DSC and XRD Crystallinity Measurements for Carbon Fiber-reinforced Polyamide-6 Laminates Processed at Different Cooling Rates

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Fiber-reinforced thermoplastic composite laminates are intriguing materials from an industrial and research point of view. Among them, carbon fiber/polyamide-6 (CF/PA6) composites have attracted interest in recent years because of their promising properties. The mechanical properties of such composites made with semi-crystalline polymers depend on the different morphologies present in the matrix. The degree of crystallinity (DOC) can be characterized as the mass fraction of the crystallized polymer. The DOC highly depends on the cooling rate (CR) of the manufacturing process. In the current investigation, thin CF/PA6 laminates are manufactured, maintaining a constant CR through the thickness of the plates (Fig. 1). Four different CRs are applied (Table 1). A uniform crystallinity through the thickness of the sample is confirmed by recording the thermal history on different through-the-thickness locations. The current work characterizes the DOC using two different techniques: X-Ray diffraction (XRD) and differential scanning calorimetry (DSC). For both cases, the overall trend of the obtained DOC confirms that fast CR results in lower DOC.

Due to the polymorphic nature of polyamides, specifically polyamide-6, difficulties may arise in quantitatively interpreting the DSC (Fig. 2) and XRD (Fig. 3) results. From the DSC curves, different phenomena are distinguished that occur in polyamide-6 during heating. These phenomena are in line with the transitions reported for PA6 samples [1-3] and include i) Brill transition that initiates at relatively low temperatures above the glass transition, ii) sub-melting transition before the main melting signal, iii) cold-crystallization that exhibits a broad exothermic peak before melting, and iv) the melting-recrystallization-remelting (MRR) of crystals that exhibit a shoulder before the melting peak temperature. The occurrence of these phenomena is investigated using a modulated-DSC technique.
The DOC results obtained using DSC and XRD are presented in Table 2. The two techniques showed a good correlation for higher crystallinity levels resulting from the CRs ranging from 0.7 to 43 °C/min. In contrast, XRD measurements yield lower DOC values than DSC for the fast CR of 770 °C/min. This difference could be attributed to the small and highly imperfect crystalline structures formed due to a high nucleation density and insufficient time for chain reorganization, resulting in imperfect β-crystals. The disordered nature of these crystals makes it hard to properly separate the diffraction peaks from the amorphous halo in XRD post-processing. Part of the diffracted X-rays is inevitably included in the amorphous halo, resulting in apparently lower DOC values obtained after XRD decomposition. For DSC, the fusion enthalpy of imperfect β-structures is added to the melting enthalpy and is thus incorporated into the DOC calculation. It can be concluded that there are no significant differences between the DOC for the CF/PA6 laminates cooled down at slow and moderate CRs. In contrast, a fast CR can lead to a DOC value as low as 29 %. Moreover, the results show that moisture absorption of CF/PA6 after plate manufacturing and before DSC measurement is significant and will cause invalid measurements and higher values of DOC. Hence, care should be taken to prevent moisture absorption before the DSC analysis of CF/PA6 samples.

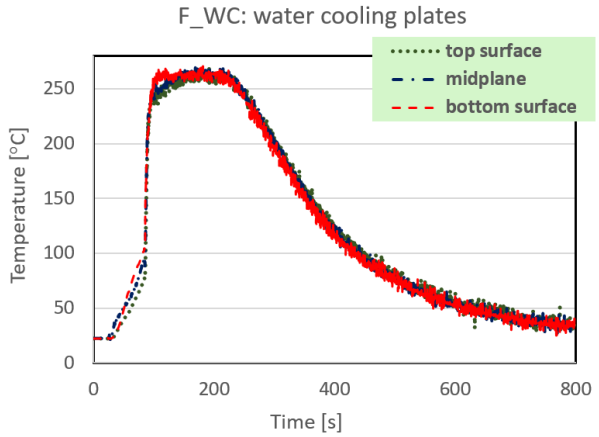

Fig. 1. Thermal history of the manufacturing process of F_WC plate recorded at three surfaces of the laminate.

Table 1. Different applied cooling rates.

Plate	Cooling method	Avg. CR (°C/min)
P_SC	Convection by air [slow CR]	0.7
P_WC	Water cooling plates [moderate CR]	7.9
F_WC	Water cooling plates [moderate CR]	43
P_CP1	Cooling on plates at room temperature [fast CR]	770
P_CP2		

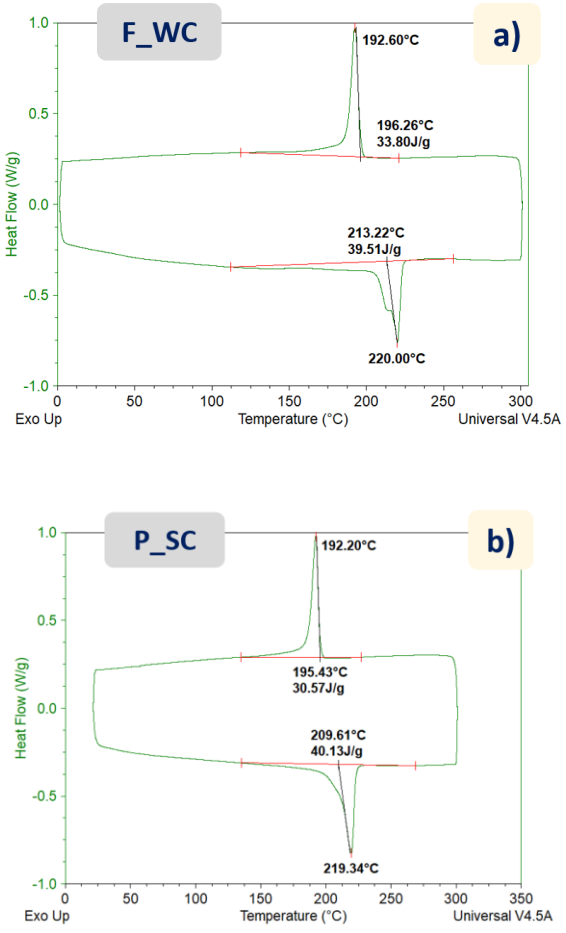

Fig. 2. DSC curves for CF/PA6 composites processed at different cooling rates: (a) F_WC, (b) P_SC.

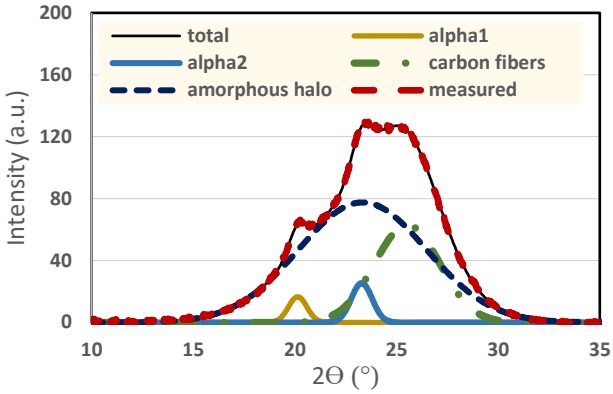

Fig. 3. Typical XRD pattern of the CF/PA6 sample with peak-fitted peaks.

Table 2. DOC measured using DSC and XRD techniques for different cooling methods.

Plate	DOC from DSC [%]	DOC from XRD [%]
P_SC	43.0 ± 1.1	42.1 ± 1.4
P_WC	46 ± 1.6	37.3 ± 1.5
F_WC	41.0 ± 1.8	32.3 ± 2.2
P_CP1	29.0 ± 1.5	16.2 ± 1.2
P_CP2	30 ± 1.3	15.5 ± 0.8

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