SYNTHESIS AND CHARACTERIZATION OF RECYCLABLE CHEMICALLY-CROSSLINKED SHAPE MEMORY MATERIALS

Thomas Defize, *Raphaël Riva, Jean-Michel Thomassin, Christine Jérôme*, Michaël Alexandre*

Center for Education and Research on Macromolecules (CERM), University of Liege, Building B6a, 4000 Liege, Belgium

Poly(ε-caprolactone) (PCL), a semi-crystalline polymer, is one of the most widely studied polymers for the development of shape memory materials when chemically cross-linked. PCL presents several advantages such as a melting transition temperature close to human body temperature, a high biocompatibility and is (bio)degradable. So, this polymer is highly relevant for both biomedical devices such as stents or resorbable suture wires and also for degradable packaging. However, after cross-linking, the material can not be reprocessed, preventing any reuse/recycling of the material. One of the purposes of this work is to find a solution to this major drawback, which would then allow, for example, to reshape packaging films after use or to recycle trimmings remaining after fabrication. Amongst current trends in the design of new polymer and composite materials, the use of organic reactions that are able to create and reversibly disrupt chemical bonds upon an external stimulus (temperature, irradiation,…) is currently gaining more and more attention as it can lead to applications in various areas such as remendable materials, drug delivery systems, stimulus-degrading materials or recyclable materials.

This contribution aims at reporting a new concept for the preparation of well defined and recyclable PCL based reversibly cross-linked shape memory polymer by the formation of reversible carbon-carbon bonds.

Amongst all the reversible links described in the literature, thermally (4+2) reversible cycloadditions present interesting features such as the creation of robust bonds and well defined reversibility conditions. As an example, the application of furan/maleimide adducts as covalent link, which cycloreversion is largely favored in the range of temperature (90-120°C), is widely reported. For this purpose, commercially-available linear and multi-arm star shaped PCL precursors have been selected and selectively modified at their chain ends either by a diene (furan, anthracene) or a dienophile (maleimide). Typically, PCL-based shape memory materials have been prepared by mixing a stoichiometric amount of diene-bearing and maleimide-bearing PCLs in a twin-screw mini-extruder at a temperature which favors cycloreversion. The polymer blend is then cured at 65°C (just above PCL melting temperature), with the purpose to increase chains mobility and improve the formation of the adducts. Cross-linked PCLs were obtained, as evidenced by swelling experiments. The shape memory properties of the materials have been studied by cyclic tensile thermomechanical analysis. The influence of the architecture of the PCL precursors as well as the nature of the Diels-Alder moieties on the cross-linking rate and on the shape memory properties has been studied [1-3]. Reversibility of the network formation in the case of furan, used as diene, has been assessed by rheology and by recycling experiment.

(1) Defize, T.; Riva, R.; Raquez, J.-M.; Dubois, P. ; Jérôme, C.; Alexandre, M.; *Macromol. Rapid Commun.* **2011**, *32*, 1264.
(2) Defize, T.; Riva, R.; Thomassin, J.-M.; Jérôme, C.; Alexandre, M.; *Macromol. Symp.* **2011**, *309/310*, 154.
(3) Defize, T.; Riva, R.; Jérôme, C.; Alexandre, M.; *Macromol. Chem. Phys.* **2012**, *213*, 187.