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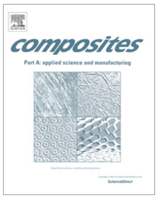

Multivariable dependency of thermal shrinkage in highly aligned polypropylene tapes for self-reinforced polymer composites

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ABSTRACT

Self-reinforced composites offer a unique combination of properties such as high specific strength, high impact resistance, and recyclability by incorporating highly aligned fibers within a random matrix of the same polymer. However, high temperatures will shrink the system to recover randomness in the aligned segments, compromising the composite thermal stability during processing as self-reinforced tapes are consolidated into the final composite through heating and pressure. Hence, the dynamic nonlinear multivariable (i.e., time, temperature, stress) shrinkage exhibited by self-reinforced polypropylene (SRPP) tapes was measured and modeled at the maximum shrinkage limit achieved in the proximity of the composite processing temperature [~140 to160 °C]. At high stress (~7.5 MPa) the thermal shrinkage of the SRPP tapes was reduced and a parallel creep mechanism was activated. The modeling, and prediction of the main factors governing the thermal shrinkage expand and diversify the dynamic design window for new SRPP composites.

1. Introduction

The improved interfacial compatibility and property versatility obtained by combining highly aligned polymer reinforcement within a lower melting point or amorphous matrix of the same material has propelled the use of self-reinforced composites for numerous applications in fields like automotive, and construction. Tapes elaborated from self-reinforced composites act as structural units that can be woven and compacted to produce unique lightweight materials exhibiting high impact resistance, and enhanced stiffness [1–6]. Self-reinforced polypropylene (SRPP) seems conventionally preferred due to its low cost, high specific properties, and recyclability [7,8] as well as controlled processability and interaction with other materials [9]. However, the molecular architecture and performance of SRPP tapes are highly dependent on the processing conditions [1,10–12].

SRPP composites are typically processed by weaving tapes of highly aligned polypropylene (PP) cores with tops and bottoms of PP that exhibit melting temperatures up to 60 °C lower than the core [11]. These weaves are then heated between the two melting points and pressed in a thermoforming-type process. The lower melting material flows into gaps and consolidates to form the matrix of the composite where the highly aligned PP conveys most of the resultant mechanical reinforcement (e.g., tensile modulus of ~20 GPa for aligned PP vs.~2 GPa for amorphous PP matrix) [5,12]. Unfortunately, due to the propensity of highly aligned materials to retract on heating, these weaves must be restrained with force to maintain alignment and prevent shape distortion [1,13,14].

Although improved consolidation can be achieved with higher temperatures, it also situates the system in a less favorable thermodynamic state where thermally activated phenomena can be triggered as temperature increases and approaches the SRPP processing temperature range ~140 to 160 °C. As temperature increases, thermal expansion, creep and thermal shrinkage can typically act simultaneously compromising the composite performance. Whereas thermal expansion and the elastic part of creep are thermo-reversible, thermal shrinkage is entropic in nature and therefore irreversible, driving the highly aligned chain segments to more relaxed coiled conformations [15,16]. As compared to highly aligned polymers, thermal shrinkage represents one of the essential factors that can potentially limit further development of SRPPs in moderate temperature applications and is extremely important for optimized processing. Exploring the variables governing thermal shrinkage can provide fundamental elements to control this complex phenomenon.

Here, we attempt to describe the simultaneous effect of time, temperature, and stress on the thermal shrinkage of SRPPs in the proximity of the composite processing temperature. The dynamic

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nonlinear multivariable response is measured and modeled by connecting it to possible acting mechanisms. We removed significant contributions from thermal expansion by minimizing thermal gradients as contracting forces act during the isothermal process. We also present the time and temperature dependent limit at which creep can overcome thermal shrinkage as the governing mechanism during constrained testing. A modeled and bounded multivariable thermal shrinkage response conveys both crucial and practical importance that can broaden the overall processing window and expand the number of applications for SRPP composites.

2. Experimental

2.1. Materials

Samples of ~8.8, 2.3, and 0.060 mm in length, width, and thickness, respectively, were cut from single flat tapes pulled from unprocessed Tritek™ provided by the Motorsport Industry Association (MIA). Tritek is a thermoplastic self-reinforced polypropylene (SRPP) composite composed of a highly oriented isotactic polypropylene core with both sides coated with random-polypropylene matrix of lower melting point similar to Pure™ from Lankhorst or Tegris™ from Milliken. SRPP tapes contain approximately 90% of highly aligned PP. The amorphous layers (~5 μm) occupy less than 10% of the volume in order to balance the elastic response of the final composite. Additional tape properties are reported elsewhere [1,8,12]. No sample pretreatment was performed on testing samples.

2.2. Experiments

Thermal shrinkage measurements were performed in a dynamic mechanical analyzer (DMA) (DMA800, TA Instruments). The DMA Controlled Force mode was employed in order to measure overall strain as forces were applied over the testing samples. A preload force of 0.01 N was found to keep the specimen straight during the different stages of measurement. Thermal shrinkage was measured under three different stress values: 0.15, 1.5, and 7.5 MPa, which capture the primary evolution of constrained thermal shrinkage in SRPP tapes. Stress levels were achieved at a ramp rate of 0.01 N/min to prevent rapid deformations and preserve the integrity of samples. A maximum stress of ~7.5 MPa illustrated the transition from thermal shrinkage to creep, whereas higher loads completely hindered the thermal shrinkage and structurally affected the tapes at the grip points (e.g., burning, necking). At each stress (i.e., 0.5, 1.5, and 7.5 MPa) the thermal shrinkage was measured at four different temperatures relevant for processing (135, 140, 145, and 150 °C) for 130 min after equilibration. Ramping the force at room temperature before increasing it to the target values minimized possible under predictions of creep during load application (~40 min). Strain values measured during temperature equilibration were neglected based on their minimal contribution, and values for time and shrinkage were zeroed at the onset of the isothermal segment.

3. Results and discussion

3.1. Thermal shrinkage of self-reinforced polypropylene tapes

The composite internal architecture is intimately correlated to the shrinkage response. Typical self-reinforced polypropylene (SRPP) tapes contain ~90% of highly aligned polypropylene chains after processing conferring enhanced mechanical properties in the composite as alignment increases [12,17]. Chain alignment can be estimated in different ways like using optically anisotropy (i.e., birefringence) or crystallinity measurements [18]. After chain alignment mechanical properties can be substantially modified, for instance, a reduction from 300% to 7% in strain to failure was reported as draw ratio of SRPP tapes changed from 0 to 17 [12,18]. Additional properties can be customized based on processing conditions of the tapes. Since, thermal expansion and creep can be minimized with low thermal gradients and low force loads, respectively, thermal shrinkage can be essentially attributed to the aligned segments along the SRPP tapes.

Thermal shrinkage is conventionally estimated either by measuring contracting forces, or free shrinkage under unconstrained conditions [12]. Since the presence of significant load forces can modify the time and temperature dependence of dynamic processes in polymers, we determined the time and temperature dependence of the constrained shrinkage of SRPP tapes at 0.15, 1.5, and 7.5 MPa (Fig. 1), in an attempt to integrally capture the complex multivariable shrinkage response and obtain a close view of the possible materials behavior during operation. The thermal shrinkage evolution over time can be modeled by an exponential damping following Eq. (1),

$$S(t) = \sum_{i=1}^{n} S_{\infty i}\left(1 - e^{-\frac{t}{\tau_i}}\right) \tag{1}$$

where $S_{\infty i}$ and τ_i represent the "ultimate" shrinkage and relaxation time of the unit i, respectively. Although thermal shrinkage and creep are independent phenomena, by using a similar analysis we can provide some physical interpretation to the overall mechanical modeling of thermal shrinkage, where springs and dashpots act analogous to creep but in opposite directions. The irreversible nature of thermal shrinkage could be represented by stretched entropic springs, and dashpots, whose length contraction is mediated by force loads and temperature. Two inverted Kelvin-Voigt (KV) units (i.e., spring and dashpot in parallel) in series Eq. (2) can closely approximate the entire shrinkage response, where the first unit captures the rapid initial response and the second damps the response at long times. One KV unit could also approach the global response by weighting the rapid initial response and yielding more conservative values for the ultimate shrinkage parameter as shown in Fig. 1 and Table 1.

$$S(t) = S_{\infty 1} * \left[1 - e^{-\frac{t}{\tau_1}}\right] + S_{\infty 2} * \left[1 - e^{-\frac{t}{\tau_2}}\right] \tag{2}$$

The experimental data shown in Fig. 1 is modeled at four different temperatures: 135, 140, 145, and 150 °C, and three conditions of stress: 0.15, 1.5, and 7.5 MPa. The numerical fitting of the model parameters (Table 1) was performed using nonlinear least squares and numerical solutions were constrained, where the maximum value of the ultimate shrinkage values has to equal the total shrinkage observed at long times, ~7200 s. As shown in Fig. 1, nearly 80% of the total isothermal shrinkage exhibited by SRPP tapes was developed between the first 10 and 30 min at any load, and specimens were almost fully contracted after an hour at low stresses (i.e., 0.5 and 1.5 MPa). This rapid combination of effects on thermal shrinkage generated by temperature and stress becomes a crucial stage for enhanced composite processing.

3.2. Maximum load, competing creep, and shrinkage

Thermally activated processes such as creep and thermal expansion can be present during the testing of thermal shrinkage of SRPP tapes. Nonetheless, their contributions remain less significant as thermal gradients and preload forces are minimized. In the absence of stresses the thermal shrinkage exhibited by SRPP tapes is a strong function of draw ratio (DR), and chains can contract up to a third of the total specimen length at DR ≈ 9.3 [12]. Further chain alignment introduces a thermal stabilization effect (i.e. less