SOLVENT BASED SELF-HEALING OF THERMOSETS WITH EMBEDDED SMA WIRES

S. Neuser[1], V. Michaud[1], N. Sottos[2] and S. White[2]

[1]Laboratoire de Technologie des Composites et Polymères (LTC), Institut des Matériaux, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
Email: sam.neuser@epfl.ch

[2]Autonomic Materials Systems Group, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign Urbana, IL 61801, USA
Email: swhite@uiuc.edu

Keywords: self-healing polymer, smart composite, solvent, SMA, diffusion

ABSTRACT

Self-healing composites are an emerging class of materials that can mend themselves after damage. Our current work focuses on a liquid-based method, where micro-capsules, embedded into a thermoset resin matrix, crack and release their content to promote healing after a damage event. Healing efficiency is generally measured through the crack propagation energy during a TDCB test before and after healing. Among the various healing systems proposed so far, Caruso et al. recently incorporated microcapsules loaded with a solvent/epoxy mix into the matrix which, when released, dramatically increase the chain mobility and allow fracture planes to heal by enabling the reaction of residual hardener with the epoxy [1].

In parallel, Kirkby et al. investigated the effect of using embedded shape memory alloy (SMA) wires to further close the crack and heat up the damage zone for the DCPD/Grubbs self-healing system. Reduced crack gap and the local heating favoured complete curing of the DCPD and further increased the healing efficiency [2].

In this research, we present results on further testing of active response systems with SMA applied to solvent based healing systems. Ethyl phenyl acetate was chosen as the solvent system, and the epoxy matrix is Epon 828. The mechanisms of solvent healing were further investigated. Diffusion experiments of the solvent in the epoxy matrix were performed by immersing epoxy cylinders in the solvent and following their weight (see Fig.1).

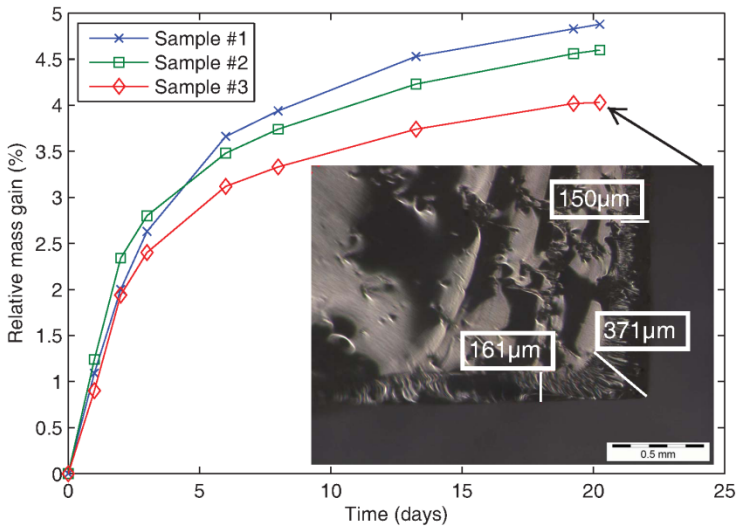

Figure 1: Weight increase vs. immersion time. Inset showing ductile surface layer.

We observed that the diffusion coefficient is very low, in the order of 10^{-15} m^2/s at room temperature. This translates into a diffusion length of about 38µm in 24h. The saturation concentration was found to be 25wt%.

As can be seen in the inset of the above mentioned figure, the samples showed a ductile surface layer when fractured after three weeks immersion. This surface layer saturated in solvent was substantially softer than the fragile epoxy in the bulk. Therefore mechanical properties of bulk epoxy and epoxy with solvent were determined. The results in Tab.1 confirm the observations above.

Table 1: Mechanical properties of the resin cured with 25% solvent

Material	Young's modulus	Ultimate strength	Elongation at break
Resin + EPA	1.10 +- 0.02	20.93 +- 0.72	3.59 +- 0.11
Resin	2.54 +- 0.16	43.51 +- 5.70	2.02 +- 0.37

Using these values, the curing of epoxy in presence of the solvent was measured using a rheometer. The gel point was largely delayed due to the presence of the solvent. 25% solvent mixed with resin and hardener delayed the gel time at room temperature from 3.5h to 10h. Compared to the well-studied DCPD/Grubbs system, the gel times are much higher. Taking into account the heating through SMA wires, the gel point of the same resin/solvent mixture decreased to 30min using the temperature profile found in a real sample while the storage modulus only achieved its final value after about 90min. We then used this knowledge to improve the healing efficiency in long groove tapered double cantilever beam samples. Healing efficiency was increased from 26% to 71% when comparing 3min and 30min of heating time. A heating time of 90min further increased the average healing efficiency to 78%. The lowest value measured for that sample batch increased from 18% for the 30min activation series to 57% for the 90min activation series, leading to a lower coefficient of variation (0.37 for 30min and 0.25 for 90min). As compared to the former protocol for the DCPD/Grubbs system, a longer activation period prevented premature cracking while the resin was still not fully cured.

Finally, we used DSC to determine the residual reactivity after exposure to the solvent. While normally cured resin had a residual reactivity of 148.50J/g, samples exposed to the solvent only had 86.46J/g of residual reactivity for 7.7wt% uptake of solvent and no residual reactivity at all for samples prepared at the saturation level of the solvent.

Table 2: Healing efficiencies with different parameters.

Chronology	Gap [µm]	Healing efficiency [%]
no SMA	28.2 +- 7.0	24.3 +- 14.8
3 min	47.9 +- 29.5	25.9 +- 23.2
30 min	15.5 +- 13.4	70.5 +- 25.8
90 min	11.9 +- 5.5	78.2 +- 19.2

REFERENCES

[1] M.M. Caruso, B.J. Blaiszik, S.R. White, N.R. Sottos and J.S. Moore, Full recovery of fracture toughness using a non-toxic solvent-based self-healing system, *Advanced Functional Materials,* **18**, 2008, pp. 1898-1904.

[2] E.L. Kirkby, J.D. Rule, V.J. Michaud, N.R. Sottos, S.R. White and J.E. Månson, Embedded shape-memory alloy wires for improved performance of self-healing polymers, *Advanced Functional Materials*, **18,** 2008, pp. 2253-2260.