CHAPTER I

INTRODUCTION

Rationale for the study

It is well-known that during polymer processing the crystallization kinetics and the final morphology; i.e. spherulite, cylindrite, or fibrillar, are deeply influenced by molecular orientation induced by flow (in the molten state) and deformation (in the solid state). Understanding and quantification of these effects are extremely important from both scientific and technological basis.

Polymer morphology or polymer crystallization is a phase transition that involves the arrangement of polymer molecules into crystalline and amorphous regions. Polymers are never 100% crystalline, and some cannot crystallize at all. At the highest dilutions, the precipitating solid polymer can be in the form of isolated crystals, called polymer single crystals. As known, in the simplest form they are isolated lamellae containing the chains in a folded conformation. At the highest concentrations and in single component melts, they generally will give rise to spherulites with their characteristic appearance (Maltese cross and often concentric banded extinction features) under crossed polars in the optical microscope. These features, at the large scale end of the crystalline structure hierarchy are radially arranged and growing lamellar aggregates (the source of the Maltese cross) [1]. Polymers are often crystallized under stress or flow to give an overall molecular orientation and enhanced properties. In such circumstances, primary nucleation is linear and the products are row structures, frequently described as shish-kebabs. Here, the shish is a linear backbone, typically tens of nanometer across, on which chainfolded lamellae (the kebabs) grow transversely [2].

Polypropylene (PP) is a semi-crystalline polymer that is different in stereospecificity and comonomer content. It is commercially produced in isotactic, syndiotactic, and atactic forms with varying degree of tacticity, the isotactic form being the most common. Depending on the solidification, PP can crystallize into four different crystal polymorphs, α (monoclinic), β (hexagonal), γ (triclinic) and a smetic form [3, 4, 5, 6]. PP is widely used in many applications due to its excellent balance of physical properties and low cost. The property profile of PP is strongly influenced by the level of crystallinity that is achieved when the polymer crystallizes from the melt. When molten PP cools during extrusion or injection molding, crystals form at nucleation sites, which are often impurity particles. These crystals radiate outward from these nucleating centers forming spherical structure known as spherulite. Eventually the spherulites impinge on one another and the part become fully solid in nature. Amorphous (non-crystalline) material is also entrained within the spherulite, so that the overall crystallinity of the final part is somewhere in the range of 40% to 60% crystalline. The modulus (stiffness) and strength of the final part is depending on the percent crystallinity, and higher crystallinity leads to higher stiffness and strength [7].

Polymer fibers have gained, over the years, abundant usage in a variety of applications from apparel to industrial fabric. Polypropylene (PP) is one of the most commonly used polymers in fiber manufacture [8]. High strength PP fiber can be used in the applications of anti-ballistics, ropes, nets, tubes, pipes, automotive part, reinforcement for cement or polymer and other similar applications. The very large commercial importance of PP fiber is due to its attractive characters of low cost, low specific gravity, high chemical resistance, ease of processing and recycling [9]. The introduction of more crystal nuclei dramatrically speeds up the rate of crystallization, and this has the effect of reducing cycle time in injection molding. Many nucleating agents have been developed to achieve these effects ranging from substances such as sodium benzoate to the high performance organophosphate salts and sorbitol clarifiers [7].

Since the mid 1980's, the dibenzylidene sorbitol (DBS) and its derivatives have been investigated as an additive for semi-crystalline polymers. Investigations of DBS-based nucleator in PP indicate that at low additive content (up to about 0.5%) clarity is enhanced. This effect lost when the content exceeds 2% [10]. In which polymer mechanical properties, such as Young's modulus of injection molded samples, increase with additive content up to 0.75% [11]. Influence of DBS and its derivatives on the orientation achieved during processing of semi-crystalline polymers has also been investigated. Enhancement of shear-induced orientation by the presence of DBS fibrils has been studied [12, 13, 14, 15]. It was found that fibrils align parallel to the applied shear while polymer crystal grow epitaxially on the fibril surface, perpendicular to the shear direction [12].

1,3:2,4-dibenzylidene sorbitol or dibenzylidene sorbitol (DBS) is a low molecular weight organic molecule. It is known as a gelator in cosmetics, biomedical materials etc. At low concentrations, it can self-organize to form a three-dimensional nanofibrillar network through hydrogen-bonding and π-interactions in variety of organic solvents and polymer melts to produce organogels [16]. The DBS molecule is a chiral molecule shaped like a butterfly having a sorbitol body and two benzylidene wings (Figure 1). Since the benzylidene attached at the 1 and 3 carbons is in an "R" chiral orientation and the benzylidene attracted at 2 and 4 carbons is in an "S" chiral orientation, DBS is designated as 1,3(R):2,4(S)-dibenzylilidene sorbitol [17].

As DBS self-assembles into a fibrillar network, two types of physical intermolecular interactions are likely to occur: hydrogen bonding and π-interactions. Hydrogen bonding refers to the interaction between a hydrogen atom bonded to an electronegative atom.

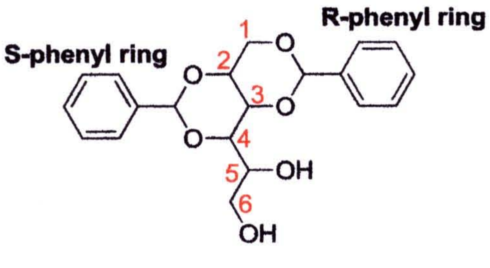

Figure 1 Chemical structure of 1,3:2,4-dibenzylidene sorbitol (DBS) [18]

In general, under quiescent crystallization condition PP exhibited the morphologies in form of spherulites. Furthermore, crystallization of PP melts under shear flow can be promoted anisotropic crystal structure, such as shish-kebab or row structures. This structure consists of the central position acted as "shish", while the lamellae perpendicularly crystallize on "shish" upon an epitaxial growth mode, termed as "kebabs" [19]. Many factors, such as intensity of applied flow, the processing temperature and molecular weight of polymer are effect on the orientation [14]. Jay and co-workers [20] measured the crystallization kinetics of PP with various molecular weights during shear in a fiber pull-out device. They observed that the sensitivity of a given PP to shear depended on its molecular weight. The high molecular weight species played an important role in melt orientation and enhancement in crystallization. If long molecular chains were present, the polymer crystallization was sensitive to shear flow and the orientation of the surface layer was much higher in these materials. Jerschow and co-workers [21] investigated isotactic polypropylene (iPP) under shear it is indicated that the long polymer chains were predominant for the formation of the highly oriented surface layers. Several practical processing means of polymer products, including injection molding, extrusion, etc. involve intensive extension or shearing flow. They are providing high validity of formation of shish-kebab structure in the prepared products. There is a prevalent consideration that formation of shish-kebab can markedly improve tensile strength [22], promote modulus and stiffness, decrease permeability and increase thermal stability.

In previous research, the shish-kebab structure has been studied in various polyolefin blend, including PP/LLDPE, LLDPE/HDPE, iPP/HDPE, HDPE/EVA (ethylene-vinyl acetate), PP/ethylene cellulose and iPP/poly(ethylene terephthalate) (PET) for formation of polyolefin shish-kebab structure [23]. So far, most of the studies have focused mainly on the role of long molecular chains in the formation of a shish-kebab structure and neglected the high density entanglement of long molecular chain. A schematic mechanism for elucidating the role of molecular weight of HDPE on shear-induced shish-kebab structure in LLDPE/ HDPE blend is illustrated in Figure 2. It is suggested that the molecular weight of HDPE plays an important role in which chains network stretched under shear to form bundles of shish taken, and then epitaxy of kebab take place at the position between adjacent entangled sites [24].

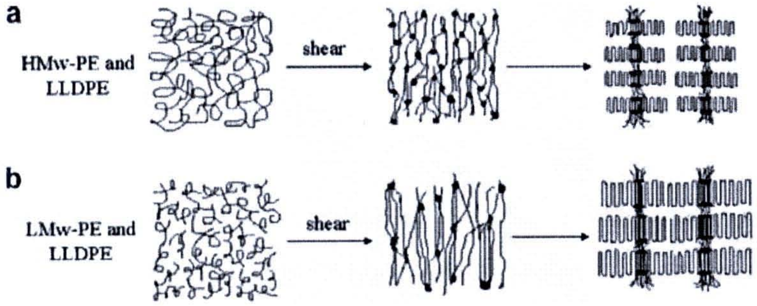

Figure 2 Schematic mechanism for the role of HDPE molecular weight on shear-induced shish-kebab structure in LLDPE/HDPE blend: (a) high molecular weight and (b) low molecular weight

The addition of DBS to polymer matrix will change in the crystallization process and the morphology that subsequently form. As already mentioned, DBS can self-organize to form a three-dimension nanofibrils network in polymer melt. When sorbitol derivatives are dispersed into the polymer matrix it can self-assemble in to fibrous structure that appears to act as nucleation centers for polymer crystals [11].

The purpose of this work is to modify the molecular structure of DBS for study the fibril morphology in more detail by electron beam of scanning electron microscope (SEM) and transmission electron microscope (TEM). The effect of modified DBS structure as a row nucleating agent for iPP will be studied.

In previous work, under shear flow DBS form highly extended nanofibrils which lie parallel to the flow direction and serve to direct crystallization of the polymer leading to a massive amplification of anisotropy present in the melt. Without DBS polymer exhibits an isotropic microstructure. In addition, DBS concentrations and flow conditions are effective to the generation of highly aligned system. Below a certain temperature, DBS self-organizes into a three dimensional network within the polymer melt. When deformation is applied to this gel state it templates the polymer lamellae that subsequently form, whereas when the melt is sheared at a temperature where the DBS is dissolved in the polymer, no anisotropic microstructure is found in resultant polymer after crystallization. Moreover, at shear rates above a threshold the orientation is almost independent of the shear rate. Very small shear strains do not produce anoisotropiy. Intermediate shear strains produce high levels of anisotropy. For very high shear strains the orientation is reduced, there is a breakage of the fibril network due to an excess of strain [13].

In this work, the formation of anisotropic semi-crystalline structures in iPP from sheared polymer melts by using sorbitol derivatives as a nucleating agent and their effect on mechanical properties on iPP fiber will be studied.

Aim of this study

The aim of this thesis is to modify molecular structure of DBS for study as a nucleating agent for iPP. Under shear flow, the presence of small quantities of these derivatives may generate highly anisotropic semi-crystalline structure and affect to mechanical properties of iPP. The shish kebab or row structure will be introduced by using the low molecular weight of gelator sorbitol derivatives on iPP. Therefore, the effect of sorbitol derivatives as a nucleating agent and their effect on mechanical properties and morphology of polypropylene fiber will be investigated.

Scope of the study

In the present study, the sorbitol derivatives i.e. *o*-Cl-DBS, *m*-Cl-DBS, *p*-Cl-DBS and *p*-Br-DBS will be synthesized for comparison the substitution position (for chloro derivative) and type of substituent (chlorine and bromine). Fibril morphology of sorbitol derivatives in low molecular weight solvent will be investigated by TEM and SEM techniques. The iPP containing sorbitol derivatives were prepared by melt blending process using two-roll mill. The effect of sorbitol derivatives on crystallization and melting temperature of iPP were studied by DSC technique. The blend samples were spun into fiber form by extrusion process. The effect of processing parameters i.e. die temperature, screw speed, cooling rate on mechanical and morphology of iPP will also be investigated. The mechanical properties of neat iPP and iPP fiber containing sorbitol derivatives were investigated by using tensile tester. Finally, the effect of sorbitol derivatives on morphology of iPP fibers were investigated by SEM, SAXS and WAXS techniques.