

THERMOPLASTIC SILICONE ELASTOMERS

Michael A. Brook, Laura C. Zepeda, Yunqing Chen and Amanda S. Grande

Department of Chemistry and Chemical Biology, McMaster University, 1280 Main St. W., Hamilton ON Canada L8S 4M1
(mabrook@mcmaster.ca)

ABSTRACT

Silicone elastomers are normally thermoset materials prepared using radical, condensation, or platinum-catalyzed addition cure to crosslink (functional) silicones oils. Like other condensation polymers, it is possible to degrade silicones back, mostly to monomers, by acid and particularly base-catalyzed hydrolysis or alcoholysis. However, the ability to repurpose silicones would be advantageous. Thermoplastic elastomers need crosslinks that are reversibly broken in response to a stimulus, including chemical or thermal stimuli. We report two distinct processes to achieve this, using boronic acids and coumarin groups, respectively.

Coumarin was introduced to silicones via a click reaction. The ultimate objective was to reversibly photocrosslink the coumarin groups in a 2+2 cycloaddition (Figure 1A). Surprisingly, the simple incorporation of the coumarin groups led to increases in modulus of several orders of magnitude, which depended on the backbone concentration of coumarin groups. The change in properties was shown to be the result of π - π physical dimerization, which led to thermal crosslinks that were readily broken above about 80 °C. It was therefore straightforward to select a desired modulus simply by selecting the coumarin density within the silicone.¹

Boronic acids have become attractive targets because of their ability to undergo cross-coupling. However, more interesting from our perspective is their ability to selectively form esters with vicinal diols, which permits them to discriminate between different saccharides. A series of boronic acid-modified silicones was prepared by hydrosilylation. Complexation with a series of amino-modified materials leads to elastomeric materials. Thermolysis did not provide a thermoplastic response unless monofunctional amines were also present (Figure 1B). These exchanged with the crosslinking amines, temporarily lowering the modulus until the monofunctional amine was removed by distillation.²

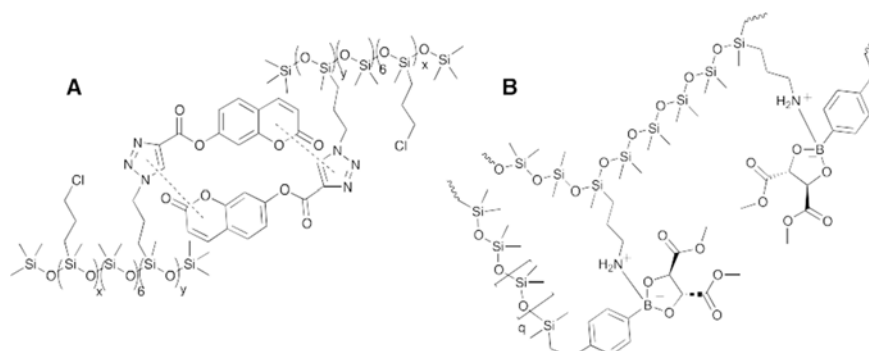


Fig. 1: A: Coumarin and B: boronate-modified silicone elastomers.

Acknowledgement: We thank the Natural Sciences and Engineering Research Council for funding.

References:

¹Fawcett, A. S.; Brook, M. A., *Macromolecules* **2014**, *47*, 1656-1663.

²Dodge, L.; Chen, Y.; Brook, M. A., *Chem. Eur. J.* **2014**, *20*, 9349-9356.