MELT-MASTICATION OF ISOTACTIC POLYPROPYLENE FOR IMPROVED THERMAL AND PHYSICAL PROPERTIES

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Abstract

Herein a new polymer processing method called Melt-Mastication (MM) is demonstrated as a method to fabricate Isotactic Polypropylene (iPP) with improved thermal and mechanical properties. Melt-Mastication is a low temperature mixing technique that subjects molten iPP to chaotic flow under simultaneous cooling, promoting flow induced crystallization (FIC). The resulting materials demonstrate an unusual crystal morphology that is highly crystalline by thermal calorimetry (57% crystallinity), melts at a temperature 10.3 K higher than conventionally processed iPP, and demonstrates melt memory after annealing at 200 °C. The crystal morphology by polarized optical microscopy and atomic force microscopy appears to be comprised of largely disorganized lamellae, with possible ordering in local regions. Melt-Masticated iPP demonstrates improved mechanical properties in compression, specifically compressive modulus (+77%) and strength (+40%). The enhanced mechanical properties are attributed to aspects of the crystal morphology produced by MM.

Introduction

Isotactic polypropylene (iPP) is an industrially important semicrystalline thermoplastic polymer that may be formed and shaped into useful articles via established melt processing techniques [1]. Specific iPP melt processing operations such as film casting or melt spinning generate mechanically anisotropic articles with oriented crystal morphology through a phenomenon termed flow induced crystallization (FIC) [2,3]. Flow induced crystallization is achieved by applying sufficiently strong flow to molten iPP at a temperature near the melting point (T_m). Under these conditions an apparent increase in the crystallization rate is observed, along with the presence of oriented crystal structures that may include fibrillar or “shish-kebab” morphologies [4–12]. These crystal structures may be oriented by the flow field resulting in mechanical anisotropy, which in the case of melt spun iPP fibers can result in a 15-20x increase in the modulus of the draw direction [13].

However, current FIC melt processing operations are generally limited to mechanically anisotropic, thin iPP articles such as films and fibers. Isotropic, thick iPP articles like plates and rods are difficult to fabricate with FIC due to the large deviatoric flow field necessary for FIC, which causes contraction in one or two dimensions. Specialized injection molding techniques like shear-controlled orientation injection molding (SCORIM) do promote FIC in bulk iPP articles through simultaneous oscillation and cooling of an iPP melt [14–16]. However, such techniques were not widely adopted, presumably due to high equipment costs and long cycle times. Accordingly, there is a desire for alternative processing methods to apply the structural and mechanical advantages of FIC to bulk iPP articles.

In this report, we explore FIC of iPP through a processing technique termed Melt-Mastication (MM). In a previous report, MM was evaluated for dispersion nanoparticles in semicrystalline polymers [17]. In the present work, we elaborate on the FIC mechanism of MM and show how this technique promotes a unique iPP crystal morphology with enhanced thermal and mechanical properties, compared to iPP prepared by conventional melt processing techniques.

Methods

Materials

Pellet form isotactic polypropylene (iPP) grade PP9999SS was kindly supplied by ExxonMobil and used as received (T_m = 164 °C, T_c = 111 °C). Antioxidant process stabilizers, Irganox 1010 and Irgafos 168, were purchased from Ciba and also used as received.

Processing of Isotactic Polypropylene

Melt-Mastication was accomplished by compounding iPP over a three step temperature process, schematically represented in Figure 1. In the first step, iPP and oxidative stabilizers (0.05 wt% Irganox 1010 + 0.05 wt% Irgafos 168) were fully melted and compounded in a batch mixer (Brabender ATR Plasticorder®). The melt temperature was then reduced under continuous mixing and forced air cooling to the mastication temperature (T_M), where T_c < T_M < T_m of iPP. The final step involved isothermal mixing at T_M for 5 minutes. After MM, samples were immediately removed from the mixer and allowed to air cool to room temperature.

For reference, control samples were prepared by melt compounding (MC) to simulate conventional melt processing. In this case, iPP and oxidative stabilizers
(0.05 wt% Irganox 1010 + 0.05 wt% Irgafos 168) were melted and blended in a batch mixer. The conditions for MC were identical to the first step of MM, except the mixing time was equivalent to the total MM time. After MC, samples were immediately removed from the mixer and allowed to air cool to room temperature. The mixing torque, stock temperature, and mixing rate were recorded continuously for all samples.

**Figure 1. Schematic of Melt-Mastication temperature program**

**Thermal Analysis**

Differential Scanning Calorimetry was performed on a TA Instruments-DSC Q200. Calorimetry was performed from 20 to 200 °C or 20 to 215 °C with 10 K/min ramp rate. Melting and crystallization enthalpies were calculated from the first heating and first cooling ramps in order to capture the thermal history imparted by the processing technique. Crystal volume fraction was calculated according to a literature value for the melting enthalpy of an infinite iPP crystal, 207.1 J/g [18].

**Optical Microscopy**

Transmission optical microscopy was conducted on an Olympus optical microscope with DP71 digital camera equipped with crossed polarizers. Sample sections were prepared with glass knife microtomy in order to ensure consistent section thicknesses. Thin sections (10 μm x 2 mm x 2 mm) were prepared at room temperature on a Reichert-Jung FC4 Ultramicrotome.

**Atomic Force Microscopy**

Atomic force microscopy (AFM) was performed on a Digital Instruments Dimension 3100 AFM instrument in tapping mode. Sample surfaces were prepared by diamond knife cryomicrotomy on a Reichert-Jung FC4 Ultramicrotome at -40 °C.

**X-ray Scattering**

Small-angle X-ray scattering (SAXS) was performed on a Ganesha 300 XL SAXS system operating in SAXS mode. The system included a Genix Xenocs Cu Kα X-ray source, wavelength 1.54 Å. The resulting 2D scattering patterns were circumferentially integrated, producing a 1D SAXS profile. The lamellar long period \( d_{ac} \) was calculated from the scattering maximum \( q \) of the 1D SAXS profile, with \( d_{ac} = 2π/q \). The lamellar crystal thickness \( d_c \) was calculated assuming a two phase model according to: \( d_c = d_{ac} \cdot \chi_c \) where \( \chi_c \) is derived from thermal calorimetry.

X-ray diffraction was achieved with a PANalytical XPertMater Research Diffractometer equipped with a ½° divergence slit, a 10 mm mask on the incident beam optics, and a 2.3° radian Soller slit on the diffracted beam optics. Isotactic Polypropylene samples prepared by either MM or MC were cryo-milled into powders via a SpexCertiprep Freezer Mill. The resulting powder samples were analyzed with a Cu Kα X-ray source, wavelength 1.54 Å.

**Uniaxial Compression Analysis**

Uniaxial compression tests were performed with an Instron 4466 testing machine between parallel steel plates at 0.5 mm/mm/min strain rate. Samples processed by MM were milled into 4.3 mm thick plaques and then a guide hollow drill bit was used to create 4.3 x 4.3 mm cylindrical compression samples. Samples prepared by MC were first compression molded into 4.3 mm thick plaques. Isotactic Polypropylene pellets were allowed to melt in the mold under atmospheric pressure for 2 minutes between polished brass plates and then the load was increased stepwise to a maximum load of 8,000 lbs over 6 minutes. The samples were subsequently quenched by transferring to a water cooled compression press. Next, the 4.3 mm thick plaques were milled into cylindrical compression samples with the guide hollow drill bit. Before uniaxial compression tests, samples were lubricated on the top and bottom surfaces with soap water and Teflon tape in order to promote affine deformation (no sample bulging) during compression.

**Results and Discussion**

**Processing of iPP**

Melt-Mastication of iPP was accomplished in a batch mixer over a three step temperature profile illustrated in Figure 1. The mixing torque recorded by the batch mixer during MC and MM is presented in Figure 2. In the first step of Figure 1, the pellets are compounded at a temperature well above \( T_m \) in order to uniformly melt the
iPP and compound with antioxidant process stabilizers. This step requires relatively large torque in order to melt and grind the iPP pellets, which is observed for both MM and MC in Figure 2 (t < 300 s). However, the torque load approaches a minimum value after 5 minutes, suggesting the iPP is fully molten and homogenized by the end of the first step. The presence of antioxidant process stabilizers is necessary to prevent oxidative degradation of iPP chains during MM and MC, as demonstrated in a previous study [17]. In the second step of Figure 1, the iPP melt is cooled under constant mixing using forced air cooling. The appearance of the iPP melt gradually transitions from translucent to opaque white and the recorded torque increases from 2.5 to 5 Nm. In the third step as iPP reaches $T_m$, it becomes an opaque white, highly viscous “pseudo melt” that resembles bread dough at room temperature. As the temperature of MM is well above the quiescent crystallization temperature for this iPP (111 °C), the white appearance and increased mixing torque suggest that FIC is occurring. The recorded torque in the third step plateaus at a maximum value of 12.5 Nm ($t > 1200$ s). After removing the “pseudo-melt” from the mixer, the iPP rapidly solidifies.

![Figure 2: Mixing torque vs. time recorded during Melt-Mastication (MM) and melt compounding (MC)](image)

### Thermal Calorimetry

Aspects of the crystal morphology produced by MM and MC were explored with thermal calorimetry. The results and analysis are summarized in Table 1. Isotactic Polypropylene prepared by MM (MM-iPP) shows elevated crystal volume fraction ($\chi_c$) and $T_m$, compared to iPP prepared by melt compounding (MC-iPP). Specifically, the crystal volume fraction by calorimetry increased by 37% and the peak melting temperature increased by 10.3 K. Wide-angle X-ray powder diffraction results (not shown) confirm that both MM-iPP and MC-iPP assume the α-crystal type. For comparison, a virgin iPP sample was annealed quiescently in the DSC under the MM temperature program (Q-MM-iPP). This sample demonstrated similar melting behavior as MC-iPP and a $\chi_c$ value between MC-iPP and MM-iPP. The elevated $T_m$ of MM-iPP is ascribed to increased lamellar crystal thickness ($d_c$), as described by the Gibbs Thomson relationship [19]. The crystallization exotherm of MM-iPP demonstrated significantly higher peak crystallization temperature ($T_c$), which remains persistent even after heating up to 200 °C. Similar so-called “memory” effects have been observed by other groups studying FIC of iPP [11,12]. The memory effect of MM-iPP was exploited as a “self-nucleating” agent for iPP by melt compounding 10 wt% of MM-iPP powder with 90 wt% virgin iPP pellets for 5 minutes at 200 °C. The resulting “self-nucleating” material (10/90 MM/MC) demonstrated an elevated crystallization temperature and the effect was erased after heating to 215 °C (10/90 MM/MC_215).

### Microscopy

Polarized optical microscopy was used to characterize the iPP crystal morphology through birefringence. Samples prepared by either MM or MC were micromotomed to 10 μm thick sample sections and were characterized in transmission mode. Both the micromotomed MC-iPP and MM-iPP sample sections have moderate striations due to imperfections in the glass microtome knife. A second MC sample was also annealed on the microscope stage for 1 minute at 225 °C and then slowly cooled to room temperature for a “stage crystallized” sample.

Quiescently crystallized iPP commonly forms radially organized crystal structures known as spherulites, which are visible through crossed polarizers due to birefringence (Figure 3B and F) [20]. The MC sample shows a moderate birefringent “Maltese cross” pattern consistent with spherulites. The stage crystallized iPP sample demonstrates a sharper pattern, likely due to the crystallization of the film on the microscope stage. However, MM-iPP analyzed under 90° crossed polarizers shows nearly total light extinction. From calorimetry, MM-iPP is clearly semicrystalline, but apparently the crystal morphology is not hierarchically organized into spherulites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
<th>$\chi_c$ (%)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>167.1</td>
<td>41.5</td>
<td>111.7</td>
</tr>
<tr>
<td>MM</td>
<td>177.4</td>
<td>57.0</td>
<td>120.1</td>
</tr>
<tr>
<td>Q-MM</td>
<td>165.7</td>
<td>48.7</td>
<td>---</td>
</tr>
<tr>
<td>10/90 MM/CMP</td>
<td>---</td>
<td>116.1</td>
<td></td>
</tr>
<tr>
<td>10/90 MM/CMP_215</td>
<td>---</td>
<td>112.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Thermal analysis results summary for MM-iPP and MC-iPP.
Figure 3: Polarized optical microscopy of iPP prepared by MC (A-B) or MM (C-D). Images E-F are MC-iPP after melting and recrystallizing on the microscope stage.

For AFM analysis, smooth sample surfaces were prepared by diamond knife cryomicrotomy and then imaged in tapping mode. The tapping phase data provided useful contrast between crystalline (dark) and amorphous (bright) regions, shown in Figure 4. At high magnification (Figure 4A and C), both MM-iPP and MC-iPP show lamellar crystals dispersed between amorphous regions without any apparent inter-lamellar orientation correlation. However, at lower magnification MC-iPP shows a cross-hatched morphology where the parent lamella extend from top to bottom of the image, and daughter lamella are oriented roughly orthogonal to the parent lamellae. There is no obvious ordering for the MM-iPP morphology, although Figure 4D may show a stacked lamellar structure in the top half of the image.

The iPP lamellar crystal thickness \( d_c \) may be estimated from AFM micrographs, however because the AFM test plane is randomly intersected by lamellae, the observed lamellar thickness \( d_{c,o} \) is greater than \( d_c \). Ikeda et al. reported a quantitative stereological technique to estimate \( d_c \) [21]. The \( d_{c,o} \) for each sample was measured at 90 positions of Figure 4A and C, and the AFM tip radius effect (2 x 4.5 nm) was subtracted from each thickness measurement. For MC-iPP, \( d_c = 10.4 \pm 3.2 \) nm and for MM-iPP \( d_c = 15.7 \pm 4.4 \). These results agree with the calorimetry results, as lamellae above a critical thickness threshold require higher \( T_m \) [22].

Small-Angle X-ray Scattering

As discussed in the thermal analysis section and the microscopy section, the elevated \( T_m \) of MM-iPP is ascribed to the enhanced \( d_c \). However, thermal calorimetry does not capture all aspects of iPP crystal morphology at elevated temperatures [22]. Accordingly, SAXS was used to directly evaluate \( d_c \). For iPP, the SAXS peak intensity corresponds to lamellar long period \( d_{ac} \), or the contrast periodicity due to the combined thickness of one lamellar crystal and one amorphous layer. In the present study, \( d_c \) is estimated from \( d_{ac} \) assuming a two phase structure of amorphous and crystalline regions. For MC-iPP, \( d_c = 6.6 \) nm, and for MM-iPP, \( d_c = 13.7 \) nm at room temperature. The results confirm that the \( T_m \) difference between MM-iPP and MC-iPP is due to enhanced \( d_c \).

Mechanical Properties

Uniaxial compression tests are a useful method to investigate the crystal morphology and network connectivity of semicrystalline polymers. Unlike uniaxial tensile tests, structural flaws are suppressed in compression which enables evaluation of the large strain responses (i.e. yield and post yield). The compressive behavior of MC-iPP and MM-iPP in Figure 5 is typical for semicrystalline polymers. At low strain, iPP responds elastically up to a yield point. Next, iPP strain softens until finally strain hardening at large deformation. In this study, the compression response curves are used to determine elastic modulus \( (E) \), yield stress \( (\sigma_y) \), and strain hardening modulus \( (G_R) \).
Melt-Masticated iPP demonstrates a notably higher $E$ (77% increase) and $\sigma_y$ (40% increase) compared to MC-iPP. The modulus disparity is ascribed to the enhanced $\chi_c$ of MM-iPP, as it is well known that mechanical modulus is strongly related to $\chi_c$ in iPP [23]. Additionally, the improved $\sigma_y$ is rationalized by Young’s model, which proposes that yield in semicrystalline polymers is due to disentanglement rearrangements during crystallization, which facilitates neo-Hookean strain in order to determine $G_R$. Dashed lines are added to emphasize $G_R$.

Interestingly, MM-iPP shows significantly higher $G_R$ compared to MC-iPP, which suggests that network connectivity of iPP is also improved through MM. In the strain hardening region of Figure 5, the compressive behavior is controlled by the connectivity of the remaining network, which consists of entanglements trapped in the amorphous phase [27,28]. A neo-Hookean description is conventionally used to describe the large strain behavior of semicrystalline polymers, which suggests that the true stress ($\sigma_t$) should be proportional to neo-Hookean strain $(\lambda^2 - 1/\lambda)$ at large strains $(\lambda \approx 2)$ [29,30]. Accordingly, Figure 5 is plotted against neo-Hookean strain in order to determine $G_R$ from the slope at high strain. Govaert et al. showed that network connectivity of iPP is influenced by the thermal history, specifically the rate of cooling from the melt [31]. Slow cooling from the melt allows more time for chain rearrangements during crystallization, which facilitates disentanglements and therefore reduces $G_R$. In contrast, rapid cooling traps entanglements in the amorphous regions and increases $G_R$. In the present study MC-iPP was prepared by quenching, therefore MC-iPP should show the highest $G_R$ (4.9 ± 1.5). However, MM-iPP demonstrates a significantly higher $G_R$ (12.9 ± 0.7). The results suggest that the unique crystal morphology from MM-iPP enables high network connectivity as well as increased $d_c$ and $\chi_c$. Accordingly, the unusual morphology produced by MM promotes desirable property combinations that cannot be achieved through conventional iPP melt processing methods.

**Conclusions**

A Melt-Mastication (MM) processing method was explored for semicrystalline isotactic polypropylene (iPP) and shown to produce iPP with irregular morphology and improved thermal and mechanical stability. The processing conditions of MM promote flow induced crystallization (FIC) of iPP within a chaotic flow field, such that the resulting material possesses a crystal morphology and melting behavior distinct from quiescently crystallized iPP. Microscopy analysis indicates that the MM-iPP crystal morphology appears to be disorganized lamellae, with possible ordering in local regions. Isotactic Polypropylene prepared by MM demonstrates significant improvements to modulus, yield stress, and strain hardening modulus in compression which are attributed to enhancements in crystal volume fraction, lamellar crystal thickness, and network connectivity, respectively.

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**References**