Self-Healing Processes in Ionomeric Elastomers

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Keywords: self-healing elastomers, ionomers, dynamic bonds, rheology

Abstract ID No : 205

ABSTRACT

The development of self-healing mechanisms that allow the repair of elastomers instantaneously on the molecular level is highly demanded in order to result in more reliable and durable elastomers. Ionomeric materials that are crosslinked exclusively by dynamic bonds are recently shown to be of potential for autonomous or on-demand self-healing in flexible polymeric materials. In this respect, the use of ionomers represents a promising approach but the implementation and parameter optimization, however, requires a profound understanding of the structure-property relationships. For this purpose, we developed a model system for self-healing ionomeric elastomers that allows a detailed insight into the interrelations of molecular structure, ion fraction, counter-ion nature, and the resulting mechanical and self-healing properties. Our results deliver a clear indication for the important impact of the inner structure of ionomer-based elastomers on their mechanical properties, both on their frequency-dependent, dynamic behavior as well as on their thermal characteristics, and that both parameters are essential for the self-healing ability and material reliability in these materials.

1. INTRODUCTION

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. Elastomeric materials exhibit enormous extensibility up to several hundred per cent, and have a wide range of commercial applications. The development of technically relevant elastomers with the ability of intrinsic and repeatable self-repairing is one of the most popular desires of modern material sciences. A reversible formation of 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]–[5] Within this class of materials, ionomers represent a promising approach toward novel self-healing elastomers.[6]–[10] 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 in correlation to their self-healing ability.

2. MATERIALS

Model ionomers based on *n*BA and neutralized acrylic acid units of various molar fraction are synthesized by copper-catalyzed atom transfer radical polymerization (ATRP) in a three-step procedure by adapting literature protocols (Figure 1).[7], [11], [12] We result in narrowly distributed linear polymer chains (polydispersity index PDI ~ 1.1) with a random comonomer sequence and a molar mass of all materials is in the range of M_w ~ 50 $kg \cdot mol^{-1}$. The polymers are encoded following the nomenclature: P*t*BA-X, PAA-X and PM-X; with *t*BA: poly(*tert*-butyl acrylate), AA: poly(acrylic acid), M: metal counter ion; P: poly(*n*-butyl acrylate) and X: mol% of *t*BA, AA or M. The balance is the *n*BA molar fraction.

3. METHODS

The molar mass and its distribution is investigated by size exclusion chromatography (SEC), ^1H- and ^{13}C nuclear magnetic resonance (NMR) are employed to elucidate the copolymer composition. The degree of neutralization and the specific metal coordination are detected by infrared spectroscopy (FT-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 $K \cdot min^{-1}$, 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 ºC with 2% strain level. Tensile testing is carried out using 15 mm x 2 mm pressed sample stripes and an elongation rate of 500 mm/ min. The self-healing efficiency is determined by elongation at break and tensile strength of macroscopically cut species compared to native ones. After cutting the fresh edges of the samples are shortly pressed together and healed either under different time scale or healing temperature in a conventional oven.

4. RESULTS AND DISCUSSION

All ionomers were carefully analyzed structurally, and mechanical properties were characterized. A predominant viscoelastic behavior is found in all investigated model polymers, prevailing an elastic behavior at high frequencies, as indicated by the condition that $G' > G''$. With decreasing frequency, *G''* exceeds the value of *G'*, and below the crossover frequency, the viscous behavior of the materials is dominant as shown exemplarily for Co^{2+}-based ionomers in *Figure 1a*. The crossover frequency is shifted to lower values and the ionic transition temperature T_i increases with increasing ion fraction (Figure 1b, c). These initial results indicate a good correspondence of the estimated cluster size with the calculated effective crosslink density of ionomers at low frequency indicating that the mean radius of ionic clusters decreases from $Na^+ > Co^{2+} > Zn^{2+}$. Rheological measurements with simultaneous *in situ* FT-IR spectroscopy at different temperatures and frequencies give information on the mechanochemistry of the system. The network dynamics and supramolecular reversibility correlates with the scratch-healing ability. [6] Materials with a dynamic bond lifetime τ_b in the range of $10s < \tau_b < 100s$ revealed in good self-healing behavior and good mechanical properties.

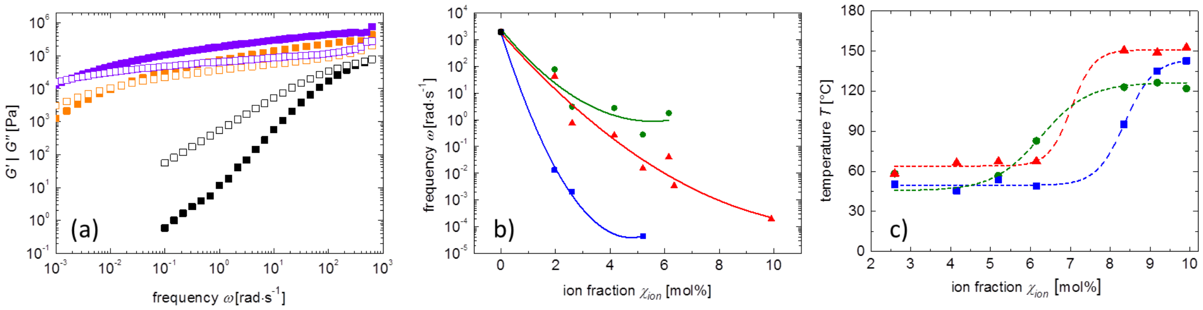

Figure 1. a) Frequency dependence of shear moduli *G*' (filled symbols) and *G*'' (open symbols) of Co^{2+}- based ionomers with different ion fraction (black: 0.3 mol%, orange: 2.0 mol%, purple: 4.6 mol%) at 25 °C; b) crossover frequency ω_{cross} and c) ionic transition temperature T_{ion} of the ionomers vs. ion fraction χ_{ion}, for PM-X with M = Na (green circles), Co (blue squares) and Zn(red triangles)

The temperature-reversible nature of the ionomeric crosslinks is an essential feature for the intrinsic self-healing behavior in these model ionomeric elastomers. Furthermore, the ion fraction needs to exceed 5 mol% in order to allow sufficient mechanical stability under load conditions.

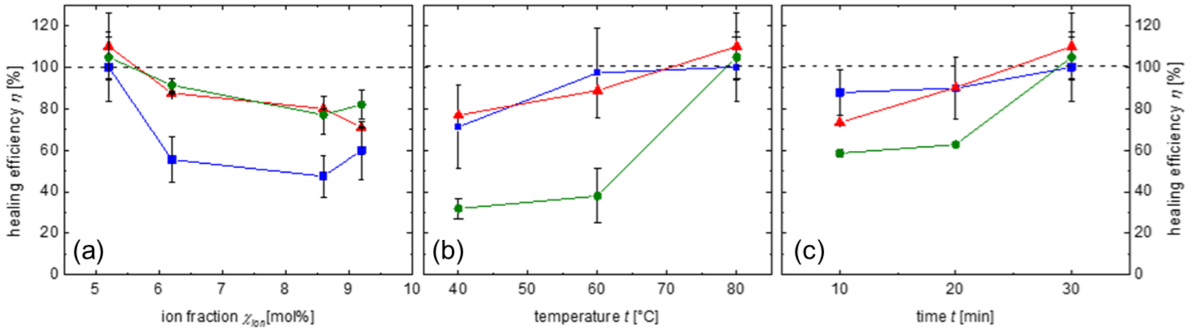

Figure 2. Self-healing efficiency η based on the tensile strength of various ionomers PM-X with M = Na (green circles), Co (blue squares) and Zn (red triangles) in dependence of the a) ion fraction χ_{ion}; b) temperature *T*, and f) time *t* for PM-5.2.

Good and reproducible healing properties were initially observed for PM-5.2 ionomers at a contact time of 30 min at 80 °C. Ionomers with higher ion fractions are compared for their healing properties based on these standard conditions (Figure 2a). Additionally the healing temperature and time for PM-5.2 ionomers are investigated. Lower healing efficiency can be attributed to slower molecular mobility, higher raptation times or high ionic transition temperatures. While the behavior under dynamic load is mainly determined by the ion fraction, the time scale of the viscous-to-elastic transition (given by ω_{cross}) is influenced by the nature of the counter ion.

5. CONCLUSIONS

The generic principle to employ ionomeric, dynamic bonds for the realization of self-healing elastomers is investigated in this project on the base of a well-defined model system. While the ion fraction correlates directly to the effective network density and elastic properties, the frequency at the crossover point between viscous and elastic behavior is influenced by the nature of the counter ion. For materials with an ionic fraction in the range of 5 mol% a reliable elastic response and good healing behavior can be observed at moderate healing temperatures and times. This clearly illustrates their principal potential for self-healing materials, and that an optimization of the effect with respect to the counter-ion nature and the ion fraction is possible.

ACKNOWLEDGEMENTS

We gratefully acknowledge the DFG (SPP 1568, “Design and Generic Principles of Self-healing Materials”) for financial support, Dr. Wim Pyckhout-Hintzen at the Forschungszentrum Jülich for SAXS measurements and Prof. Sybrand van der Zwaag for IR-coupled thermorheology measurements.

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