

SELF-HEALING SUPRAMOLECULAR POLYMER NANOCOMPOSITES

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ABSTRACT

Polyborosiloxanes (*PBSs*) are viscoelastic, transparent, colourless, self-healable polymer matrices, synthesized by reacting linear polydimethylsiloxanes (*PDMSs*) with boric acid (*BA*) above 150°C. *BA* takes part not only in cleaving the *PDMS* chains, but also contributes boronic-acid like moieties to the cleaved chain ends, which provide supramolecular self-healing capabilities. *PBSs* can be regarded as supramolecular elastomers, owing to the reversible cross links formed by the abundant hydroxyl groups. Therefore they are able to recover both the microscopic and macroscopic fractures intrinsically via hydrogen-bonds. Additionally, a glass transition temperature (T_g) as low as -90°C ensures chain mobility to *PBSs* molecules to heal cracks autonomously without extra heat supply. Compared to traditional carbon-based polymeric materials, *PBSs* provide a higher resistance to heat and light owing to the siloxane backbone. Upon increasing the degree of modification, *PBSs* get stronger on the one hand. However, *PBSs* also become less adhesive and start suffering from brittle fracture. Interestingly, the addition of nano-clay (*Cloisite 30B*) solves this problem. It does not make *PBSs* more brittle as it does in traditional thermal plastics. Instead, it renders *PBSs* ductile but strong. Comparing to *PBSs*, the *PBSs/Cloisite 30B* nanocomposites even exhibit an additional filler-induced mechanical relaxation at high frequency. This phenomenon implies that *PBSs/Cloisite 30B* nanocomposites can be applicable as self-healing shock absorber. Further investigations will be focusing on characterization of the self-healing capacity, on strengthening the composites and on tuning the position of the filler-induced rheological response.

Upon applying other (nano-sized) reinforcements, *PBSs* can be endowed with wide variety of targeted functionalities, for instance, stiffness by nano-clay; thermal conductivity by graphite or boron nitride; piezoelectric properties by lead zirconate titanate (*PZT*), etc. The presence of particles is also advantageous for the adhesive properties of the composites, because particles lower the number of hydrogen-bonds by, either isolating molecules or forming particle-molecule interaction.

1. INTRODUCTION

Polyborosiloxanes (*PBSs*) were invented during the World War II in the U.S.. The goal was to look for synthetic rubber compounds to solve the shortage of natural rubber. However, *PBSs*, possessing reversible physical cross-links, were born accidentally, and served the world for decades under the names, Silly Putty, bouncing putty¹, Solid-liquid², dilatant compound³, etc.

In the field of self-healing materials, two main mechanisms exist, encapsulated systems and intrinsic systems. One ‘family’ relies on the implanted capsules, which contain healing agents. Upon loading, capsules may break and the released healing agent in order to close local cracks. In intrinsic systems, the cross-links among molecules are physically reversible. So in principle, the intermolecular disconnection due to fractures can reconnect autonomously whenever it appears. PBSs constitute an important contribution to the intrinsic self-healing family, as they are outstanding self-healing matrices, which have the potential to deliver abundant self-healing composites by adding functional filler particles. For instance, nano-clay increases the stiffness of PBSs; graphite and boron nitride give rise to thermal conductivity; lead zirconate titanate (*PZT*) enhances piezoelectric property, etc.

This paper will present the characterization of the lab-synthesized *PBSs*, the properties of *PBSs*/filler composites, and efforts to quantify the self-healing capabilities of *PBSs* and their composites.

2. MATERIALS AND METHODS

Trimethylsiloxy terminated polydimethylsiloxanes (*PDMSs*) and boric acid (*BA*) are heated at 200°C to produce the viscoelastic *PBSs*. The siloxane backbone of *PDMS* cleaves in the presence of *BA*, which leads to a $-\text{SiOB}(\text{OH})_2$ structure at the new chain ends. n-Hexane is used to dissolve the products, in order to filter out unreacted *BA* and other unexpected side-products.

Nano-sized clay platelets (*Cloisite 30B*), graphite, and lead zirconate titanate (*PZT*) give rise respectively to stiffness, thermal conductivity, and piezoelectric properties. Brabender blander is used to mix the filler particle with *PBSs* matrix, in order to prepare the *PBSs* composites.

Fourier transform infrared (*FTIR*) spectroscopy is used to characterise the cleavage of the siloxane backbone, generation of Si–O–B linkages, and the presence of *BA* as impurity. By means of a TA AR-G2 rheometer, the self-healing capacity of *PBSs* matrices was also quantified in the plate-plate geometry.

3. RESULTS AND DISCUSSION

Figure 1 shows the *FTIR* spectra of pure *PDMSs* that have been held at 240°C for different durations. The absorption bands correspond to specific chemical groups, for instance, peaks in the range of 1020–1090 cm^{-1} present the vibrations of the siloxane backbone⁴. Other bands⁵ correlated to our research assign to, $-\text{Si}(\text{CH}_3)_2$ at 880 cm^{-1} and 1260 cm^{-1} , $-\text{CH}_3$ at 2905 cm^{-1} , and $-(\text{CH}_3)_2$ at 2960 cm^{-1} , etc. Upon heating, the spectra of pure *PDMSs* do not change with time, except for a slight decrease of the band corresponding to the siloxane backbone. This implies *PDMSs* are quite resistant at 240°C, besides a minor degree of backbone cleavage, due to residual water molecules.

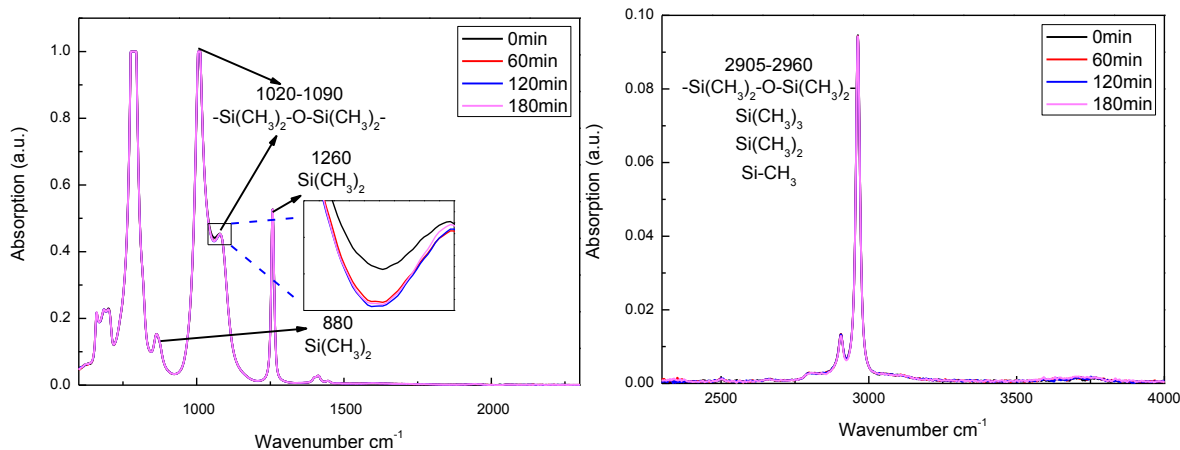


Figure 1: FTIR spectra of the pure PDMSs heated at 240°C

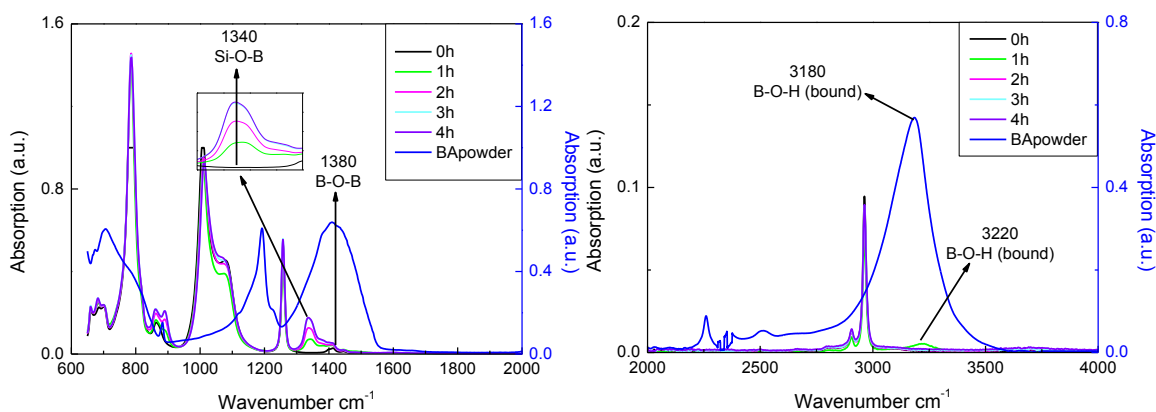


Figure 2: FTIR spectra of a mixture of *PDMSs* and *BA* reacted at 200°C for different reaction times

Boric acid (*BA*) plays a crucial role in the cleavage of polydimethylsiloxanes (*PDMSs*) backbone. In the presence of *BA*, *PDMSs* undergo backbone cleavage in a less rigid condition (above 150°C⁶⁻⁸). Polyborosiloxanes (*PBSs*) were synthesized by mixing *PDMSs* and *BA* at a weight ratio of 10:1 at 200°C in this work. To observe the change in the molecular structure of *PDMSs*, *FTIR* spectroscopy was applied on samples with various reaction times. Figure 2 introduces three relevant new bands. At 1340 cm^{-1} , a peak appears and grows as the reaction continues, which is assigned to the Si-O-B linkage. Its appearance signifies that *BA* has connected to the siloxane backbone. Bands around 1380 cm^{-1} and at 3180 cm^{-1} correlate with the B-O-B and the bound B-O-H structures in the crystalline boric acid. The absence of B-O-B assigned band in our *PBSs* indicates that our reaction procedure does not involve significant boric acids polymerization, Hence no big, branched molecule is produced. The B-O-H assigned band exists in *PBSs* in the early stages (1h), but vanishes later. The reason is, the B-O-H structure in *BA* crystals dissociates and is consumed during the reaction.

We have designed an approach to quantify the self-healing capacity using the rheometer, where we program the rheometer to perform cyclic pulling and squeezing. By measuring the normal force of each step, the self-healing behaviour can be roughly quantified. Pure *PDMSs* served as reference (in black) and experiments were

run at two operation temperatures (Figure 3). In both cases, the normal force vs. gap (sample deformation, in μm) plot of the 2nd pulling step (in pink) is well overlapping with the 1st pulling step (in red) after resting, which indicates the deformed *PBSs* have healed cohesively and autonomously. Additionally, an increase in healing temperature shortens the healing time.

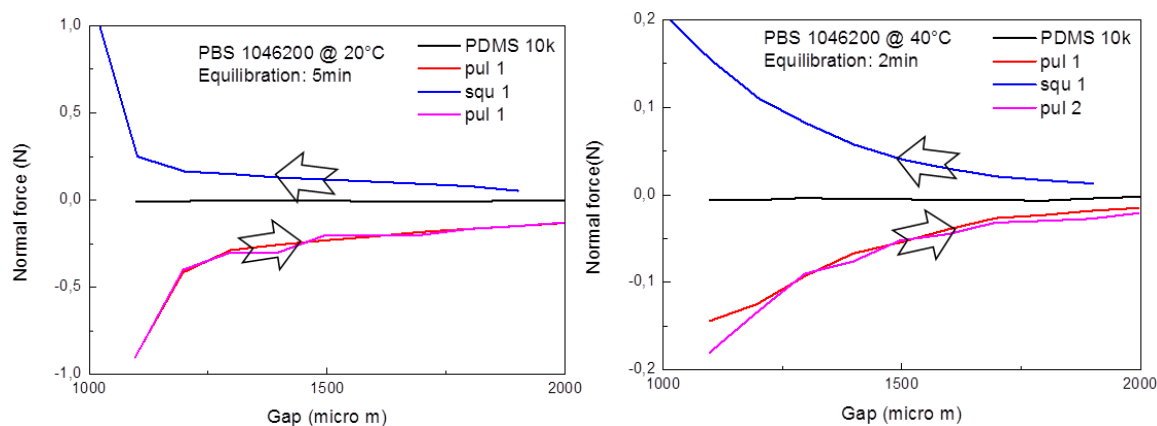


Figure 3: Quantification of the self-healing capacity.

4. CONCLUSIONS

Formation of the Si–O–B moieties in polyborosiloxanes (*PBSs*) has been demonstrated by *FTIR*. Together with the absence of B–O–B, we announce that the intention of producing a class of supramolecular self-healing materials has been accomplished. A cyclic pulling and squeezing experiment has proved that *PBSs* are capable of self-healing, intrinsically and autonomously.

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