VIBRATION ASSISTED INJECTION MOLDING OF POLY(LACTIC ACID) - THERMAL, SPECTROSCOPIC, AND MECHANICAL ANALYSIS OF HYDROLYTIC DEGRADATION

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Abstract

Hydrolytic degradation of PLA was studied, and a comparison was made between samples molded using vibration-assisted injection molding (VAIM) technology and those through conventional injection molding. Data from an earlier study is revisited to observe hydrolytic degradation effects by analyzing thermal, spectroscopic, molecular weight, and tensile strength trends. The trends show that degradation causes an apparent decrease in crystal order, reduction in molecular chain length and weight. Comparison between molding cases shows that VAIM results in a relatively higher strength of molded PLA, with apparently a more ordered crystal structure. It is interesting to note however that comparison in data trends as degradation of the samples proceeds throughout the study does not show any significant differences between VAIM and conventionally molded PLA, especially in terms of changes in thermal and spectroscopic data.

Introduction

Poly(lactic acid) (PLA) is a bio-based, biocompatible, and biodegradable thermoplastic polymer that has rapidly evolved into a competitive commodity material over the past decade, and has become what is now a billion dollar industry. As it is derived from bio-based renewable resources, PLA is increasingly sought as eco-friendly product alternatives to its petroleum-based counterparts for an expanding range of applications.

Due to its biocompatibility and biodegradability, PLA is viewed as an ideal material for biomedical devices designed for applications involving human interface [1]. A major issue in this regard however is the lack in understanding and control of its degradation behavior.

The effect of vibration on injection molded plastics requires further research. There have been investigations on various forms of vibration technology applied to injection molding and its effect on the percentage crystallinity [2] and mechanical properties [3, 4, 5] of the molded products. However, the scientific fundamentals of what happens to the polymer as it undergoes oscillatory motion during solidification needs to be further researched. The scientific questions of how it affects melt dynamics and rheology, and crystallization kinetics is still unanswered. Research furthering scientific understanding of the relationship between PLA processing and these parameters is important since they directly influence the final product’s mechanical, physical, thermal, optical, and degradation properties.

The VAIM technique has been explained in previous literature [3, 4, 6]. In brief, it is injection molding augmented with an in-built system that instructs the machine plunger to oscillate at a specific low frequency, amplitude, and duration as the melt is shot into the mold cavity, and continued as the polymer is packed, up to its solidification.

This paper continues past work in investigating the effects of VAIM and molecular orientation on degradation activity [6, 7]. Existing data is revisited and presented in terms of analysis on thermal and spectral data trends, molecular weight drop, and tensile strength deterioration as the molded samples degrade. This paper also presents how VAIM may have influenced the molecular and crystal structure of molded PLA, in addition to its impact on the material’s degradation behavior.

Materials

PLA 3051D provided by NatureWorks LLC were used in this study. The material is composed of 96% L-Lactide and 4% D-Lactide content. It has a melt flow rate of 14 g/(10 min) at 210°C, with a glass transition temperature between 55°C and 60°C and the melting temperature between 145°C and 160°C.

Experiments

Injection Molding

The PLA samples were molded into Type I tensile test specimens according to the ASTM D638-01 standard. The samples were categorized according to the following injection molding conditions: i. conventional (without vibration); ii. VAIM at 4 Hz for 10s; and iii. VAIM at 6 Hz for 15s. Injection and cooling times were maintained at 20 seconds for all specimens. Specific injection molding parameters that were applied for these categories are listed in Table 1. Temperatures at the nozzle, front, middle, and rear sections of the injection screw were set at 400°F(204.4°C), 380°F(193.3°C), 360°F(182.2°C) and 350°F(176.7°C) respectively.
Table 1. Injection molding parameters for the PLA samples

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>4Hz, 10s</th>
<th>6 Hz, 15s</th>
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</thead>
<tbody>
<tr>
<td>Injection speed [cm/s]</td>
<td>42.6</td>
<td>42.6</td>
<td>42.6</td>
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<tr>
<td>Injection pressure [MPa]</td>
<td>36.7</td>
<td>55.0</td>
<td>91.6</td>
</tr>
<tr>
<td>Packing pressure [MPa]</td>
<td>73.3</td>
<td>73.3</td>
<td>73.3</td>
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Hydrolytic Degradation

Phosphate Buffered Saline (PBS), diluted to a concentration of 1X and an adjusted pH of 7.6 was used. All samples were sterilized by immersion in 80% ethanol for 30 minutes, followed by pure ethanol for 10 minutes. The samples were finally washed with 1X PBS to completely eliminate ethanol prior to placement in containers for incubation. Incubation was performed by complete submersion of the samples in 1X PBS at 37°C for 39 weeks. Throughout the incubation period, the samples were tested in multiple ways to assess degradation activity.

Tensile Testing

Tensile tests were conducted on an INSTRON 5667 C 9620_30 kN Tensile Testing Machine. The extension speed was set at 5mm/min according to the ASTM D638-01 standard.

Results and Discussion

Optical Birefringence

Figure 1 shows the optical birefringence pattern on the dog bone samples prepared at the three injection molding conditions. The images clearly show differences in molecular orientation levels that were locked along the gage length section of the specimens. Since anisotropic arrangement of crystals in polymers is expected to increase with molecular orientation, hence observation of light retardation and fringe patterns on the molded part can be used to qualitatively indicate the orientation levels in the specimen. As observed in Figure 1, the more frequent fringes observed in the VAIM specimens indicate a corresponding higher level of molecular orientation. In this regard, it can thus be inferred that the 6Hz-applied frequency (Figure 1a) results in a higher level of molecular orientation in relation to the 4Hz (Figure 1b) and conventionally molded (Figure 1c) specimen.

Molecular Weight

Molecular weight measurements were made via Gel Permeation Chromatography (GPC). Polystyrene with a molecular weight ranging from 600 – 3,800,000 g/mol was used for calibration. All samples were dissolved in Tetrahydrofuran (THF) at a concentration of 0.1 %w/w. GPC data was analyzed using PL Caliber Version 7.03 from Polymer Laboratories.

DSC-Thermal Analysis

An interesting observation is made when analyzing the thermogram for the three injection molding cases in an
overlay plot (Figure 2). VAIM is observed to cause: (i) a marked decrease in the first endothermic melting peak with an apparent shift to the to higher temperatures which indicates that the polymer has a more ordered crystal structure. It is noted that similar observations were made by others using polyethylene [2] and polypropylene [8]; (ii) broadening and lowering of the cold crystallization exothermic peak, and an apparent shift to lower temperatures. Broadening and decrease in peak intensity is as expected as this indicates less chain mobility and ability to reorganize towards crystallization upon heating. The left shift however, may be due to shorter molecular chains and weights, caused by the vibration, resulting in lower temperatures to cause cold crystallization. The overlay plot also shows an observable decrease in aging due to vibration. In this regard it is interesting to note that applied vibration during molding, causes a similar trend to extruding the polymer at higher rates [9], and also annealing the material at higher temperatures and duration [10, 11].

Figures 3, 4, and 5 show the DSC thermogram for the three injection molding conditions, over the 39 weeks of degradation. In all three cases, two clear endothermic melting (Tm) peaks for the material are be observed, as also found by others working with NatureWorks Ingeo™ 3051D [11] and PLA [12]. It is thought that the first is for the disordered α'-phase that melts at a lower temperature, which then attains mobility and reorganization to form the more ordered α-phase. The latter then requires a higher energy and temperature to melt. In this regard, it has been hypothesized that the double peak is due to the result of annealing during the DSC scan, whereby crystals of low perfection [13], or crystals that are thinner [14], have time to melt and recrystallize at a few degrees higher in temperature, and to then remelt; and that this phenomenon decreases with increasing optical purity of the material. Researchers have remarked that these two endotherms may also be attributed to the gradual melting of the lamellae of different thickness or morphologies [12], or molecular weight distribution [15]. It is also apparent that as degradation advances, the samples exhibit a deeper endotherm peak at the higher temperature, as also observed by others [16], and a left-shifting of the first endotherm peak to lower temperatures. This leftward shift may indicate crystals with lower ordered structure.

Figure 2. Overlay plot comparison of the DSC thermograms for samples molded under different conditions at Week 1.

Figure 3. DSC thermogram for injection molded PLA over varying degradation periods.

Figure 4. DSC thermogram for injection molded PLA (vibration assisted at 4Hz for 10s) over varying degradation periods.
Figure 5. DSC thermogram for injection molded PLA (vibration assisted at 6Hz for 15s) over varying degradation periods.

The cold crystallization temperature (Tcc) for all cases is observed to decrease in broadness, shifting to the left and increasing in sharpness as degradation proceeds. This may be due to hydrolytic scissions resulting in smaller chains with lower molecular weights [16], which in turn requires a lower temperature to cause crystallization. The enthalpy is also higher due to more chain mobility, and more molecular chains that can be reorganized upon heating. It should be pointed out that even though the second endotherm melting peak accentuates with degradation, taking into consideration the corresponding increase in exothermic cold crystallization, this may indicate a decrease in the material’s %crystallinity with degradation.

The decreasing trend in glass transition temperature (Tg), as shown for all cases in Figure 6, with advancing degradation may be attributed to reduced crystallinity, molecular weight (shorter chains), and increased chain flexibility. This is in part, inferred from claims by others who state that an increase on the other hand, indicates a decrease in molecular mobility [9].

The endotherm which occurs immediately after the Tg is attributed to physical aging of the samples [12, 14]. Others working with IngeoTM 3051D have also reported this observation [17]. In terms of degradation, this peak is an indication of a drop in its molecular weight. Similar observations were reported by others investigating PLA degradation [18]. This phenomenon is also commonly observed in amorphous PLA as the material has more free-volume for the polymer chains to relax, whereas oriented and unoriented semi-crystalline PLA may prevent the material from aging to a more stable state [19].

The trends observed in the DSC thermograms with advancing degradation show an apparent reduction in the material’s crystallinity. It has been postulated that hydrolysis of PLA first occurs in the amorphous regions (hence the gradual change in crystallinity – difference between the melting endotherm and the slight crystallizing exotherm), forming low molecular chain segments. Finally, hydrolysis of the crystalline section occurs causing loss in the material’s molecular weight and mechanical properties [20].

Figure 6. Apparent decreasing Tg trend with advancing degradation – a comparison between the three injection molding cases.

**ATR-FTIR Spectroscopy**

Figure 7 shows the overall FTIR spectrum of PLA, for the different degradation periods with spectral peak band assignments typical to the conventionally molded material [21, 22]. The PLA spectrum shows a broad band between 3450 – 3700 cm⁻¹ related to the stretching of the OH group. The stretching bands for –CH are at 2997 (asymmetric), 2944 (symmetric), and the methyl group -
CH$_3$ with a weaker bonding is assigned at 2877 cm$^{-1}$. A strong transmittance at about 1759 cm$^{-1}$ is attributed to the stretching of C=O bond with variation in intensity that is thought to be attributed to the molecular arrangement in the polymer chain. This together with the –C=O bend at 1268 cm$^{-1}$ are important indicators of PLA. Bending vibration of –CH$_3$ can also be found at 1453 cm$^{-1}$.

–CH- deformation including symmetric and asymmetric bending can be found 1382 and 1362 cm$^{-1}$. The bands for the C-O ester bonds stretch are assigned at 1194, 1130, and 1093 cm$^{-1}$. The -OH bend is assigned at 1047 cm$^{-1}$, and –C-C- stretches are at 926 and 868 cm$^{-1}$ respectively. Similar spectra are observed for the samples molded at 4 and 6 Hz and are thus not shown.

Figure 7. FTIR spectrum of PLA (conventional) with advancing degradation (Weeks 1, 5, 13, 31, and 39, as indicated).

ATR-FTIR plots comparing the different injection molding cases are shown in Figures 8, 9, and 10 at Week 39. Comparison between molding conventionally, and with VAIM at 4 and 6 Hz does not reveal any obvious shifting or change in peak intensities.

Figure 8. FTIR spectra showing the carbonyl stretch for the three molding cases at Week 39

Figure 9. Close-up of the FTIR spectrum of PLA at the –OH stretch for the three molding cases at Week 39. There does not appear to be any differences between the three cases.
Figure 10. FTIR spectra showing the C-O stretch for the three molding cases at Week 39. The plot shows no apparent shift or change in peak intensities between the three cases.

Focusing on the spectral data trend over the degradation period however, revealed changes for certain ranges of peaks as the samples degrade. Figure 11 shows that the strong carbonyl C=O stretch at 1759 cm\(^{-1}\) does not shift or change with advancing degradation - an observation that is corroborated by others [23]. However hydrolytic degradation causes the OH group to further broaden (Figure 12), as the ester linkages are cleaved. It is also apparent that hydrolytic degradation causes shifting and intensification of the C-O bond peak frequencies (Figure 13). This was also observed by others [24, 23] who further add that the –CH\(-\) bonds at transmittances of 2997 and 2955 cm\(^{-1}\) do not degrade. It is noted that although when an ester such as PLA hydrolyzes, the OH group should undergo stretching, but the sharp peaks at the early stages of degradation is unexpected.

Figure 11. FTIR spectra showing the carbonyl stretch (C=O) that does not appear to shift or change in intensity over the degradation period.

Figure 12. Close-up of the PLA FTIR spectral region (conventional) showing the –OH stretch broadening and intensifying over the degradation period.
Figure 13. FTIR spectra showing the C-O stretch that appears to shift slightly to higher frequencies and intensity over the degradation period.

TGA

Figure 14 shows the apparent onset temperature drop for the samples molded under the three molding cases. It is noted that for all three cases, there is an initial increase in onset temperature for samples taken during the initial weeks (up to week 10) of degradation. Perhaps at the beginning weeks, there are irregularities acting as weak points for thermal degradation to start. As these weak links have been removed during the initial degradation period, thermal degradation under TGA occurs at a higher onset temperature, as more energy is required to break the long polymer chains. As the samples undergo hydrolytic scissions over time, the polymer’s molecular weight (and hence inferred chain length) decreases. The Van Der Waals inter-molecular forces, which may be the dominant restriction for the smaller molecule polymer after degradation, would require less energy to break. This may be the reason for the apparent drop in onset temperatures from Week 10 to the end of the experiment, after the initial increase.

Molecular Weight

The drop in molecular weight due to hydrolytic degradation is shown Figure 15. Although an apparent drop is observed over the degradation period, there does not appear to be any significant differences between the three molding cases. The drop of roughly 10% at Week 5 is less than that of 20% at 28 days as reported by others [25] working with the same material but incubated in H₂O for hydrolysis. The PBS medium used in this work may have inhibited the autocatalysis of the carboxyl (COOH) end group.


**Tensile Strength**

Figure 16 plots the reduction in ultimate tensile strength of the samples for the three molding cases, over the degradation period. The plot shows that the drop is generally less in the vibration molded samples. It is thought that although vibration does not necessarily increase the material’s %crystallinity, it does however induce a more ordered molecular structure and this may be the reason for this observation.

Tensile test plots for the three molding cases are shown in Figures 17, 18, and 19 respectively. The vibration-molded samples are observed to generally have a higher ultimate tensile strength reading throughout the degradation period. For all molding cases, the samples are also observed to acquire a reduction in tensile strength, and progressively break at shorter strains during testing. Hence there is a marked reduction in the material’s pliability with degradation. This may be attributed to the scissions resulting in a shorter backbone of molecular chains, and reduced intermolecular forces throughout the specimen.

![Figure 16. Comparison of the drop in ultimate tensile strength between samples molded at different vibration conditions](image)

![Figure 17. Variation of stress over strain for the conventionally injection molded samples.](image)

![Figure 18. Variation of stress over strain for the injection molded samples, at 4 Hz 10s of vibration.](image)
Hydrolytic degradation was observed to effect changes in the DSC thermograms of the PLA samples throughout the duration of study. In summary, the DSC data shows an apparent loss in crystal structure with reduced crystallinity with degradation. It can also be inferred from the DSC data that hydrolytic scissions results in lower chain lengths, and thus lower molecular weights and chain flexibility. ATR-FTIR data shows that degradation causes a broadening of the OH group, and intensification and shifting of peaks of the C-O bond to higher frequencies.

Our data does not show any significant differences in data trends when comparing between molding cases (VAIM vs. conventional) throughout the period of study. It is noted that there is a difference in tensile strength however where VAIM molded PLA consistently recorded a higher value compared to the conventionally molded sample, although there is a general loss in strength for all samples throughout the degradation period.

Conclusions


