CHAPTER VII

SUMMARY & RECOMMENDATIONS REGARDING THE MEAUS PROCESS FOR PMP AND POM

7.1 SUMMARY

This section of the dissertation has addressed the investigation of the three stage process (melt-extrusion/annealing/uniaxial-stretching) (MEAUS) for making both poly(4-methyl-1-pentene) and polyoxymethylene microporous membranes. The reader may recall that these two semicrystalline polymers were selected to test the crystalline mobility (α_c relaxation) requirement regarding the MEAUS method since both PMP and POM display an α_c relaxation. In addition, other prerequisites were proposed for the formation of a microporous film but will not be restated at this time. The important observations obtained regarding the PMP and POM studies are now reiterated respectively.

PMP:

In the first stage (melt-extrusion), the process variables studied included melt-extrusion temperature, extrusion speed, line speed, and quench height. For the three PMP resins (A, B & C) utilized, the variables were the weight average molecular weight (M_w) and comonomer content. The reader may remember that resin B possessed a higher comonomer content relative to resins A and C. Upon melt-extrusion of resin A, parallel planar lamellar morphologies with relatively high crystalline orientations along the machine direction (MD) were promoted. Some resin B films were noted to have sheaf-like structures while other samples possessed parallel planar lamellar textures with high chain axis orientation along MD. The resin C films could be made to possess either sheaf-like structures or slightly twisted lamellar textures with an absence of any superstructure. For a given resin, the orientation development and the formation of the fibril nucleated morphologies were concluded to be a consequence of the extrusion stress as controlled by the process conditions. However, for films extruded under equal conditions but from different resins, the film morphology and orientation were strongly dependent upon the characteristic melt-relaxation times of the PMP resins. The dissimilar melt-relaxation times between resins were a consequence of their M_w differences. The comonomer differences between resins A (or C)

and B were not found to play a significant role in either the morphological features or the crystalline orientation for this study. The additional comonomer present in resin B did, however, affect the values of T_m and X_c.

The structural modifications promoted by annealing were also studied. The important variables included the temperature (T_a), time (t_a) and tension level (percent extension) applied during annealing. Annealing at the higher temperature of 205°C was found to induce greater values of crystallinity. Additionally, for a given T_a, longer t_a values were recognized to produce higher crystallinity. The T_a and t_a utilized were also observed to effect the α_c relaxation. It is this thermal relaxation that makes it possible for the structural changes to occur within the crystalline phase below the melting point of the polymer. In contrast to T_a or t_a, tension was not found to influence the crystalline level. It was, however, noted to influence the morphology; as the specific tension level was increased, the degree of lamellar deformation and separation increased. In fact, nanovoids were observed in the case(s) of higher tension levels via AFM.

Following annealing, the films were uniaxially stretched along the MD to produce microporous membranes. For the two step (cold and hot) stretching stage, the parameters varied in each step were the temperature (T_{cs} & T_{hs}) and percent extension (%CS & %HS). Each variable was determined to be influential in the final film permeability/Gurley number and the microporous morphology for the *resin A* films. Higher overall extension levels (i.e. high %CS & %HS) produced the highest membrane permeability and largest observable pore structure when utilized at relatively high stretching temperatures *for the processing window investigated*. From AFM and SEM, it was observed that the resin A microporous film morphologies are composed of lamellae “islands” bridged together by microfibrils oriented along the MD. At times, a relaxation step was implemented following the hot stage, however, it was found to be detrimental to the final film permeability. In addition to the stretching variables, the effect of the precursor orientation and morphology were found to be crucial in controlling the resin A final film permeability. Specifically, higher starting orientation and more parallel planar lamellar textures were recognized to facilitate higher Gurley values. The annealing parameters also influenced the final films for resin A. As noted, the tension level applied during annealing affected the annealed film morphology. This lead to a less porous stretched film as the tension level became greater during annealing. Higher annealing temperature and longer times also affected the porosity for the processing window studied.

Specifically, the level of microporosity for a resin A final film was improved if higher temperatures and times were employed for the processing window studied.

In contrast to the resin A films, microporous membranes from resins B and C could not be produced into microporous membranes using the MEAUS process within the processing window studied. In the case of resin B films, this was in spite of relatively high crystal orientation and parallel planar morphologies. The reader may recall that these characteristics are two of the proposed criteria required for the production of a microporous membrane. The inability of the resin B films to form microporous films was attributed to the additional comonomer present, which adversely impacted the α_c relaxation. Resin C possessed lower comonomer levels, analogous to resin A, and it was characterized by a crystalline α_c relaxation that was also similar to resin A. Thus, sufficient crystal thickening and perfection was promoted with annealing. The inability of the resin C films to form microporous membranes, however, was attributed to the lower crystalline orientation values and twisted lamellar morphologies that typified its precursors. In conclusion, the resin A films met the proposed criteria that have been mentioned throughout this document and thus "quality" microporous films were produced via the MEAUS method. In contrast, the resin B and C materials did not meet the criteria, which explains the lack of microporous character their films displayed upon annealing and stretching the melt-extruded precursor.

POM:

In reiterating the important results of the POM study, many of the same observations made in the PMP study were reaffirmed here, specifically regarding the proposed prerequisites to the formation of microporous films via the MEAUS method. In addition, new findings presented themselves at each stage of the process.

Three POM resins (D, E & F) were studied, where each resin was characterized by a different M_w, specifically resin D > resin F >> resin E. Resins D and E also had similar MWD values while resin F was much broader. The reader may also recall that resin F was polymerized with a small amount of ethylene oxide comonomer while resins D and E were not. Upon melt-extrusion of these resins, a number of different types of morphological features were found. In fact, it could be concluded that almost a continuous spectrum of morphologies were obtained, spanning from spherulitic-like textures to planar stacked-lamellar. This so-called spectrum of morphologies was found to be dependent upon both the molecular characteristics of the resin as well as the melt-extrusion conditions, which control

the line-stress applied to the melt during crystallization. In the case of the latter, the processing conditions were found to influence the precursor properties where a higher melt temperature, slower line speed/extrusion speed, or higher quench height produced a lower f_c or Δ_T value and more quiescent-like (spherulitic) morphology. The resin characteristic M_w was found to be responsible for the differences in morphology and the orientation state between similarly processed precursors of resin D and E. Resin D possessed the higher M_w of the two resins and thus those films had less of a quiescent-like morphology with higher f_c and Δ_T values. The higher MWD of resin F was noted to produce a more planar lamellar morphology with higher f_c and Δ_T values than resin D regardless of the slightly higher M_w for the latter resin. The effects of the molecular characteristics on the morphology and orientation state of the precursor films from different resins extruded under equal conditions were found to be a consequence of their influence on the melt-elasticity or relaxation time between resins.

In terms of the annealing effects on the resin F films, the following conclusions were made. As the T_a or t_a were increased, the crystallinity and long spacing (lamellar thickness) increased as a consequence of crystalline mobility (α_c relaxation). For these films, the melting temperature did not appear to be affected in a systematic manner as a function of either T_a or t_a. The application of tension to the annealed film was also found not to effect the melting temperature or the crystallinity. This annealing parameter did, however, influence the annealed film morphology. The annealing tension effects on the morphology were similar at lower T_a values to results reported in the previous PMP investigation.

These morphological alterations by annealing impacted the final microporous morphology for resin F films, as did the effects induced by the T_a and t_a utilized. The stretching variables were also found to influence the final film porous structure as well as the permeability. From AFM, it was observed that the POM micropores are a result of interlamellar splaying between individual lamellae. This is in contrast to the "islands" of lamellae that splay apart, creating the microvoids, in the PMP stretched films. However, in either case, microfibrils oriented along the MD bridge together the splayed lamellae. The initial melt-extruded morphology and f_c were also noted to be influential on the microporosity and permeability of the final film. In fact, a lower f_c and a slightly twisted lamellar morphology were believed to be the main reason why the precursors from resin D were not able to form microporous membranes.

In conclusion, the resin F films met the proposed criteria that have been mentioned throughout this document and thus "quality" microporous films were produced via the

MEAUS method. In contrast, the resin D materials did not meet the criteria, which explains the lack of microporous character these films display upon annealing and stretching the melt-extruded precursor.

7.2 RECOMMENDATIONS

The above content summarizes what has been accomplished in this dissertation regarding the formation of PMP and POM microporous membranes via the MEAUS method. In light of the future research direction of this study, a few recommendations are provided below:

1) A next step might be the selection of a semicrystalline polymer that does not possess an α_c relaxation as is the case for isotactic poly(1-butene). However, this polymer was previously investigated by T. H. Yu[1]. Note that in order for this particular investigation to be a rigorous test of the α_c supposition, the remainder of the prerequisites must be fulfilled, i.e. planar stacked lamellar morphology and relatively high crystal orientation must be attainable upon melt-extrusion. A possible candidate includes poly(3-methyl-1-butene). This is somewhat of an unlikely choice because of the overlap between its melting point 350°C the start of its degradation point (ca. 300°C).[2] Thus, significant polymer degradation would likely occur during melt-extrusion. However, fibers produced from this polymer were found to exhibit hard-elastic character.[3]

2) Another possibility is the investigation of another semicrystalline polymer that satisfies the proposed criteria for the formation of a microporous membrane via the method in question. The main reason why such a studied would be beneficial is that it would lend further credence to the proposed criteria. The results from such a study likely would facilitate an improved working knowledge of the mechanisms behind each stage, i.e., melt-flow behavior during melt-extrusion, structural modifications occurring while thermal annealing, and the deformation processes taking place during stretching. Additionally, the influence of the MEAUS processing parameters on film porosity and the reproducibility of the film porosity could lead to a better understanding of the MEAUS process. Thus, such a study would be beneficial to both the engineering and scientific communities. If successfully produced into a microporous membrane, a product potentially would be available for commercial sale. A suggested possibility includes poly(vinylidene fluoride) (PVDF). This polymer is currently being produced into

microporous or nanoporous membranes for use in the areas of water filtration and battery separation specifically in lithium ion batteries.[4,5] In all cases, these membranes are produced via the phase inversion method[6] as discussed in Chapter 2. Thus, PVDF membranes from the MEAUS process could be utilized for these applications where the MEAUS process would likely provide a more cost-effective means of production relative to the phase inversion process.

3) In the studies reported thus far, it was shown that the melt flow behavior for either the PMP or POM resins can be controlled to a degree by varying the melt-extrusion process conditions. To further probe this statement, a wider processing window is suggested that include both higher and lower stress conditions than those utilized here. Another POM resin may also be selected that is a product of the same polymerization mechanism that produced resin F, but that possesses a higher M_w than resin F. Such a resin would be expected to produce a more planar lamellar morphology than the films previously discussed. Upon annealing and subsequently stretching such a film, a higher permeability would likely result when compared with the POM final films reported above.

4) In the case of the PMP resin C, the reason believed for its films not forming "quality" microporous membranes was their lower f_c and slightly twisted lamellar morphology. Thus, the statement regarding a higher extrusion stress condition has special implications, especially since this resin was shown to possess an α_c relaxation similar to that of the resin A films. If a more oriented crystal phase and flatter lamellae (non-twisted) could be melt-extruded given the appropriate conditions, it is likely expected that a microporous film possessing a uniform distribution of micropores would be produced upon subsequently annealing and stretching at the proper conditions.

5) The morphological and orientation results due to the application of tension during annealing were not straightforward for the POM films. The reader may recall the difference in the deformation modes that occurred, which depended upon the annealing temperature. Hence, a systematic study should be undertaken, where higher levels of tension are employed for the T_a values already utilized in this study (i.e., 130 & 145°C). Analysis of the bulk morphology may also aid in this investigation. Since POM is a polymer unable to be stained by traditional agents such as RuO_4 or OsO_4, the analysis of

the bulk morphology by the conventional technique of transmission electron microscopy could, however, prove to be a difficult task.[7]

6) The POM microporous films were not able to achieve significantly high permeability levels, e.g. Gurley levels below 50 seconds. Possible solutions to this problem include the use of larger levels of total stretch than those studied here, i.e. %TS > 180%, which might lead to greater lamellar separation. Additionally, a sequential machine direction/transverse direction stretching process would likely improve the final film porosity and thus should be investigated.

References

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