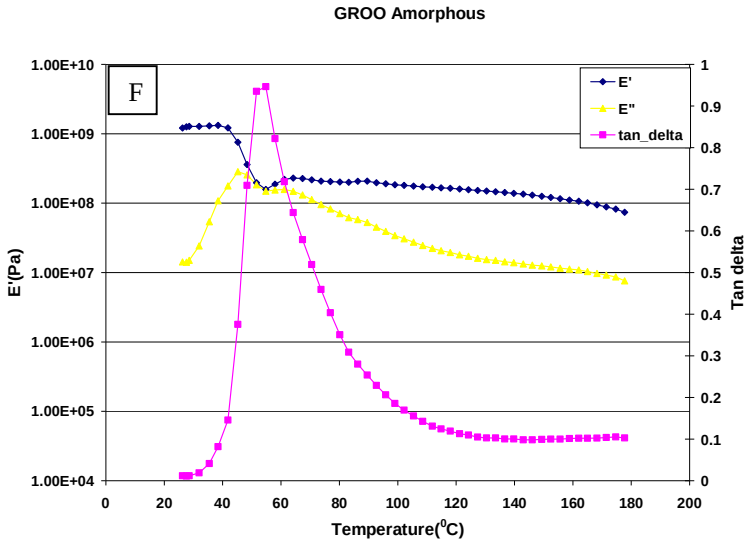


Fig: 6.5(c): *DMTA data on PBT (D), PET (E) and GR00 (F)*

Table 6(c): *T_g data: PBT, PET and GR00*

Sample	PBT	PET	GR00
T_g@10Hz (^{0}C)	30	74	45

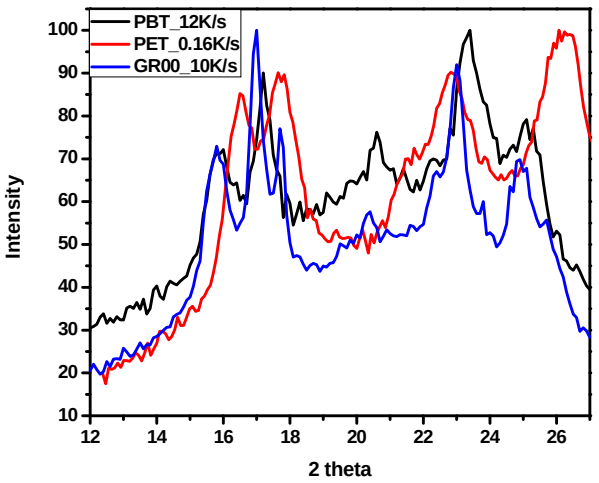


Fig: 6.5(d): *WAXS patterns of PBT_12K/s, PET_0.16K/s and GR00_10K/s*

6.6 Conclusions:

1. In the case of blends where grinding is accompanied before blending, two separate density drops due to the decrease in crystallites of PET and PBT can be clearly seen, while such clear cut is not evident in non grinded blends.
2. The plasticizer dispersion and their action is more pronounced in blends where grinding is performed before blending as the density drop shifted to higher cooling rate in comparison with non grinded ones.
3. PBT/PET blend shows amorphous miscibility, the existence of co-crystallization is excluded from the WAXS studies and the blend shows a unique density drop which is in between those of PET and PBT.
4. The blend behaves as a single homogeneous phase in the melt as revealed from the unique solidification curve and from single T_g observation. In comparison with the ideal behavior one can propose a 'complete' demixing of the PET and PBT moieties, at least those giving rise to the crystalline phases, had taken place from the homogeneous equilibrium melt to satisfy the requirement of the onset of two independent non-miscible crystalline phases.

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7.PLASTICIZERS ON PBT/PET(60/40)BLEND CRYSTALLIZATION

7.1 Introduction:

In chapter 6, we proposed demixing is a quite common mechanism taking place before crystallization in macromolecular systems whose conformations are constrained by the complex topology. Under these circumstances one can think about the factors influencing the kinetics of demixing. One such factor is the addition of plasticizers which increases the free volume and there by polymer chain mobility. Two miscible plasticizers PEGDME (P) and DOP (D) were melt mixed with the blends for the solidification studies. The selection of plasticizers was done according to the literature which is discussed in the **State of Art** section. Two different wt % (1 and 5) melt mixed with the blends [GR1P, GR5P, GR1D, & GR5D] to study whether there is a threshold in the amount of plasticizer for their action.

Polyesters such as poly (ethy1ene terephthalate) (PET) or poly (buty1ene terephthalate) (PBT) commonly undergo chemical reactions at elevated temperatures in the solid state and in the melt. Trans-esterification reaction is very common in such polyester blends [M. Kotliar 1981; J. Devaux 1982; F. Pilati 1985]. The extent of such reactions highly controlled by the processing conditions (Temperature, holding time in the melt, blending technique etc.) and can affect the morphology and properties of the blend [M.F. Cheung 1989; K.R. Carduner 1990; H.Wang 1990; M.E. Stewart 1993]. As interchange reaction proceeds, blends convert initially to block copolymers and then finally to random copolymers. ^{13}C NMR [S. Backson 1991; B. Jacques 1996] and ^{1}H NMR [H. Matsuda 2002] studies gives the evidence for such randomization processes. In order to study such randomization reaction melt crystallization studies were carried out by different holding times in the melt and are discussed in the final section.

7.2 Density studies on blends and plasticized blends:

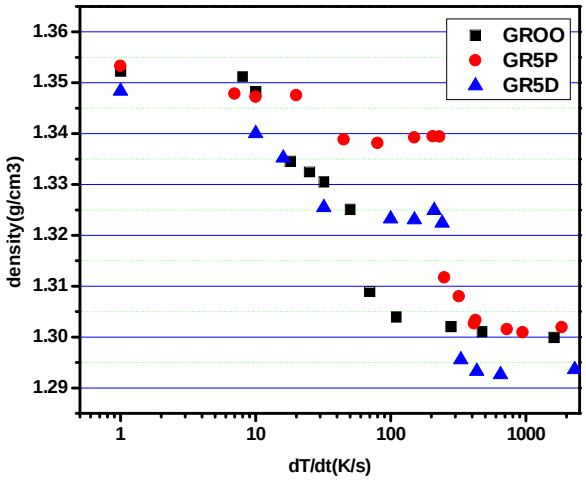
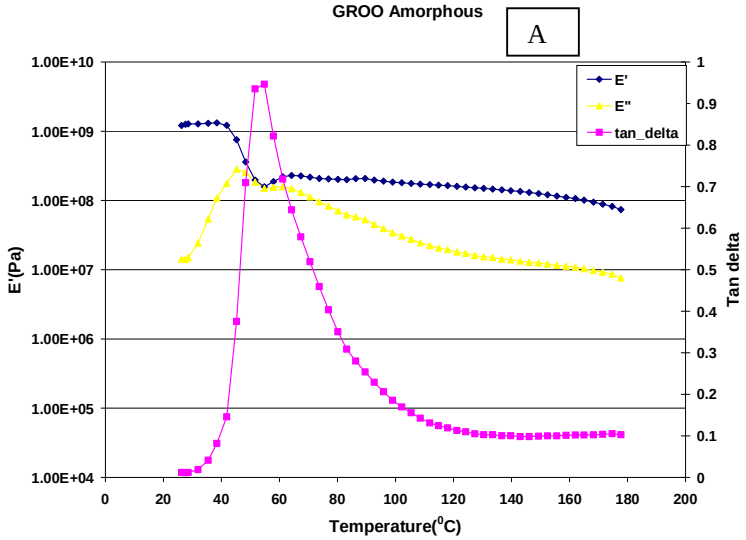
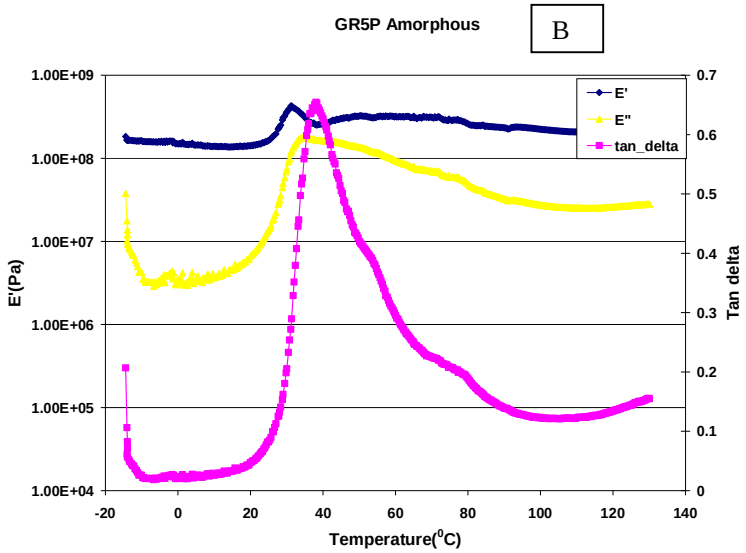


Fig: 7.2 (a): *Solidification Curve: Density (g/cm^3) Vs cooling rate (K/s) for the plasticized and non plasticized blends*

From the solidification curve in **figure 7.2(a)**, one can clearly observe that the plasticizer action is pronounced at intermediate cooling rate region where the density behavior is different for plasticized and non plasticized samples. In non plasticized samples the transition from more stable crystalline phase to meta-stable or amorphous phase occurs at a cooling rate of ~50K/s while for the latter it takes place at ~250K/s i.e. In plasticized blends, the density drop significantly shifted to the higher cooling rate region. Previous studies shown that the crystallinity obtained from PET/PEG oligomer gel is 20% higher than all other methods such as annealing, solvent crystallization, stretching techniques etc. From fluorescence spectra Gi Xue *et al*. have reported that PEG reduces the entanglements to a level similar to that of freeze extracting from a dilute solution (PET 0.5 wt %) in phenol [Gi Xue, 1998]. Furthermore the plasticizer occupies positions in between the polymer chains, which imparts more free volume and diminishes the possible frictions among them. All such factors enhance the flexibility and degree of freedom of the possible polymer conformations [Z. Kulinski 2006] and thus in plasticizer

incorporated samples, the density drop occurs at higher dT/dt region. The plasticization effect can be seen from the DMTA data as the plasticized samples give a T_g lower than the pure ones **[Figure 7.2(b) and Table 7(a)].**





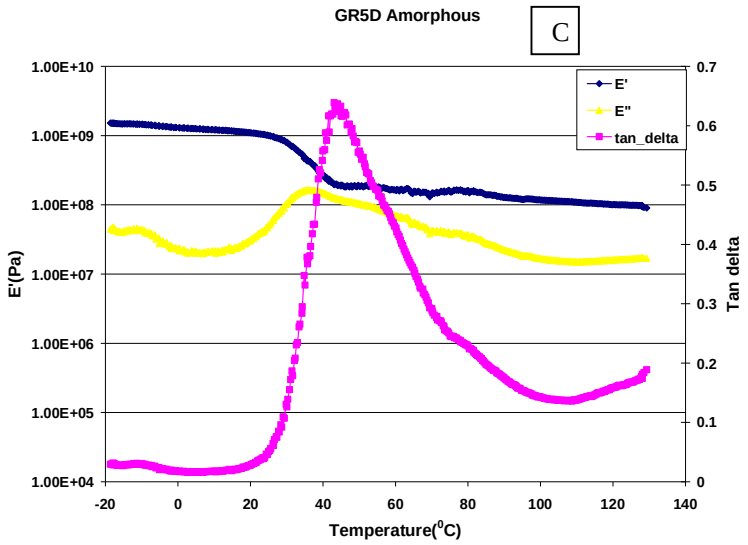


Fig: 7.2(b): *DMTA plots: GROO (A), GR5P (B) and GR5D(C)*

Table 7(a): *T_g data PET, PBT, GR00, GR5P and GR5D*

Sample	PET	PBT	GR00	GR5P	GR5D
Tg@10Hz	74	30	45	32	36

In the previous chapter, we proposed complete demixing of PET and PBT moieties takes place from a homogeneous melt before crystallization to form non miscible crystalline phase. In presence of plasticizer, the rate of demixing is facilitated due to less entanglements and mobility imparted by the plasticizers. Another striking point from the solidification curve is that the plasticizing action is more pronounced in P incorporated samples than D. This is due to the plasticizers containing long aliphatic chains are more flexible and effective than those containing bulky cyclic groups. In D blends, the amorphous density is low compared to those of P, this can be attributed to the bulky phthalate groups in D, which imparts more free voids and decreases the overall density as seen from **figure 7.2(d)**.

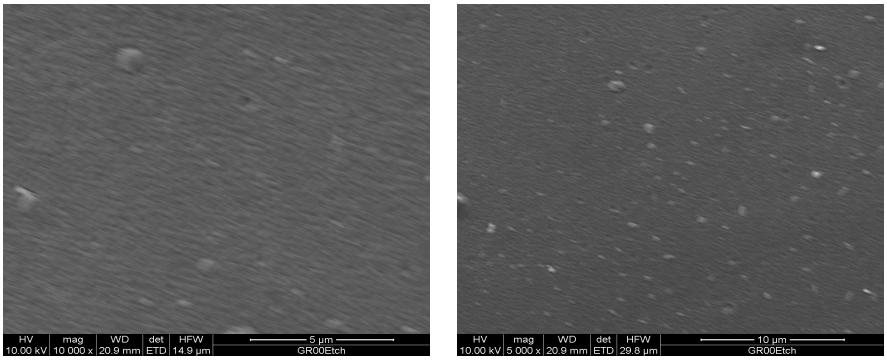


Fig: 7.2(c): *SEM Scans on GROO*

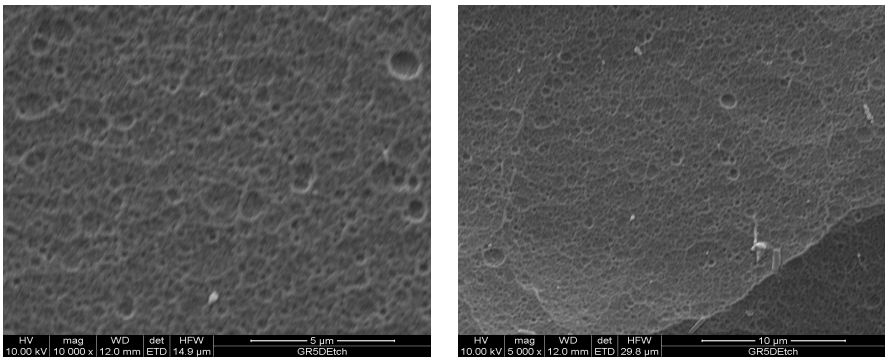
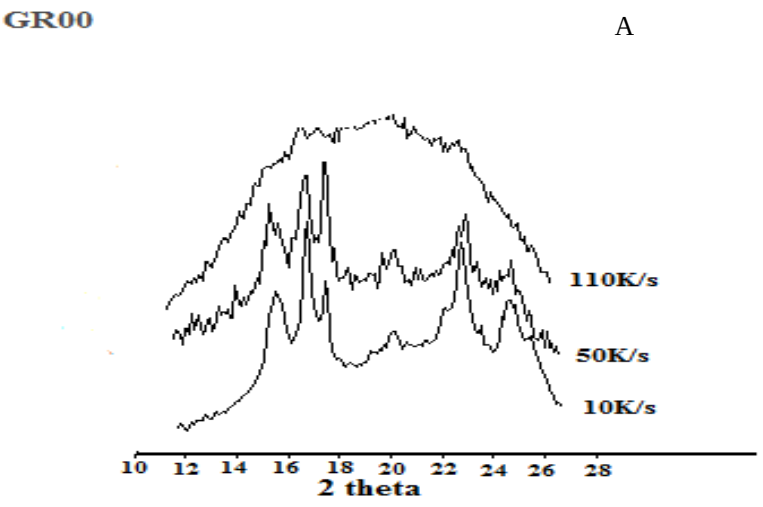
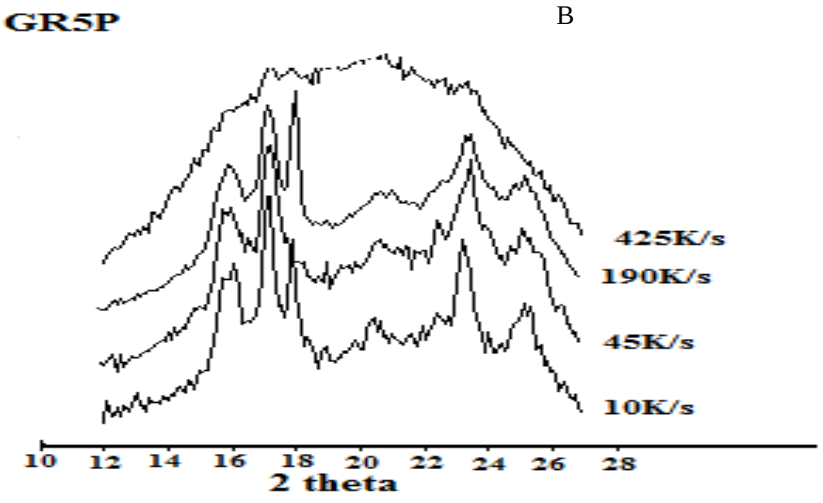


Fig: 7.2(d): *SEM Scan on GR5D*

7.3 WAXS studies on plasticized and non plasticized blends:

The crystal form of PET is triclinic [T. Asano 1999; D. Raabe 2004] and for PBT both monoclinic and triclinic forms are reported [J. Liu 1997; M.L. Di Lorenzo 2003]. The PET showed characteristic peaks at scattering angles at 2θ values of 16.6, 17.4, 22.9, 25.9, and 32.7°, which correspond to the (0 1¯ 1), (0 1 0), (1 1¯ 0), and (1 0 1) scattering planes, respectively [Z.G. Wang 2000]. For PBT, the characteristic X-ray peaks were observed at the scattering angles 2θ of 15.8, 17.0, 20.5, 23.2, and 25.0°, refers to the reflection planes of (0 1¯ 1), (0 1 0), (0 1 1), (1 0 0), and (1 1¯ 1) [R.K.Y. Li 2000]. In the last chapter WAXS patterns of crystalline PET, PBT and those of the PBT/PET blends were compared and found that both crystallizes separately as a result of mismatch in their unit cell.


GR00
A
110K/s
50K/s
10K/s
10 12 14 16 18 20 22 24 26 28
2 theta


GR5P
B
425K/s
190K/s
45K/s
10K/s
10 12 14 16 18 20 22 24 26 28
2 theta

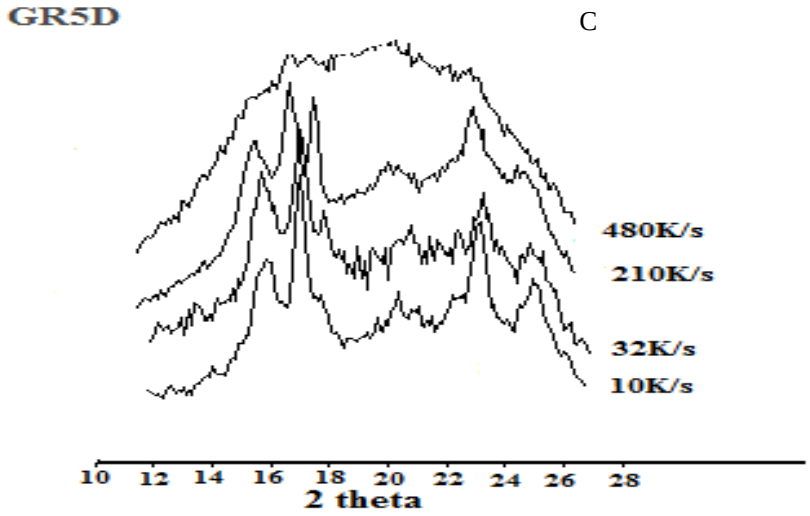


Fig: 7.3(a): *WAXS Patterns: GR00 (A) GR5P (B) and GR5D (C)*

The qualitative interpretation of the pure blend showed the presence of crystalline content up to a cooling rate of 50K/s and for the plasticized samples which is even up to a quenching rate of ~250K/s; above this the material tend to be substantially amorphous **[Figure 7.3(a)]**. However, separation of the crystalline peaks, which are related to two individual crystalline phases of PET and PBT is very difficult due to the close positions of most intense peaks **[Figure 7.3 (b)]**.

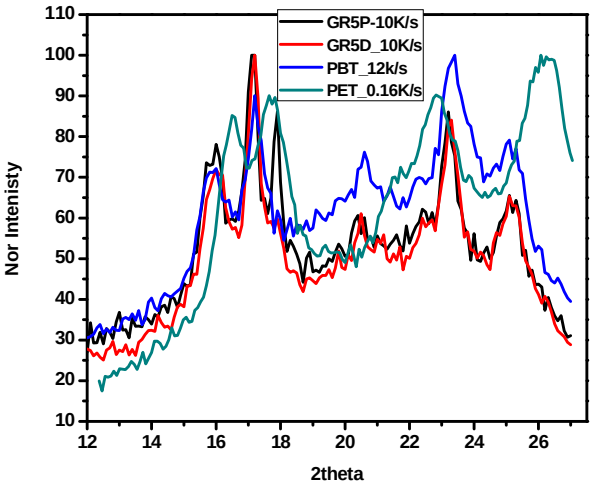


Fig: 7.3(b): *WAXS Patterns Comparison on PET, PBT, GR5D and GR5P*

Attempts have been done in order to separate the percentage of PET and PBT crystallites by applying a Lorentian function template for both PET and PBT. Deconvolution of the WAXS pattern of the blend by peak fitting is shown in **figure 7.3(c)** and the results are shown in **table 7(b)**. In GR00, on increasing the cooling rate, a remarkable decrease in the crystallization of PET exists while on the plasticized samples the percentage of PET and PBT crystallites remain almost constant even at higher cooling rates. In GR5D comparatively lower density especially in the intermediate cooling rate is due to the lesser percentage of both PET and PBT crystallites **[Table 7(b)]**. The obtained WAXS data are in good agreement with the density data.

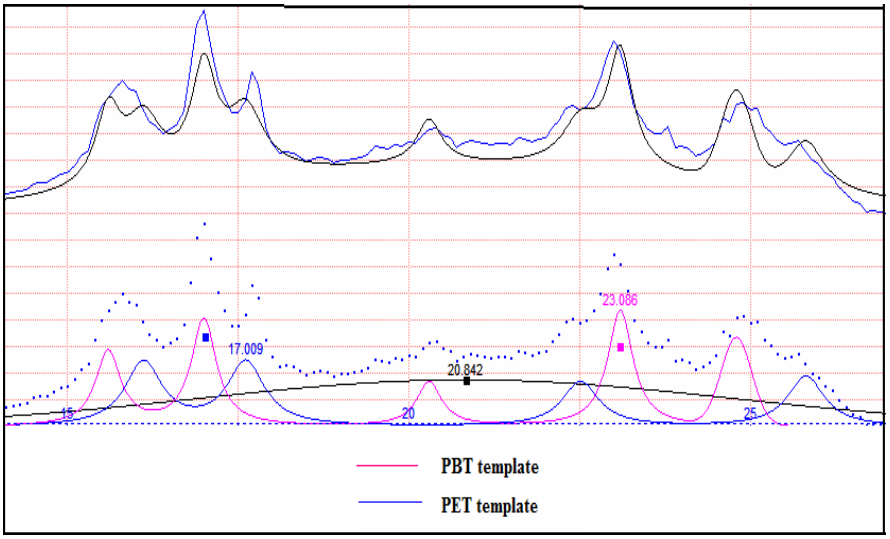


Fig: 7.3(c): *Deconvolution pattern of PBT/PET blend by peak fit*

Table 7(b): *Percentage of PET and PBT crystallizes*

Sample	% PET Crystallinity	% PBT Crystallinity	% Amorphous content
GR00_10K/s	23.7	23.5	52.6
GR00_18K/s	14.5	25	61
GR00_50K/s	14.7	19	66.3
GR 5P_10K/s	26.3	26.8	46.8
GR 5P_45K/s	25.1	24.6	50.2
GR5P_190K/s	24.8	28.5	46.5
GR 5D_10K/s	24.6	23.4	51.8
GR 5D_32K/s	19	20	60
GR5D_210K/s	16	16.5	66.8

7.4 One wt% plasticizers on PBT/PET (60/40 w/w) blend solidification:

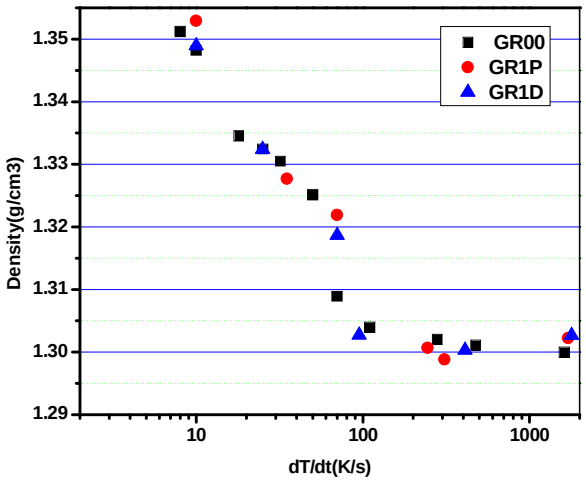


Fig: 7.4(a): *Solidification curve comparison GR00, GR1P and GR1D*

In order to see whether there is a threshold in the amount of plasticizer for the plasticizing action, the blends were prepared with 1% P & D plasticizers (GR1P &GR1D). From **figure7.4 (a)** it is clear that 1% is not sufficient for the plasticizing action to take place while on the other hand 5% has significant effect as shown in **figure 7.2(a)**.

7.5 Evidence for trans-esterification reaction: Effect of holding time on melt crystallization temperature:

Figure 7.5(a) shows the melt crystallization data for the pure and plasticized PET, PBT after 3 and 6 min holding in the melt (280^0C and 260^0C) where both exotherms exactly coincides as there is no unwanted reactions such as hydrolysis or decomposition. But in the case of blends, as we increase the holding time from 3 to 6 min in the melt (280^0C), the extent of trans-esterification reaction is more and the melt crystallization temperature shifted to lower values as shown in **figure 7.5 (b), (c), (d) and table 7.(c)**. Attention must be given in order to minimize such trans-

esterification reactions since it inversely affects the crystallization rate. Thus for the blends melting temperature and holding time in the melt must be chosen carefully so that extent of such reactions are minimum and must ensure that there exists complete mixing of the individual components.

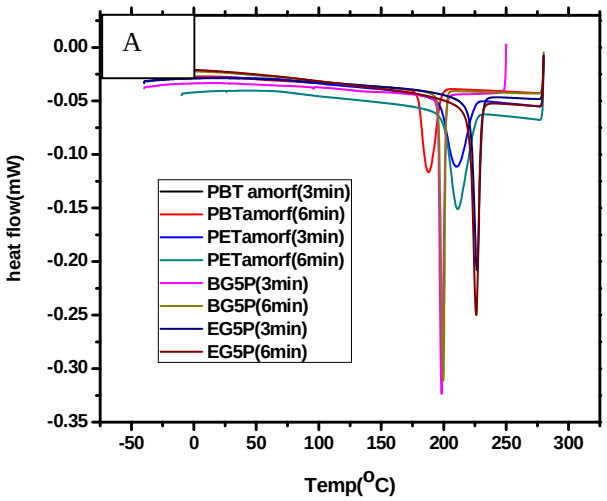
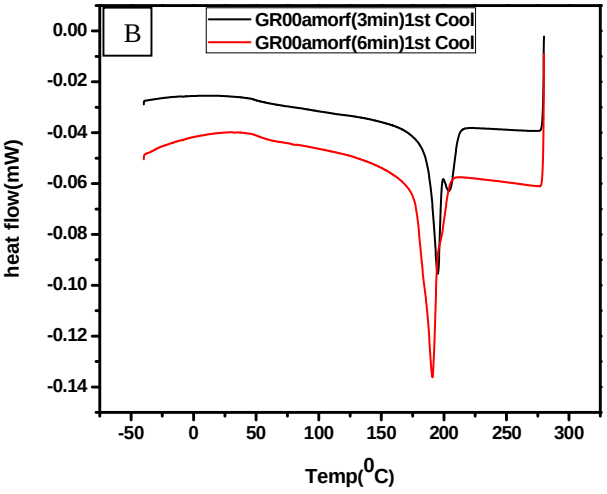


Fig: 7.5(a): *Melt crystallization curves of PBT, PET and Plasticized samples after 3 and 6 min holding time in the melt (A)*



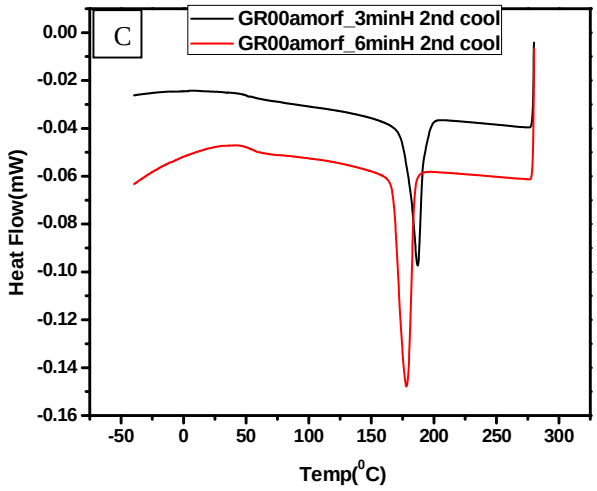
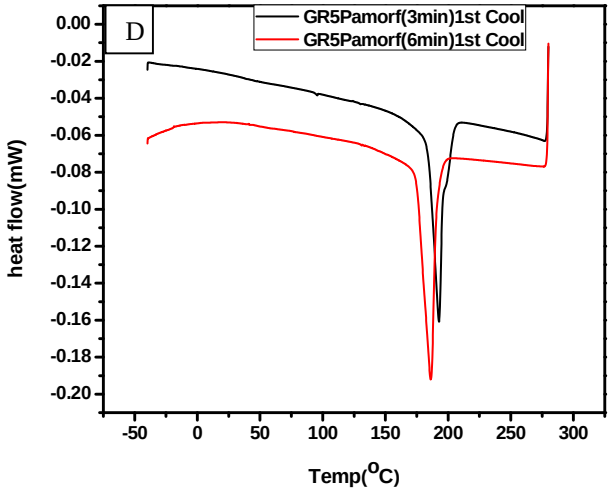


Fig: 7.5(b): *Melt crystallization curves of GR00 after 3 and 6 min holding time in the melt [first (B) and second cool(C)]*



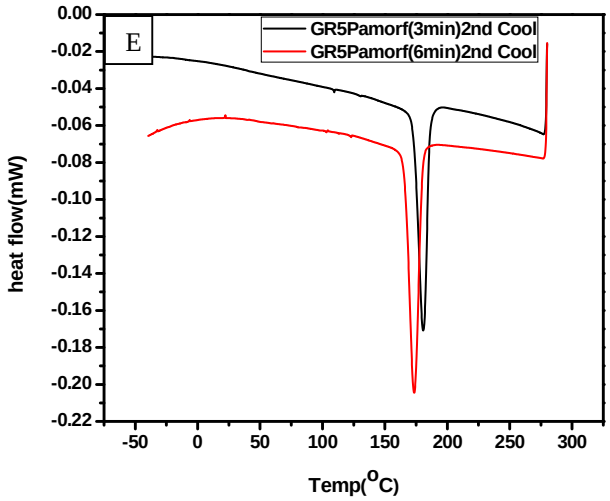
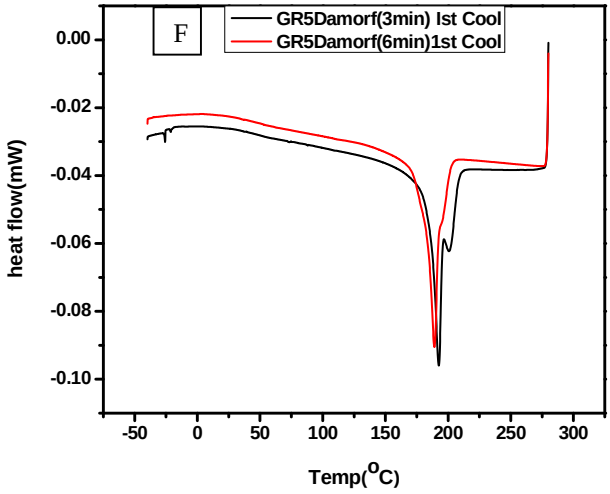


Fig: 7.5 (c): *Melt crystallization curves of GR5P after 3 and 6 min holding time in the melt [first (D) and second cool (E)]*



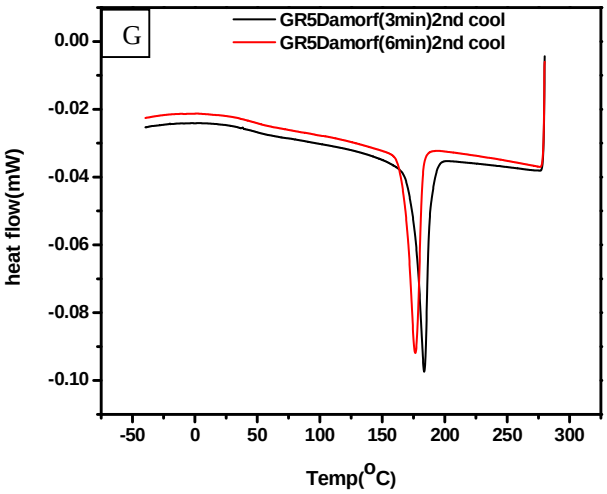


Fig: 7.5(d): *Melt crystallization curves of GR5D after 3 and 6 min holding time in the melt [first (F) and second cool (G)]*

Table 7(c): *Melt crystallization data Ist and 2nd cool*

Sample (Amorphous)	**T_c (melt crystallization) Ist cool**	**T_c (melt crystallization) 2nd cool**
PBT(3min)	188	188
PBT(6min)	188	189
PET(3min)	210	210
PET(6min)	211	211
PBT+5P(3min)	198	198
PBT+5P(6min)	199	199
PET+5P(3min)	226	226
PET+5P(6min)	226	226
GR00(3min)	195	187

GR00(6min)	191	178
GR5P(3min)	193	181
GR5P(6min)	186	173
GR5D(3min)	193	183
GR5D(6min)	189	176

7.6 Conclusions:

1. Both plasticizers enhance the rate of crystallization as the transition from crystalline to amorphous phase takes place at higher cooling rate on comparison with pure ones. For the pure blends the density drop is at 50K/s while for the plasticized ones is at ~250K/s.
2. P is more efficient plasticizer than D. In comparison with P (linear) the mobility of D plasticizer is limited due to the bulky nature and such samples shows lower amorphous density as evidenced from SEM pictures (voids).
3. The rate of demixing is facilitated due to less entanglements and mobility imparted by the plasticizer.
4. WAXS studies exclude the possibility of co-crystallization and from deconvolution studies it is shown that PET crystallizes at higher cooling rate (~50K/s) when it is blended with PBT and in plasticized blends (even up to ~200K/s) while the pure PET crystallizes only up to 2K/s.
5. There is a threshold in the amount of plasticizer for plasticizing action to takes place.
6. Increasing the holding time in the melt i.e. from 3 to 6 min, the melt crystallization temperature (T_c) shifts towards the lower temperature region due to trans-esterification reactions.

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8. PLASTICIZERS AND NUCLEATING AGENTS ON POLYESTER CRYSTALLIZATION

8.1 Introduction:

Relevance of polymer crystallization in material science does not need to be further pointed out if one thinks that out of the overall synthetic polymers production the most important materials and material classes are those of crystalline polymers. This situation has certainly given rise to continuous interest on the understanding and gathering of relevant information whenever this was made possible by the experimental approaches. By far the most important technique is Differential Scanning Calorimetry which could collect (in different modes) data on crystallization and melting with characteristic times down to 10-100s, certainly the 'fastest' method if one compares with the majority of available methods. It is very accurate and can collect all sort of information related to temperature dependence of overall crystallization kinetics or identify peculiar mechanisms [B. Wunderlich 2008]. It is clear that the time range explored is far different with respect to processing conditions where characteristic times are of the order of $1\text{-}10^{-3}$ seconds at least 4 orders of magnitude smaller.

In polymer processing environment two situations determine a dichotomy of crystallisable materials depending on whether they are amenable to processing by injection molding or not, i.e. fast or slow crystallizing polymers. At first glance it is even more surprising that crystallization kinetics of fast crystallizing polymers is not easily experimentally available. The latitude of cooling rates or temperatures under non-isothermal or isothermal crystallization kinetics, available is relatively modest. The upper bound of cooling rates is determined by instrumental dynamics while the bounds for studying crystallization under isothermal conditions depend on instrumental sensitivity or by instrumental dynamics on decreasing temperature, i.e. if the cooling rate had not been large enough, the material might already partially crystallize upon dropping to crystallization conditions. For slowly crystallizing polymers it is even possible to inhibit crystallization by either increasing cooling

rate or decreasing isothermal crystallization temperature to an extent that the typical pattern obtained by WAXD is replaced by a broad diffuse halo, apparently related to the onset of the fully amorphous phase. In such polymers it is possible to study the crystallization kinetics over a broad range of conditions to discriminate the underlying mechanisms. It is for this reason that those materials are often used as a model for interpreting and quantifying the mechanisms.

Here we compare the influence of a plasticizer on the density drop, and therefore the disappearance of any long range order crystalline phases after fast controlled quenching of some polyester {PET+5% P &D plasticizers (EG5P, EG5D); PBT+5% P &D (BG5P, BG5D)}. The polyesters for the study are so selected that it shows different crystallization behavior, i.e. low crystallizing stiffer polymers poly(ethylene naphthalate) (PEN) & poly(ethylene terephthalate) (PET), fast crystallizing soft polymer poly (buthylene terephthalate) (PBT) and an intermediate one poly(trimethylene terephthalate) (PTT).

8.2 Materials:

PET01:

PET having an intrinsic viscosity of 0.62dl/g, kindly supplied by DSM Netherland (phenol/tetrachloro ethane (60/40) solution at 30^0C).

PBT02:

Supplied by DSM Engineering plastics & has an intrinsic viscosity of 0.85dl/g (phenol/tetrachloro ethane (60/40) solution at 30^0C).

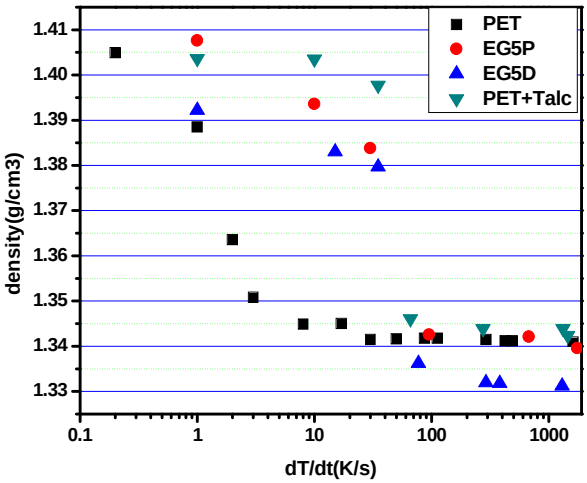
PTT clear:

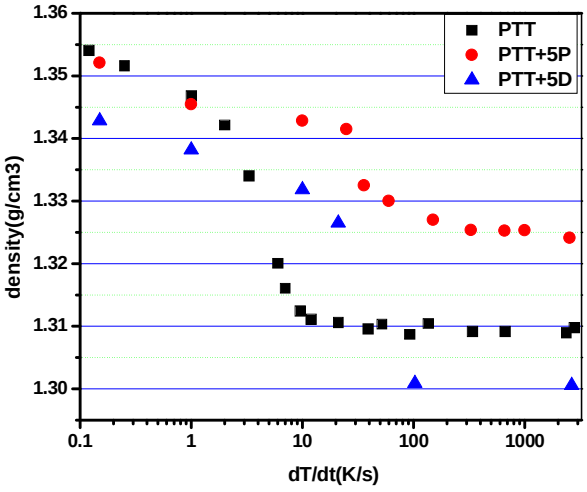
PTT clear is from shell chemicals which has a number average M_w 43000 and an intrinsic viscosity of 0.84ml/g when calculated in phenol/tetrachloro ethane (60/40) solution at 25^0C.The glass transition temperature is around 45-50^0C and its melting temperature is 245±4°C

PEN:

PEN is having an intrinsic viscosity 0.55 dl/g.

8.3 Influence of plasticizers on crystallization of individual components:





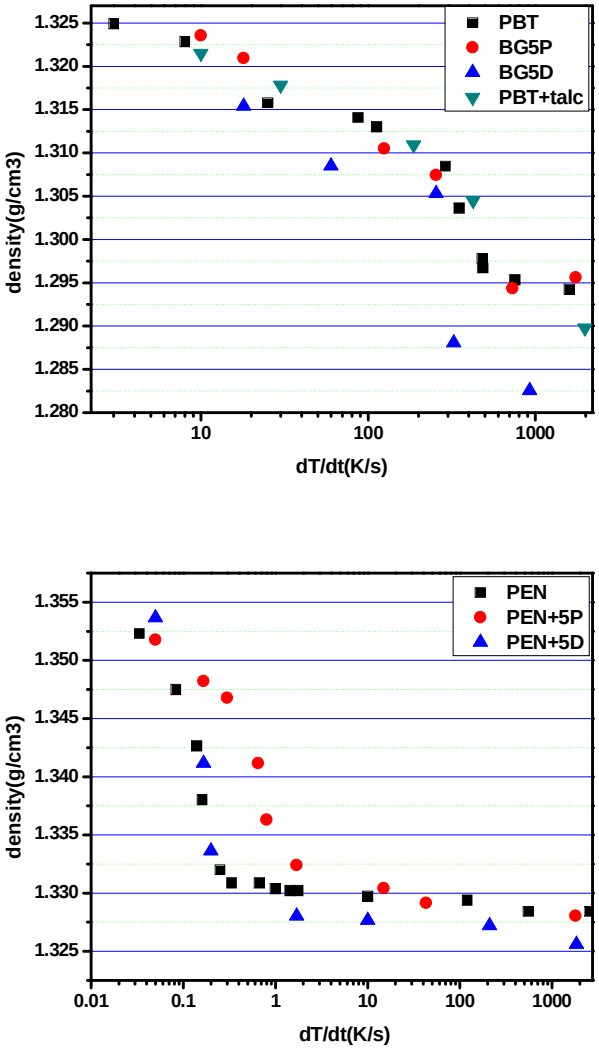
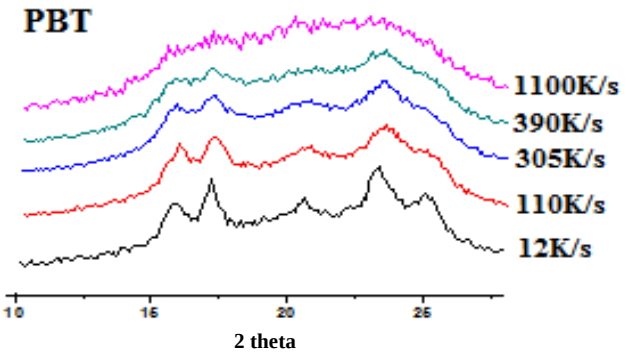


Fig: 8.3 (a): *Solidification curves: PET, PBT, PTT, and PEN with plasticizers and Nucleating agents*

The solidification behaviour of several polymers investigated under conditions emulating polymer processing by a heuristic approach whereby a thin sample is solidified in a mould by controlled continuous cooling approach very similar to that adopted in metallurgy to investigate the morphology developed in steels [S.

Piccarolo 2002]. In contrast to the usual approaches adopted to study crystallization, nothing is known on the evolution of the morphology during cooling but its thermal history is recorded with the help of fast responding thermo couples. By suitable design of experimental conditions a homogeneous morphology is obtained throughout the sample, amenable for use of macroscopic probes for the characterization of its overall structure [V. Brucato 2002]. Sample density, plotted versus suitable cooling rate describes the non-isothermal crystallization behaviour, it is the solidification curve and is shown in **figure 8.3(a)** for four polyesters; Poly (ethylene terephthalate) (PET), poly (trimethylene terphthale) (PTT), poly (butylene terephthalate), (PBT), and poly (ethylene naphthalate), (PEN). Common feature to all curves is a smooth decrease of density with cooling rate and a sudden drop at particular cooling rate above which the material is substantially amorphous (i.e. above this cooling rate crystalline phases giving rise to distinct WAXD peaks disappear) **[Figure 8.3(a), (b) and (c)]**. It is this critical cooling rate, CR*, we shall examine and compare in the following discussion. The difference between the so called slow and fast crystallizing polymers is apparently related with CR*, fast are those with CR* on the order or above 100K/s, (PBT and PTT), slow are those with CR* below 1-2K/s (PEN and PET). Between the two classes there are two orders of magnitude in the cooling rate determining the disappearance of phases carrying the fingerprint of long range order [**Figure 8.3 (b)**]. This does not necessarily mean that above such cooling rates the materials are completely amorphous, as mesomorphic phase, where the degrees of organization ranging between those of crystalline and amorphous are reported in literature for many polymers, PET [T. Asano 1999; K. Fukao 2003] and PBN [Takashi Konishi 2008]. The WAXS data **[Figure 8.3(b) and (c)]** obtained are in good agreement with the density measurements.

A



B

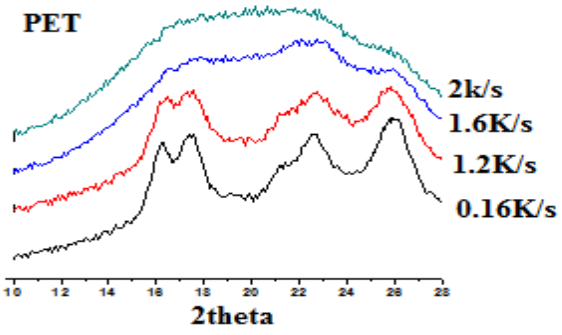
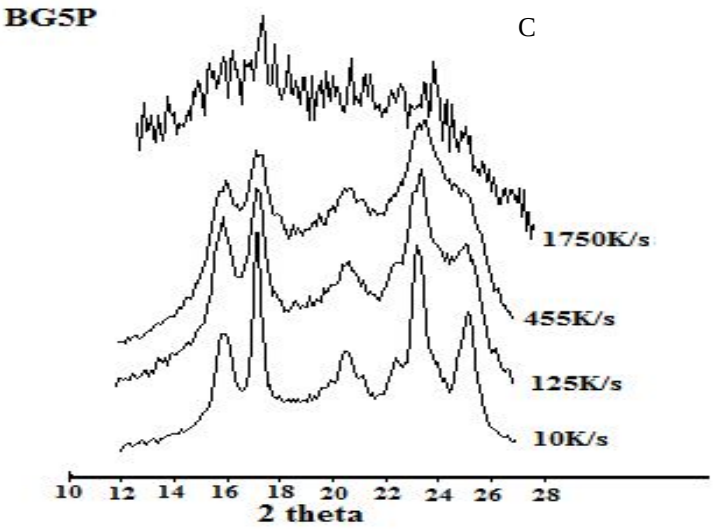
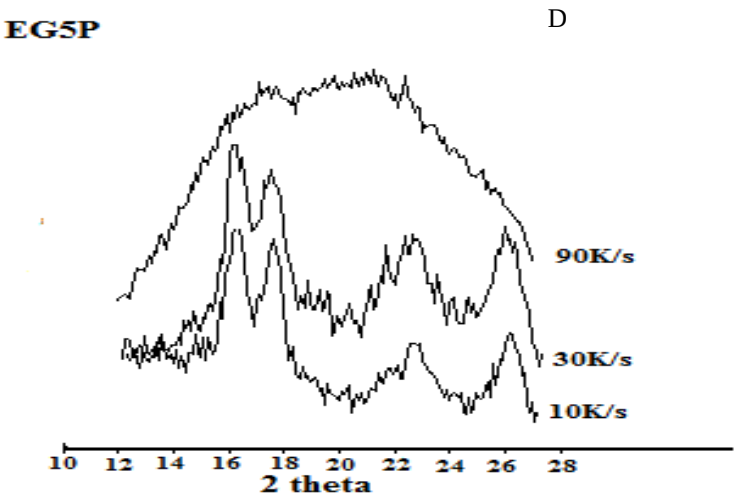
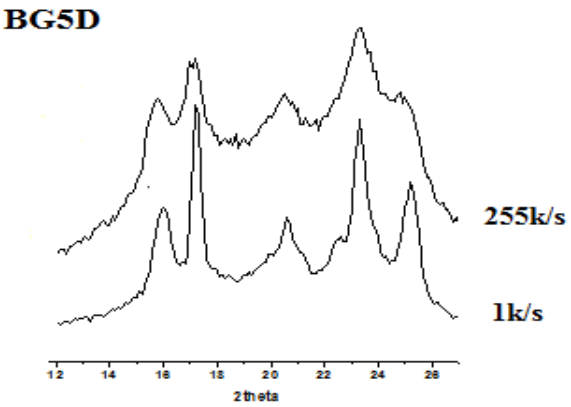


Fig: 8.3 (b): *WAXS Pattern on PBT (A) and PET (B)*


BG5P
C
1750K/s
455K/s
125K/s
10K/s
10 12 14 16 18 20 22 24 26 28
2 theta


EG5P
D
90K/s
30K/s
10K/s
10 12 14 16 18 20 22 24 26 28
2 theta

E


BG5D
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1k/s
12
14
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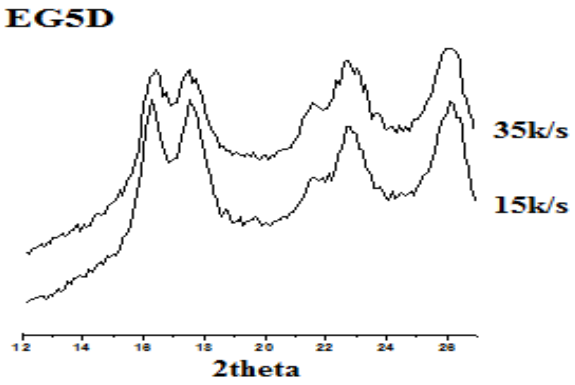
22
24
26
2theta

F


EG5D
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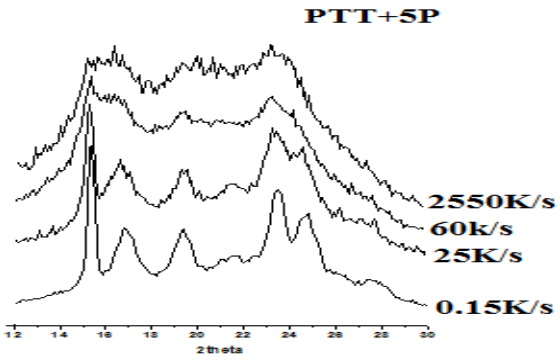
G



H

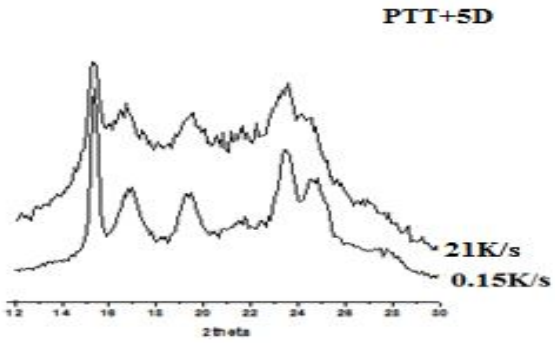


Fig: 8.3 (c): *WAXS Pattern on Plasticized samples(C, D, E, F, G, & H)*

Figure 8.3 (c) shows the influence of a plasticizer on the solidification of PET, PTT, PBT and PEN. The Plasticizers on PET, PEN and PTT crystallization is very significant since CR* increases by one and a half order of magnitude and the

plasticization can be clearly seen from the decrease in T_g from DMTA experiments **[Table 8.3(a) and (b)]**. On comparing the action of P and D on polyester crystallization one can say that P is more effective plasticizer as seen from the **figure 8.3(a)**. This is because plasticizers containing long aliphatic chains (P) are more efficient than those containing bulky cyclic groups (D) since plasticizer migration is restricted due to less mobile bulky rings and thus T_g decrease is more relevant in P plasticized sample than D **[Table 8.3(a) and (b)]** [D.J Meade 1942].

The mechanism of action of nucleating agents and plasticizers are different as we can see from the different solidification curve for nucleated and plasticized PET **[Figure 8.3(a)]**. Nucleating agents provide nucleating sites for the polymer to crystallize while plasticizers often migrate among the polymer chains and increases the free volume and mobility of the polymer chains which facilitates the rate of crystallization.

Table 8.3(a): *T_g data PET & PBT with additives*

Sample	**PET**	**EG5P**	**EG5D**	**PET+ Talc**	**PBT**	**BG5P**	**BG5D**	**PBT+ Talc**
T_g@10Hz	74	58	64	75	30	28.5	30	40

Table 8.3(b): *T_g data PTT & PEN with plasticizers*

Sample	**PTT**	**PTT+5P**	**PTT+5D**	**PEN**	**PEN+5P**	**PEN+5D**
T_g@10Hz	45	27	40	108	88	96

The plasticizer P does not affect any significant extent on the CR* of PBT. The different behaviour of plasticizer in this context, i.e. on determining a faster crystallization of PET while barely affecting on PBT crystallization is surprising.

Crystallization in polymers is a complex phenomenon where the mechanisms involved might not simply those reported for simple systems, i.e. nucleation and growth. However when consider this simplified approach there is only difference in the surface energy contribution between primary and secondary nucleation so that nucleation in any case is the rate determining step. There are mainly three approaches to interpret the nucleation in polymers. The first by Turnbull and Fisher [D.Turnbull 1949] and then directly borrowed by Hoffman and Lauritzen is the most established viewpoint of polymer crystallization [J.I. Jr. Lauritzen 1960] which accounts of a thermodynamic balance. The second due to Strobl [G. Strobl 2007] is based on a thermodynamic interpretation albeit it postulates, on the basis of experimental evidence, the presence of a mesomorphic precursor which should overcome steps like the conformational regular arrangement of chain sequences necessary for stem deposition on the growing surface.

The third approach by Wunderlich, recently reviewed by W. Hu, [W.Hu 2007] assumes a molecular nucleation to occur during stem deposition although the evidence for its occurrence is inferred from experimental indirect observations. Finally another approach is from Rault [J. Rault 1978] bearing many similarities to the one described by Strobl. In all the cases cited, the experimental tests of these approaches are based on solidification conditions not much departed from equilibrium, i.e. conditions which give the possibility to follow the solidification in real time by some macroscopic method of characterization, therefore the timescale of the experiment is above the one quoted above ~10s. In all approaches mentioned above no explicit role is attributed to melt topology. This issue has been recently taken in due consideration by Hikosaka [M. Hikosaka 2005] where the disentanglement mechanism is postulated to occur as a prerequisite for nucleation to take place. Certainly disentanglement occurs in crystallization and it may even be pushed to such an extent that the separation of different molecular weight fractions in a process called Crystaf, [B. Monrabal.1996] the acronym standing for crystal fractionation. A beautiful experiment in this context should be acknowledged; it starts from the observations of Lemstra and co-workers, obtained high modulus PE

fibers from very dilute solutions of UHMWPE, a process patented by DSM [P. Smith 1980]. Very high draw ratios can be obtained upon drawing the solid precipitate although if molten solid cannot be drawn anymore to the same extent. These results led Rastogi [S. Rastogi. 2007] to observe the onset of a metastable melt once the disentangled solid polymer, is slowly heated, whatever the route adopted for its development. This melt will eventually crystallize much faster than the normal one obtained by fast heating above the melting point. Furthermore fluorescence spectra on PET/PEG oligomer gel shows that PEG could reduce the entanglements to a level similar to that of freeze extracting from a dilute solution (0.5 wt% PET) in phenol solvent [Gi Xue 1998]. These are striking evidences of the importance of entanglements on polymer crystallization.

In order to interpret the different behaviour of plasticizers on PET and PBT, **[Figure 8.3(a)]**, we deliberately overlook the general framework of understanding the phenomena involved in crystallization and focus on the specific data of two polymers with particular reference to the nature of the amorphous phase whose local mobility influenced by a plasticizer; plausibly a good local solvent. In the literature there are several sources of information regarding entanglement density and tube diameter for several polymers but, at least to our knowledge, not that many. One major information is reported in the series of papers of Fetters *et al*. where several parameters reported, including M_e (onset entanglement molecular weight) and its relationship with other molecular parameters [L. Fetters. 1994; L. Fetters. 1999]. In a review by Aharoni on M_c, the critical molecular weight for the onset of entanglement dynamics, for a broad range of materials reported. [S.M. Aharoni 1986]. PET is certainly among the materials listed, no mention is made on PBT, and therefore for this polymer one may infer a trend on the basis of polymers with similar chemical structure or on the basis of a comparison with the parent polymer PET, attributing a larger mobility to PBT due to the four methylene groups. The collection of several data on other materials is supported by the packing model [N. Heymans.2000], albeit criticized in a recent work [S. Wang 2007], mentioned that M_e decreases with chain stiffness because stiffer chain pervades larger volume that

can accommodate the same number of chains at a shorter chain length. This observation should be compared with the Kuhn length for several polymers which decreases for stiffer chains [L. Fetters 1999]. The different behavior of PET and PBT, if one excludes specific interactions with the plasticizer adopted in this work, should therefore come from a stiffer and a softer chain polymer respectively. Although this statement reconciles with the experimental evidence, the results account of a threshold like behavior difficult to interpret on the basis of such understanding. These remarks are some hints to reconsider the role of topology in polymer crystallization whose influence can remarkably affects the kinetics particularly under relevant experimental conditions. Only new methods for studying polymer crystallization can give perspectives on the understanding of polymer solidification with crystallization under the drastic conditions during the processing.

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9. EFFECT OF PLASTICIZERS ON SOLIDIFICATION OF PTT

9.1 Introduction:

Poly (trimethylene terephthalate) (PTT), first patented by Whinfield and Dickson [J.R. Whinfield 1946] in 1946 and its commercial introduction is by Shell Chemicals in 1990s. It combines the desirable physical properties of PET (strength, stiffness, toughness, and heat resistance) with the processing advantages of PBT (low melt and mold temperatures, rapid crystallization, and faster cycles), retaining basic polyester benefits of dimensional stability, electrical insulation, and chemical resistance. These characteristics make PTT suitable for uses in fibers, films, packing, and engineering thermoplastic markets [K. Dangayach 1997]. The isothermal crystallization studies on PTT by Avrami equation suggested that the crystallization rate of PTT is in between those of PET and PBT when they were compared at the same degree of cooling rate. [H. Chuah 2001; P. D Hong 2002]. PTT has high birefringence and luminous transmittance and is expected to be applied in the fields of optical communications, optical data processing, directional couplers and nonlinear optics [G.K Singh 2004; S.J Bai 1996].

The influence of plasticizers on the crystallization of comparatively fast crystallizing polymers like PTT is an interesting topic and is rarely studied. Two different plasticizers P and D melt blended with PTT and the crystallization studies were carried out by density measurements, WAXS, DMTA and are discussed in the following section.

9.2 Density studies on PTT and plasticized PTT:

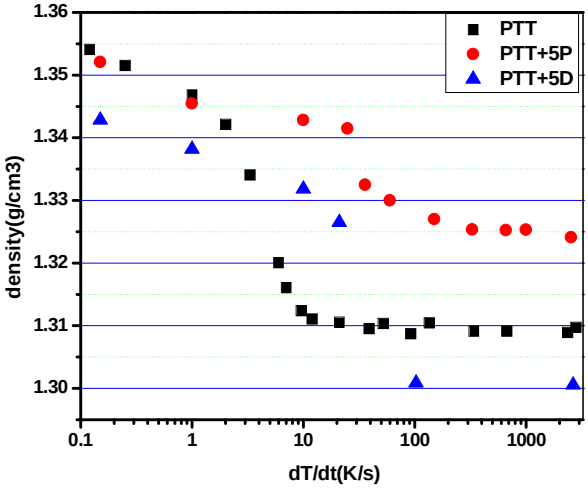


Fig: 9.2 (a): *Solidification Curve PTT, PTT+5P, and PTT+5D*

Figure 9.2(a) shows that PTT can be made to crystallize effectively at a cooling rate of 100 K/s, more than one decade larger with respect to clear PTT by P plasticizer. On comparing the solidification curve of P and D, it is more evident that linear plasticizer P is more effective than the plasticizer containing bulky groups which often decreases the mobility of the plasticizer and their intrusion among the polymer chains. The lower amorphous density in D incorporated PTT can be attributed to voids created by such bulky groups. It is surprising that even at the largest cooling rates we obtained a mesomorphic phase which is more stable than amorphous phase as evidenced by the higher density behavior in the higher dT/dt region.

9.3 WAXS studies on PTT and Plasticized PTT:

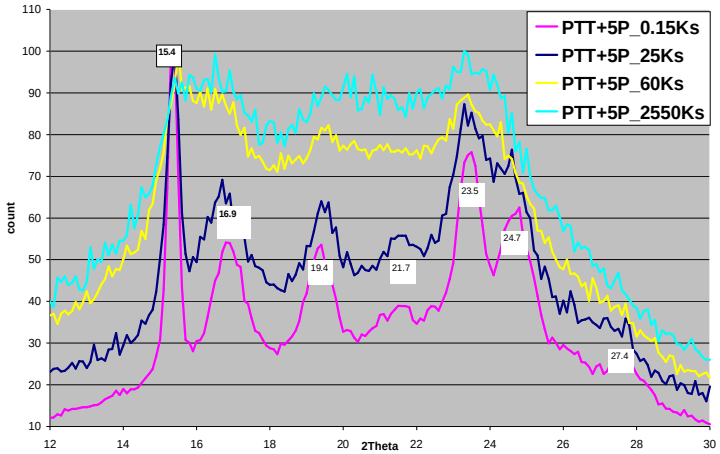


Fig: 9.3 (a): *WAXS pattern on PTT+5P samples*

PTT has triclinic unit cell with characteristic 2θ of 15.3, 16.8, 19.4, 21.8, 23.6, 24.6, and 27.3°, corresponding to the reflection planes of (010), (01$\bar{2}$), (012), (102$\bar{}$), (102), (11$\bar{3}$) and (104$\bar{}$), respectively [**Figure 9.3(a)**] [Wei ang Luo 2008]. From the solidification curve **figure 9.2(a)** we suggested that the presence of unusual higher density at higher dT/dt is due to the presence of an oriented mesomorphic phase and is further confirmed from the WAXS pattern at 2550K/s. The issue of mesomorphic phase has been widely studied and suggested that the mesomorphic phase, if oriented is very stable and tough, e.g. for PET [T. Asano 1999; K. Fukao 2003] and PBN [Takashi Konishi 2008].

9.4 DMTA studies on PTT and plasticized PTT:

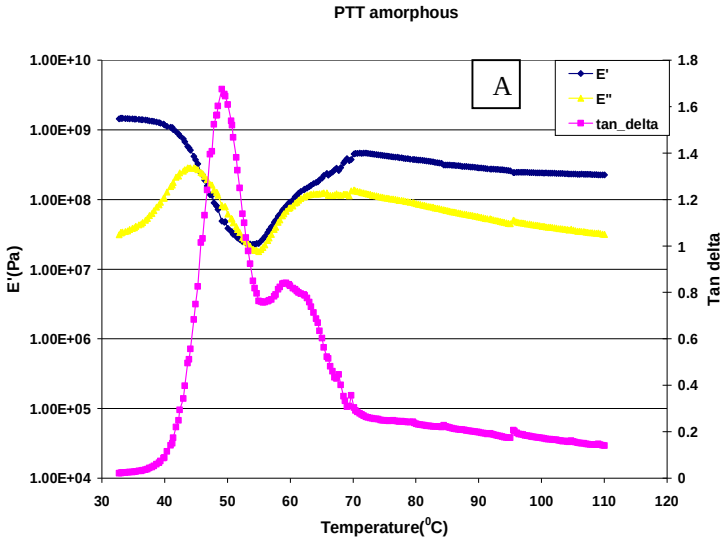
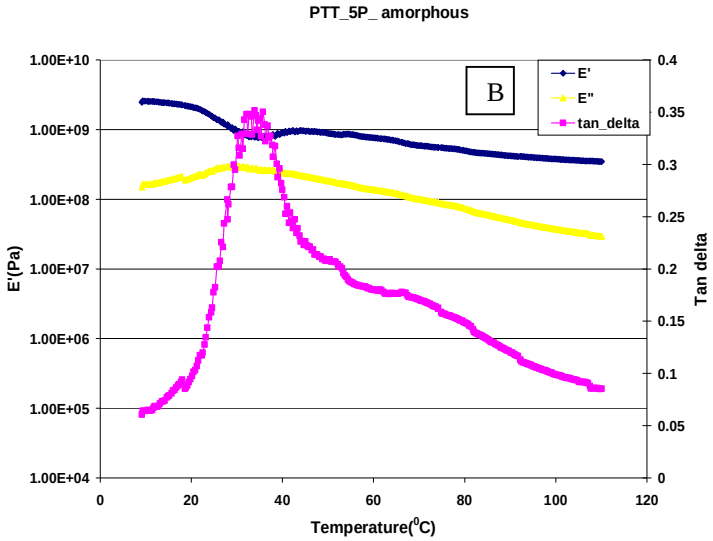


Fig: 9.4 (a): *DMTA data on PTT sample (A)*



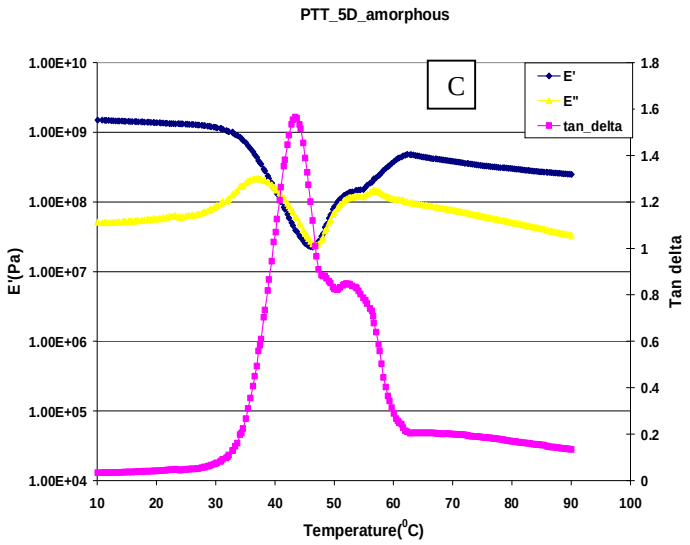


Fig: 9.4 (b): *DMTA data on plasticized PTT (B &C)*

Table 9(a): *T_g data PTT, PTT+5P and PTT+5D*

Sample	PTT	PTT+5P	PTT+5D
T_g@10Hz	45	27	40

From DMTA data [**Figure 9.4(a), figure 9.4(b) and table 9(a)**], it is clear that the P plasticizer is more effective as T_g decrease is more relevant in P incorporated samples. In such sample one can observe broad T_g and decrease of modulus at T_g is less relevant. This gives a hint that even at low temperature P incorporated samples are not completely frozen in comparison with the pure samples. Furthermore in P plasticized samples the crystallization from the mesomorphic phase is not as evident as in pure and D incorporated samples. This is because in presence of P plasticizer, the chains are very much mobile and crystallizes soon even at the early stages of heating and one could not observe a sharp modulus increase above T_g as in other samples.

9.5 Conclusions:

By suitable plasticizer PTT can be made to crystallize effectively at a cooling rate of 100 K/s, more than one decade larger with respect to clear PTT. Density and WAXS studies suggest that samples plasticized with P; an oriented mesomorphic phase is formed at larger cooling rates (~1000K/s). The plasticization is more pronounced in PTT where it is blended with P plasticizer as seen from the DMTA and density data. One can say, the crystallization rate of PTT with 5% P is comparable to that of fast crystallizing PBT.

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