3D PRINTING OF BIOCOMPOSITE BY COLD MATERIAL EXTRUSION

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Additive manufacturing (AM) of composites enabled the production of highly customized parts with excellent mechanical properties, compared to the neat polymer used ordinarily in AM [1]. However, the majority of the used materials are still fossil-based which does not align with the ever increasing ecological awareness. Nevertheless, in the polymers market, one can find various bio-based thermosetting polymers with remarkable thermal properties such as poly furfuryl alcohol (PFA). Historically, PFA resin's most common use was metal-core molds but it has recently been used as a matrix for composites mainly using closed molding techniques and prepregs [2–6]. Despite the good potential of this resin, it is not yet used in additive manufacturing. Accordingly, in the present work, a fully biomass-based composite material was developed using PFA as a bio-based matrix filled with up to 30 wt% cellulose powder as a pasty ink for AM.

Printable ink formulation

The addition of cellulose powder conferred to the uncured composite paste viscosity and a shear-thinning thixotropic behavior (Fig.1) compatible with injection molding and 3D printing by liquid deposition modeling (LDM). The oscillatory rheology proved also an increase in the yield stress and the stiffness of the slurry which reached respectively 770 Pa and 200 kPa, thus ensuring the shape maintenance of the printed object prior to curing.

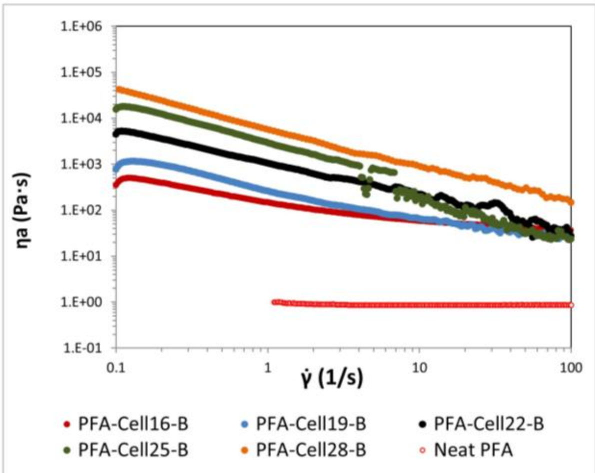

Fig.1- Cellulose effect on the flow curves of different slurries.

Resulted composite

In addition to the rheology tuning, the added cellulose powder limited pores formation during atmospheric curing by favoring vapor degassing through the percolating cellulose network and slightly improved the mechanical properties of the cured composite with 3 GPa Young's modulus. Indeed, this renewable and cost-effective composite has good mechanical performances and thermomechanical stability with only a 20% drop of modulus when stressed at 200°C.

Additive manufacturing by LDM: toward in-situ curing

Although the developed ink is successfully printable (Fig.2), many challenges can occur when printing pastes without solidification, especially for complicated parts. To overcome these limitations a special printer with a heated oven was developed for and in-situ curing. Moreover, this machine has two different printing heads which allow printing supports to successfully print complex models.

Fig.2- Printing of a cylinder with 0.7 mm nozzle.

Conclusions

In the present work, a PFA/cellulose composite was successfully printed with the LDM technique. The renewable and cost-effective composite exhibited adequate mechanical and thermomechanical properties outstanding some of the commonly used thermoplastic filaments. The printability of the developed ink is acceptable and can be further enhanced with an in-situ curing process using a personalized printer.

References

(1) Ngo, T. D.; Kashani, A.; Imbalzano, G.; Nguyen, K. T. Q.; Hui, D. Additive Manufacturing (3D Printing): A Review of Materials, Methods, Applications and Challenges. *Compos. Part B Eng.* **2018**, *143*, 172–196. https://doi.org/10.1016/j.compositesb.2018.02.012.

(2) Wang, T.; Sun, H.; Long, J.; Wang, Y.-Z.; Schiraldi, D. Biobased Poly(Furfuryl Alcohol)/Clay Aerogel Composite Prepared by a Freeze-Drying Process. *ACS Sustain. Chem. Eng.* **2016**, *4* (5), 2601–2605. https://doi.org/10.1021/acssuschemeng.6b00089.

(3) Deka, H.; Misra, M.; Mohanty, A. Renewable Resource Based "All Green Composites" from Kenaf Biofiber and Poly(Furfuryl Alcohol) Bioresin. *Ind. Crops Prod.* **2013**, *41*, 94–101. https://doi.org/10.1016/j.indcrop.2012.03.037.

(4) Lems, E.-M.; Winklehner, S.; Hansmann, C.; Gindl-Altmutter, W.; Veigel, S. Reinforcing Effect of Poly(Furfuryl Alcohol) in Cellulose-Based Porous Materials. *Cellulose* **2019**, *26* (7), 4431–4444. https://doi.org/10.1007/s10570-019-02348-6.

(5) Pohl, T.; Bierer, M.; Natter, E.; Madsen, B.; Hoydonckx, H.; Schledjewski, R. Properties of Compression Moulded New Fully Biobased Thermoset Composites with Aligned Flax Fibre Textiles. *Plast. Rubber Compos.* **2011**, *40* (6–7), 294–299. https://doi.org/10.1179/1743289810Y.0000000017.

(6) Guigo, N.; Mija, A.; Vincent, L.; Sbirrazzuoli, N. Eco-Friendly Composite Resins Based on Renewable Biomass Resources: Polyfurfuryl Alcohol/Lignin Thermosets. *Eur. Polym. J.* **2010**, *46* (5), 1016–1023. https://doi.org/10.1016/j.eurpolymj.2010.02.010.