ESRF	**Experiment title:** A scanning microfocus SAXS/WAXS investigation of ordering in the vicinity of a crack in a self-healing supramolecular polymer	**Experiment number**: SC3070
Beamline:	**Date of experiment**: from: Apr 2 2011 to: Apr 4 2011	**Date of report**: 20/6/11
Shifts:	**Local contact(s)**: Dr Emanuela di Cola	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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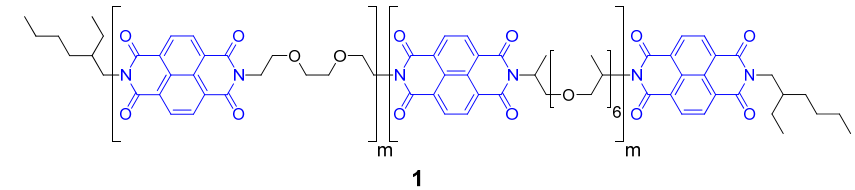
Report:

This was a highly successful session. Scanning XRD was performed on two self-healing polymer systems. Representative data from one of these materials is presented below. Scheme 1 shows the two polymeric components which form a supramolecular non-covalently linked complex due to hydrogen bonding and aromatic stacking interactions of polydiimide **1** and polyamide **2.** Details of synthesis and characterization were published previously.[1]



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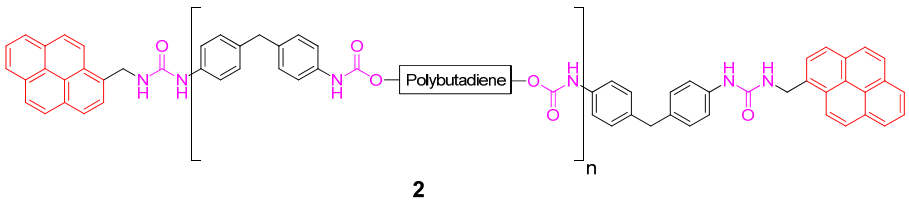

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Scheme 1. The two components of the supramolecular healing polymeric system.

The size of the microfocus beam was 350 × 400 nm and the sample was scanned through the beam with two configurations: (a) low magnification - horizontal step size of 53 μm, vertical step size of 20 μm; (b) high magnification – horizontal step size of 4 μm, vertical step size of 16 μm .

Arrays of microfocus XRD patterns are shown in Fig.1 for a specimen in which damage was induced by cutting the edge of a film, perpendicular to the edge as shown in Fig.1 (right-hand side). Fig.1a shows a scanned array of XRD patterns obtained with the larger step size (scale shown), the cut can clearly be seen top centre because the XRD patterns are shaded darker, corresponding to reduced transmission, thus mapping the damaged regions. Further detailed analysis of integrated 1D intensity profiles will be discussed shortly. Fig.1b shows a zoom-in (smaller scan step size). Fig.1c,d show arrays of XRD patterns over the same two scan areas, for the sample during annealing at 120 ^{o}C. The XRD patterns appear homogeneous across the sample, i.e. XRD patterns with reduced intensity are no longer observed in the damaged regions. Fig.1e,f show the corresponding XRD pattern arrays after cooling to 30 ^{o}C, again no evidence of damage is observed, and apparently self-healing has occurred.

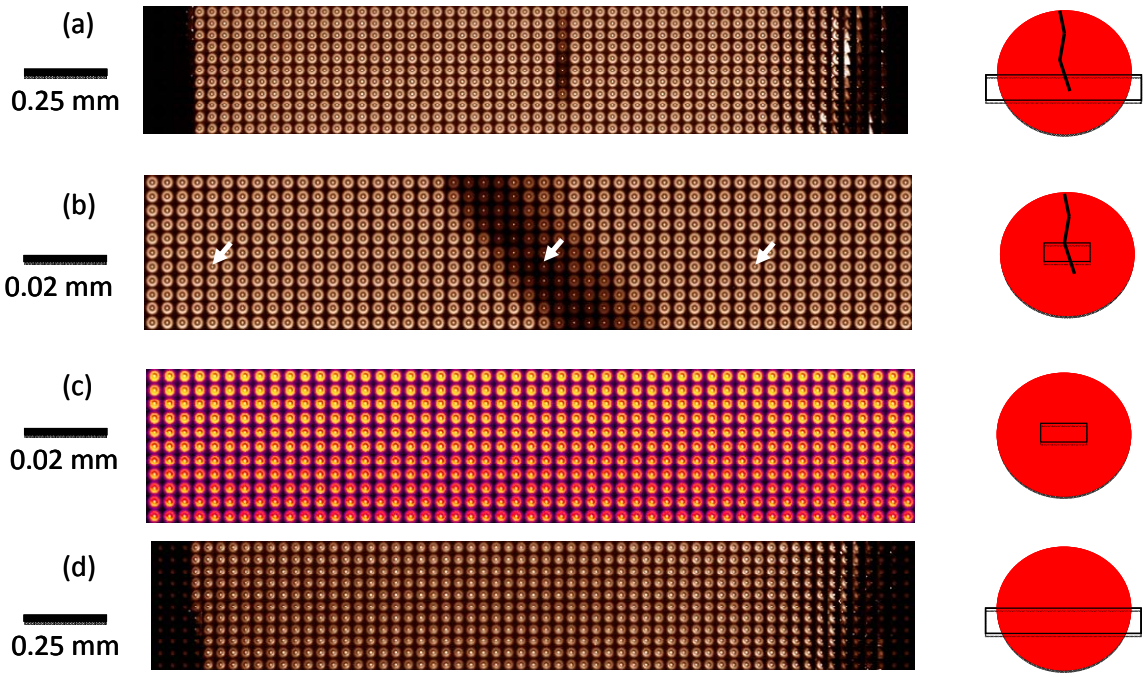

Fig.1. Scanned array of microfocus XRD patterns: (a,b) Sample at room temperature before healing, with cut region at sample edge, (c,d) Corresponding regions of sample during heating at 120 ^{o}C. The white arrows show the location of representative patterns analysed in more detail in Fig.2 and Fig.3. The right-hand side shows schematics of the sample.

Fig.2a shows profiles obtained for the sample before annealing. In agreement with our previous report,[1] the primary peaks in this pattern correspond to spacings of 3.4 Å and 5.1 Å. The former spacing has been assigned to a π-π stacking distance of the pyrenemethylurea units, and the latter has been ascribed to the distance between hydrogen bonded urea/urethane units within the polymer. An additional broad peak is observed at 2.1 Å (outside the *q* range previously investigated). At low *q*, two sharper peaks are observed with spacings of 13.2 Å and 15.9 Å. The three profiles in Fig.2a show that the XRD patterns in the undamaged regions are the same (similar profiles were obtained from patterns elsewhere outside the damaged area), however the profile in the damaged region is different. The main difference is the reduced intensity (due to a reduction of the amount of sample in the beam). However, there is an additional change in the shape of the background. Detailed analysis (*vide infra*) of the region comprising the 3.4 Å and 5.1 Å peaks shows in fact no qualitative difference in these peaks in the damaged area. During annealing, differences in XRD profiles between previously damaged and surrounding areas disappear as shown in Fig.2b. This in fact is a central finding of this work. The fact that the microfocus XRD patterns in the previously damaged regions recover, and that the 3.4Å and 5.1 Å reflections are retained shows that self-

healing occurs within the damaged region. In other words, the supramolecular structure with π-π stacking and hydrogen bonding interactions is involved in the self-healing in the damaged region. Alternative possibilities such as fractionation on heating, or the involvement of non-supramolecular interactions in the healing process, can be excluded. Fig.2b also contains profiles obtained on cooling back to 30 ^{o}C, following annealing. The three profiles plotted (two in undamaged regions, one in the previously damaged location) all superpose. The profiles have a different background to those measured during annealing, but contain the same diffraction features confirming that the healed structure is retained.

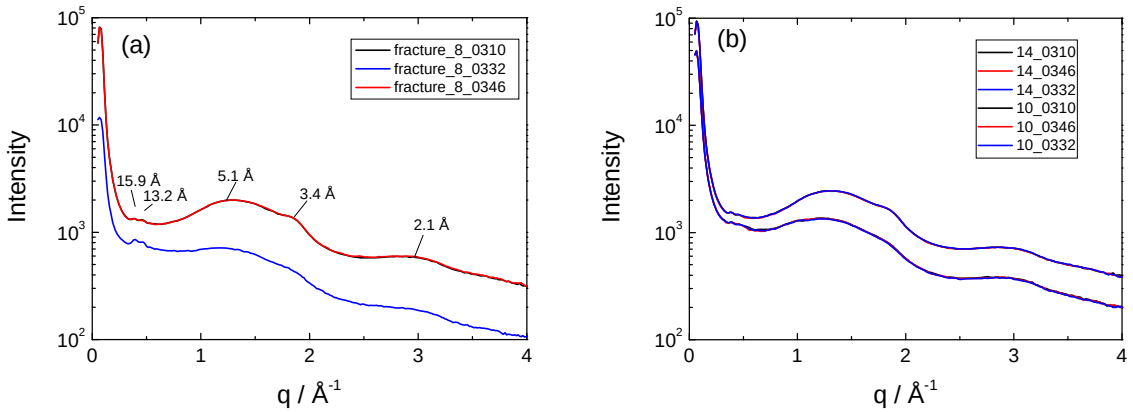

Fig.2. Integrated XRD profiles corresponding to arrowed patterns in Fig.1. (a) At room temperature, prior to healing (b) top (superposed) profiles – during annealed at 120 ^{o}C, bottom (superposed) profiles – cooled to 30 ^{o}C after annealing.

In summary, these data indicate that self-healing occurs via re-establishment of hydrogen bonding and π-π stacking interactions in the damaged region. This work is presently being prepared for publication.[2]

References

1. Burattini, S.; Greenland, B. W.; Merino, D. H.; Weng, W. G.; Seppala, J.; Colquhoun, H. M.; Hayes, W.; Mackay, M. E.; Hamley, I. W.; Rowan, S. J. *J. Am. Chem. Soc.* 2010, 132, (34), 12051.
2. Greenland, B. W.; Burattini, S.; Hayes, W.; Colquhoun, H. M.; Hamley , I. W.; di Cola, E. *Macromolecules* 2011, to be submitted.