

# UNDERSTANDING THE MOLECULAR MECHANISMS INVOLVED IN THE INTERFACIAL SELF-HEALING OF SUPRAMOLECULAR RUBBERS

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Keywords: supramolecular rubbers, self-healing efficiency, tapered double cantilever beam, rheology

## ABSTRACT

Supramolecular rubbers based on 2-aminoethylimidazolidone and fatty acids with epoxy crosslinks have been shown to self-heal via multiple hydrogen bonding sites. In this work, several tools are used to investigate the molecular mechanisms taking place at the interface to understand cohesive healing in these polymers. The quantification of self-healing was performed via a tapered double cantilever beam (TDCB) geometry. The TDCB geometry is especially amenable to studying multiple healing cycles due to the fracture toughness, and subsequently healing efficiencies being independent of crack length. Healing was carried out for multiple fracture-healing cycles and varying fracture testing experimental parameters to track the change in efficiency of interfacial healing. Strain rate and rate of crack closure are both shown to affect the self-healing efficiency.

## 1. INTRODUCTION

Self-healing in supramolecular rubbers based on 2-aminoethylimidazolidone and fatty acids with epoxy crosslinks has been shown to occur via multiple hydrogen bonding sites [1]. Previous work has shown that these hydrogen bonding systems undergo a “deactivation” of the surfaces under certain conditions [2]. On the other hand, it was also shown that damage or fracture processes can cause “activation” of the surfaces leading to enhanced self-healing upon bringing the fractures surfaces together. Annealing of the fractures surfaces at different temperatures before healing also affects the healing efficiencies. Moreover, surfaces undergo time dependent polymer chain rearrangements which lead to differences in the healing efficiency. In this work, experiments have been designed to further investigate and understand the interfacial molecular mechanisms of these fractured surfaces. Firstly multiple cycles of crack propagation and healing was carried out in a tapered double cantilever (TDCB) setup. The TDCB geometry was chosen due to the independence of fracture toughness on crack length [3], thus providing the advantage of self-healing efficiency that is independent of crack length for multiple healing cycles. Furthermore, rheology in a strain-controlled mode was used to understand the parameters affecting the cohesive strength between fractured surfaces.

## 2. MATERIALS

Supramolecular rubbers based on 2-aminoethylimidazolidone and fatty acids with epoxy crosslinks (provided by Arkema) were used as the self-healing system under investigation. Modified tapered double cantilever (TDCB) specimens were prepared as described previously [4]. The geometries were shaped out of aluminium and used with 10 x 6 x 2 mm polymer samples inserted in the region of interest. The entire TDCB setup was held inside a rigid aluminum mould to ensure uniform pressure between fractured surfaces during each healing cycle. A sharp 1 mm pre-notch was made on the polymer using a razor blade. For the rheology experiments 20 mm diameter polymer discs with a thickness of 2 mm were used.

## 3. METHODS

Healing was carried out for five subsequent loading (i.e. fracture) and healing cycles and varying fracture testing experimental parameters to track the change in efficiency of interfacial healing. For the first set of experiments, polymer samples were fractured at different strain rates (5, 10 and 300 mm/min) in a universal tensile testing machine (Zwick, 20 kN) to monitor the relationship between loading and crack propagation. Samples were allowed to heal in the TDCB mould for 1 hour at room temperature between fracture cycles. For these tests, the fractures surfaces were brought together at a fast strain rate of 300 mm/min.

In a separate set of experiments, samples were fractured at a constant strain rate of 10 mm/min but the fractured surfaces were brought together at different speeds (1, 10 and 100 mm/min) in a controlled fashion using the tensile testing machine. This allowed for a study of the mechanism of deactivation and rearrangement of the surface polymer chains. Rheology (ThermoFisher, Haake Mars III) was used to study the viscoelastic behaviour of these polymers. A tack type adhesion testing was carried out in the strain-controlled rheometer to determine cohesive strength between two discs of the same polymer. Two discs of 20 mm diameter and 2 mm thickness were pressed together between parallel plate geometry of a rheometer at 80 °C for 5 minutes. The samples were then separated at a constant strain of 10 mm/min and the force-displacement curves were plotted.

## 4. RESULTS

Previous work on these polymer films has shown two mechanisms of fracture: cavitation occurring at low strain rates; and brittle fracture which is dominant at high strain rates or low temperatures [2, 5]. Study of the transition from one mechanism to other could provide helpful information regarding healing self-healing. The load vs. displacement behaviour (Figure 1) shows a constant force plateau at 5 and 10 mm/min which corresponds to a steady crack propagation. Whereas, in case of the 100 mm/min loading rate, a markedly different behaviour is observed. The polymer undergoes an initial linear elongation, which rapidly turns into a nucleation and cavitation type of failure. The first signs of cavitation were seen at the displacement value at which the force displacement curve changes slope. Thus, in the TDCB geometry, the polymer has two dissimilar responses under low and high strain rates, which is contradictory to that observed previously [2], and therefore requires further research. However, this strain rate dependence behaviour does provide further

insight into the timescale of the dynamic network formation. Previous work has shown a similar behaviour for other supramolecular polymer networks [6].

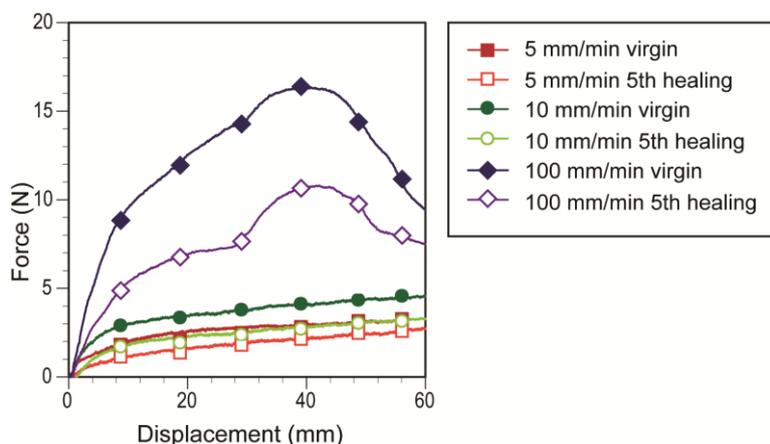


Figure 1: Differences in force displacement curves with different fracture rates indicate two separate mechanisms of fracture.

Since chain relaxation is likely a very important phenomenon at the surface, another set of experiments was performed by varying the rate of crack closure, while keeping loading rate constant. As shown in Figure 2(a) the rate of crack closure also has a major effect in the after healed properties, suggesting a process of polymer chain relaxation at the crack surface plane. This effect can be quantified by plotting healing efficiency as a function of the rate of crack closure as shown in Figure 2(b). The healing efficiency at closure rates of 1-10 mm/min reaches values of 90% while higher closure rates (i.e. 300 mm/min) lead to a clear decrease in healing efficiency, a likely indicator of the time dependent polymer chain relaxation. It is supposed that high crack closure rates do not allow sufficient chain entanglement, leading to a lower bond strength.

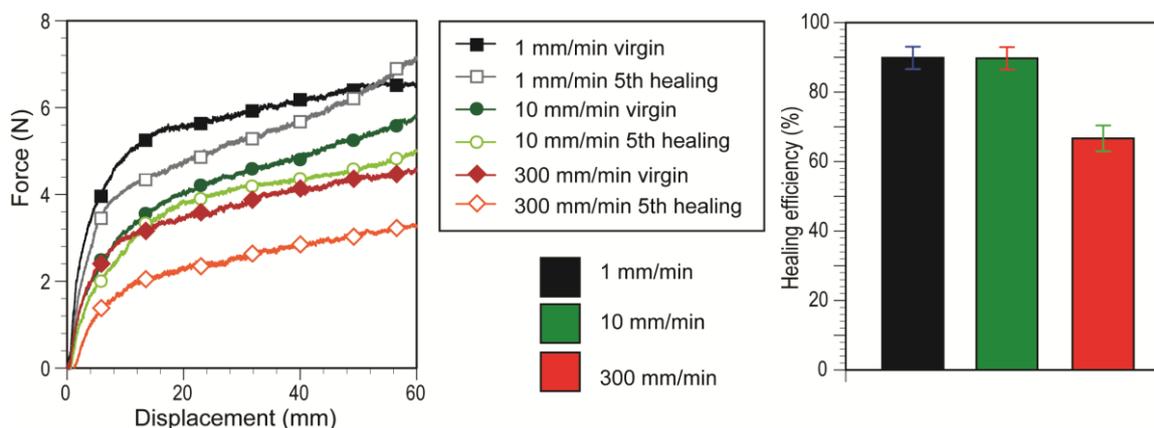


Figure 2: (a) While keeping loading rate constant, different rates of crack closure lead to a difference in the healing phenomena, an indication of the chain relaxations on the surface, and (b) healing efficiency, defined as ratio of force of healed to virgin polymer, is higher for slower rates of crack closure.

## 5. CONCLUSIONS

As seen in these results, for supramolecular self-healing a study of the interfacial mechanism is necessary and yields interesting information regarding self-healing in these hydrogen bonding networks. Different mechanisms of fracture and crack closure have been observed as function of the rates of loading and crack closure rates. A detailed study of parameters affecting self-healing and the quantification of the fracture energy are expected to yield further information regarding the activation and deactivation of polymer chains on the surface.

## ACKNOWLEDGEMENTS

The authors are grateful to Jean-Pierre Disson at Arkema for providing the supramolecular polymers used in this work.

## REFERENCES

- [1] Cordier, P., et al., Self-healing and thermoreversible rubber from supramolecular assembly. *Nature*, 2008. 451(7181): p. 977-980.
- [2] Maes, F., et al., Activation and deactivation of self-healing in supramolecular rubbers. *Soft Matter*, 2012. 8(5): p. 1681-1687.
- [3] Brown, E.N., Use of the tapered double-cantilever beam geometry for fracture toughness measurements and its application to the quantification of self-healing. *The Journal of Strain Analysis for Engineering Design*, 2011. 46(3): p. 167-186.
- [4] Brown, E.N., S.R. White, and N.R. Sottos, Microcapsule induced toughening in a self-healing polymer composite. *Journal of Materials Science*, 2004. 39(5): p. 1703-1710.
- [5] Montarnal, D., et al., Synthesis of self-healing supramolecular rubbers from fatty acid derivatives, diethylene triamine, and urea. *Journal of Polymer Science Part A: Polymer Chemistry*, 2008. 46(24): p. 7925-7936.
- [6] Hentschel, J., et al., Self-Healing Supramolecular Block Copolymers. *Angewandte Chemie International Edition*, 2012. 51(42): p. 10561-10565.