EVALUATING SOLVENTS AS HEALING-AGENTS IN THERMOPLASTIC MATRICES VIA DYNAMIC SYNCHROTRON X-RAY MICROTOMOGRAPHY

Steven D. Mookhoek[1,2], Hartmut R. Fischer[3], Sybrand van der Zwaag[1] and W. Ludwig[4]

[1] Delft University of Technology, Faculty of Aerospace Engineering, kluyverweg 1, 2629 HS Delft, The Netherlands
Email: s.d.mookhoek@tudelft.nl

[2] Dutch Polymer Institute (DPI), P.O. box 902, 5600 AX Eindhoven, The Netherlands

[3] TNO Science & Industry, Department of Materials Performance, De Rondom 1, 5612 AP Eindhoven, The Netherlands

[4] European Synchrotron Radiation Facility (ESRF), BP220, 38043 Grenoble, Cedex 9, France

Keywords: Self-healing, thermoplastics, x-ray tomography, synchrotron

ABSTRACT

Since the introduction of self-healing materials the use of encapsulated liquids has been demonstrated to be a good concept to introduce self-repair in (composite) polymer systems. In liquid-filled microcapsules based self-healing materials functional liquid is stored inside microcapsules dispersed in a matrix material. The encapsulated liquid is released when the surrounding matrix fractures or cracks. The released liquid then is able to close the crack and repair the damage by chemo-physical processes, *e.g.* polymerization. In this work the design of a one-component solvent-induced self-healing mechanism is presented for amorphous linear thermoplastics, solely based on the activation of polymer reptation and re-entanglement. The potential of solvent-induced healing of thermoplastics was investigated by dynamical Synchrotron X-ray tomography measurements focussing on the solvent deployment and mechanism of healing after cracking as a function of time. Here we present the results of an analysis of a detailed on a PMMA/PS material system embedded with bromobenzene filled microcapsules, which comprises the fracture, release and healing processes upon cracking under loading. Using synchrotron radiation, fast tomographic scans allow a detailed investigation of the solvent release and solvent sorption within minutes after crack formation.

Introduction of a crack in the sample caused rupture of the microcapsules in the crack-path and at a limited distance away from the crack. In contrast to expectations, the solvent release from the capsules outside the direct line of the crack is not quasi instantaneous but occurs over a period of minutes after cracking. The reconstructed tomographic slices located just below the crack-tip clearly show how several embedded capsules appear to be intact after introduction of a crack but release the solvent into the matrix up to 20 min after crack formation. The solvent is absorbed by the PMMA-PS matrix after capsule rupture which leads to a detectable volume of solvent affected matrix around the position of the capsule. This affected volume increases in time as the solvent penetrates further into the matrix but does not show full homogenisation over the measuring time of the experiment (35 min). The solvent remains in high concentration around the ruptured capsule and solvent 'clouds' of approximately twice the capsule diameter can be observed. From full 3D analysis and segmentation of the data-sets on the solvent sorption around the crack it can be observed that the solvent spreading inside the crack for PMMA-PS matrices is minimal and absorption of solvent into the matrix is very fast. Figure 1 illustrates the evolution of solvent absorption by the matrix after fracture as a function of time. The volume of solvent affected material is segmented from the matrix volume and is indicated in yellow. For purpose of reference, the segmented volume of the microcapsules (purple) and the matrix material (white) are also given in Figure 1, showing where the crack was introduced. In Figure 1 at t=0 min a small volume of solvent affected matrix can already be detected prior to cracking, caused by the preliminary rupture of capsules. At t = 0.5 min after fracture the large volume of solvent absorbed

around the crack is clearly visible. It is shown by subsequent images at t = 10.5 and 20.5 min that the affected volume expands away from the crack in time, caused by limited diffusion and delayed capsule depletion outside the crack-line.

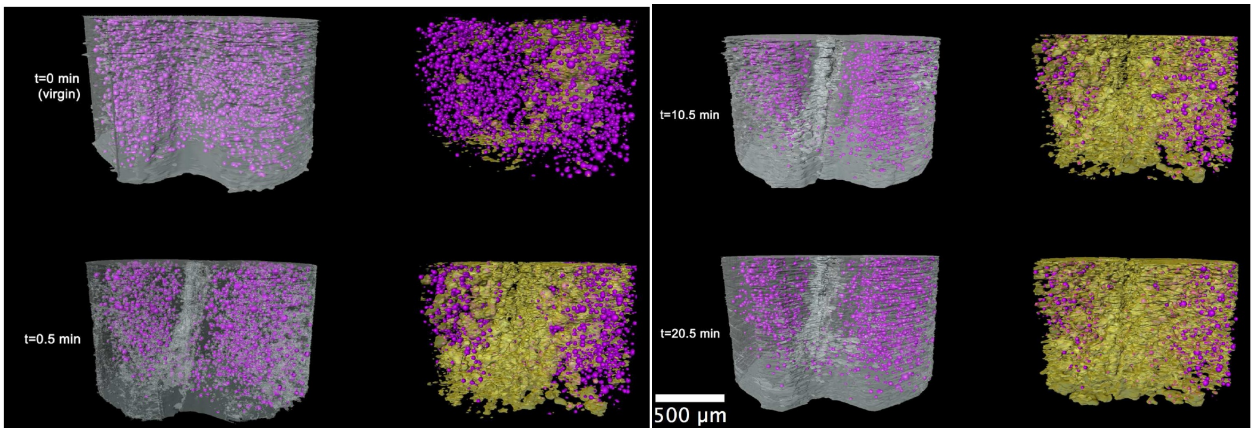

Figure 1: Evolution of the matrix solvent absorption after crack introduction for a 15 wt% ca. 45 µm UF(BB) PMMA-PS system

Detailed segmentation of the different features within the broken sample allows the quantification of the reduction of filled microcapsules (released solvent volume) and the affected volume by the solvent in the vicinity of the crack. Figure 2a displays the released volume per crack area for samples with different capsule sizes as a function of time after fracture.The evolution of solvent affected volume with time is displayed in Figure 2b. This figure shows that the rate of increase after fracture depends on the capsule diameter and shows a delay for larger capsules. The sorption of solvent is initially retarded for larger microcapsules due to their small surface to volume ratio. At longer time the increase in the solvent fraction is found to be more or less comparable for all three capsule sizes.

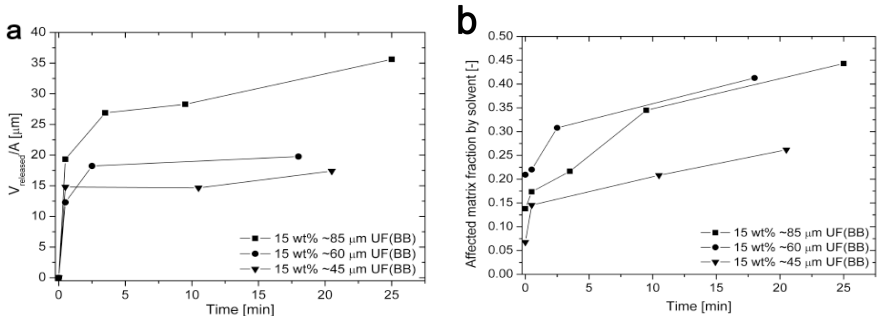

Figure 2: The released solvent volume per crack area and b) the fraction of solvent affected matrix as a function of time for PMMA-PS matrices embedded with UF(BB) microcapsules of different sizes

The dynamic tomographic experiments have shown that solvent sorption for this solvent/thermoplastic system is very fast and the material directly absorbs nearly all the solvent released, without spreading inside the crack. It can be rationalised however that spreading of solvent over the surface should be fast in comparison to solvent sorption in order to achieve optimal healing over the total surface. The effect of solvent sorption and as a consequence plasticizing the thermoplastic matrix is also observed when measuring healing-efficiencies mechanically. For these experiments healing times are found long and healing efficiencies are relatively low. Hence, it is demonstrated that in order to achieve (optimal) healing for solvent based self-healing thermoplastic materials, the careful selection of a suitable solvent/matrix combination is crucial.