Cross-Linking of PBT by Reactive Extrusion Using Zn(II) Epoxy-Vitrimer Chemistry

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Vitrimers[1] are networks made of chemically cross-linked polymers in which thermally stimulated exchange reactions permit network topology rearrangements while keeping constant the number of bonds and cross-links. In contrast to the two other categories of polymers, i.e., thermoplastics and thermosets, vitrimers combine insolubility and ability to flow when heated. The viscosity of vitrimers is controlled by the rate of the exchange reactions.

Prototypes of vitrimers were based on exchangeable links by transesterification and implemented by using classical epoxy chemistry. The objective of this study is to show how the original Zn(II) − epoxy chemistry can be applied to synthesize semi-crystalline polyester vitrimers from commercial thermoplastic grades by a cross-linking method that can be used on an industrial scale. Our efforts focused on poly(butyleneterephthalate) (PBT)[2].

PBT is characterized by a high degree of crystallinity, a high melting point and rapid crystallization. One of its limitations is that just above the melting point (230 °C) any mechanical strength disappears and the polymer tends to drip under its own weight. In demanding applications, it is necessary to use crosslinked PBT but the existing crosslinking processes are complex and the polymer obtained is not recyclable. In the process that we envisioned, PBT is modified by epoxy resins in the presence of a transesterification catalyst, directly into an extruder. To devise an effective formulation, we studied in detail the exchange reactions and catalysis in model systems and in the polymer. The polymer thus obtained maintains the essential properties of a semi-crystalline thermoplastic polymer and acquires the new properties of vitrimers such as heat resistance, mechanical strength and solvent resistance. Transformation of ordinary PBT into a vitrimer could open up new areas of application for PBT.

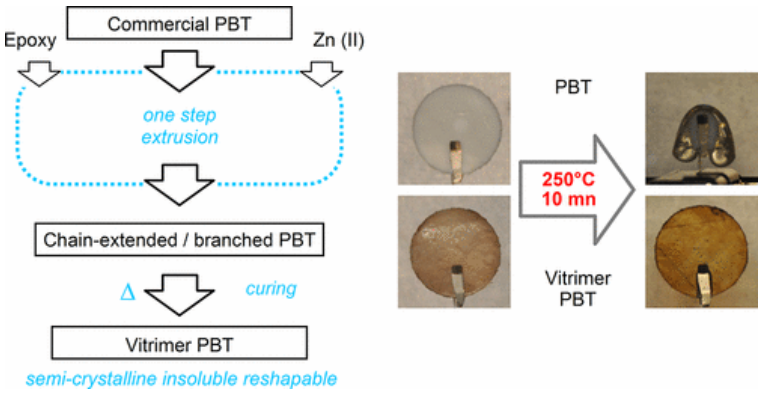

Figure 1. *Strategy used to obtain a vitrimer PBT by an easily upscalable means. In the right part, we show how this transformation enhance the heat resistance of PBT above its melting point.*

[1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965–968.
[2] A. Demongeot, R. Groote, H. Goossens, T. Hoeks, F. Tournilhac, L. Leibler, *Macromolecules* **2017**, *50*, 6117–6127.