EFFECT OF PROCESS- AND ANNEALING-INDUCED SHRINKAGE ON THE THERMOMECHANICAL PROPERTIES OF GLASS FIBER-REINFORCED POLYPROPYLENE

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Abstract
Thermoplastic composites undergo shrinkage during the cooling phase of the process and the annealing post-process step. We investigate the thermomechanical behavior of laminates made of glass fiber reinforced with a copolymer polypropylene matrix. The shrinkage is monitored using optical fiber Bragg gratings embedded in unidirectional laminates that are manufactured with a static hot-press (SHP) and a double-belt press (DBP). The processes have very different cooling rates and pressure levels. Results show, unexpectedly, that laminates processed with SHP are subjected to much lower shrinkage during cooling phase as compared to laminates manufactured with the DBP. The metallic mold used in this process has a constraining effect which inhibits shrinkage. This effect induces the build of residual stresses that cannot be entirely removed by an annealing treatment. Consequently, the transverse expansion coefficient of the laminates manufactured with the SHP is lower than that of the laminates manufactured with the DBP.

1. Introduction

Thermoplastic materials are subjected to shrinkage when they are cooling from the melt to room temperature. Process induced shrinkage may cause detrimental deformation of the manufactured part, and the factors that are responsible for this are numerous [1]. Therefore predicting shrinkage and the final shape of a thermoplastic part is important but remains a challenge. Experimental testing and results still provide substantial help to the designers. Increasing cooling rates may be a solution to minimize the absolute shrinkage, as it gives less time to the crystalline structure to develop [2]. An interesting outcome from fast cooling is the enhanced ductility of thermoplastics composites, which is a key property regarding resistance to impact loading [3,4]. In thermoplastic composite manufacturing, dimensional variation is also due to the differential thermal expansion behavior between reinforcing fibers and the thermoplastic matrix. This mismatch results in a build-up of residual stresses that are related to the cooling rate [5]. Our observations indicate that in hot-press molding of glass fiber reinforced polypropylene (GFPP), fast cooling generates a higher residual strain [6]. Internal residual stresses are not desired as they may induce unstable thermal and mechanical properties. To reduce these stresses and improve some mechanical properties, annealing procedures are commonly carried out [7]. For polypropylene (PP), annealing to a temperature between 100°C and 120°C would double its impact resistance [8].

In the automotive industry, the production of semi-structural parts made of GFPP is steadily increasing. These components are usually subjected to a broad range of temperatures, so it is important

to have at the early design phase, precise knowledge of the GFPP thermomechanical behavior and to know how this behavior is related to shrinkage and process parameters.

In this study, we investigate the thermomechanical behavior of continuous glass fiber-reinforced polypropylene (copolymer) unidirectional laminates. Laminates are manufactured using two different industrial processes, static hot-press (SHP), and double-belt press (DBP). Each process allows the application of very different cooling rates and pressure levels. Samples are then subjected to annealing to evaluate further shrinkage, and finally, we calculate coefficients of linear thermal expansion (CLTE). We use fiber Bragg gratings (FBGs) that are embedded in the core of the material to monitor the shrinkage (or process-induced strains) from solidification to mold release [6]. The same embedded sensors are used to determine shrinkage after annealing and coefficients of thermal expansion during further heating tests. Dilatometry (DIL) is used to validate the thermomechanical behavior and the CLTEs. Finally, differential scanning calorimetry (DSC) allows us to clarify the change of crystallinity after annealing.

2. Experimental

2.1 Material and samples

The GFPP composite material was supplied by SABIC in the form of a unidirectional (UD) prepreg tape, typically with a thickness of 250 μm and a width of 110 mm. It is reinforced with continuous E-glass while the matrix was a copolymer PP, a blend of isotactic polypropylene and rubber components. The material has a fiber volume fraction of 41%. The laminates were unidirectional and made of eight plies ($[0_8]$).

2.2 Instrumentation and manufacturing processes

FBG sensors and thermocouples (TCs) were inserted in the mid-plane of the laminate. The polyacrylate coating was removed from the FBG region. To compensate for the temperature effect when measuring strain in varying thermal conditions, we used a method based on an encapsulated FBG and another method based on a thermocouple [6]. For the acquisition of the Bragg peak shifts, we used a MicronOptics interrogator. For temperature measurements, we used a PICO TC08 data logger. The process conditions for the SHP were the following: a heating ramp at 10˚C/min up to 210˚C, an isothermal dwell of 20 minutes, a cooling phase with an average cooling rate (CR) measured at 12˚C/min and a pressure of 6.8 bar set at the beginning of the isothermal dwell and released when the temperature cooled down to 28˚C. The process conditions for the DBP were the following: a heating ramp at 225˚C/min up to 210˚C, an isothermal dwell of 1 minute, a cooling phase with an average CR measured at 300˚C/min and a pressure of 0.1 bar set from the beginning to the end.

2.3 Post-process experiments

The annealing process and the thermomechanical behavior were monitored using FBGs embedded in the samples. They were subjected to a temperature cycle in an oven featuring a dedicated opening on the side to enable the passage of cables. This allowed for measuring temperature and strain in the instrumented laminates. The temperature cycle consisted of a heating phase at 1˚C/min up to 80˚C starting from room temperature (RT ≈ 23˚C) and a cooling phase ending at RT (fan cooling). This temperature range is representative of the composite end-user conditions.

The FBG results were compared with those obtained using a Netzsch DIL 402C dilatometry unit. Each GFPP sample was submitted to 3 consecutive cycles. Non-annealed samples with dimensions of 2 x 4 x 20 mm^3 were cut from the laminates just after manufacturing. The thermal analysis was performed using a Netzsch 204 F1 Differential Scanning Calorimeter (DSC). Samples with a mass of approximately 20 mg were heated at 10˚C/min, from 25˚C up to 190˚C, well above the melting point. We tested five samples, unannealed and annealed.

3. Results and discussion

3.1 Process-induced shrinkage

SHP and DBP strain monitoring results are shown in Fig. 1. Melting and solidification points were identified by a sudden change in the strain progression (corresponding temperatures are indicated on the graphs). Between these two points, the strain response stays constant while the temperature varies, since the matrix is in a liquid state and thus no strain transfer is possible. We can see that, in each case, strain starts to change again after the solidification point. From this point, a full strain transfer from matrix to fiber is made possible. In the case of the SHP process, residual strains were measured after the laminates were removed from the mold. Shrinkage is the absolute value of the residual strains. For the DBP manufacturing, no mold was used, so shrinkage was simply measured at the end of the process when the temperature inside the laminate reached 23˚C.

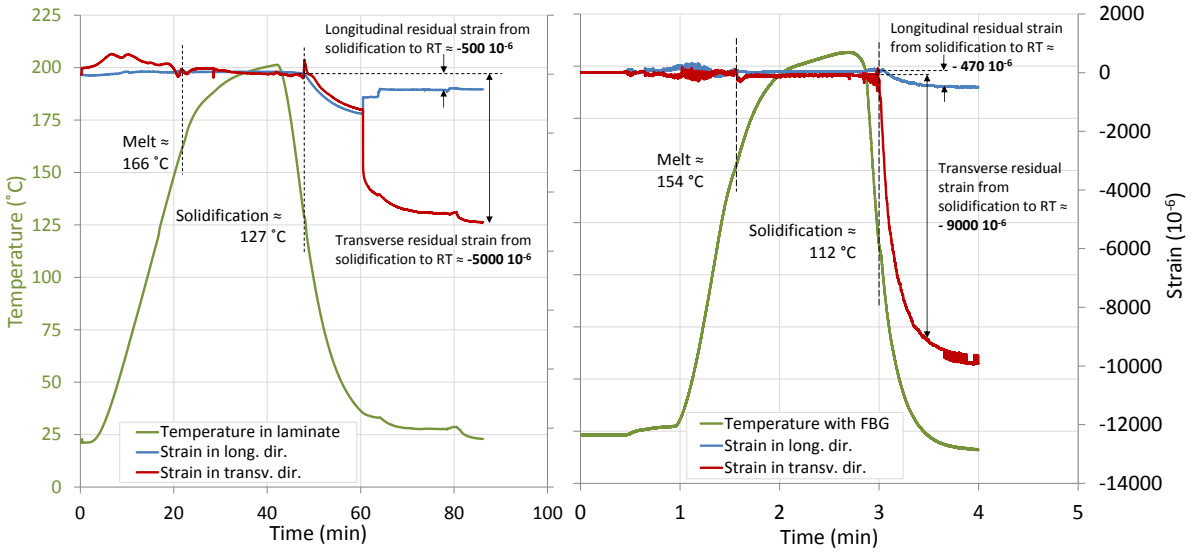

Figure 1. Process-induced shrinkage measured with FBGs of UD copolymer GFPP during SHP molding (using a steel mold) where a CR measured in the core of the laminate is 12˚C/min (left) and during DBP manufacturing where a CR measured in the core of the laminate is 300˚C/min (right).

The blue curves plotted in Fig. 1 represent the longitudinal strain changes (reinforcing fiber direction). The residual strains are $500x10^{-6}$ and $470x10^{-6}$ for the SHP and DBP, respectively. The longitudinal behavior of the laminate is mainly driven by the reinforcing glass fibers. The red curves represent the strain changes in the transverse direction.

A significant difference between SHP and DBP process-induced shrinkage is observed, $5000x10^{-6}$ and $9000x10^{-6}$, respectively. We were expecting an opposite trend due to the cooling rate being much lower with the SHP process. We assume that the steel mold used in SHP plays a significant role in this difference. The coefficient of thermal expansion (CTE) of stainless steel is approximately seven times lower than that of PP. When the laminate is confined inside this mold, it is forced to expand or contract just as the mold does. During the cooling phase the contraction of the laminate is limited by the thermomechanical behavior of the mold due to a frictional (or sticking) process that is promoted by the SHP pressure. The applied pressure (6.8 bar during SHP molding compared to 0.1 bar during DBP processing) can probably influence the efficiency of the load transfer between the mold and the molded parts and thus increase the mold/part interaction.

3.2 Annealing-induced shrinkage

The left graphs of Fig. 2 and Fig. 3 show FBG measurements of thermally-induced strain in SHP- and DBP-processed laminates subjected to an annealing cycle. Longitudinal behaviors are very similar, confirming that the thermal expansion is mainly controlled by the reinforcing glass fibers. From this point onwards, our study mainly focused on the transverse behavior of the UD laminates.

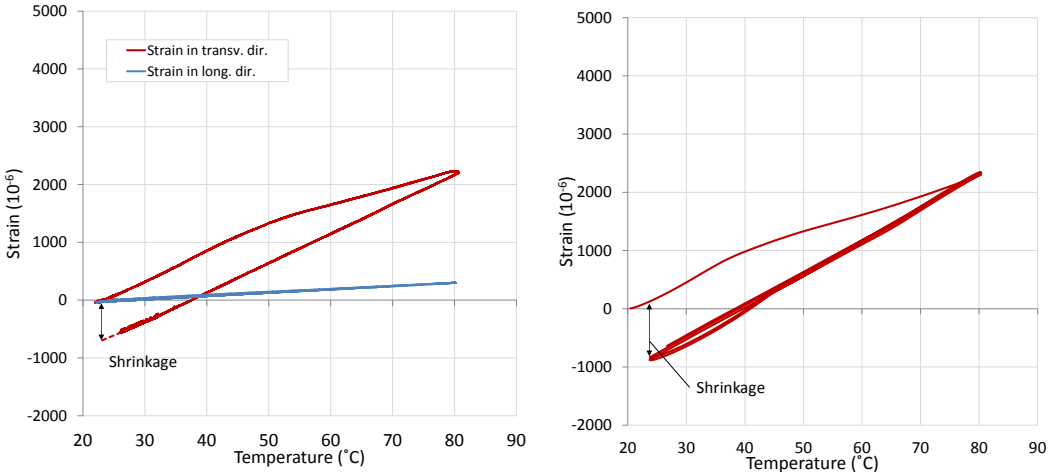

Figure 2. Thermal expansion measurements of a UD laminates made with the SHP. Left, strains are measured using FBGs. Right, strains are measured in the transverse direction using a dilatometer.

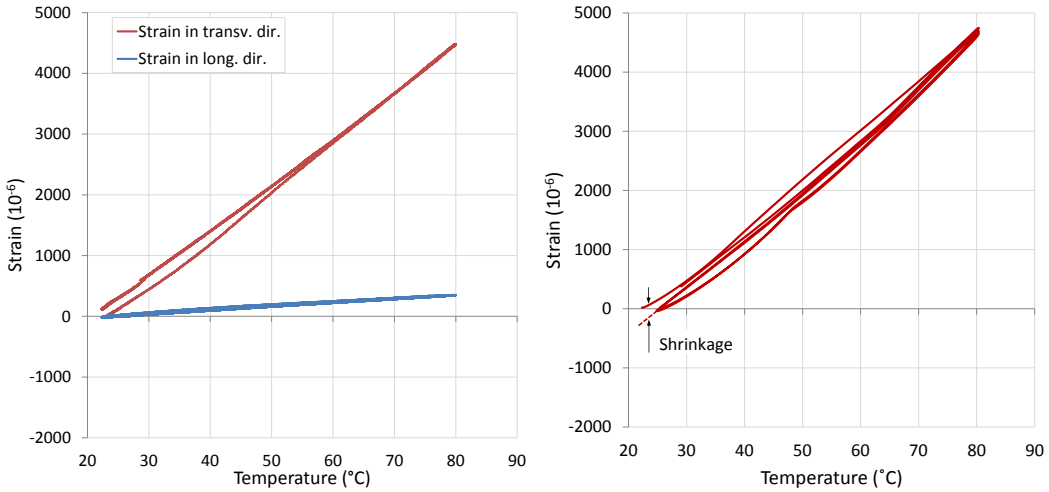

Figure 3. Thermal expansion measurements of a UD laminate made with the DBP. Left, strains are measured using FBGs. Right, strains are measured in the transverse direction using a dilatometer.

For the SHP-made laminates (Fig. 2, left), the transverse strain change measured with FBGs revealed a hysteresis after cooling to room temperature showing that there was an additional shrinkage due to annealing. Equivalent samples were annealed using a dilatometer and results showed (Fig. 2, right) a similar hysteresis after cooling. When performing the heating cycle a second and third time, we do not observe any significant hysteresis. This indicates that most of the annealing effect was completed during the first cycle. The left graph of Fig. 3 shows FBG measurements of thermally-induced strain in DBP-processed laminates subjected to an annealing cycle. The change in strain is rather linear during both heating and cooling. Here, the observed shrinkage is limited. Measurements obtained with the dilatometer (Fig. 3, right) revealed comparable trends. Repeating the cycle a second and a third time

confirmed this quite linear behavior and did not significantly increase shrinkage. Annealing-induced shrinkages are $980x10^{-6}$ and $400x10^{-6}$ with the SHP and DBP process, respectively. SHP-molded laminates shrink much more than DBP-processed laminates. This trend is the opposite of that presented in the process-induced shrinkage, although the annealing-induced contraction is one order of magnitude lower. Annealing has two main effects on a fiber-reinforced semi-crystalline matrix: stress relaxation, and secondary crystallization. To understand which of these two effects is responsible for the unexpected results, we performed DSC analysis.

3.3 DSC analysis

DSC tests were carried out to evaluate the change of crystallinity due to annealing. GFPP samples manufactured with SHP and DBP processes were subjected to DSC, before and after annealing. Five samples of each type were investigated, representing a total of 20 tested samples. Typical DSC curves of copolymer GFPP samples are presented in the left graph of Fig. 4. The total enthalpy consumed by each sample was evaluated by measuring the area under the large endothermic peak due to the melting of the polymer. The crystallization degree was determined on the basis that heat of fusion of 100% crystalline PP is 207 J/g [3]. Results are gathered in a bar chart shown in the right graph of Fig. 4. Annealing up to 80˚C enhances crystallinity for 10.7% and 11.5% in SHP and DBP conditions, respectively. To estimate how much shrinkage this crystallinity change represents, and knowing the density of the amorphous PP (0.899 g/cm^3) and the crystalline PP (0.946 g/cm^3), we estimated the total volumetric shrinkage generated by the phase transformation. **A** large amount of the shrinkage is found to be related to the enhancement of crystallization. The right graph of Fig. 4 also reveals that there is only a small difference of degree of crystallinity between the SHP- and the DBP-made laminates (1.6 %), even though the latter provides a much higher cooling capacity.

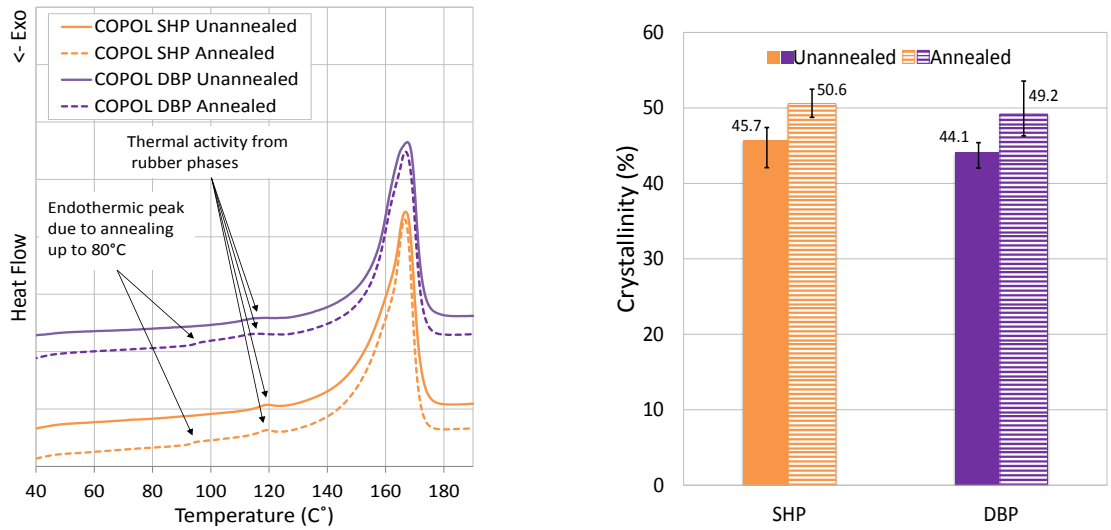

Figure 4. DSC graphs of unannealed and annealed GFPP samples (left) and degree of crystallinity of unannealed and annealed laminates (right).

3.4 Coefficients of linear thermal expansion (CLTE)

The transverse CLTEs were measured using the data set obtained from the FBGs and the dilatometer, after the first annealing cycle. Results are presented in Table 1. The CLTEs measured by FBGs are slightly lower than those measured by dilatometry. This may be due to a misalignment of the embedded sensor, a light local stiffening effect of the optical glass fiber or a scale effect due to the DIL samples being much smaller than the instrumented plate.The CLTEs for the SHP-made samples are approximately 40% lower than the DBP-made samples.

Table 1. Transverse CLTEs measured during the 2nd heating run with FBGs and with DIL.

Transverse CLTE (10^{-6}/°C)	Static hot-press	Double-belt press
Measured with FBG	50	80
Measured with DIL	55	97

4. Conclusion

The influence of SHP- and DBP-induced shrinkage, as well as the influence of annealing on the transverse thermomechanical behavior of copolymer GFPP UD laminates, was investigated. In this aim, the use of embedded FBGs has shown to be a very efficient tool. Process-induced transverse shrinkage of GFPP UD laminates is found to be much lower with SHP molding than with DBP manufacturing although the latter provides much faster cooling. Due to the mismatch of thermal expansion between the GFPP and the metallic mold in SHP molding, stresses are induced in the laminate. In the confining and sticking conditions of the metallic mold under pressure, the shrinkage development is constrained during solidification, whereas in the DBP conditions the laminates are free to expand or contract at any time in the process. Annealing induces twice as much shrinkage in SHP-processed laminates as in DBP. However, in both cases, most of the shrinkage is caused by the secondary crystallization. After annealing, the thermomechanical behavior of the GFPP laminates is more linear and consistent, allowing reliable identification of CLTEs. However, the process-induced stresses are only partially relieved. Laminates made with SHP molding exhibit much lower CLTEs than laminates made with the DBP process. Hence, the initial stress state of a GFPP laminate has a major influence on its thermomechanical properties.

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References

[1] D. Stan, A. Tulcan, L. Tulcan, I.T. Clanzan. Influence factors on the dimensional accuracy of the plastic parts. *Materiale Plastice*, 45 (1): 119–124, 2008.
[2] A.S Nielsen., R. Pyrz. The effect of cooling rate on thermal residual strains in carbon/polypropylene microcomposites. *Science and engineering of composite materials*, Vol. 7, Nos. 1-2, 1998.
[3] H. Wafai, G. Lubineau, A. Yudhanto, M. Mulle, W. Schijve, N. Verghese. Effects of the cooling rate on the shear behavior of continuous glass fiber/impact polypropylene composites (GF-IPP) *Composites: Part A*, 91 :41–52, 2016.
[4] A. Yudhanto, H. Wafai, G. Lubineau, R. Yaldiz, N. Verghese. Characterizing the influence of matrix ductility on damage phenomenology in continuous fiber-reinforced thermoplastic laminates undergoing quasi-static indentation. *Composite Structures*, 183: 324-334, 2018.
[5] P.P. Parlevliet, H.E.N. Bersee, A. Beukers. Residual stresses in thermoplastic composites, a study of the literature-Part I: Formation of residual stresses; *Composites: Part A*, 38:1847–1857, 2006
[6] M. Mulle, H. Wafai, A. Yudhanto, G. Lubineau, R. Yaldiz, W. Schijve, N. Verghese. Process monitoring of glass reinforced polypropylene laminates using fiber Bragg gratings. *Composites Science and Technology*, 123:143-150, 2016.

[7] Q. Meng, Y. Gu, L. Luo, S. Wang, M. Li, Z. Zhang. Annealing effect on crystalline structure and mechanical properties in long glass fiber reinforced polyamide 66. *J. Appl. Polym. Sci.*, 44832, 2017.
[8] JW. Chen, J. Dai, JH. Yang, T. Huang, N. Zhang, Y. Wang. Annealing-induced crystalline structure and mechanical property changes of polypropylene random copolymer. *J.Mater.Res.* 28: 3100-3108, 2013.