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Severe graphene nanoplatelets aggregation as building block for the preparation of negative temperature coefficient and healable silicone rubber composites

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ABSTRACT

With the request of higher performance in automotive products, sealing components and materials resisting to severe conditions, the performance requirements for silicones are becoming ever more diverse and sophisticated. In this article we prepared silicone rubber (SR)-graphene nanoplatelets (GNPs) composite via liquid mixing method; the mechanical strength of the GNPs estimated by applying quantized fracture mechanics suggested a severe GNPs agglomeration that was confirmed by scanning electron microscopy analysis. We observe that such SR/GNP composite behaves as a negative temperature coefficient material, exhibiting electrical resistance decrease with temperature increase. It was also shown how the damaged SR/GNP composite can be healed by simple thermal annealing. The healing mechanism was rationalized in terms of "living" reactive species that are not consumed by curing at room temperature and promote, when thermally activated, the crosslinking among the damaged network of oligomers. The healing efficiency, expressed as crack length vs. annealing temperature, has been estimated again applying the principles of quantized fracture mechanics. These results could satisfy many of the demanding requirements of the silicone rubber materials used in daily life and indicate that SR/GNP composites can act as healable and temperature sensor materials e. g. for seals, hoses and automotive sector.

1. Introduction

Rubber materials are commonly considered the workhorse of the industrial and automotive rubber products industries [1–3]. As a significant candidate of them, the silicone rubber (SR) offers a unique combination of chemical and mechanical properties that organic elastomers cannot match. Silicone rubber withstands high and low temperatures far better than organic rubbers. Silicone rubber can be used indefinitely at 150 °C with almost no changes in its properties. It withstands use even at 200 °C and some products can withstand heat of 350 °C for short periods. Silicone rubbers are thus suitable as a material for rubber components used in high temperatures environments. These properties make silicone rubber the most used material for applications in extreme temperature conditions due to its good thermal stability and especially excellent elasticity [4,5]. Moreover, such soft and flexible materials have attracted attention due to their potential applications in advanced strain sensors [6–8].

Silicone rubbers are usually reinforced with carbon black, carbon nanotubes and graphene nanoplatelets to obtain improvements in thermal and electrical properties [9–11]. Compared with the traditionally used reinforcing fillers like silica, graphene nanoplatelets (GNPs) have recently attracted attention as a negative temperature coefficient material [12], exhibiting rapid electrical resistance decrease with temperature increase. Kong et al. [12] demonstrated how the electrical resistance is size dependent,

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decreasing with increasing the graphene thickness. These findings could suggest that agglomeration can be a viable method to produce negative temperature coefficient materials. It was also found that GNPs were similar to conventional negative temperature coefficient materials and this finding suggests the potential use of GNP based composites for temperature sensors in rubber made automotive components.

Elastomeric applications are also susceptible to mechanical and chemical damage (e.g. scratches, cuts and punctures). Such damages result in the loss of the originally intended functions of the elastomers leading to spillage, contamination, safety hazards or just lost of performance. Such damages are particularly problematic when the elastomers are used as seals, hoses and coatings. After the occurrence of the first cracks or surface damage, the material is especially susceptible to further damage. For this reason, seals, hoses or coatings have to be frequently checked and mended or even replaced with the subsequent cost. The development of elastomers with self-healing properties, i.e. the realization of structures able to repair mechanical damage, is an important challenge from industrial point of view for the development of polymeric materials that have much greater lifespans than currently available.

For decades, the scientific community focused the attention to developing self-healing polymeric materials to improve the safety and lifetime [13]; the storage of healing agents in the materials that are released upon damage is the most used approach. This technology generally consists in the exploitation of microcapsules [14–16] which store the healing agents into the polymer matrix. The healing agent is released from the crack to then restore it. The main drawbacks of such approach consist in the possibility to heal the material only once at the same location and the reduction of mechanical properties due to the inclusion of microcapsules in the polymer matrix that behaves as defects. Some outstanding results to overcome the utilization of microcapsules came from Leibler et al. [17] that used a mixture of fatty diacid and triacid condensed with diethylene triamine and then reacted with urea giving a cross-linked rubber that in contrast to conventional cross-linked rubbers made of macromolecules, when cut, can be repaired by bringing together fractured surfaces to self-heal at room temperature. A step forward toward silicone based elastomers has been obtained recently by Bao et al. [18] who synthesized a network of poly(-dimethylsiloxane) polymer chains crosslinked by coordination complexes that combines high stretchability and autonomous self-healing. The most common silicones are the polydimethylsiloxanes, trimethylsilyloxy terminated, with the following structure $Me_3SiO(SiMe_2O)_nSiMe_3$ and many of such silicone polymer systems involve the reaction of a silane-hydrogen (SiH) component with a silanol (SiOH) component. Thus the presence of free silanol groups can be used to catalyse the healing of such polymers when activated by temperature. For example, very recently it was shown [19] that silicone-based sealants exposed to a hydrocarbon flame, can be easily healed. In this case healing did not require the delivery of coordination complexes [18,19].

As stated by the above recent works the research on self-healing organic polymers has grown recently, but one simple self-healing mechanism from more than 60 years ago has been nearly forgotten until Zheng et al. [20] have demonstrated that silicone rubber that has been cut in half can completely repair itself through heat-activated reversible bonding. They showed that the healed interface had strength comparable to the cohesive strength of the undamaged elastomer. They obtained a completely self-healed silicon rubber at 90 °C for 24 h. The temperature thus is a crucial parameter that can be used to heal silicone rubbers and a viable method could be the addition of thermally conductive inclusions into the polymer matrix for a better heat transfer.

Because thermal conductivity of elastomers is very low, the heat build-up is harmful to elastomers, because elastomers are susceptible to thermal degradation [21,22]. Composites with carbon-based fillers showed thermal stability, light weight, and high thermal conductivity [23,24].

These properties prompt us to believe that integrating GNPs with SR with free silanol groups might generate a novel healable composite material, which deals self-repairing by thermal annealing and temperature activation of the electrical conductivity. Our material paves potential applications in sealing and temperature sensors of automotive components.

2. Experimental details

Liquid rubber (GLS-50 purchased from PROCHIMA®) was used for casting with a cold cure by poly-condensation. Before using, we add to the rubber 5% of T30 catalyst (purchased from PROCHIMA®). The complete vulcanization takes 18–20 h at room temperature. To accelerate this process, the blend was put in a warm place (30 C°), but the reaction was too fast and did not allow the escape of air bubbles.

GNPs were purchased from Cheaptubes (bulk density 0.04g/cm^3, thickness 8–15 nm, lateral dimension about 1.5 μm). GNPs were dispersed in liquid silicone rubber (1%wt.) through the utilization of a Dispermat (500 rpm for 1 h) to facilitate the dispersion of GNPs. Then the catalyst was added. The liquid composite was deposited onto a silicone mould and the vulcanization was obtained in 18–20 h at room temperature.

The melting behaviours of the samples were tested by differential scanning calorimeter (DSC) using a TA Q200 DSC analyser under nitrogen atmosphere. Samples were heated from −80 °C to 150 °C, cooled to −80 °C, and heated to 150 °C again. In all heating and cooling cases, the rate was set at 10 °C min^{-1}. Thermogravimetric analysis (TGA) were performed in nitrogen with a TG/DTA Extar 6300 at a heating rate of 10 °C min^{-1}. Field emission scanning microscopy (FESEM) was used to investigate the cross section of the samples obtained by fracture in liquid nitrogen.

Neat silicon rubber (SR) and silicon rubber added with GNP (SR/GNP) were characterized with Fourier transform infrared spectroscopy (FTIR) to verify the occurrence of the polymerization and the effects induced by the GNP presence. The measurements were realized using a JASCO FT/IR-615 spectrometer, in the 500–4000 cm^{-1} range transmission mode.

The tests were performed on a thin film of the SR and of the SR/GNP: the reactive mixtures consisting of neat SR, SR/GNPs and T30 catalyst were deposited onto silicon substrates and the measurements were recorded before and after the polymerization of the samples that was performed at room temperature for 24 h. A substrate of neat silicon was used to subtract the background spectrum.

SR and SR/GNPs polymerized samples were then post annealed in an oven at 150 °C and at 250 °C for 2 h and FTIR spectra were recorded to investigate the modifications induced by the annealing to their chemical structure.

The electrical characterization of both neat SR and SR/GNP composite was performed, by using a computer controlled Keithley 4200 source measure unit. The electrical current was recorded by biasing the samples at 50 V and 100 V at different temperatures.

The samples were cut into strips of ~100 mm × 10 mm × 2.5 mm. Before healing, a 3 mm cut was made in the middle of the sample along the strip traverse direction, and then the cut sample was healed by thermal annealing in an oven up to 250 °C for 2hr. The mechanical properties were measured by a universal tensile testing machine (Lloyd Instr. LR30K) with a 250 N load cell at room