SELF-HEALING PROCESSES IN IONOMERIC ELASTOMERS

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ABSTRACT

The use of dynamic bonds in self-healing polymeric systems allows restoring of the chemical structure and mechanical properties multiple times. In this respect, the use of ionomers represents a promising approach. The strong interaction between ionic moieties within a non-polar matrix leads to microphase separation and a behavior similar to covalent crosslinks in a thermally reversible network. The implementation and parameter optimization, however, requires a profound understanding of the structure-property relationships.

Motivated by recent findings on the excellent self-healing behavior of ionomeric NBR-based systems, we report on an ionomer model system designed to explore the thermal and viscoelastic properties of these materials by varying the ionic content, neutralization degree and nature of counter-ions.

The dynamic mechanical properties of the materials are investigated by rheological oscillation measurements in dependence on the ionic content and the nature of cation.

The temperature-reversible formation of ionic cross-links, an essential feature for the ability of extrinsic self-healing by thermal activation, is shown to be possible by incorporation of magnetic nanoparticles. The transfer of the basic results to NBR elastomers is successfully demonstrated.

1. INTRODUCTION

Environmental stress and weathering may lead to micro- and macro-cracks in elastomers resulting in a catastrophic failure of the material performance, especially when the device material is difficult to access and hence difficult and expansive to repair. This raised the scientific interest in self-healing elastomers towards more reliable and durable materials. Up to now, many concepts have been successfully developed on autonomous self-healing thermo- and duroplasts e. g. microcapsule and fiber approaches [1,2], but their transfer to elastomers is still a challenge due to their drastic processing and working conditions. In addition, the reversibility of the healing processes in such systems is limited, while the use of dynamic bonds allows to rearrange the chemical structure and to restore mechanical properties multiple times.

Non-covalent intermolecular bonds based on π-π stacking, hydrogen bonds, or metal-ligand interactions thus open pathways to unique, structurally dynamic materials that
may be designed to be sensitive to a wide range of stimuli [3]. When properly
designed, they show great potential as self-healing systems, and within this class of
materials, ionomers represent a promising approach toward novel self-healing
elastomers [4,5]. As such, a properly designed system requires a highly viscous flow
at low strain conditions, while it shall behave like an elastomer under working
conditions. Based on these material requirements, we developed an ionomer model
system with a flexible polymer backbone including only ionic crosslinks [6,7].
Dynamic mechanical and thermal properties of the model ionomers are studied in
dependence of the ionic content and the nature of the counter ions. As an additional
feature, magnetic nanoparticles are incorporated in order to allow for a local heating
effect in an oscillating electromagnetic field (OEMF) as an external trigger for self-
healing.

2. MATERIALS

The model system is based on copolymers of n-butylacrylate and a varying fraction of
t-butylacrylate prepared by Atom Transfer Radical Polymerization (ATRP). The
polymers show an adjustable molecular weight up to 80,000 g/mol and a narrow
molecular weight distribution (PDI: 1.08- 1.2). After selective hydrolysis of the t-butyl
groups, carboxylic acid moieties are formed that are neutralized with basic sodium,
zinc or cobalt salts to produce the corresponding ionomer. Similarly, carboxylated
NBR (XNBR) is transferred to ionomeric elastomers. For composites that allow a
local heating activation, cobalt, magnetite and cobalt-ferrite nanoparticles are
incorporated in different contents into the model copolymer and NBR matrices,
respectively.

3. METHODS

$^1$H- and $^{13}$C nuclear magnetic resonance (NMR) and respective 2D methods are
employed to elucidate the copolymer composition and sequence structure. The
degree of neutralization and the specific metal coordination are detected by infrared
spectroscopy (FT ATR-IR). 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$^{-1}$, while small-angle
X-ray scattering (SAXS) measurements are performed for the superstructure of the
copolymers. 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.
The measurements are performed on homogeneous polymer samples with a
frequency sweep from 3.14 to 628 rad/s at 25 °C with 2% strain level.
Thermorheology is used to study the influence of temperature on dynamic properties
in the range of 20 – 90 °C at a heating rate of 10 K·min$^{-1}$. The magnetic heating
behavior of ionomeric composite samples is investigated using a high frequency
generator equipped with a water-cooled copper induction coil, operated at 247 kHz
with a magnetic field amplitude of 31.5 kA·m$^{-1}$. The sample temperature is recorded
with an optic temperature sensor. Tensile testing is carried out using 15 mm x 2 mm
pressed sample stripes and an elongation rate of 500 mm/ min.
4. RESULTS AND DISCUSSION

All methods indicate a successful formation of model ionomers with predetermined structure by using the employed synthetic pathway. As well SAXS as DSC experiments indicate an influence of the nature of the cation on the phase separation, increasing in order Co$^{2+} < \text{Zn}^{2+} < \text{Na}^+$. All model ionomers 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. The loss angle $\tan\delta$ defined as the ration of $G''$ and $G'$ serves as a significant value to describe the frequency-dependent viscoelastic behavior of the employed systems (Fig. 1, left). Temperature-dependent rheology experiments reveal a shift of the crossover point to higher frequencies with increasing temperature, and a shift of the ionic transition (indicated by a strong increase of $\tan\delta$) to higher temperatures with increasing frequency (Fig. 1, right).

By incorporation of magnetic nanoparticles into the ionomer matrix, a local heating effect is possible employing an alternating magnetic field that is correlated to the particle content (Fig. 2, left). The temperature effect accelerates the healing effect of the materials, and a transfer of the concept to XNBR systems is successfully shown. We have demonstrated a dependence of the self-healing efficiency on the healing temperature, and the impact of the external magnetic field is evident (Fig. 2, right). Tensile tests show a nearly 100% recovery of the original breaking elongation of ZN-HNBR healed at 55°C.

**Figure 1:** Frequency dependency of the loss angle $\tan\delta$ for Co$^{2+}$-based ionomers with different ionic content (left), and temperature dependence of $\tan\delta$ for a Zn$^{2+}$ based ionomer (right).
Figure 2: Magnetic heating profiles for magnetic ionomer composites with varying particle content (left), and tensile profiles of a Co@Zn-HNBR (0.5 wt%) healed at RT with and without magnetic field application, respectively (right).

5. CONCLUSIONS

The self-healing behavior of ionomeric elastomers is of high interest for prospective applications, and a profound understanding of their structure-property correlation is required for the optimization of the effect. The presented ionomer model system clearly shows the relationship between the dynamic and thermal properties, the nature of the cation and the ionic content. It is further shown that the ionic aggregates can be stimulated by different heating methods. Local heating in alternating magnetic fields is a selective and effective activation mode as well in the model systems as in NBR matrices, and correlates to the content of incorporated magnetic nanoparticles. A proof of concept for self-healing MNP filled elastomers is demonstrated.

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REFERENCES