



## RECENT PROGRESS IN DEVELOPING POLYURETHANES SHOWING FAST INTRINSIC SELF-HEALING AT ROOM TEMPERATURE

Currently, there is an interest in developing self-healing polymeric materials, including adhesives, polyurethanes (PUs) in particular. Because of the formation of hydrogen bonds between the urethane and/or urea groups in PUs, micro-phase separation is produced and this may favor self-healing. Several PUs exhibited self-healing induced by an extrinsic (isocyanate encapsulation in the polymeric matrix) [1] or an intrinsic (dynamic reversible covalent or non-covalent/ionic bonds) [2] mechanism.

The most PUs showing intrinsic self-healing are synthesized with polyester or polyether polyols. Due to the high polarity and strong carbonate bond with respect to ether and ester bonds, self-healing should be more favored. In fact, different self-healing PUs synthesized with polycarbonate diol polyols have been already described, but they need heating (80-120 °C) and/or they show somewhat long time for complete self-healing. In our recent study [3], a PU made with polycarbonate of 1,6 hexane diol (hard segments content : 22 wt.%) showed fast and efficient intrinsic self-healing at 20 °C. The self-healing was ascribed to the existence of a significant number of free carbonate groups, a relatively low percentage of free and hydrogen-bonded urethane groups, and high mobility of the soft segments. A mechanism based on the existence of dynamic non-covalent exchange interactions of the carbonate groups in the soft segments was proposed (Figure 1). However, that polyurethane showed low mechanical properties.

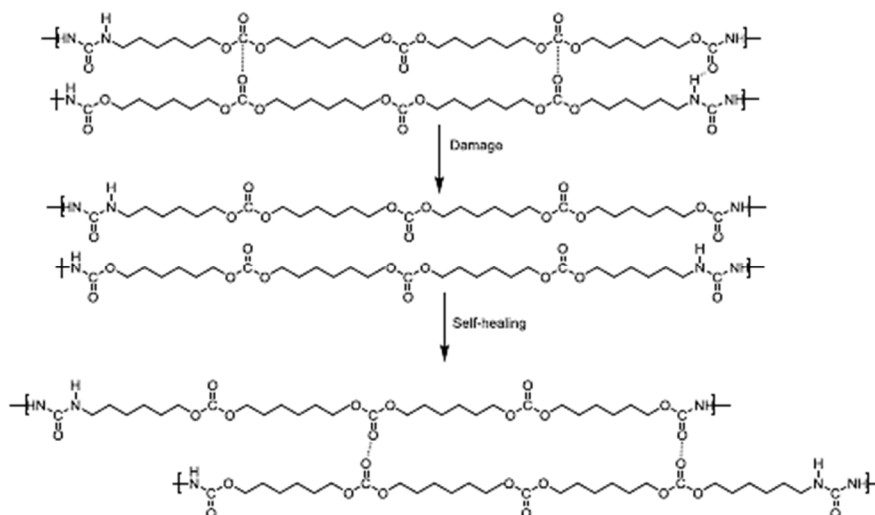


Figure 1. Proposed self-healing mechanism of polyurethane synthesized with polycarbonate diol polyol.

In order to confirm the proposed mechanism of self-healing, different PUs with similar low hard segments content were synthesized with blends of polycarbonate of 1,6 hexanediol and polyadipate of 1,6 hexanediol polyols, i.e., the content of carbonate groups in the soft segments was decreased. If the interactions between the carbonate groups in the soft segments are the main responsible of the intrinsic self-healing at 20 °C, the decrease of the amount of carbonate groups should decrease the extent of self-healing.

On the other hand, considering that the mechanical properties of the PU made with polycarbonate diol polyol are low and the ones of the PU made with polyester polyol are high, the PUs made with blends of polycarbonate diol and polyester polyols may improve their mechanical properties.

### References

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3. Paez-Amieva, Y.; Martín-Martínez, J. M. Dynamic non-covalent exchange intrinsic self-healing at 20 °C mechanism of polyurethane induced by interactions among polycarbonate soft segments. *Polymers.* 2024, 16, 924. <https://doi.org/10.3390/polym16070924>