CHAPTER I

INTRODUCTION

The processing-structure-property response of semicrystalline polymers (as well as polymers in general) has always been of interest to many polymer engineers and scientists. This interest is a consequence of the effect morphology has on the properties of a given polymeric product. Furthermore, the morphology is a direct consequence of the processing conditions. From an engineering standpoint, qualitative comprehension of the particular process variables that maximize the product's performance is crucial while from a research point of view, the molecular mechanisms that influence the structure and its properties are of fundamental interest.

In semicrystalline polymers, it is the structural order on the molecular, lamellar, and superstructure levels that affect the material properties. For many semicrystalline polymers, e.g. high density polyethylene (HDPE), isotactic polypropylene (iPP), isotactic poly(4-methyl-1-pentene) (PMP), and polyoxymethylene (POM), when melt-extruded under the appropriate conditions into fibers or films, a stacked lamellar morphology is induced as a result of stress induced crystallization. Upon its deformation perpendicular to the lamellae, high short-term recovery from nearly 100 percent extension is possible. In addition, films possessing voids on the order of microns, i.e. microvoids, can often be produced from these stacked lamellae materials after annealing and subsequently stretching in the machine direction (MD). This three-stage process (melt-extrusion/annealing/uniaxial-stretching) (MEAUS) for producing microporous films is industrially utilized for generating HDPE and iPP microporous membranes. The end use for these materials is often for blood-oxygenation and battery separators.

It is evident from the literature that a number of features regarding the theoretical and experimental framework exist for understanding the property-structure-property relationships for each stage of the MEAUS method. An analysis of the "resin-to-final-film" has already taken place within this laboratory on HDPE and isotactic poly(1-butene) (PB-1).[1] As stated previously, HDPE and iPP are commercially available microporous products produced by the method of interest. Interestingly, both of these polymers possess one or more α_c crystalline relaxations. An α_c relaxation, as will be described later in greater detail, is associated with chain axis mobility in the crystalline phase. It has also been noted that PB-1, which lacks an α_c relaxation, is not able to be made into microporous films with high permeability to air even though a planar lamellae morphology can be promoted in the extruded precursor. Thus, the question arises, are specific prerequisites required of a semicrystalline polymer in order for it to be produced into a microporous membrane via the MEAUS process. Additionally, it is still unknown what specifically occurs at each of the processing stages based upon variations in process conditions as well as molecular weight and its distribution.

It is believed that the orientation state and morphological features of the initial melt-extruded precursor film are critical to controlling the final pore structure. Of course, the orientation and morphology are a function of the process conditions (e.g. extrusion temperature, line speed, extrusion speed, & quench height) as well as the resin characteristics (e.g. molecular weight distribution, MWD, & weight average molecular weight, M_w). To generate a well-oriented and highly planar lamellae, the literature suggests the utilization of a "higher" extensional stress during extrusion with polymers of a highly uniform chemical composition that rapidly crystallize. Additionally, skin-core differences are not desirable and thus the well-oriented planar lamellae must exist throughout the film cross-section. This can be controlled through a rapid cooling process during extrusion in conjunction with a limited film thickness. After melt-extrusion, an annealing treatment (second stage) is utilized to induce molecular alterations such as crystalline perfection and lamellar thickening. This requires that chain mobility exist in the crystal phase (α_c relaxation) and that the annealing temperature is sufficient enough to activate this relaxation. Following annealing, the film is then deformed uniaxially (third stage) along the extrusion direction or MD causing the stacked lamellae to splay and initiate a microporous structure. This is accomplished through a two step stretching stage composed of a cold and hot stretching step. The cold stretching step is utilized to "nucleate" the micropores while the hot stretch step induces larger scale lamellar separation utilizing lower rates of draw at higher temperatures. From this brief overview, a set of criteria can now be hypothesized to aid in the selection of semicrystalline polymers capable of forming controllable microporous materials via the MEAUS process. The proposed criteria are as follows:

1. "Fast" crystallization kinetics
2. A highly planar lamellae morphology for the extruded precursor
3. "High" orientation of the crystalline phase in the precursor

4. Proper film thickness (1mil) and quenching rate to facilitate rapid heat transfer of the film
5. Presence of a α_c relaxation

The proposed study of the MEAUS method will involve two selected polymers that will be shown to fulfill the proposed criteria: isotactic poly(4-methyl-1-pentene) and polyoxymethylene. Three resins of each polymer will be utilized to investigate the effects of the property-structure-property relationships of the three stages. The main goal is to produce a PMP film that displays a high level of microporosity uniformly distributed throughout the final stretched membrane. This is also desired overall goal for the POM study. A selective number of melt-extrusion conditions with certain physical requirements will be utilized for each semicrystalline polymer with the goal of producing a highly planar stacked lamellar morphology with "high" crystal orientation. From these extruded films (precursors), the orientation, morphology, α_c relaxation, and other properties will be measured. These same properties will then be analyzed after the annealing stage and in some cases the stretching stage. Film analysis after each stage will generate information regarding how and why specific variations in the process parameters affect the properties of the film. In addition, this type of analysis will aid in determining the key operating mechanisms for the formation of "quality" microporous films.

In this selective testing of specific process parameters, their influence on the microporosity and its reproducibility for PMP and POM films will be elucidated. Further, the effect of the MEAUS processing variables on microporosity will aid in understanding how to produce better microporous films (i.e. films with higher microporosity). Comprehending the mechanisms of micropore production and the effect of the process parameters on the porosity will facilitate one's ability to "dial-in" the desired level of porosity. This control of porosity will ideally allow the manufacturer greater flexibility for marketplace requirements.

Another study that is separate from the MEAUS investigation will also be undertaken within this dissertation. It will focus on the processing-structure-property relationships of the molecular characteristics such as M_w and MWD in relation to the optical properties of blown and cast roll polyethylene films. This topic is of importance since it is often desirable for films to be clear and glossy.

This dissertation is therefore divided into three main parts. In order to aid the reader in an understanding of the MEAUS process, a literature review of relevant topics is first provided. This information is presented and discussed within Chapter 2. The second part of this document concerns the investigation of the MEAUS process regarding poly(4-methyl-1-pentene) presented over the course of Chapters 3 (melt-extrusion) and 4 (annealing & stretching). Chapters 5 (melt-extrusion) and 6 (annealing & stretching) represent the results of the sequential study of polyoxymethylene with respect to the MEAUS method. Summary and recommendations of the MEAUS studies (Chapters 3-6) will then follow in Chapter 7. The last portion of this dissertation (Chapter 8) addresses the processing-structure-property relationships of a number of polyethylene resins melt-extruded using both blown and cast film processes. The goal of this last study is to comprehend and control film haze through an understanding of the molecular characteristics affecting this film property. While this last report deviates from the microporous film study, it is still an investigation of the extrusion and resin characteristics on the resulting structure and morphology. Finally, the summary and recommendations regarding the polyethylene blown and cast films will follow in Chapter 9.

References

[1] Yu, T. H., Ph.D. Dissertation (advisor: G. L. Wilkes) Virginia Tech, 1995; Private communication.