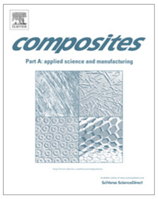
Composites: Part A 53 (2013) 34–45

Contents lists available at SciVerse ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa



# Warpage analysis of a micro-molded parts prepared with liquid crystalline polymer based composites

Hwa Jin Oh[a], Doo Jin Lee[a], Chae Gyu Lee[a], Ki Yeon Jo[a], Dong Hyun Lee[b], Young Seok Song[b,*], Jae Ryoun Youn[a,*]

[a] *Research Institute of Advanced Materials (RIAM), Department of Materials Science and Engineering, Seoul National University, 56-1, Silllim-Dong, Gwanak-Gu, Seoul 151-742, Republic of Korea*

[b] *Polymer System Division, Fiber System Engineering, Dankook University, 126, Jook-Jeon Dong, Suji-Gu, Gyeong-gi Do 448-701, Republic of Korea*

ARTICLE INFO

*Article history:*
Received 2 April 2013
Received in revised form 3 June 2013
Accepted 8 June 2013
Available online 15 June 2013

*Keywords:*
A. Hybrid
B. Anisotropy
C. Micro-mechanics
E. Injection molding

ABSTRACT

The purpose of this study is to understand the warpage behavior of a micro-injection molded part induced by anisotropy of the material. Microstructural anisotropy was characterized to understand warpage behavior of liquid crystalline polymer based composites. A new definition of the microstructure was introduced along the thickness of a molded part, i.e., "skin–shear–core" layer was proposed depending on the orientation of LCP molecules and fillers. The microstructural anisotropy of LCP composites was verified by using WAXD, CT, and SEM analyses. The anisotropic elastic modulus and coefficient of thermal expansion (CTE) of micro-injection molded parts were investigated by using a new numerical method with the modified Mori–Tanaka (M–T) model. The interaction coefficient, $C_I$, and coefficient of thermal expansion (CTE) were the most important factors determining the warpage of a micro-injection molded part made of an anisotropic material. The control of warpage due to the orientation of glass fibers was investigated by simulation.

## 1. Introduction

Liquid crystal polymers (LCPs), exceptional plastics, have had a subordinate role in the multibillion-dollar microsystem industry. Their commercial breakthrough strongly depends on the means of low cost mass fabrication that can provide dimensional accuracy and good part quality. Widely used mass-production methods of polymeric materials such as injection molding, however, need to be modified significantly if they are to be adopted for micro-molding applications [1–5].

The mechanical and thermal properties of an LCP based hybrid composite need to be improved. For instance, reinforcement with glass fibers has increased its stiffness, mechanical strength and heat resistance. Mineral filled LCPs typically have higher impact strength and elongation at break than glass fiber reinforced LCPs. In addition, they provide an attractive surface finish and good flow properties. Furthermore, the degree of anisotropy increases with an increase in the fraction of glass fibers [6–9].

Micro-injection molding, an innovative solution to fabricate precise and durable polymeric parts, is attracting large attention recently due to its outstanding feature that various microplatforms can be commercialized for applications in microelectronics, micromechanics, microfluidics, and biological and medical fields [7–10]. In micro-injection molding, micron-sized patterns on polymeric parts are replicated from a mold insert. This process requires convergence of such different technologies as MEMS and new systems and materials. For instance, high performance material properties such as good mechanical and thermal characteristics, processability, and low shrinkage are needed for micro-injection molding compared with conventional injection molded parts. Those physical features are indispensable for introducing the structural and thermal stability of micro-injection molded parts. Among commercially available polymers, liquid crystalline polymer (LCP) is regarded as one of the most appropriate candidates satisfying the aforementioned physical requirements. The LCP is an exceptional polymeric material that possesses rigid molecular chains (i.e., liquid crystals) even in the liquid state after melting because rigid molecules in the LCP resin consisting of aromatic units and ester linkages behave as rigid rods in the molten state. The rigid molecules provide good mechanical and thermal properties as well as low melt viscosity (in other words, good processability), which are compelling features for application to the micro-injection molding process. Complex flow patterns including shear and elongation flows are developed in a flow conduit and cavity especially during filling stage of the micro-injection molding. High tempera-

---

* Corresponding authors. Tel.: +82 31 8005 3567 (Y.S. Song), tel.: +82 2 880 8329 (J.R. Youn).

*E-mail addresses:* ysong@dankook.ac.kr (Y.S. Song), jaeryoun@snu.ac.kr (J.R. Youn).

1359-835X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesa.2013.06.006

ture gradient arises across the flow direction in a molded part due to the low thermal conductivity of polymers. Such thermophysical circumstances have significant influence on crystallization and orientation of molecules. In this sense, it is critical to control the orientation of rigid anisotropic LCP molecules in an effort to materialize the potential of LCPs in the micro-injection molding process [6,11–17]. One the other hand, LCPs become less anisotropic when incorporated with various reinforcements such as mineral fillers and glass fibers, which is an opposite characteristic compared with other commodity polymers.

Micro-injection molding process was investigated in this study where LCPs were selected as the matrix and glass fibers and minerals as reinforcing fillers. Prior to characterizing the anisotropic properties of LCP composites, layer microstructure was defined as "skin–shear–core" layers based on the orientation and configuration of LCP molecules and fillers. Random orientation of LCP molecules yields an isotropic matrix but partial or complete orientation of molecules leads to an anisotropic matrix. The anisotropic nature that depends upon flow and transverse directions is induced by the orientation of fillers or LCP molecules and affects the warpage of a molded part. In most studies reported in the literature, macroscopic anisotropy has been investigated with typical injection-molded specimens. The anisotropic property that was measured macroscopically is an average value of each microscopic layer across the thickness of the part. The anisotropic property measured macroscopically for the entire sample thickness cannot represent the exact material property of each layer affected by the degree of anisotropy since it is not possible to control the molecular orientation in a robust fashion and to sample a targeted section exclusively. Therefore, evaluation of material properties of each microscopic structure is needed for numerical prediction of anisotropic behavior of composite parts. The purpose of this study is to identify the internal structure of micro-injection molded parts and to classify it with respect to its morphology, i.e., skin–shear–core layers. The exact material property of the LCP composite was determined by considering the orientation of fibers in each microscopic layer. The exact material property of micro-injection molded composite part was determined in this study and a new methodology was provided to determine the exact physical properties of composite materials such as mechanical properties and thermal expansion coefficient of the anisotropic micro-injection molded parts.

Numerical simulation of micro-injection molding has several major advantages. Flow can be visualized, and the last-filled sections of the mold can be predicted. Such visualization is usually done by the short-shot method, where the mold is filled with different amounts of the material to see how the flow would proceed during injection. That method is useful in identifying defects, such as incomplete filling, weld lines and voids. Furthermore, it can economically optimize the design of the mold. In other words, because it is usually expensive to manufacture an injection molding mold, it would be very useful to simulate different geometrical designs, sprue and gating systems and then to determine the optimum mold design before manufacturing. In addition, the thermal conditions of the flow during filling and cooling can be simulated, and the results can be used to estimate the cycle time and determine the processing bottlenecks. Furthermore, relevant experiments can be designed to determine the processing parameters that most influence the part quality and to identify post-processing properties, such as residual stresses, shrinkages, and warpage.

In this paper, we discussed the anisotropic properties of the microstructure of LCP hybrid composites. The mechanical and thermal properties of an anisotropic material have strongly depended on how experimental conditions were applied, especially in fabrication of samples for tests. Based on our previous study on the anisotropic properties of LCP composites, here we seek to verify the effect of anisotropic properties on the warpage of micro-injection molded parts. Two kinds of parts, a simplified micro-connector and a micro-connector with combed structures (both 250 μm thick) as shown in Fig. 1a and b, were addressed in this study. Unlike macro-injection molded parts encompassing skin, shear, and core layers, micro-injection molded parts consist of only the skin and the core layer in our definition of layers, as shown in Fig. 1c. In this sense, micro-injection molded parts should be regard as having a different structure from macro-injection molded parts in that the skin layer can be ignored in macro-injection molded parts, whereas the skin layer in micro-molded parts takes up a rather large portion of the whole layer.

The finite element method (FEM) was adopted for predicting the fiber orientation and warpage of the micro-connectors. Micro-computed tomography (CT) and the toolmaker's microscope were used to assess the numerical predictions of fiber orientation and warpage. In addition, MATLAB™ was used to calculate the fiber orientation tensor for a micro-CT image.

## 2. Experimental

### 2.1. Materials

A commercially available and injection-grade LCP resin, Vectra A950 (Hoechst-Celanese, USA), was used in this study. The LCP resin is copolyester consisting of about 70% *p*-hydroxybezoic acid (HBA) and 30% 6-hydroxy-2-naphthoic acid (HNA). Its melting temperature is 285°Cand its rod-shaped molecules are oriented along the flow direction during injection molding. Mechanical properties and shrinkage of the LCP parts depend on the flow field developed during filling of the mold cavity. Two different samples, glass fiber reinforced composites and both mineral and glass fiber reinforced composites, were prepared to examine the influence of fillers and molecular orientation on the microstructure and material properties. The composition of the selected material is listed in Table 1. Three different kinds of systems were fabricated for specimens: single phase system (pure LCP), two phase system (glass fiber incorporated LCP), and multi-phase system (glass fiber and mineral particle incorporated LCP).

### 2.2. Injection molding

Manifold flat and dog-bone-shaped samples were injection-molded with an injection molding machine (Sumitomo SE-18DU, Japan). Fig. 2 shows the image of the dog-bone specimen, which was 150 mm long, 20 mm wide, and 1 mm thick. The injection speed was 50 mm/s, the injection pressure was 500 kg/cm$^2$, and the cooling time was 10 s, and the mold temperature was set at 120 °C.

### 2.3. Wide-Angle X-ray Scattering (WAXS)

Wide-angle X-ray scattering was employed to identify the orientation of molecules in the pure LCP specimen. The X-ray patterns were obtained for the thermoplastic LCP layers of an injection molded part by using a 2-D areal detector connected to the General Area Detector Diffraction System (GADDS, Bruker, Germany) generating Ni-filtered Cu K$\alpha$ radiation.

### 2.4. Observation of fiber orientation

A high-resolution desktop X-ray micro-tomography system (Micro-CT, 1172, Skyscan, Belgium) was employed to acquire microstructural information of the talc/glass fiber reinforced composites as previously reported [18]. A 100 kV and 10 Mp X-ray