Flow-Induced Warpage of Injection-Molded TLCP Fiber-Reinforced Polypropylene Composites

W.S. DePolo, D.G. Baird
Department of Chemical Engineering and Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211

The most common belief is that warpage in injection-molded fiber-reinforced thermoplastics is primarily attributed to residual thermal stresses associated with shrinkage and thermal contraction of the parts. Therefore, it is assumed that flow-induced stresses generated during mold filling do not play a significant role. Injection-molded plaques of polypropylene (PP) reinforced with pregenerated thermotropic liquid crystalline polymer (TLCP) microfibrils were generated in order to investigate the role of residual flow-induced stresses relative to that of thermal stresses on the warpage. In an effort to relate the material parameters to warpage, the rheological behavior of these fiber-filled systems was investigated. The shrinkage and the thermal expansion of the TLCP/PP composites, and hence, the thermally induced stresses decreased with an increase in fiber loading while the flow-induced stresses increased. The increase in the flow-induced stresses was attributed to increased relaxation times (this is not the only cause, but is a significant factor) with an increase in fiber loading. Therefore, it was found that in order to accurately predict the warpage of fiber-reinforced thermoplastics, the flow-induced residual stresses must be accounted for. It is expected that the results reported here can be extended to glass-reinforced PP composites as well.

INTRODUCTION

Warpage and dimensional stability of fiber-reinforced thermoplastics have drawn much attention in recent years [1–7]. This is especially the case for the automotive industry where there is an ongoing desire for more fuel efficient cars by replacing high-density metallic parts with lower density fiber-reinforced thermoplastics. Reinforcement with high-aspect ratio fibers is required to increase the stiffness and strength of the thermoplastic. However, when reinforced thermoplastics are injection molded to produce flat panels, such as for use in the exterior of cars, there is a considerable tendency for the part to not remain flat when removed from the mold. Both warpage (a bend around the centerline) and twist (a bend around the diagonal) of the part are observed. Furthermore, it is observed that warpage and twist of thermoplastics reinforced with low-aspect ratio particulates, such as mineral or talc, are considerably less than that for systems reinforced with high-aspect ratio fibers, such as glass or carbon fibers. For example, Kikuchi and Koyama [1–4] injection molded center-gated discs of mineral-filled nylon 6,6 and glass fiber-filled nylon 6,6 at filler loadings of 40% by weight. The mineral used for the study had an average aspect ratio of 4.0, while the glass fibers had an average aspect ratio of 55. It was observed that the warpage of the higher aspect ratio glass fibers was two and a half times greater than that of the mineral filled system.

The most common belief is that warpage is caused by an imbalance in the residual stresses that remain in an injection-molded part after it has been ejected from the mold and cooled down to ambient temperatures. These residual stresses originate from two main sources: (primarily) thermally induced stresses and (secondarily) frozen-in flow-induced stresses [5, 8–12]. Thermally induced stresses are associated with differential shrinkage and thermal contraction (coefficient of linear thermal expansion, CLTE) during nonuniform cooling of the molded part, both inside and after ejection from the mold. The flow-induced stresses are associated with the viscoelastic behavior of the melt during mold filling. During the filling stage, the viscoelastic flow of the melt promotes orientation (alignment in the direction of flow) of polymer chains due to the high shear and elongational deformation rates that are developed. The rate of stress relaxation of the oriented macromolecules once flow is stopped seems to be retarded by the presence of the fibers, and hence, stress is not completely relaxed due to rapid solidification of the molded part. Therefore, flow-induced stress becomes locked into the molded part. In the case of polymer composites, the reinforcing filler will further inhibit the oriented polymer chains from relaxing, which leads
to a greater buildup of frozen-in flow-induced residual stresses. Typically, the frozen-in flow-induced residual stresses are assumed to be at least an order of magnitude smaller than the thermally induced stresses due to almost instantaneous relaxation of the orientation of the polymer melt at high temperature, and, therefore, they are often omitted in analyses [5, 8–14].

Although thermally induced stresses generated during the cooling and solidification process may be the primary cause for warpage in unreinforced composites, the additional warpage observed for fiber-reinforced matrices cannot be accounted for merely by the mechanism of residual thermal stresses for various reasons. For example, the warpage of fiber-reinforced composites is generally much greater than that of the neat resin even though the shrinkage is significantly less in the fiber-reinforced composites. In fact, neat polymers typically do not warp to any measurable extent even though they shrink significantly on cooling. Furthermore, if low-aspect ratio particles are used to reinforce the same neat resin, then the warpage is found to be significantly less relative to the fiber-reinforced system even though the reduction in shrinkage is similar. Kikuchi and Koyama [1–4] showed that the warpage of the glass fiber-reinforced nylon 6,6 was 30 times greater (6.4 × 10⁻³ m) than that of the neat resin (0.2 × 10⁻³ m), while the shrinkage of the glass fiber-reinforced composite was reduced by 20% relative to that of the matrix. A mineral-filled composite containing low-aspect ratio particles had much lower warpage (2.5 × 10⁻³ m) than the glass-filled composite, but a similar reduction in shrinkage was observed. The warpage was attributed to increasing anisotropy in the CLTE with increasing filler aspect ratio. The anisotropy of the CLTE, which is defined as the ratio of the CLTE in the flow direction to that of the transverse direction, was 1.0 for the unfilled matrix, 0.5 for the mineral-filled nylon 6,6, and 0.4 for the glass fiber-filled nylon 6,6. It is interesting to note that for a small difference in the anisotropy of the CLTE between the glass fiber and mineral-filled system, there was a large difference in the magnitude of warpage. However, the difference in the anisotropy of the CLTE between the mineral-filled composite and base resin is large, but the difference in the magnitude of warpage is rather small.

It is our belief that the greater anisotropy and warpage of the fiber-filled system is most likely due to an increase in the orientation of the polymer chains, and hence, stresses, as well as to a greater degree of inhibition of stress relaxation relative to the mineral filled and unfilled systems rather than residual thermal stresses (CLTE and shrinkage). The high-aspect ratio fibers promote increased chain alignment and, therefore, orientation, and increased relaxation times, thereby retarding the process of stress relaxation on cessation of the filling process. As the polymer melt cools inside the mold, frozen-in flow-induced stresses are generated. If any imbalance in the cooling process of the part occurs, then one can expect a nonuniform variation in relaxation of stresses and, therefore, an increase in warpage of fiber-reinforced thermoplastics.

Warpage of injection-molded plaques that are reinforced with high-aspect ratio fibers is of primary interest in this study. In particular, our goal is to evaluate the role of the residual flow-induced stresses relative to the thermal stresses on the warpage of injection-molded rectangular plaques consisting of polypropylene (PP) reinforced with pregenerated microfibrils of a thermotropic liquid crystalline polymer (TLCP). Although we are primarily interested in the effect that pregenerated TLCP microfibrils have on the warpage of PP composites, it is expected that the results will be applicable to other high-aspect ratio reinforcing fibers, such as glass. It is apparent that the addition of fibers and an increase in the aspect ratio of the fibers that are used to reinforce thermoplastics enhance the degree of warpage of injection-molded parts. Although it is widely believed that warpage is caused by residual thermal stresses (shrinkage and anisotropy of the CLTE), we show that the effect of residual stresses generated during melt flow cannot be overlooked. In this study, we investigate the effect of the TLCP microfibril concentration and aspect ratio on the warpage of the TLCP/PP composites.

EXPERIMENTAL PROCEDURES

Materials

The thermotropic liquid crystalline polymer used in this work is HX3000 provided by DuPont, and the thermoplastic matrix used is a polypropylene (PP) homopolymer Profax 6823 provided by Basell. The HX3000 is composed of unspecified ratios of terephthalic acid, 4-hydroxybenzoic acid, hydriquinone and hydroquinone derivatives [15]. The solid density is 1.38 g/cm³, its melting temperature is 320°C, and there is no discernable glass transition temperature. The PP used for composite generation is Profax 6823, and it has a melting temperature of 165°C, a melt-flow rate of 0.5 g/min (2.16 kg, 230°C), a solid density of 0.902 g/cm³, and a weight average molecular weight of 600,000. This PP was selected because of the loss of some MW during the process by which the pregenerated microfibrils were created as discussed below.

Composite Strand Generation

Pregenerated strands of HX3000/PP at a composition of 55% by weight of HX3000 were extruded using a patented dual extrusion process consisting of two Killion extruders each with 1 in. barrels and a mixing head [15–19]. The mixer assembly consisted of a mixing head including three helical elements and a Koch static mixer with four elements. The HX3000 was melt processed in one of the extruders at a process temperature in the range of 260–
270°C. Gear pumps were used to control the flow rate of each stream produced by the two extruders, and hence, the final concentration of the generated composite strand. Once the TLCP is passed through the gear pump, its melt temperature was dropped to 340°C, while the PP stream was increased to 290°C after passing through the gear pump of the second extruder. The TLCP stream was then joined with the PP stream from the second extruder before passing through the mixing head. The combined TLCP/PP stream passed through the mixing head to further divide the TLCP fibers into smaller layers. Upon exiting the mixers, the strands were drawn at a draw ratio in the range of 50–56, quenched in a cooling bath, and then chopped into 3, 6, or 12 mm pellets. Sabol et al. [15] have shown that the generated TLCP microfibrils are nearly continuous in the strand. Therefore, it is believed that the aspect ratio (L/D) of the generated microfibrils is increased with an increase in the pellet length of the chopped strand. The pellets could then be processed at a temperature where the PP melted, but not the TLCP microfibrils as discussed next.

**Injection Molding**

The 6-mm pellets containing 55% by weight of TLCP that were generated by the dual extrusion process were further diluted to loadings of 10, 20, 30, and 40 wt% TLCP by dry blending them with PP (Profax 6823) as the diluting agent in a mechanical mixer. The 3- and 12-mm pellets containing 55% by weight of TLCP were also further diluted to a loading of 30 wt% TLCP by dry blending them with the PP as the diluting agent. The dry-blended composites were then injection molded using an Arburg Allrounder Model 221–55-250 injection-molding machine. The Arburg Allrounder has a 22 mm diameter screw, a check ring nonreturn valve, and an insulated nozzle that is 2 mm in diameter [16]. The composites were injection molded, using a melt temperature of 210°C, a mold temperature of 70°C, a hold pressure of 100 bars, and a screw speed of 200 RPMs, into a rectangular film-gated mold with dimensions of 80 mm by 76 mm by 1.6 mm.

To maintain uniform cooling of the part while it was in the mold, both sides of the mold were heated by using cartridge heaters, two for each side, equidistant from one another at approximately 20 and 60 mm from the bottom of the mold. Furthermore, the mold was allowed to heat for 5 h prior to molding to ensure thermal equilibrium. The first 10–15 molded plaques during each molding run were also discarded to allow the mold to reach an equilibrium temperature.

**Warpage and Shrinkage Testing**

Warpage and twist measurements of the 80 mm by 76 mm plaques were performed by using a Trans-Tek Model 1003 Linear Variable Displacement Transducer. The warpage and twist measurements were normalized to a 914 mm by 914 mm plaque in accordance with ASTM standard D229–96. The percent warpage was calculated by the following equation:

$$ W_{36} = \left( \frac{D}{L} \right) \times 100 $$

where $W_{36}$ is the percent warp or twist that is observed for a molded part that is 914 mm in length, $D$ is the maximum deviation in millimeters that is observed from the molded parts originally flat shape, and $L$ is the length in millimeters of the dimension along which the warp or twist is observed. A minimum of 10 samples was tested at room temperature, and the average value and standard deviation were calculated from the data.

The shrinkage measurements in the flow and transverse direction of the molded plaques were made in accordance with ASTM standard D955–00. The percent mold shrinkage was calculated from the following equation:

$$ MS = \left( \frac{DC - DS}{DC} \right) \times 100 $$

where $MS$ is the percent mold shrinkage that is observed, $DC$ is the dimension of the mold cavity in millimeters, and $DS$ is the dimension of the specimen. A minimum of 10 samples was tested at room temperature, and the average value and standard deviation were calculated from the data.

**Dynamic Mechanical Thermal Analysis of Solid Plaques**

Dynamic mechanical thermal analysis (DMTA) of the TLCP/PP composites was measured in the flow and transverse direction on rectangular strips cut from the plaques using a Rheometrics RMS-800. Along with measurements of the storage ($G'$) and loss ($G''$) moduli, the CLTE was also measured. When using a torsional rectangular geometry, the Rheometrics RMS-800 contains a function called autotension, which maintains a small tension on the samples as it expands during heating. When autotension is enabled, the displacement of a sample can be measured as the material is heated from an initial testing temperature. Therefore, the CLTE of a sample can be measured experimentally within the range of temperatures tested. To perform the tests, rectangular strips approximately 75 mm long by 8 mm wide were cut near the center of the plaques. Once the strips were mounted in the rheometer, $G'$, $G''$, and the change in length as a function of temperature were measured. The temperature range of 30–120°C was investigated at a temperature ramp rate of 5°C/min under a continuous nitrogen atmosphere. For each composite generated, three samples were tested to check for reproducibility. The CLTE of each composite generated was determined by plotting the change in length normalized to the initial length at 30°C as a function of temperature. The slope of the line is the CLTE for that material, and it has units of (mm/mm)/°C.

**Injection Molding**

The 6-mm plaques were performed by using a Trans-Tek Model 1003 Linear Variable Displacement Transducer. The warpage and twist measurements were normalized to a 914 mm by 914 mm plaque in accordance with ASTM standard
Rheological Measurements of the Composite Melts

The complex viscosity, $\eta^*$, and storage modulus, $G'$, of the TLCP/PP composites in the melt state were measured using a Rheometrics RMS-800 with 25 mm diameter plates. Specimens that were 1.6 mm thick were prepared by cutting 25 mm diameter disks from the center of the injection-molded plaques. The tests were performed at a melt temperature of 210°C and a strain of 5% under nitrogen. A minimum of three samples was tested to check for reproducibility.

RESULTS AND DISCUSSION

Effect of Concentration on Dimensional Stability

Concentration effects on the dimensional stability of the TLCP/PP composites were investigated by varying the loading level of TLCP (0, 10, 20, 30, and 40%). For the concentration study, a starting pellet length of 6 mm was used for all generated composites. In Fig. 1, the warpage and twist of the injection-molded TLCP/PP plaques are shown as a function of the TLCP loading. Generally, both the warpage and twist increase with an increase in concentration of TLCP up to about 30 wt% of TLCP. Beyond 30 wt% of TLCP, the increase in warpage and twist relative to the unfilled PP matrix remains unchanged with further addition of the TLCP fibers, 16% warp and 14% twist, respectively. It is also worth noting that there is a significant jump in the level of warpage and twist from a 10 to 20% loading level of TLCP (4–12% change in warpage).

To determine the origins of the warpage and twist that are observed in the molded plaques of PP reinforced with TLCP fibers, the effect of shrinkage on TLCP concentration was first investigated, and the results are shown in Fig. 2. As the concentration of TLCP increases, the shrinkage in the flow and transverse direction decreases. Furthermore, the anisotropy in the shrinkage in the transverse and flow direction also decreases as the concentration of TLCP is increased. This is a very interesting result because it shows that shrinkage due to crystallization, and nonuniform cooling is not an important contributor to warpage for these fiber-reinforced materials. If anything, the reduction in the anisotropy between the flow and transverse shrinkage with an increase in fiber loading should reduce the warpage of the molded plaques if shrinkage is the cause.

Next, the thermal expansion and CLTE as a function of TLCP loading were investigated, because the anisotropy in the CLTE has been correlated to warpage of injection-molded plaques by many authors [1–4]. These material properties are shown in the flow direction (Fig. 3) and the transverse direction (Fig. 4) as a function of TLCP concentration in the temperature range of 30–120°C. The numerical values on the right-hand side of Figs. 3 and 4 are the CLTE values (mm/mm/°C) determined by the slopes of the lines within the temperature range of 60–120°C. We note that the CLTE values of the TLCP/PP composites are similar to those found in the literature for short-glass fiber-reinforced PP. In the flow direction, the thermal expansion and CLTE decrease with an increase in fiber loading. Even though the CLTE values only decrease slightly with an increase in the TLCP concentration, there are still significant reductions in the overall dimensional change of the molded plaques with an increase in fiber loading. At a 20 and 40 wt% loading of TLCP, the dimensional change in the flow direction is reduced by 30 and 50%, respectively, relative to the base resin (PP) at a temperature of 120°C. However, in the transverse direction, an increase in TLCP fiber concentrations has little to no influence on the thermal properties of the TLCP/PP molded plaques. This leads to a significant increase in the anisotropy in the CLTE with
increasing fiber concentration. This is also a very interesting result because it shows that the dimensional change and the anisotropy in the CLTE are still greatly increasing between TLCP loadings of 20–40 wt%, while the warpage ceases to increase further at a loading of 30 wt% and only slightly increases by 4% in the concentration range of 20–40 wt%. This suggests that the anisotropy in the residual thermal stresses cannot account for the observed plateau in the warpage as the TLCP fiber concentration is increased.

To determine the effects of TLCP concentration on the viscoelastic flow behavior of the composite melts, the storage modulus ($G'$) as a function of frequency for all tested loading levels of TLCP is shown in Fig. 5 at a temperature of 210°C. As the loading level of TLCP increases, the magnitude of $G'$ also increases in the low-frequency region (long relaxation times). At the 30 and 40 wt% loading of TLCP, $G'$ in the low-frequency region is a little more than an order of magnitude larger than that of the matrix, and a plateau at high loadings can be observed. The observed plateau at the high TLCP loadings is indicative of a yield stress. For the 10 wt% loading, there is only a slight increase in the storage modulus in the low-frequency region. This increase in $G'$ is believed to reflect the stress relaxation of the composite as it is indicative of enhanced long relaxation times. As the magnitude of $G'$ increases, stress relaxation is inhibited and, therefore, a greater degree of flow-induced stresses are frozen into the part. If the magnitude in $G'$ at the low-frequency region is truly indicative of an increase in relaxation times and, therefore, an increase in residual stresses, then by inspection of Fig. 5, one would expect that warpage and twist would increase as the loading level increases up to about 30–40 wt% of TLCP. These results are in qualitative agreement with the observed warpage of the TLCP/PP composites up to about 30 wt% TLCP. The magnitude of $G'$ in the low-frequency region of the unfilled matrix and the 10 wt% TLCP-reinforced plaques are very close to each other, as is the observed warpage. There is a significant jump in the magnitude of $G'$ in the low-frequency region, which correlates with the large increase in the observed warpage from 4 to 12%, when the level of fiber reinforcement is increased from 10 to 20 wt% of TLCP. Furthermore, the magnitude in $G'$ in the low-frequency region increases while the warpage also increases when the fiber reinforcement is increased from 20 to 30 wt% of TLCP. It is interesting to note that there is a lack of increase in the observed warpage when the fiber reinforcement is increased from 30 to 40 wt% of TLCP, while the magnitude of $G'$ at low frequencies continues to increase. This unex-

FIG. 3. Thermal strain (mm/mm) and CLTE values (mm/mm/°C) in the flow direction of the TLCP/PP composites for different TLCP concentrations. The TLCP/PP composites were generated with pellets that were 6 mm in length. A temperature ramp of 5°C/min was applied. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 4. Thermal strain (mm/mm) and CLTE values (mm/mm/°C) in the transverse direction of the TLCP/PP composites for different TLCP concentrations. The TLCP/PP composites were generated with pellets that were 6 mm in length. A temperature ramp of 5°C/min was applied. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 5. Storage modulus as a function of frequency of the TLCP/PP composites for different TLCP loadings at a melt temperature of 210°C. The TLCP/PP composites were generated with pellets that were 6 mm in length. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
pected result will be discussed in more detail in the later section.

**Effect of Aspect Ratio on Dimensional Stability**

The dependence of fiber aspect ratio on warpage was also investigated by varying the pellet lengths of the TLCP/PP fiber composites (3, 6, and 12 mm), while maintaining the TLCP reinforcement level at 30% by weight (Fig. 6). The unfilled PP matrix has a small percentage of warpage, but with the addition of fiber reinforcement, the warpage increases markedly from an average value of 1.5–16%. The warpage of the TLCP/PP composites generated with the 3 and 6 mm pellets is approximately the same at an average value of 16%, while the warpage of the composites generated with the 12 mm pellets is much larger having an average value of 26%.

In Fig. 7, the dependence of fiber aspect ratio on shrinkage is shown. The flow direction shrinkage significantly decreases with the addition of TLCP fibers, but there is little change with increasing fiber aspect ratio. However, the shrinkage in the transverse direction slightly decreases with an increase in fibril aspect ratio, even though there is an increase in warpage. This shows that the warpage increases with a reduction in shrinkage, and, therefore, shrinkage cannot be a major contributor to the warpage of fiber-reinforced composites.

The thermal expansion and the CLTE values are shown in the flow direction (Fig. 8) and the transverse direction (Fig. 9) for the TLCP/PP composites in the temperature range of 30–120°C. In the flow direction, the thermal expansion and CLTE decrease with an increase in fiber aspect ratio and, as observed in the case of TLCP concentration, the aspect ratio of the fibers had little to no influence on the thermal properties in the transverse direction. Therefore, the anisotropy in the thermal properties increases with an increase in aspect ratio. It is interesting to note that there is very little difference in the dimensional change and CLTE values of the composites generated with 3 and 6 mm pellets relative to those generated with the 12 mm pellets. These results are in qualitative agreement with the observed warpage.

Finally, the dependence of fiber aspect ratio on $G'$ is presented in Fig. 10. The magnitude of $G'$ increases at low frequencies for the 12 mm long pellets relative to that of the values for the 3 and 6 mm fibers, but there is no increase in $G'$ between the 3 and 6 mm long pellets. The lack of increase in warpage (Fig. 6) in going from the 3 to 6 mm long pellets is consistent with the $G'$ values. However, the composites generated with starting pellet lengths of 12 mm only show a slight increase in the magnitude of $G'$ in the low-frequency region, indicating only a slight increase in the long relaxation time. This is inconsistent with the 60%
increase in the observed warpage that occurs when the TLCP/PP composites are generated with 12 mm long pellets relative to that of the composites generated with the 3 or 6 mm long pellets.

**Estimation of Thermally Induced Stresses**

To estimate the residual thermal stresses that are locked into the molded parts upon ejection from the mold and the subsequent cooling to ambient temperature, Hooke’s law was applied, which assumes that there is a linear relationship between the stress and the strain. Assuming the flow direction is \( x \) and the transverse direction is \( y \), then the thermal stress in the flow direction is given by:

\[
\sigma_{xx} = E\epsilon_{xx}
\]  

(3)

where \( \sigma_{xx} \) is the residual thermal stress, \( E \) is Young’s Modulus, and \( \epsilon_{xx} \) is the thermal strain. *Equation 3* can be applied to the transverse direction to calculate \( \sigma_{yy} \) using the appropriate values of \( E \) and \( \epsilon_{yy} \). The Young’s Modulus at ambient temperature was approximated as \( 3G' \), where \( G' \) is the storage modulus.

The thermal strain imposed on a solid object can also be expressed as:

\[
\epsilon_{xx} = \alpha_{l}(\Delta T)
\]  

(4)

where \( \alpha_{l} \) is the CLTE, and \( \Delta T \) is the change in temperature. *Equation 4* can be applied to the transverse direction to calculate \( \epsilon_{yy} \) using the appropriate value of \( \alpha_{l} \). The CLTE of the TLCP/PP composites was measured by running DMTAs of the solid plaques as described in the experimental section. As a first approximation, the change in temperature is represented by the temperature difference of the mold to that of the ambient air.

**Estimation of the “Frozen-in” Flow-Induced Stresses**

Flow-induced stresses are generated during mold filling due to the high shear and elongational deformation rates that are developed during the viscoelastic flow of the composite melt. The generated stresses are subsequently locked into the molded part due to rapid solidification. The flow behavior during mold filling is further complicated by the fountain flow effect as described by Tadmor [20]. Using axes attached the fluid and moving with the average velocity, Tadmor describes the kinematics of the advancing front as a stagnation flow where the particles appear to decelerate as they approach the advancing front, and then the particles stretch in an orthogonal direction towards the wall of the mold. The stretching generates considerable orientation, and thus, as the particles are laid up on the wall, they are rapidly solidified into a highly oriented state. Hence, the extensional flow at the melt front leads to a higher state of orientation at the surface of the molded part than in the core.

To simplify the complex flow behavior that is typically observed during mold filling, it is assumed that the flow behavior of the melt into the rectilinear end-gated mold can be represented by parallel-plate pressure driven flow. A power-law model is used to model the shear rate dependent viscosity and is defined as:

\[
\eta = m|\dot{\gamma}|^{n-1}
\]  

(5)

where \( \eta \) is the viscosity, \( \dot{\gamma} \) is the shear rate, \( n \) is the power-law index, and \( m \) is the consistency. With these assumptions, the additional orientation that is generated by

\[FIG. 9. \text{ Thermal strain (mm/mm) and CLTE values (mm/mm/°C) in the transverse direction of unfilled PP and the TLCP/PP composite for different starting pellet lengths. Concentration of TLCP in PP is 30 wt\%. A temperature ramp of 5°C/min was applied. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.] } \]

\[FIG. 10. \text{ Storage modulus as a function of frequency of unfilled PP and the TLCP/PP composites for different starting pellet lengths at a melt temperature of 210°C. Concentration of TLCP in PP is 30 wt\%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.] } \]
the extensional flow at the melt front during mold filling is neglected. Based on the above-mentioned assumptions, the governing fluid flow equations become:

\[ Q = \frac{WH^2}{2(s + 2)} \left( \frac{H\Delta P}{2mL} \right)^s \]  
(6)

\[ \dot{\gamma}_w = \left( \frac{H\Delta P}{2mL} \right)^s \]  
(7)

\[ \tau_w = \frac{H\Delta P}{2L} \]  
(8)

where \( Q \) is the volumetric flow rate of the viscoelastic fluid, \( \Delta P \) is the pressure drop, \( \dot{\gamma}_w \) is the shear rate at the wall, \( \tau_w \) is the shear stress at the wall of the mold, \( H \) is the thickness of the mold, \( L \) is the length of the mold, and \( s \) is the reciprocal of the power-law index, \( n \) [21]. The height and thickness of the mold are known values, and the power-law parameters \( m \) and \( n \) are determined by fitting Eq. 5 with experimental viscosity-shear rate data that is obtained by performing the rheological measurements of the composite melts as described in the experimental section. Therefore, the pressure drop can be obtained by using Eq. 6 if the volumetric flow rate of the fluid is experimentally determined. The volumetric flow rate was experimentally determined by assuming a constant screw injection speed and dividing the total volume, which consists of the volume of the mold, sprue, and gate, by the fill time. The fill time is the time for the polymer to flow from the entrance of the mold to the point where the mold is filled, and it is calculated from the injection time by subtracting the time the screw advances from the retracted position to the point where the polymer composite begins to enter the mold. Once the pressure drop is known, the shear stress at the wall can be calculated by using Eq. 8.

In addition to the shear stress, the primary normal stress difference, \( N_1 \), also contributes to the overall buildup of stress during mold filling of the composite melt. \( N_1 \) was estimated by using the White-Metzner model [21], and for steady shear flow, it is expressed as:

\[ N_1 = 2\eta\lambda \dot{\gamma}^2 \]  
(9)

where \( \lambda \) is the relaxation time of the polymer chains, and it is a function of shear rate. To accurately predict \( N_1 \), it is necessary to fit \( \lambda \) to experimental results. \( N_1 \) is very difficult to measure for reinforced composites, but for a number of polymers, \( N_1 \) is approximately two times the storage modulus, \( G' \) [21]. Therefore, as a first approximation, one can calculate the relaxation time at any given frequency (or shear rate) by substituting \( 2G' \) for \( N_1 \) in Eq. 9, provided that the \( G' \) is known. However, shear rates much greater than 100 s\(^{-1}\) are typically reached during mold filling [20]. To estimate the relaxation time at high rates of shear, Read and Baird [22] found that by rearranging Eq. 9 in terms of \( \lambda \) and taking the natural log of both sides, one gets a curve that can be fit by a power-law model. Once the power-law parameters are determined, the relaxation time of the polymer composites can be estimated at the high rates of shear that are generated during mold filling. Because the shear rate during mold filling can be calculated by using Eq. 7, one can estimate \( N_1 \). By calculating \( N_1 \) using this method, it is assumed that \( N_1 \) was approximated by \( 2G' \) at high shear rates. It has been shown that at high frequencies \( G' \) levels off while \( N_1 \) continues to increase as the shear rate increases [23]. Therefore, \( N_1 \) is underestimated by using \( 2G' \) at high rates of shear, which should lead to an underestimate of the flow-induced stresses that are generated during mold filling. Finally, the total flow-induced stresses at the mold wall, that are generated during mold filling, can be estimated by calculating the principal stress difference, \( \Delta \sigma \), which in shear flow is expressed as:

\[ \Delta \sigma = \sqrt{4\tau^2 + N_1^2}. \]  
(10)

**Thermally induced and flow-induced residual stresses of the injection molded composites**

To calculate the residual thermal stresses, the CLTE and \( G' \) at ambient temperature were measured. The CLTE values in the flow and transverse direction of the TLCP/PP composites that were generated using a starting pellet size of 6 mm at the various TLCP loadings are presented in Figs. 3 and 4. In addition to the thermal expansion and CLTE values of the generated composites, \( G' \) at 30°C was also measured by running the DMTA of the solid plaques, and the results are shown in Table 1 for the flow and transverse direction. With the CLTE values, \( G' \) at 30°C, and the mold temperature of 70°C, the residual thermal stresses in the flow and transverse direction were calculated by using Eqs. 3 and 4. The results will be presented later.

<table>
<thead>
<tr>
<th>TLCP concentration (% by weight)</th>
<th>Flow (Pa)</th>
<th>Transverse (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.54E8</td>
<td>1.58E8</td>
</tr>
<tr>
<td>10</td>
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<td>1.78E8</td>
</tr>
<tr>
<td>20</td>
<td>2.05E8</td>
<td>2.03E8</td>
</tr>
<tr>
<td>30</td>
<td>2.15E8</td>
<td>1.95E8</td>
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<tr>
<td>40</td>
<td>2.56E8</td>
<td>2.35E8</td>
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</table>

To calculate the flow-induced stresses, the volumetric flow rate and the power-law parameters of the generated TLCP/PP composites were determined experimentally. The fill time and the volume of the mold, including the sprue and gate, were constant at 1.5 s and 14820 mm\(^3\), respectively, during injection molding of the TLCP/PP composites that were generated using a starting pellet size of 6 mm at the various TLCP concentrations. Hence, the volumetric flow
rate of the composite melts was the same at 9.88E-6 m³/s for all injection molding runs.

In Fig. 11, the complex viscosity, $\eta^*$, as a function of frequency for all tested loading levels of TLCP, is shown at a temperature of 210°C. The power-law parameters for each composite are also shown in Fig. 11, and they were obtained by fitting Eq. 5 to the high-frequency region of the viscosity-frequency curves. As expected, $\eta^*$ in the low-frequency region increases with an increase in fiber loading and the increase in viscosity becomes more pronounced with an increase in concentration of the TLCP fibrils. At low concentrations (20% by weight or less), the addition of the TLCP fibers results in a small increase in viscosity, typically half an order of magnitude or less, relative to the base resin. Also, a Newtonian plateau is still observed at low-shear rates when the concentration is 10% by weight or below. At the high-fiber loadings, $\eta^*$ in the low-frequency region is about an order of magnitude larger than that of the base resin. Also, there is no observance of a Newtonian plateau, which is indicative of a yield stress at the high TLCP concentrations. In the high-frequency region, there is still a significant increase in the complex viscosity of the TLCP/PP composite melts with an increase in fiber loading. These results suggest that during mold filling the shear stress at the wall of the mold will increase with an increase in TLCP concentration.

The flow-induced stresses, $\Delta \sigma$, of the injection molded TLCP/PP plaques that were generated using a starting pellet size of 6 mm at the various TLCP loadings were calculated by using Eqs. 5–10, and the results are presented in Table 2 along with the thermally induced stresses in the flow, $\sigma_F$, and transverse direction, $\sigma_T$. Generally, the flow-induced residual stresses increase with an increase in concentration of TLCP up to 30 wt% of TLCP, whereas the thermally induced residual stresses decrease in the flow direction due to the significant reduction in thermal expansion and shrinkage attributed to the incorporation of the TLCP fibers. Beyond 30 wt% of TLCP, both the flow-induced and thermally induced stresses remain unchanged with further addition of the TLCP fibers. It is interesting to note that the warpage of the molded parts increases with increasing TLCP concentration even though the thermally induced stresses are reduced. Furthermore, the ratio of the magnitude of the flow-induced stress to that of the thermally induced stress are within an order of magnitude of one another and, as the concentration of the TLCP increases, this ratio decreases until it plateaus at a TLCP concentration of 30% by weight. The ratio of the magnitude of the flow-induced stresses to that of the thermally induced stresses would even be further reduced if the additional flow-induced stresses that are generated by the advancing front were taken into account. This is especially the case for fiber-filled polymer systems, where the fountain flow effect leads to highly oriented fibers at the surface of the molded part.

There are two possible reasons for the observed increase in warpage with increasing TLCP concentration: (1) the anisotropy between the thermally induced residual stresses in the flow and transverse direction is increased and (2) the greater generation of orientation of the polymer chains as well as the increased inhibition of stress relaxation of these chains. If the increase in warpage were truly due to the increase in the anisotropy, then one would expect that the warpage of the molded plaques would continue to increase with an increase in the fiber loading, but this is not the case. At TLCP loadings of 30 and 40 wt% of TLCP, the magnitude of the flow-induced and thermally induced residual stresses that are locked into the molded parts are nearly equivalent, which results in warpage values that are nearly equivalent within experimental error. These results correlate well with the observed warpage and twist of the TLCP/PP composites and show that the flow-induced stresses may have a more significant impact on the warpage of fiber-reinforced injection-molded parts than previously thought. Therefore, to accurately predict the warpage of fiber-reinforced injection-molded parts, the flow-induced residual stresses must be accounted for.

![FIG. 11. Complex viscosity as a function of frequency of the TLCP/PP composites for different TLCP loadings at a melt temperature of 210°C. The TLCP/PP composites were generated with pellets that were 6 mm in length.](image)
CONCLUSIONS

This study was concerned with ascertaining the main causes of the enhanced warpage observed for injection thermoplastics reinforced with high-aspect ratio fibers. In this case, the warpage of PP composites reinforced with TLCP fibers was investigated and correlated to enhanced flow-induced residual stresses in the presence of the high-aspect ratio fibers. The increase in warpage was attributed to an inhibition of stress relaxation of the polymer chains and greater generation of frozen-in flow-induced stresses with an increase in the concentration of the fibers. As the concentration of fibers increased, the warpage increased up to a TLCP loading of 30% by weight at which point a plateau was reached, where further addition of the TLCP fibers had no affect on the warpage. The observed plateau in the warpage could not be accounted for by changes in the thermally induced residual stresses. The shrinkage and the thermal expansion of the TLCP/PP composites were significantly reduced in the presence of the fibers with the decrease being enhanced by further addition of the TLCP fibers. Therefore, the warpage increased with an increase in TLCP concentration, while the thermally induced residual stresses decreased. On the other hand, the flow-induced stresses increased with an increase in fiber concentration. This suggests that, for fiber-filled thermoplastics, the flow-induced stresses may have a more significant impact on the warpage than previously thought. Therefore, in order to accurately predict the warpage of fiber reinforced thermoplastics, the flow-induced residual stresses must be accounted for.

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REFERENCES