MULTIPLE HEALING IN MULTI-FUNCTIONAL POLYMER COMPOSITES

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ABSTRACT

In this work, we investigate the formation of self-healing systems that are able to recover more than once more than one (mechanical or other physical) functionality. To this aim composites were created consisting of a polysulfide thermoset rubber matrix having intrinsic self-healing properties filled with thermally/electrically conductive particles.
The cohesion, adhesion and thermal/electrical conduction recovery of these composites are investigated, monitored and quantified as function of the filler type and content. Moreover, the effects of healing temperature and the intrinsic polymer structure on the kinetics and degree of property recovery are explored.

1. INTRODUCTION

With the introduction of self-healing concepts in material science, materials having the ability to recover their functionality autonomously or upon a mild thermal stimulus did become a reality. To date, self-healing concepts have been applied mainly to structural materials that have to carry mechanical loads or materials that have a protective function against mechanical impact. In this respect, only one functionality (strength) is to be “healed” via the imparted self-healing mechanism. Intrinsic self-healing polymeric materials [1-3] enable the creation of self-healing composites that have the in-built capability of multiple healings at sample locations having failed earlier [4]. This approach is expected to enhance and increase the reliability of composite functionality as a function of the service time and is very promising for opto- and microelectronic applications [5]. In the present work, we investigate the synthesis and characterization of a new type of thermally and/or electrically conductive self-healing composites using a polysulfide rubber thermoset as the matrix [1] and either hexagonal BN or graphite particles as the conductive fillers. The recovery of the functional (electrical and thermal conduction) and mechanical (cohesion and adhesion) properties upon low temperature annealing is described. A very high degree of multiple healing of both mechanical and physical properties was demonstrated for composites containing up to 40% of conductive filler particles.

2. MATERIALS

The composites were produced by mixing an uncured thermoset rubber with sub-micrometre graphite flakes or 5 μm hexagonal BN particles as filler. The amount of the fillers in the composite was varied from 10 to 40 vol%. The synthesis procedure is based on a basic catalysed condensation of epoxy functions with thiols. In a typical procedure, a stoichiometric amount of epoxidized polysulfide Thioplast™ EPS25-aliphatic (640 g/equ.) provided by AkzoNobel BV is mixed with Pentaerythritol tetrakis(3-mercaptopropionate) (~122 g/equ) from Aldrich. 4-dimethylaminopyridine (Aldrich) was used as the catalyst and it was applied at a 1 (wt)% level. Finally, the composites were prepared by adding the fillers to this slurry. After mixing for 2 minutes at 2500 rpm using a high speed mixer, the pastes obtained were poured into a 1 mm thick mould, levelled and cured at 65°C for 2 hours.

3. METHODS

The thermal conductivity of the materials was investigated using the modified transient source technique using a TCi C-Therm apparatus. The adhesive behaviour of the composites was investigated by means of single lap shear tests. To this aim, a known surface of already cured resin (12.5*25 mm, thickness 1 mm) was sandwiched between two identical aluminium 6082-T6 strips (L*W*T = 100*25*2 mm) with an overlap length of ~12.5 mm. The adhesion to the plates was promoted by a 2 h thermal treatment at 65°C. During the thermal treatment the composite and the two parts of the sample were kept in contact using a paper clip. In order to study the adhesion recovery upon thermal healing, the sample ends were repositioned carefully at the end of each lap shear strength test and the thermal treatment was repeated. To investigate the cohesive healing ability, the composites were cut using a fresh razor blade. The cut pieces were put back together and placed between two glass slides. The quantification as function of the healing time of the cohesive healing ability was investigated both at 65 and at 100°C. For this purpose, the samples were taken out from the oven during the healing procedure at different time interval and the evolution of the dimension of the initial cut (width and area) was monitored using a Leica optical microscope. Recovery of electrical contact upon healing was investigated using impedance spectroscopy with an Autolab potentiostat–galvanostat in combination with a frequency response analyser.

4. RESULTS

The composites produced are based on a rubber thermoset that does not exhibit any adhesive or cohesive functionality at room temperature. However, by annealing at 65^0 C for several minutes the composite materials, irrespective of the filler fraction, shows clear adhesive healing (Figure 1). Moreover, after each failure/healing cycle, the composites are able to regain the same level of adhesion. The adhesive strength varied with the filler type and content. A maximum adhesive strength of 0.4 and 0.5 MPa was achieved for the composite loaded with 30 vol% of graphite and BN, respectively.

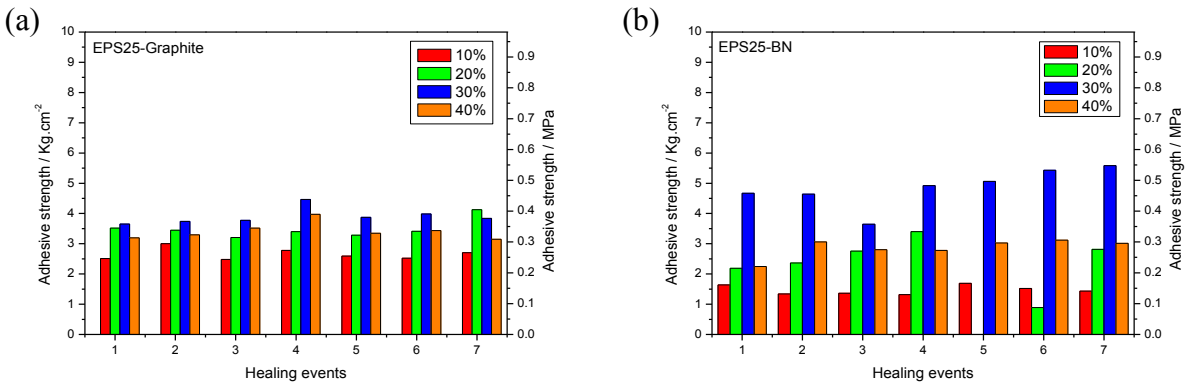

Figure 1: Adhesion as function of the healing events at 65°C for (a) graphite and (b) BN filled composite with different filler content.

In addition to adhesion recovery against an aluminium substrate, the composites also demonstrated a very attractive cohesion recovery behaviour. At lower filler contents (up to 20%) an annealing temperature of 65°C was sufficient to obtain full healing in 10 minutes (Fig 2b), while at higher filler contents (40%) full healing could only be obtained at 100°C (Fig 2a).

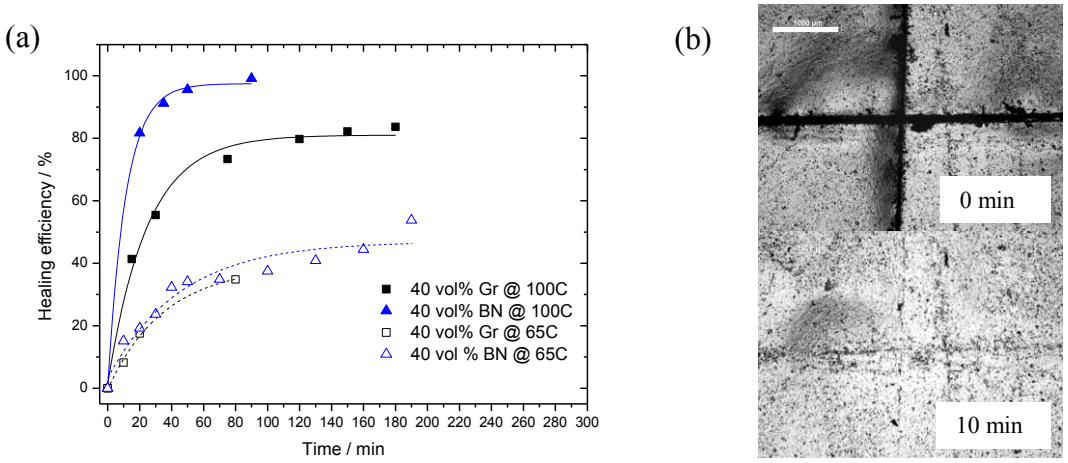

Figure 2: (a) Comparison of the cohesive healing efficiency at 65°C (open symbol/dotted line) and at 100°C (full symbol /full line) of EPS25 and EPS70 composites loaded with 40 vol % of graphite or BN. (b) Micrograph showing the cohesive healing recovery of EPS25-20 vol% graphite composite before and after 10 min healing time at 65°C (scale bar 1 mm).

The healing behaviour is more or less similar for BN fillers as for graphite fillers: the cohesive healing efficiency is 75 and 40% for the composite loaded with 30 and 40 vol% of BN, respectively. If the healing temperature is increased to 100°C, the cohesive healing efficiency and the healing kinetic are increase in almost all cases, leading to 100% efficiency for all BN filled composites.

The thermal conductivity of the composites increased with the filler content. While the pristine polymer has a thermal conductivity of 0.25 W/mK the composites reached values of 2 and 1 W/mK at 40 vol% loading using graphite and BN filler, respectively. The restoration of the thermal conductivity proceeds with the restoration of the mechanical properties. By nature the BN based composites are electrical insulators

whereas the graphite-based composites are electrical conductors. Hence graphite based composites also show an increase in the electrical conductivity with increasing graphite content. The graphite loaded composites showed recovery of both their thermal and electrical conductivity upon restoration of their adhesive or cohesive properties.

5. CONCLUSIONS

Multifunctional healing in functional polymer composites showing a good thermal and/ or electrical conductivity can be created by combining a matrix with intrinsic self-healing properties and loading it with conductive fillers. The resulting self-healing response can be tuned as function of the matrix polymeric backbones and the filler type. Fillers enhance the adhesive and conductivity properties of the composites whereas the cohesive response is mainly hampered when the filler content is relatively high. This decrease in cohesion recovery can be tackled by increasing the healing temperature to enhance the system mobility. The self-healing composites are able to restore their interfacial strength values as well as their bulk (thermal and electrical) conductivity even after multiple failure events.

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