Heal-on-Demand by Local Heating in Ionomeric Nanocomposites

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ABSTRACT

The research interest on remote-controlled multiple responsive materials has increased over the last few decades. Magnetic nanoparticles have the potential to convert magnetic energy of external alternating fields into thermal energy. The combination of magnetic nanoparticles with soft materials offers new possibilities towards smart adaptive materials that can be manipulated by external magnetic fields. In particular, the local heat dissipation by magnetic nanostructures in oscillating electromagnetic fields (OEMF) provides the option to increase the temperature locally and thus stimulate dynamic processes, e. g. for self-healing. In this work, we systematically investigate the influence of the size, shape, composition and magnetocrystalline anisotropy of the magnetic nano-antennas in an acrylate-based ionomeric elastomer on the heating and healing characteristics. Furthermore the influence of the particle on the dynamic and mechanical properties of the used ionomers is taken into account. The locally dissipated thermal energy in the particles' environment triggers a thermal transition in dynamic polymeric matrices activating the self-healing process. In comparison to known thermally activated systems, the incorporation of nanoscopic heat sources leads to a faster response and allows the contactless, remote-controlled triggering of the sample shape. Under optimized conditions, a particle volume fraction as low as 0.05 vol% is sufficient to reach a healing efficiency of 90 % and higher after 15 min of irradiation.

1. INTRODUCTION

Ionomers have shown to be a promising approach for self-healing elastomers.[1], [2] A particularly promising approach for the initiation of healing is the incorporation of a component into the polymer matrix which can undergo local heating upon the application of external stimuli. This localized heating provides a non-destructive method through an electronic feedback mechanism at the damage site, healing the sample and restoring its original properties. Electrically stimulated self-healing has been reported by the use of conductive component in the form of carbon fiber or metals [3]–[5]. A major disadvantage of this method is the need for direct electrical contact with the material to cause the warming effect. Alternatively, magnetic components can be incorporated into the material and heated remotely (without contacts) via electromagnetic induction. This method of inductive heating has been studied mainly for biomedical applications and is used already in bituminous mastic and asphalt concrete applications.[6] The overall objective of this study is the development, optimization and application of tailor-made, self-healing ionomeric elastomer materials activated by local heating. For this purpose, magnetic nanoparticles will be incorporated into the elastomer matrix which leads to a local and selective heat dissipation in OEMF. These "nano-hotspots" act as antennae for

electromagnetic energy dissipation in order to heat the material intrinsically across the transition temperature and activate the self-healing process.[7]

2. MATERIALS

The ionomer PZn-5.2% (M_w ~ 60.000 g·mol^{-1}, PDI ~ 1.3) used in this study is prepared according to our previously published procedure.[8] Fe_3O_4 nanoparticles (200 nm range) Bayoxid E8706 (FS), E8712 (FC), and E8840 (FR) are provided by Lanxess in 99.5 % purity. Spherical magnetic nanoparticles with a diameter of about 15 nm are performed by thermal decomposition of $Fe(acac)_3$ and $Co(acac)_2$ and cyclic growth. oleyl alcohol, oleic acid and oleylamin have been used as stabilizer and dibenzyl ether as a solvent. Magnetic ionomer nanocomposites are prepared by ultrasound-assisted homogenisation of the respective mixtures (paricles and matrix) in a concentrated solution, followed by slow removal of the solvent.

3. METHODS

Differential scanning calorimetry (DSC) is used to detect the glass transition temperature of the polymer matrix T_g and the transition temperature of ionic aggregates T_i with a heating rate of 10 K·min^{-1}. The dynamic shear storage (*G'*) and loss (*G''*) moduli are measured by oscillatory rheometry using parallel plates of diameter 40 mm and a gap of 1.0 mm. Tensile testing is carried out using 25 mm x 3.3 mm x 2.5 mm pressed sample stripes and an elongation rate of 500 mm/ min. The magnetic heating behavior of ionomeric composite samples is investigated using a high frequency (HF) generator equipped with a water-cooled copper induction coil, operated at 247 kHz with a magnetic field amplitude of 31.5 kA·m^{-1}. Magnetic content was reported through Quasi-statistic magnetic measurements of the nanoparticles and composites, which are performed on a vibrating sample magnetometer (VSM) with a maximum field strength of $2.8 \cdot 10^9$ A·m^{-1} at a sample oscillation frequency of 75 Hz. For self-healing experiments under OEMF irradiation, the samples were cut and healed in a self-made teflon mold.

4. RESULTS AND DISCUSSION

A comparative investigation concerning particles with different composition (Fe_3O_4, $CoFe_2O_4$, Co), size, and shape, with the ultimate goal to result in a tailored design for an effective energy harvesting has been done (Figure 1a). The resulting composites were carefully analyzed on their magnetic, thermal and mechanical properties showing an overall viscoelastic behavior. The respective crossover frequency at ambient is requested to be low, with a low thermal transition of the ionomer aggregates (T_i = 66.5°C) in order to allow a thermal activation of the self-healing capability. Figure 1b shows the thermograms for a series of P@FC composites. A Langevin-like temperature increase with time is noticed due to the remaining heat loss to the environment and a steady-state temperature T_s at long times. T_s as well as the initial heating rate $(dT/dt)_{t\rightarrow 0}$ increase with increasing particle fraction, and already at volume fractions as low as 0.1 vol%, the heating is fast enough to reach 150 °C in 10 minutes. At ν_{NP} = 0.05 vol%, the ionic transition temperature T_i is reached within a few minutes.

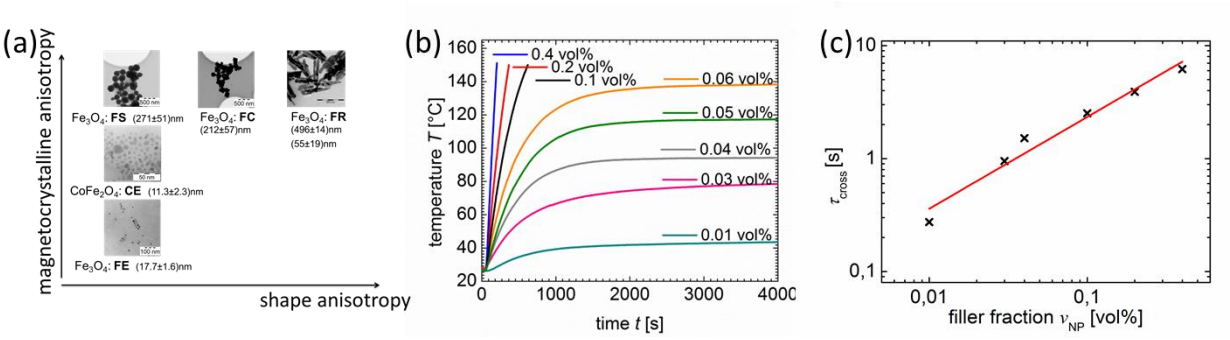

Figure 1. a) Overview of the magnetic nanoparticles of different magnetocrystalline and shape anisotropy; b) HF measurements of P@FC with increasing filler fraction and c) relaxationtime at τ_{cross} with increasing FC filler fraction.

When comparing the dependence of the steady-state temperature T_s and heating rate $(dT/dt)_{t\to 0}$ on the filler fraction for different particle types, the cubic (**FC**) particles show the best heating efficiency among the particles, followed by single-domain particle (**FE**) and (**CE**) then the spherical (**FS**) and the rod-like (**FR**) particles. All composites show a qualitative similar dynamic mechanical behavior in oscillatory rheology. At low frequencies, the shear loss (*G''*) modulus is dominant, indicating a prevailing viscous behavior. With increasing frequency, the shear storage (*G'*) modulus increases, and a *G''/G'* cross-over to a dominating elastic behavior is observed at a frequency that depends on the ion content and the nature of the counter ion. Figure 1c show a nearly linear scaling of the respective characteristic times $\tau = 2\pi/\omega_{cross}$ for composites based on (**FC)** particles, as these are shown to be the most suitable for the heating efficiency. The impact of the particulate filler fraction can be attributed to a slow-down of the sticky reptation process and can be interpreted as an involvement of the filler particles in the phase behavior of the materials.[7]

A typical shape of thermoplastic elastomers has been observed with tensile test with elastic moduli in the range of 1 MPa and hardly affected by the filler content for filler fractions up to 0.05 vol% (Figure 2a). By comparing the tensile properties after damage and healing to those of the pristine materials, the self-healing efficiency of the materials has been addressed (Figure 2b). Under magnetic stimulation, P@FC-0.05 experiences a full property restoration after 15 min, while P@FC-0.03 with a lower filler fraction show a considerable slower healing profile.

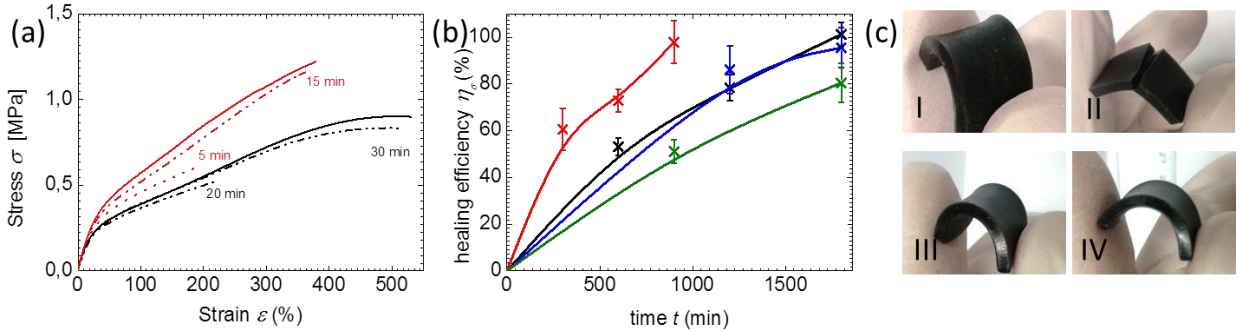

Figure 2. a) Stress-strain curves of native (straight line) and healed (dashed line) samples of ionomer (black) and P@FC-0.05 (red); b) healing efficiency based on the tensile strength $\boldsymbol{\eta_\sigma}$ for zinc ionomer (black) and P@FC-0.05 (blue) healed in oven, P@FC-0.05 (red) and PFC-0.03 (green) healed under OEMF and c) Illustration of cut `n heal experiments of P@FC-0.05.

4. CONCLUSION

The incorporation of magnetic nanoparticles of various nature into the polymer matrix by simple solution blending allows an acceleration and remote controlled activation of the self-healing effect in elastomeric ionomers. The influence of the particles on the dynamic-mechanical properties has been systematically investigated. The trend of the characteristic time constants with particle fraction is attributed to a slowed-down sticky reptation process. The cubic shaped (FC) multi-domain magnetite-based particles indicated under the employed field conditions the best heating efficiency. A particle volume fraction as low as 0.05 vol% is sufficient to reach the transition temperature T_i in short time.

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