ProPeL - PPROCESS AND PERFORMANCE SIMULATION OF LIGHTWEIGHT STRUCTURES
M3-Project

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

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Questions? Remarks? Feel free to contact

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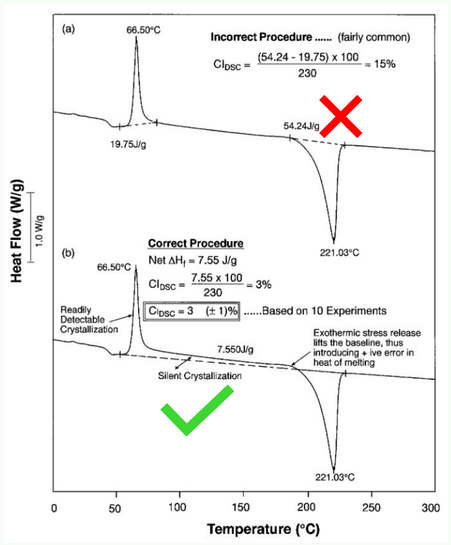
Introduction

- Polyamide-6 (**PA6**) as an engineering thermoplastic, possess excellent mechanical properties, heat and chemical resistance.
- It has been extensively used in carbon-fiber (CF)-reinforced composites (**CF/PA6**) for various applications.
- Different mechanical properties can be obtained with semi-crystalline polymers depend on the crystallinity and different morphologies present in the matrix.
- The current work characterizes the crystallinity using different techniques: **XRD** and (modulated)-**DSC**.

KELLYS THEOS F-series - Thermoplastic Hybrid Steel-Carbon Composite a.k.a. FEATHER®

Problem statement

- Different processing techniques can induce different degree of crystallinity (**DOC**).
- The **DOC** highly depends on the cooling rate (**CR**).
- Due to the polymorphic nature of polyamides, specifically PA6, difficulties may arise in quantitatively interpreting the **DSC** and **XRD** results.



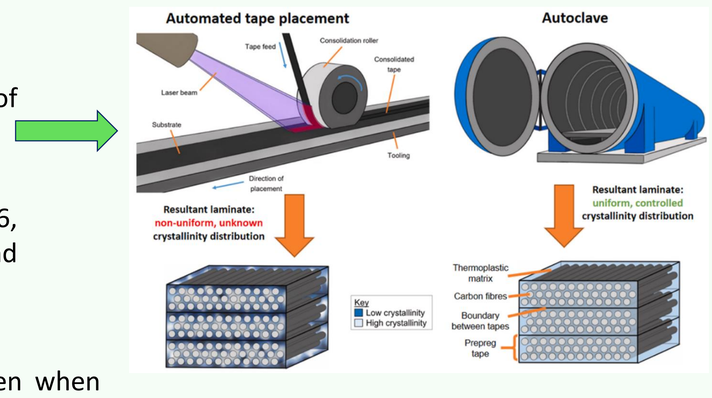
[Khanna YP, Kuhn WP., Journal of Polymer Science Part B: Polymer Physics. 1997]

Incorrect and correct approaches for processing of PA6 DSC results

- Care should be taken when interpreting the DSC curves of PA6 and its composites:

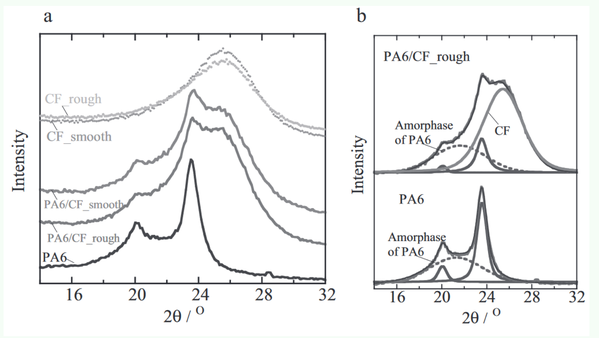
Not to exclude the broad "**silent crystallization**" peak.

- Based on the thermal cycle, PA6 form **α**, **γ**, or metastable **β** crystalline phases.
- Less stable **γ**-crystals will transform to stable **α** phase during annealing below T_m.



[Perez-Martin, Helena, et al., Comp Part B, 2021]

Schematic ATP and autoclave consolidation process and associated crystallinity uniformity through the thickness

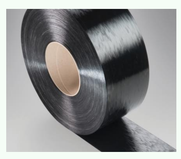


[Uematsu, H., et al., Polymer Journal, 2020]

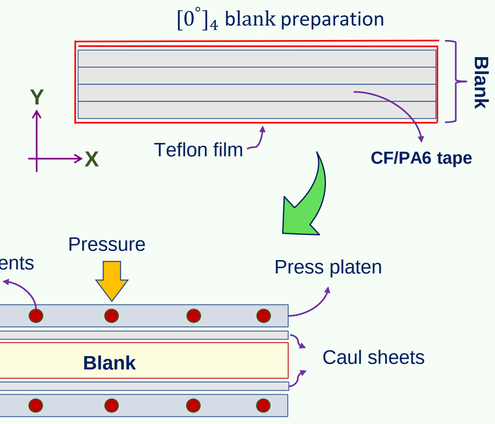
XRD pattern of (a) PA6 and CF/PA6 composites, (b) deconvoluted curves to find amorphous and crystalline structures.

Specimen preparation

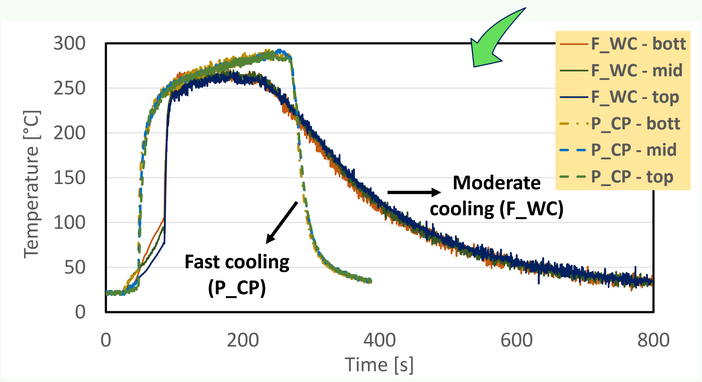
- Thin CF/PA6 laminates are manufactured, maintaining a constant CR through the thickness of the plates:



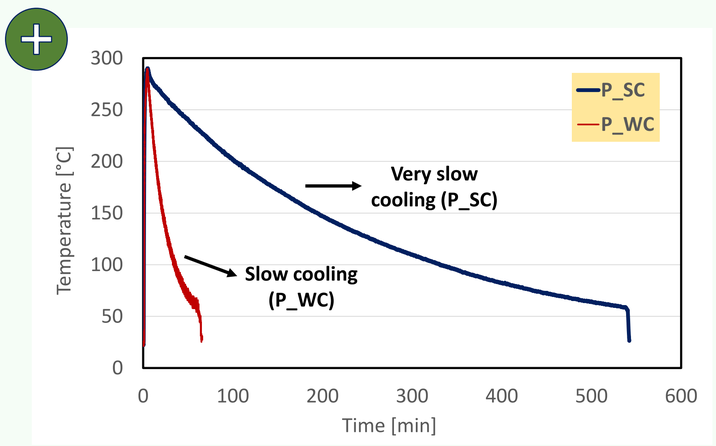
Toray Cetex® TC910 UD CF/PA6 tape



Compression molding process able to induce four **different CRs:**



Temperature cycle of compression molding for laminates: fast cooling (**P_CP**) and moderate cooling (**F_WC**) rates.

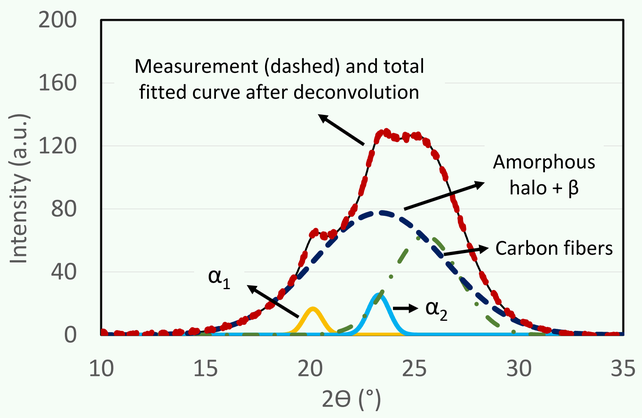


Temperature cycle of compression molding for laminates: Very slow cooling rate (**P_SC**) and slow cooling (**P_WC**) rates.

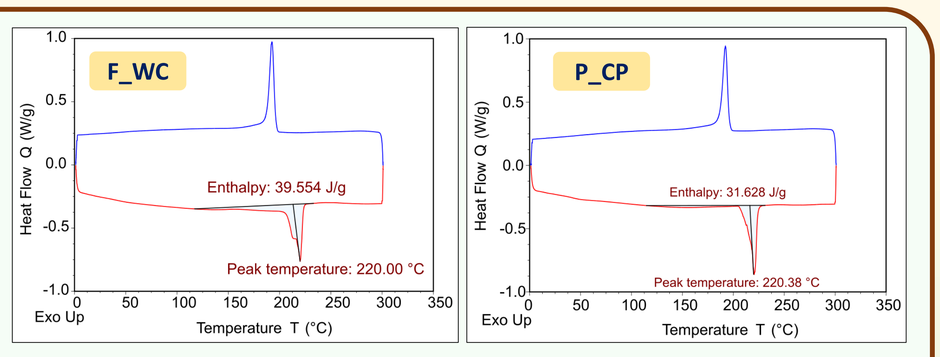
Results and discussion

Produced laminates with four different cooling rates.

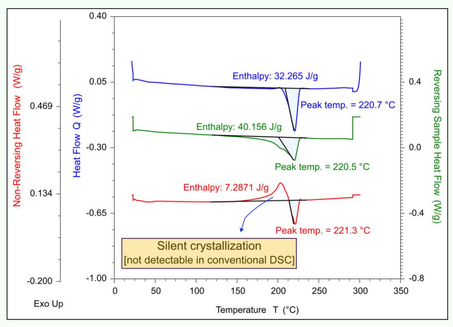
Plate	Cooling method	Avg. CR (°C/min)
P_SC	Convection by air [slow **CR**]	0.7
P_WC	Water cooling plates [moderate **CR**]	7.9
F_WC	Water cooling plates [moderate **CR**]	43
P_CP1 / P_CP2	Cooling on plates at RT [fast **CR**]	770



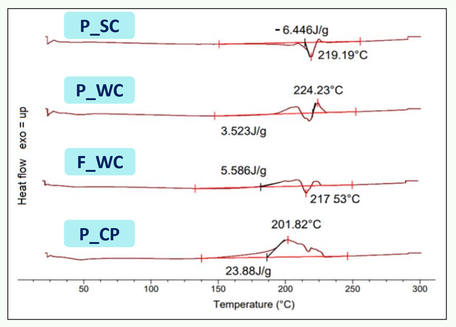
Typical XRD pattern of CF/PA6 after deconvolution of amorphous halo and crystalline structures.



DSC heat-cooling curves for F_WC and P_CP samples



mDSC result for P_CP distinguishes reversing and non-reversing heat flow

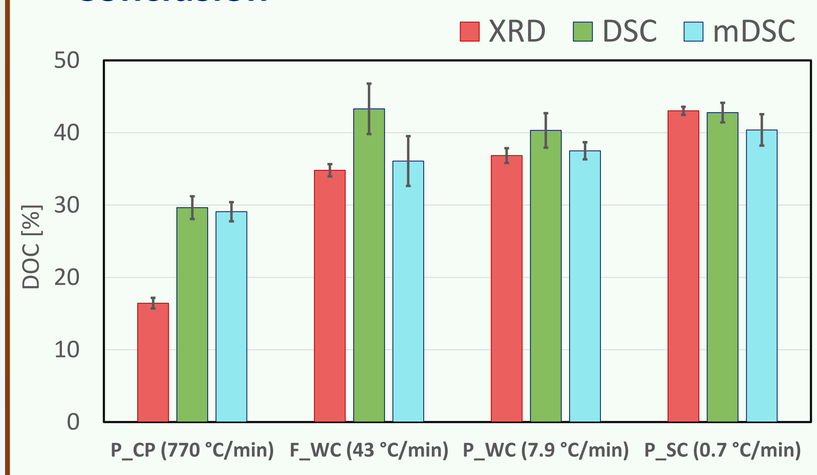


Effect of different CRs on Non-reversing heat flow from mDSC

❑ Different phenomena are distinguished:

I. Brill transition ➔ initiates above Tg,
II. Sub-melting transition ➔ before the main melting signal,
III. Cold-crystallization ➔ broad exothermic peak before melting, and
IV. Melting-recrystallization-remelting (**MRR**) of crystals ➔ a shoulder before the melting peak temperature.

Conclusion



Resulting DOC of plates measured using (m)DSC and XRD techniques.

- Slow **CR** of **0.7** °C/min ➔ Similar (**m**)**DSC** and **XRD** results
- Moderate to **7.9** to **43** °C/min ➔ Lower crystallinity from **XRD**
- Fast **CR** of **770** °C/min ➔ Much lower DOC from **XRD**

- At fast **CR** ➔ imperfect **β-crystals** form
- Small and highly imperfect **β-crystals** form due to a high nucleation density and insufficient time for chain reorganization
- Presence of **β**-crystals ➔ makes it hard to separate the diffraction peaks from the amorphous halo in XRD.

✓ **XRD** results are not accurate, specially at high CRs.
✓ Moisture in **DSC**-scanned samples lead to overestimated DOC.
✓ **DSC** heat flow curves hide possible exothermic crystallizations.
✓ **mDSC** analyses can give better understanding and results.

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