

EFFECT OF ANNEALING ON THE THERMAL EXPANSION COEFFICIENT OF BIDIRECTIONAL THERMOPLASTIC COMPOSITES

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SUMMARY: It is known that $[(\pm 30)_N]_S$ laminates fabricated by combining different types of matrix and fibers have a negative coefficient of thermal expansion (CTE) in the specimen length, i.e. the X direction of the global laminate coordinate system. In a previous work [1], it was shown that a reproductive thermal expansion is obtained when the composite is annealed at a temperature high enough to completely release the residual stresses induced during the molding phase and stabilize the crystalline structure of the matrix. To get more insight on the influence of residual stresses and crystallization on the CTE of $[(\pm 30)_N]_S$ laminates, this paper presents the results of a series of dynamic scanning calorimetric (DSC) tests performed on the same materials as those used for CTE testing. Close correspondences between the DSC results and the CTE deviations of unconditioned specimens is shown, thus corroborating the results on the influence of residual stresses and crystallization on laminate CTEs.

KEYWORDS: layered structures, thermal properties, laminates, residual stress, Dynamic Scanning Calorimetry (DSC), annealing

INTRODUCTION

It is well known that the anisotropy of composite laminates can be tailored such that, under specific thermal conditions, the overall expansion of a part in pre-determined directions can be minimized or even eliminated. For example, for $[(\pm 30)_N]_S$ composite laminates, a negative CTE along the x-axis direction (reference direction for θ measurement) of the laminate is obtained [1-3]. Such behavior is mainly attributed to in-plane normal-shear and shear-shear coupling coefficients of the laminate, which are such that a negative CTE is obtained even for fibers and matrix having both a positive CTE. On the other hand, for composites made of a semi-crystalline thermoplastic matrix, the processing history has implications on the embedded thermal residual stresses because the specific volume of semi-crystalline materials depends on the level of

crystallinity attained (crystalline phases reaching lower specific volumes than amorphous phases upon cooling and solidification, while the specific volume of fibers remain almost constant) [4, 5]. Because the release of residual stresses in a part is possible for temperatures above the glass transition temperature (T_g), due to the increase of mobility of the polymer chain in the amorphous phase, composite parts made with these materials will distort when exposed to higher temperatures. In this work, the influence of T_g and matrix crystalline structure on the coefficient of thermal expansion (CTE) of $[(\pm 30)_N]_S$ polypropylene/carbon (PP/C), polyamide12/carbon (PA12/C) and PEEK/carbon are evaluated. To help decoupling crystallization effects from thermal effects, differential scanning calorimetry (DSC) tests have been performed and compared with the CTE data.

EXPERIMENTAL

CTE and DSC Measurements

CTE measurements on $[(\pm 30)_N]_S$ composite laminates have previously been performed and the detail of these tests are given in ref. [1]. The reader is invited to consult these works for more details. Table 1 lists the most relevant of these tests for the present analysis. DSC tests have been performed on PP/carbon, PA12/carbon and PEEK/carbon composite specimens as specified in Table 2. Two tests per testing conditions have been performed as specified by the test numbers in the first column. All tests were performed on the unidirectional tapes used to mold the plaques except tests 15 and 16, taken at mid-thickness of the molded plaque (plaque-core). The temperature ranges for testing are shown in the last column of Table 2. The annealed conditions are specified in columns 4 and 5. TMA-test 1, TMA-test 5 and TMA-test 6d mean that the specimens were annealed following the same heating and cooling runs for these TMA tests. Tests 9 and 10 were preheated similar to TMA tests 2, 3, 4 prior DSC testing. All these annealings were performed directly in the DSC apparatus. All DSC tests were conducted at a heating rate of $20^\circ\text{C}/\text{min}$.

RESULTS

During the annealing, it is expected that the release of the residual stresses (induced in the plaques during molding), accompanied of by a reorganization of the microstructure of the matrix when heated over T_g , result in the obtention of deviations in the CTE traces of composites. In what follows, PP/carbon, PA12/carbon and PEEK/carbon are successively analyzed and discussed. The individual effects of cristallization and residual stresses are observed by comparing the DSC and CTE traces.

Table 1 TMA tests performed for CTE measurements

Test #	Materials	Annealing range (°C)	Temperature range (°C)	Heating rate (°C/min)	Cooling rate (°C/min)
1	PP/carbon	----	-60 to 120	1.0	1.0
2, 3, 4	PA12/carbon	80°C – 24 hrs	30 to 95	2.0	----
5	PA12/carbon	----	30 to 120	0.5	0.5
6	PEEK/carbon	----	30 to 150	2.0	----
6b	PEEK/carbon	----	30 to 150	2.0	----
6c	PEEK/carbon	----	30 to 180	0.5	0.5
6d	PEEK/carbon	----	30 to 250	0.5	0.5

Table 2 DSC Tests performed

Test #	Materials	Type	Annealing range (°C)	Annealing rate (°C/min)	Temperature range (°C)
1, 2	PP/carbon	U/D tape	----	----	-60 to 250
3, 4	PP/carbon	U/D tape	TMA–test 1	1.0	-60 to 250
5, 6	PA12/carbon	U/D tape	----	----	30 to 280
7, 8	PA12/carbon	U/D tape	TMA–test 5	0.5	30 to 280
9, 10	PA12/carbon	U/D tape	80°C – 24 hrs	----	30 to 280
11, 12	PEEK/carbon	U/D tape	----	----	30 to 400
13, 14	PEEK/carbon	U/D tape	TMA-test 6d	1.0	30 to 400
15, 16	PEEK/carbon	Plaque-core	----	----	30 to 400

PP/Carbon Composite

The CTE and DSC traces of PP/carbon composites are shown in Figure 1 and 2. Comparing PP/C-test 1 in Figure 2 with the 1st heating run in TMA-test 1 of Figure 1, three deviations are observed, one at T_g of the matrix (around -10 °C), one between 20°C and 45°C and one around 90°C. This is enlightened by the dashed lines drawn in these temperature ranges over both traces. In Figure 1, the theoretical CTE calculated at ambient temperature is also shown (dotted line). The first small variations in both traces observed when passing T_g of the matrix are representative of the molecular reorganization and softening (smaller modulus of elasticity caused by the melting of amorphous phase). A drop in the modulus of elasticity results in an increase of the shear coupling effect in the laminate and a corresponding drop of the CTE as raised by Rogers et al. [3]. A larger CTE variation is observed in Figure 1 between 20°C and 45°C. Stored at ambient temperature (20°C) before testing and being over T_g of the matrix, this second CTE variation is probably caused by the release of residual stresses when heating the

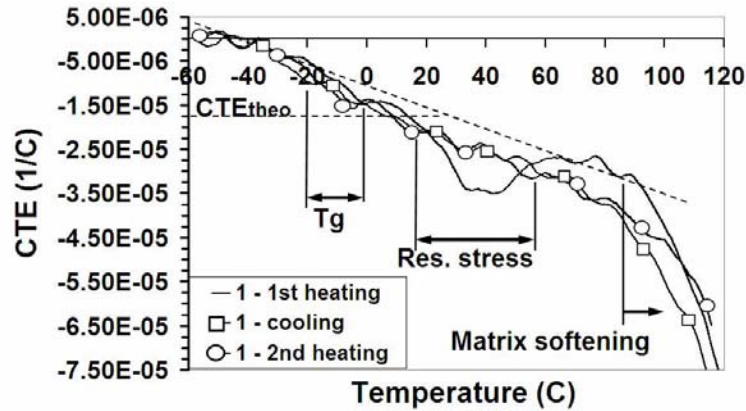


Fig. 1 CTE plots for the first cooling and second heating runs of PP/carbon, test 1.

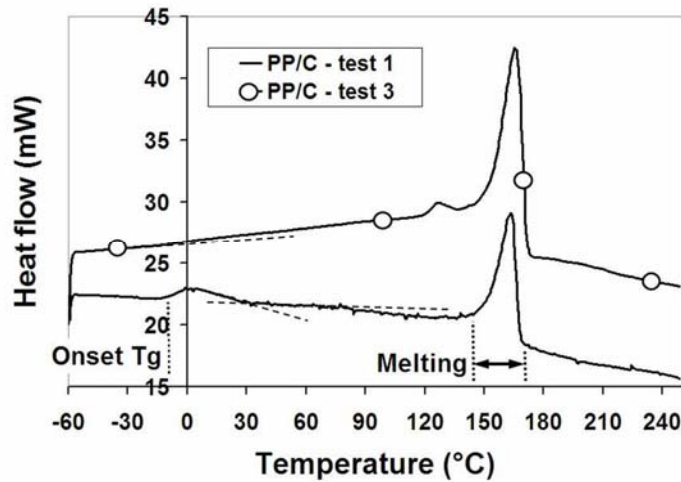


Fig. 2 DSC plots for an unconditioned specimen (PP/C-test 1) and one annealed following the PP/Carbon TMA-test 7.

specimen over 20°C for the first time (the residual stresses having already been released up to this temperature). This is supported by Figure 2 where, between 20°C and 45°C, the PP/C-test 1 trace shows small curvatures (delimited by dashed lines), suggesting few thermal molecular activities. For the 2nd heating and cooling traces in Figure 1, no more deviation is observed between 20°C and 45°C, the residual stresses having been removed by the first heating run, thus producing repetitive CTE traces. This is again supported by the PP/C-test 3 curve of Figure 2, annealed following TMA-test 1 first heating run, where no more thermal activities are observed between 20°C and 45°C (the residual stresses having been removed by the annealing). Finally, the CTE drop observed around 90°C is caused by the softening of the matrix. At this temperature, still far from the melt temperature of the matrix (165°C), the softening of the matrix with increasing temperature would increase the shear coupling effect such that a rapid drop of the CTE is observed, consistent with the observations made when passing T_g . For the cooling and 2nd heating CTE traces in Figure 1, at the glass transition temperature and especially around 90°C the CTE drops are still present, so are the deviations in the DSC traces at these temperatures.

PA12/Carbon Composite

Similar observations can be made for PA12/carbon specimens by comparing Figure 3 and 4. By comparing the specimens annealed the same way, we observe CTE variations and thermal activities (for DSC traces) for exactly the same temperatures. TMA test 5-1st heating shows an increase of the CTE around T_g of PA12 (45°C) for which temperature a thermal activity is observed in DSC test 5 in Figure 4. This CTE increase probably corresponds to the release of the residual stresses which is made possible by the molecular activity occurring after reaching T_g for the first time (no annealing). If we now compare TMA test 5-2nd heating with DSC test 7 annealed following the first heating of TMA test 5, both specimens show uniform graphs up to 120°C, representative of a stable matrix microstructure with no other deviation observed. A deviation is however observed at 120°C in DSC test 7, the maximum annealing temperature reached before testing. If we finally compare the mean CTE traces (mean of tests 2, 3 and 4) with the correspondent DSC test 9, both traces show deviations when approaching T_g , as shown by the rapid CTE drop between 30 and 45°C in Figure 3 and in the enlarged view of Figure 4, and around 80°C corresponding to the highest temperature reached by the specimens before TMA and DSC testing. At this temperature, well over the glass transition temperature of PA12, the matrix crystallizes and release residual stresses. The thermal expansion results of PP/carbon and PA12/carbon suggest that the CTE of the composites is affected when the temperature reaches T_g of the matrix and when it reaches the (previous) annealing temperature (the highest temperature reached by the composite after molding) for the first time. More evidence about these interpretations are obtained for PEEK/carbon specimens.

PEEK/Carbon Composite

The PEEK/carbon tests 6 to 6d in Table 1 have all been performed with the same sample, originally unconditioned, by increasing gradually the maximum temperature reached from test to test. The displacement versus temperature traces for the four tests are shown in Figure 5. Test 6 started to expand around 80°C, until the end of the test (150°C). This behavior is different to that of PP/carbon and PA12/carbon composites for which the CTE variations started at temperatures closer to T_g of the matrix (143°C for PEEK). Residual stresses generated in unidirectional PEEK/carbon plaques during molding were measured by Chapman et al. [6]. Compressive stresses at the surface of the plaque and tensile stresses in the middle were measured and these stresses reached respectively 53% and 25% of the ultimate transverse tensile strength. It could thus be possible, if such high levels of residual stresses are present in the TMA specimens for this material, that molecular movements (matrix deformation) occur even if the temperature is much below T_g of the matrix. This seems to be correlated by the DSC results of Figure 6 by comparing test 11 and test 13 traces with that of test 15. The small curvature in the DSC curve of test 15 between 60°C and T_g (delimited by the dashed line and not present in tests 11 and 13) suggests few molecular activities, which could correspond to the release

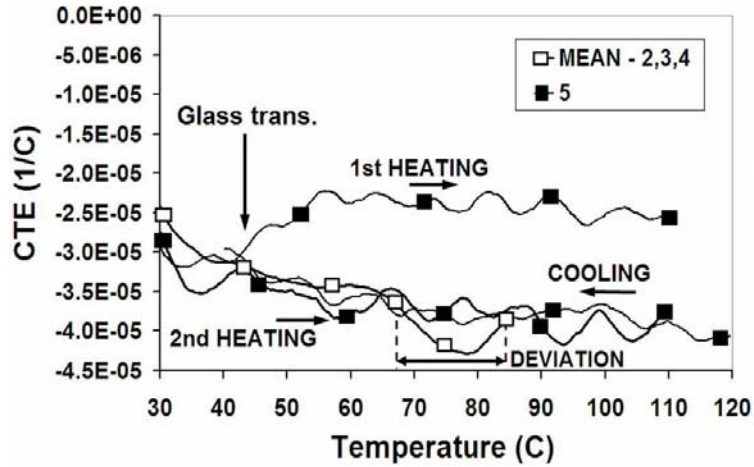


Fig. 3 Influence of repeated heating and cooling on the CTE of a PA12/carbon laminate measured with TMA.

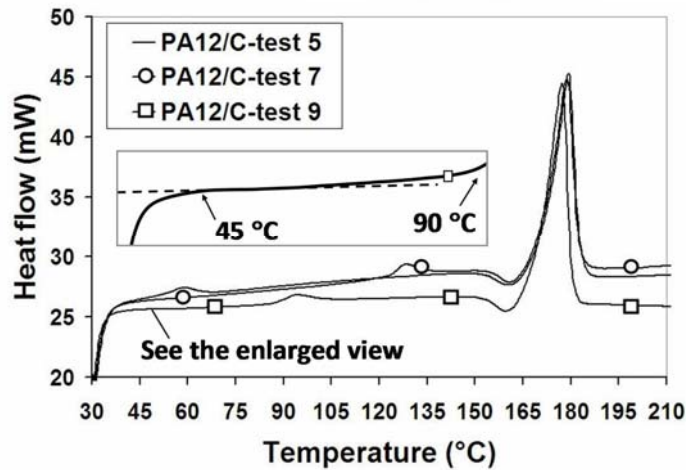


Fig. 4 DSC traces of PA12/carbon specimen for three different original conditions: No annealing (PA12/C-test 5), annealed following TMA-test 11 (PA12/C-test 7) and annealed at 80°C for 24 hours (PA12/C-test 9).

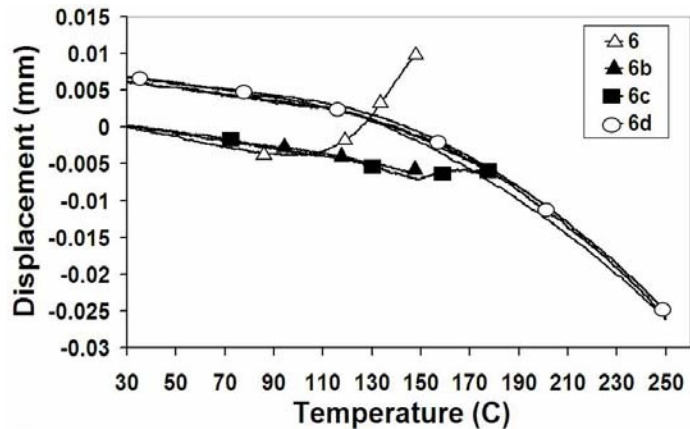


Fig. 5 Displacement as a function of temperature plots for PEEK/carbon tests 6 to 6d, realized with the same specimen but with increasing annealing temperatures.

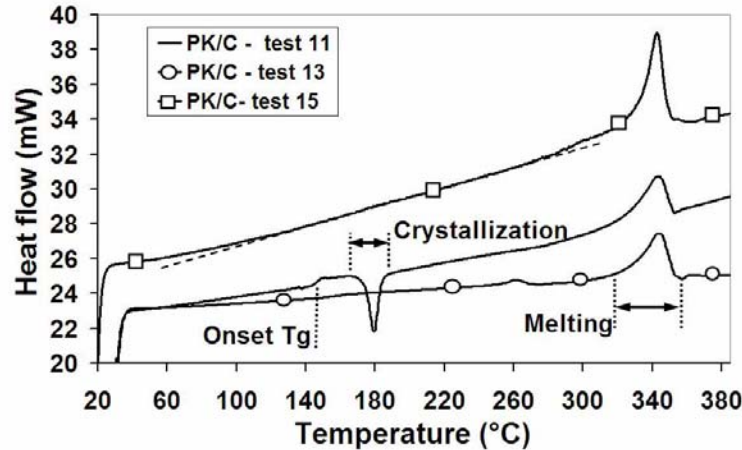


Fig. 6 DSC traces of PEEK/carbon specimen taken from the base UD tape (test 11 and 13) and from the core (mid-thickness) of composite plaques used for CTE measurements.

of residual stresses in this temperature range. However in Figure 5, the expansion around 80°C is not shown for test 6b, performed over the same temperature range that test 6, but as soon as the specimen was heated over 150°C in test 6c, it pursued the expansion started in test 6, until the maximum temperature of 180°C was reached. Finally, in test 6d, the three runs performed between 30 and 250°C show no more expansion of the specimen after 180°C, only contraction starting at T_g , and the three traces show very reproducible CTE results. This is in agreement with the results of Unger and Hansen [4] who demonstrated, with the matrix originally in the solid amorphous state (obtained under very large cooling rates), how annealing of a unidirectional PEEK/carbon coupon realized between the minimum crystallization temperature (T_c) and the melt temperature (T_m) can be performed to make reproducible the thermal expansion behavior in the transverse direction to fibers. Similar results are obtained here for tests 6 to 6d in figure 5. The reproductiveness is obtained for each new (higher) annealing temperature reached and once completed the first heating run of test 6d (equivalent in fact to annealing the specimen at 250°C), the specimen displacement was reproducible, as shown the subsequent heating and cooling runs performed on the specimen. Finally, the CTE drop from T_g to 250°C is attributed to the softening of the matrix when reaching T_g , similar to the observations made for PP/carbon.

CONCLUSION

In this work, the CTE traces obtained from TMA analysis were compared with the DSC traces obtained on specimens submitted to similar annealing before testing. Globally, the results show that the CTE of the composites is affected when the temperature reaches T_g of the matrix, when it reaches the annealing temperature (the highest temperature reached by the composite after molding) for the first time and when it approaches the melting temperature. When reaching T_g , the amorphous phase of the matrix softens and crystallization combined to a release of residual stresses can occur. Combined to an increase of the shear coupling effect in the laminate, this allows the fibers to dominate the behavior of the composite and reduce the CTE with rising temperatures. After the specimen has been annealed, the CTE of the composite is reproducible as

long as it is maintained below the annealing temperature. A further release of the residual stresses in the specimen appear when heating over the (previous) annealing temperature, after which a new (larger) temperature range of stable response is obtained.

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