

SELF-HEALING SUPRAMOLECULAR POLYMER AND POLYMER NANOCOMPOSITES

Zhen Liu, Nicolaas. A. M. Besseling, Eduardo Mendes, Stephen J. Picken

Delft University of Technology, Faculty of Applied Science, Department of Chemical Engineering,
NanoStructured Materials (NSM) group,
Julianalaan 136, 2628BL, Delft, the Netherlands.
Email: zhen.liu@tudelft.nl

Keywords: Self-healing, Supramolecular polymers, Nanocomposite, Mechanical testing,

ABSTRACT

Self-healing supramolecular polymer and polymer nanocomposites are systems capable of recovering their initial appearance and restoring their mechanical properties after loading and damaging. Different from 'one-time' self-healing materials, in which solvent or reactant stored in micro-pockets are consumed upon self repair, supramolecular systems may in principle retain their self-repairing capabilities indefinitely. Reversible physical cross-links drive the dynamic self-healing mechanism, therefore damage cures spontaneously after fracturing occurred. Reversible physical bonding, such as hydrogen-bonding (H-bond) and the low glass transition temperature (T_g) are the main factors determining the healing process, since chain mobility is necessary to form new reversible bonds when the initial intermolecular cohesion broke. In order to combine such self-healing capability with good material properties, nano(sized) particle reinforcement is investigated. Nanoparticles in various morphologies (platelet, rod, fibre and sphere) and grafted with appropriate surface modifiers will be investigated for their potential to provide mechanical strengthening without causing phase separation. A combination of the chemical cross-linking and the physical cross-linking is considered, where the permanent chemical cross-links assist with maintaining and restoring the shape, while supramolecular bonds do their healing work. If the permanent cross-linking structure can be evenly introduced into the supramolecular polymer and serve as a compatible frame as it is expected, the supramolecular polymer will be able to prevent creep.

The material currently investigated is boric acid terminated low molecular weight (Mw) hydrolysate of polydimethylsiloxane (PDMS). The idea is that PDMS hydrolyzes randomly in the presence of trace of water at elevated temperature, to produce hydroxyl terminated low Mw PDMS (diol), then boric acid is grafted to the ends of PDMS by a condensation reaction with the $-OH$ ends of PDMS. These polar, H-bonding chain ends tend to cluster thereby forming a reversibly cross-linked network. Since there is not enough space around the oxygen atoms in the backbone (Si-O-Si) due to the methyl groups, they will not be significantly involved in H-bonding. The polycondensation product of dichloromethylsilane (CH_3SiHCl_2), whose general formula is given as $-(CH_3SiHO)_n-$, is considered as an interesting alternative of PDMS and scheduled as a next-step matrix in our work. In this case, lateral H-bonding becomes feasible due to the extra space in the siloxane backbone.

Although boride (boric acid, borax, boron oxide, etc) modified PDMS has been around for quite some time and used rather extensively, surprisingly not much has been published about the actual mechanisms and chemical structures responsible for the pronounced effects of these modifications, besides three hypothetical molecular structures [1]. Therefore, we are currently investigating the modification of PDMS through Fourier Transform InfraRed (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy, in order to characterise the chemical nature of the Boride modification. FTIR has been applied to the boric acid terminated PDMS, which has been named as polyborodimethylsiloxane (PBMS) by previous researchers. Figure 1 shows the FTIR spectra of the PBMS, shoulder between 1000 and 1100 cm^{-1} indicates the Si-O-Si backbone, and peak located at 1260 cm^{-1} corresponds to the Si-(CH_3)₂ segment. Peaks at 1340 cm^{-1} and 1380 cm^{-1} are assigned to the

formation of Si-O-B and B-O-B [2] bonds, respectively. A weak cut-off around 3250cm^{-1} demonstrates bonded B-O-H segment, which might attribute to the dynamic physical cross-links (H-bonds). Peaks at 3650 cm^{-1} and 3700cm^{-1} are the characteristics of free B-O-H [3] and Si-O-H [4] segments. Peña-Alonso [5] has proposed that the formation of Si-O-B bond also results a shoulder in the region of $880\text{-}930\text{cm}^{-1}$, unfortunately it is not seen in our inspection.

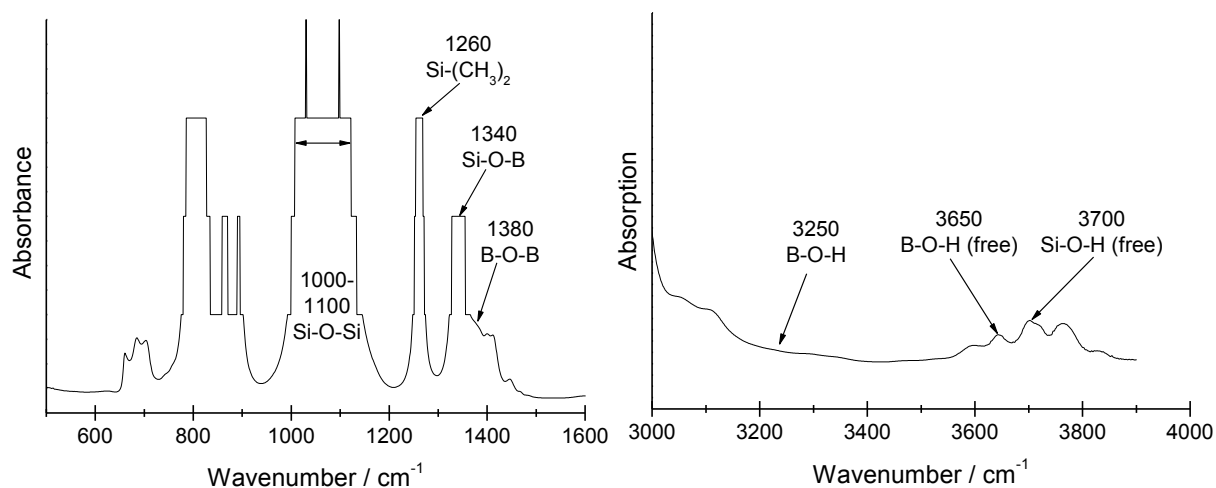


Figure 1: High resolution FTIR spectra of the boric acid terminated PDMS (PBMS).

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