Polymer - Particle Dual Network: Towards concomitant self-healing & load-bearing properties in intrinsically SH materials

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We have designed, prepared, and characterized a class of advanced intrinsic self-healing polymer nanocomposites (SHPC). It consists of a self-assembled filler skeleton formed by nanoparticles embedded in a continuous phase of a supramolecular elastomer. The ability for an intrinsically self-healing material (SHM) to repair itself is achieved by keeping the required mobility in the system while using nanoparticles to enhance the overall stiffness and resilience. This means that it is indeed possible to design a material that reconciles both mobility and stiffness. The reinforcing skeleton that interpenetrates through the polymer matrix not only prevents the supramolecular elastomer matrix from flowing, but also provides the nanocomposite with load-bearing capabilities. By fine tuning the nanoparticle-molecule adhesion, the particle aspect ratio, and the particle network formation, we are able to obtain either a load-resistant nanocomposite without prolonging the healing time, or a thixotropic composite.

1. INTRODUCTION

A variety of self-healing mechanisms has been proposed in the past where for polymer materials most methods rely on the use of encapsulated reagents, solvents, or adhesives to supply the damaged zone with a healing agent[1]. However, the mobility and associated healing mechanism is not an inherent part of the material. In the inherent SH mechanism proposed here, we make use of insight in the dynamics of supramolecular polymer nanocomposites to design a material that has stiffness while maintaining local molecular mobility[2]. The local mobility provides the material with the capability to repair itself multiple times at the same location as no chemicals are consumed during the healing process.

Normally any level of local molecular mobility will cause a substantial loss of stiffness and may lead to spontaneous flow. However, in the case of high aspect ratio polymer nanocomposites it is possible to achieve a sensible level of stiffness and resistance to flow, a yield stress, while maintaining the dynamic nature of the molecular interactions. Thus stiffness and mobility are not mutually exclusive.

In this work we describe the properties of boric acid end group modified poly(dimethylsiloxane), PBS, implanted with various high aspect ratio nanofillers such as graphene oxide, and the organically modified clay. A yield stress was indeed induced by the application of high aspect ratio particles, but the particle-molecule adhesion determines if it results in a stiff elastomer, or a thixotrope.

2. MATERIALS AND METHODS

Chemicals

Polydimethylsiloxane (PDMS) (ABCR, Germany.), and boric acid (BA) BP168-1 (Acros Organics, Belgium.) were purchased for the synthesis of polyborosiloxanes (PBSs). Cyclohexane of reagent plus grade (Sigma-Aldrich), and isopropyl alcohol (IPA) (Fisher Scientific) were used for refining, and preparing nanocomposites.

Organo-modified clay (OMC) were provided by Rockwood Additives (BYK-Chemie, Germany). Graphene oxide (GO) flakes were purchased from Graphene Supermarket (USA). Dimethyldioctadecylammonium chloride (DDA-Cl) was purchased from Sigma-Aldrich and used for the surface modification of GO.

Sample preparation

Polyborosiloxane (PBS) was synthesized by heating the mixture of polydimethylsiloxane and boric acid at 200°C at a weight ratio of 10:1. The synthetic and refining procedures, basic characterization are available in our preview paper[3].

0.82 g of GO flakes and DDA-Cl (ca. 1.88 mmol) were separately dispersed and sonicated in 500 ml of demineralized (demi) water. Their mixture was stirred at 60 °C and 400 mbar for 40 hours. We filtered this mixture and washed the filter cake with demi-water until the pH value of the filtrate was close to 7. After freeze drying, and we could collect a brown fluffy powder in the end.

Self-healing nanocomposites were prepared by dissolving PBS into the pre-sonicated filler/IPA mixture. The mixtures were heated with heating plate at 60 °C, until most of IPA vanished. The samples were processed into thick films (≈1 mm) for rheology.

3. RESULTS AND DISCUSSION

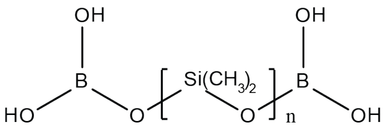

Figure 1. Molecular structure of an inorganic-organic hybrid PBS molecule.

Figure 1 shows that a PBS molecule possesses an apolar siloxane backbone and two polar borono groups. The average molar mass and glass transition temperature of the synthetic PBS are about 1600 g/mol and -90 °C respectively[3].

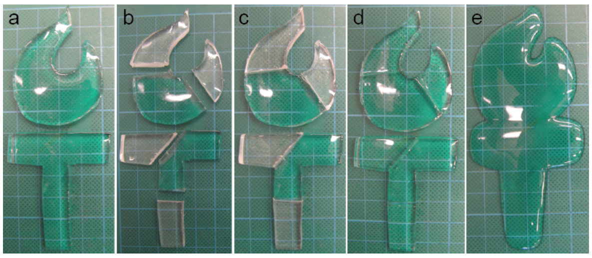

Figure 2. Graphic demonstration of the self-healing process of a PBS sample.

Figure 2 is a record of the complete self-healing process of a torch-shaped sample of PBS. It was cut (Fig. 2b), reassembled (Fig. 2c), healing for 5 min (Fig. 2d) and 10 h (Fig. 2e), without compression yet in a mold. It rendered a scar free and plumper torch in the end. This confirms the mobility of PBS molecules, which is essential for the self-healing mechanism of PBS.

We announce a ’separation of time-scales’ concept. The relatively fast dynamics, associated with the terminal relaxation time of the supramolecular elastomer, which enables recovery of the cross-links after fracture, should be preserved. At the same time the dynamic elastic modulus at low frequencies (long time scales), which vanishes for a supramolecular elastomer, should be enhanced.

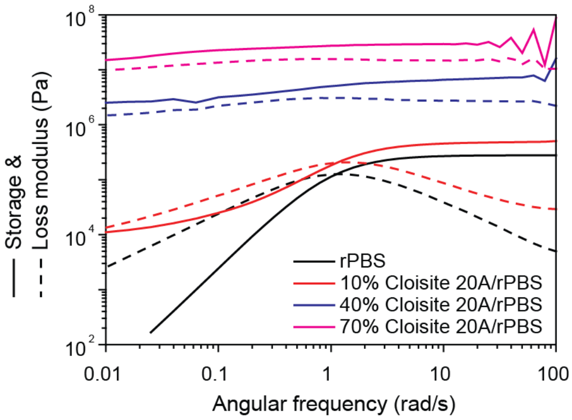

Figure 3. Dynamic shear moduli of the OMC/PBS nanocomposites.

Figure 3 shows upon increasing the filler content, both G’ and G” are dramatically enhanced, as well as the broadened G” curves. At a filler mass fraction of 0.7, G’ and G” of the nanocomposite is no longer frequency dependent. As expected, the OMC/PBS nanocomposites show an unaltered terminal relaxation time (1.26 s), which hardly deviate from that of PBS (0.9 s). The OMC/PBS nanocomposites show additional plateau at the lowest programmable frequency (G’ at 0.01 rad/s is abbreviated as $G'_{0.01}$). If we assume $G'_{0.01}$ as the elasticity of the static filler-skeleton and represent the mechanical contribution of the skeleton as a second spring connecting in parallel to the Maxwell arm, we can interpret the rheological results with the standard linear solid (SLS) model.

Incorporation of GO platelets in PBS leads to an extraordinary softening effect. The shear rate *vs.* shear stress plot in Fig. 4 clearly demonstrates that the 1% GO/PBS nanocomposite is a shear thinning fluid with a yield stress, but PBS is a Newtonian fluid. The inserted graph in Fig. 4 shows the same plot over a smaller shear stress range, which clearly demonstrates the presence of a yield stress for the 1% GO/PBS nanocomposite. To describe this behaviour we used the Herschel-Bulkley equation[4].

$$\sigma = \sigma_Y + \kappa \cdot \left(\frac{d\gamma}{dt}\right)^n \qquad \text{Eq (1)}$$

where σ, σ_Y, and d_γ/d_t represent the shear stress (Pa), yield stress (Pa) and shear rate (1/s), respectively. The κ and n parameters are empirical constants. The Herschel-Buckley model fits the experimental results precisely, and provides us with a yield stress of about 19 Pa. The two fitting constants are κ = 4.5 and n = 0.7.

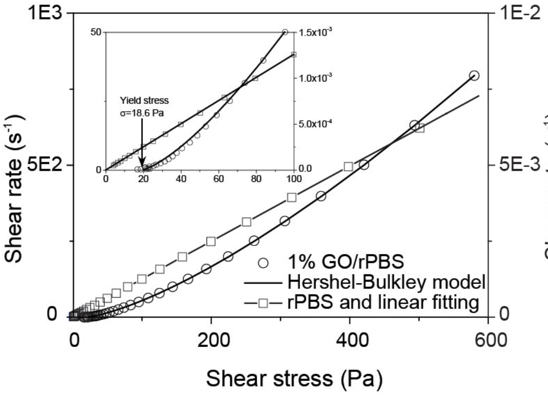

Figure 4. The Shear rate vs. shear stress relation of the PBS (right y-axis) and the 1% GO/PBS nanocomposite (left y-axis).

Furthermore, this liquid nanocomposites can be transformed into a self-standing elastomer upon dehydration, as condensation can occur between a fraction of borono groups (PBS) and the polar groups of GO at elevated temperatures. It thus leads to a solid composite, in which the outstanding mechanical properties of GO are able to take over and function. As the condensation reaction is reversible, it provides a fully reversible liquid-solid transformation.

4. CONCLUSIONS

We are able to manufacture a fast-healing free-standing nanocomposite, or a thixotropic fluid by carefully design the particle-molecule interactions. This class of materials we believe is particularly promising for dynamic and intermittently loaded samples e.g. for impact and ballistic performance. The studied materials are not only very cheap and easy to make but also provide nearly ideal model systems for further study e.g. they are perfect Maxwell and Herschel-Bulkley fluids.

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