

Relationship between the network dynamics, supramolecular relaxation time and healing kinetics of cobalt poly(butyl acrylate) ionomers



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ABSTRACT

The aim of this work is to contribute to the understanding of the relationship between the timescales of molecular processes in ionomers and that of macroscale autonomous healing. For this purpose, poly(butyl acrylate-co-acrylic acid) model ionomers with varying fractions of cobalt counter ions were used. Three temperature dependent timescales were quantified and linked: (i) the terminal relaxation time (t_d) as determined by creep relaxation experiments; (ii) the supramolecular relaxation timescale (τ) as determined by frequency sweeps in oscillatory shear rheology; and (iii) the macroscopic healing timescale (t_{heal}) as obtained by quantifying the time for full interfacial strength recovery for two ionomer surfaces brought in contact. Using the temperature dependent values of t_d , τ , and t_{heal} , the activation energies of the ionic cluster formation, the flow of the polymer backbone, and the interfacial recovery respectively, were calculated. It was found that the kinetics of healing closely follows the timescales of network and cluster formation.

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1. Introduction

Supramolecular polymer networks are based on reversible crosslinks, such as hydrogen bonds [1–3], metal-ligand interactions [4–6], ion complexations [7–9], or π - π stackings [10,11]. The two factors that contribute to the mechanical properties of these networks are the strength and concentration of the reversible interactions and the nature of the polymer backbone [1]. These factors determine load transfer properties at the molecular scale, resulting in elastic and solid-like mechanics on the supramolecular scale [12]. Therefore, for designing supramolecular materials that self-heal, there has to be a compromise between the strength of the tie-points and the mobility of the polymer network [13]. There have been several recent publications on the network and supramolecular relaxations involved in the dynamic and self-healing behavior of these polymers. Feldman et al. showed that bulk mechanical properties such as plateau moduli and relaxation timescales were primarily determined by the average distance

between the quadruple hydrogen bonding moieties along the polymer chain [14]. Binder et al. used different hydrogen bonding moieties to study the interplay between intermolecular association strengths and self-healing ability [2,3]. The G' - G'' crossover frequency was used as the cluster relaxation parameter, and self-healing was observed by visual scratch disappearance. Rossow, Seiffert et al. developed several modular polymer toolkits by systematically varying the strength and concentration of supramolecular crosslinking, resulting in polymers with tunable mechanical characteristics [12,15,16]. However, to the best of our knowledge there have been no reports establishing a relation between the various polymer relaxation timescales and the timescale of bulk macroscopic autonomous healing, which is the key focus of the present paper.

In this work, we study a subset of supramolecular polymers known as ionomers. A typical ionomer has ionic groups randomly distributed along the polymer backbone. The polar ionic groups phase separate and aggregate into nanometer-sized domains along the non-polar polymer backbone. These phase separated regions promote the formation of ionic multiplets and clusters which act as dynamic reversible crosslinks. A schematic of this hierarchical structure is shown in Fig. 1. The clustering in ionomers is described

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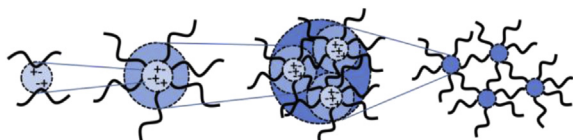


Fig. 1. Schematic of hierarchical structure in ionomers. Due to difference in polarity, ion pairs phase separate from the polymer backbone to give ionic clusters and multiplets which are regions of restricted mobility and act as dynamic crosslinks. [Reprinted with permission from [7]].

quantitatively in the Eisenberg, Hird and Moore (EHM) model [17]. According to this model, the clusters can be dissociated upon application of thermal energy and this thermal transition is known as the cluster/de-cluster temperature or ionic transition temperature (T_i). The ionic clusters add an additional factor of complexity because they are reversible linkages and act as physical crosslink points thus increasing the strength of the network.

Relaxations in polymers are directly related to the molecular mobility and these relaxations manifest themselves in the macroscopic mechanical behavior. These relaxations are associated with the dynamic nature of the reversible interactions or arise from the chain relaxations of the polymer backbone itself. For bond dissociation to occur, the reversible supramolecular bond should be in the open state and the two molecular segments should move away from each other. In this work, the parameter supramolecular relaxation lifetime (τ) is obtained from the inverse of the crossover frequency of a rheological frequency sweep. This timescale encompasses the several steps involved in the reversibility of the network, namely the disentanglements and the chain–chain dissociation resulting from the multiple ionic dissociations in a cluster.

In our previous work, we correlated supramolecular relaxation lifetime and network mobility to scratch healing behavior in a series of poly(butyl acrylate-co-acrylic acid) ionomers neutralized with various amounts of sodium, zinc and cobalt. We found that a supramolecular relaxation lifetime between 10 and 100 s resulted in samples with complete surface scratch healing and good mechanical robustness [7]. Previous work on supramolecular networks has shown that the rate of bond dissociation, rather than the crosslink thermodynamics, most strongly affects the dynamic properties of the network [18–20]. According to recent work by Stukalin et al. a supramolecular self-healing network based on hydrogen bonding can be modeled by a reversible network consisting of dangling chains with reversible stickers on one end and attached to a permanently crosslinked network at the other end [21]. Depending on the time scale and concentrations of open stickers, the recombination occurs via different mechanisms. According to this theory, in order for a material to be self-healing rather than self-adhesive, one needs: (i) a high non-equilibrium concentration of broken reversible bonds at the fractured surface that persists for a sufficiently long time as a result of restricted mobility of the reactive groups, and (ii) a low equilibrium concentration of broken bonds at the undamaged surface because of their high energy. As a result there is a large separation of time scales between self-healing and self-adhesion. However, the model fails to capture the behavior at long (model) time scales, which may actually be close to experimental time scales. Several theoretical models based on either equilibrium gelation or network growth have been proposed to describe the transition between the open and closed states of supramolecular networks [22]. Other mechanisms such as chain connectivity and mesoscopic organization such as clustering could also affect the rate of healing. In this work, we investigate the timescales of various relaxations in cobalt poly(n-butyl acrylate-co-acrylic acid) ionomers and relate the rheological and network timescales to that of thermally activated healing.

2. Experimental

2.1. Polymer synthesis

Various ionomers with different cobalt concentrations yet comparable molecular weights ($M_w \sim 42,000$ g/mol) were synthesized according to previously published routes [7]. Copolymers of *n*-butylacrylate and *tert*-butylacrylate were obtained by atom-transfer radical polymerization (ATRP) with CuBr/PMDETA, with 2–10% molar fraction of *tert*-butylacrylate. The pendant *tert*-butylacrylate was hydrolyzed to carboxylic acid groups using trifluoroacetic acid. Neutralization of the carboxylic acid groups was achieved by addition of cobalt acetate in 1,3-dioxane at 80 °C for 2 h. After synthesis, the ionomers were pressed at 80 °C and 1 MPa pressure to yield fully dense and optically homogenous free standing films with a thickness between 0.5 and 1 mm.

2.2. Frequency sweep oscillatory shear rheology

20 mm diameter discs were punched out of the ionomer films and used in a plate–plate rheometer (ThermoFisher Haake Mars III with temperature control chamber). Frequency sweep experiments from 100 Hz to 0.001 Hz were performed at temperatures of 25, 40, 60, 80 and 100 °C, with an isothermal hold for 20 min prior to each temperature step. To be able to perform a time–temperature superposition operation, frequency sweeps were made between 10 Hz and 0.1 Hz at constant temperatures between 0 and 100 °C, at increments of 5 °C and a 5 min isothermal hold prior to each frequency scan.

2.3. Creep relaxation

Creep relaxation experiments were performed in a parallel plate rheometer to determine the terminal relaxation times. Measurements were conducted at 25, 40, 60, 80, 100 and 120 °C. A constant rotational stress of 100 Pa, which is within the linear viscoelastic regime, was applied for 10 min, which was sufficient to achieve a steady state shear rate. Each interval of shearing was followed by a relaxation step of 2 h during which the sample response was measured under a zero-stress condition. The shear compliance was calculated from the plateau value for the shear rate during the relaxation step.

2.4. Thermally activated healing

8 mm diameter discs were punched out of the ionomer films and glued onto disposable aluminum plates. The rheometer was used in the strain-controlled axial testing mode to study the joining of the top and bottom ionomer discs onto each other, similar the protocol described earlier [23]. The samples were separately heated to about 20 °C above their ionic transition temperature and then brought into contact for varying amounts of time at a fixed load of 1 N. After this initial contact at the elevated temperature, the joined samples were cooled to room temperature and held there for various lengths of time. The samples were then pulled apart at a controlled strain rate of 10 mm min^{−1}. The maximum force required for separation of the two interfaces from load–displacement curves was used to study the extent of thermally-activated healing.

3. Results and discussion

The supramolecular relaxation lifetime (τ) has recently been presented as a key characteristic to describe the dynamic nature of supramolecular interactions [15,18,19,3,25]. When the relaxation lifetime is short, the macromolecular assembly is amenable to flow,

whereas a long lifetime yields materials without dynamic behavior. It has also been reported that materials with attractive and tunable properties such as adaptability, responsiveness and autonomous self-healing behavior have relaxation times in the range $1 \mu\text{s} < \tau < 1 \text{ min}$, with a preferred dominant relaxation time in the order of 60 s to have attractive healing behavior at room temperature [26]. A typical frequency sweep for the Co-5% ionomer at two different temperatures is shown in Fig. 2(a). The supramolecular relaxation lifetimes obtained from the G' - G'' crossover of a rheological frequency sweep are shown as a function of temperature for various cobalt contents in Fig. 2(b).

In the amorphous ionomer considered in this work there are two primary network relaxations: the lifetime of ionic clusters and the terminal relaxation of polymer backbone [27,28]. The terminal relaxation time (t_d) depends on the ionic content because the ionic groups are bound to the polymer backbone and each ionic dissociation and re-association allows a relaxation of only a small section of the polymer backbone. It has been reported that flow in these polymers occurs due to an “ion-hopping” mechanism, wherein the bound ionic group dissociates and re-associates with another ion pair in another cluster [28,29]. In order to understand the full picture of the network dynamics in these ionomers, we therefore determine t_d in addition to τ .

The terminal relaxation (t_d) is given as follows [28]:

$$t_d = aJ_e^0 \eta_0 \quad (1)$$

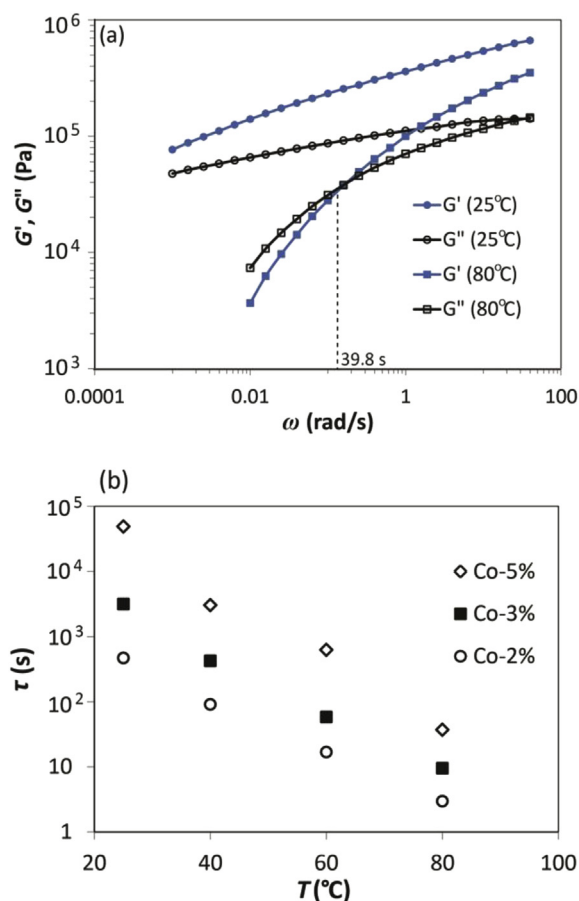


Fig. 2. (a) Representative graph showing a typical frequency sweep of Co-5% ionomers where the supramolecular relaxation lifetime (τ) is obtained from the inverse of the crossover frequency, and (b) supramolecular relaxation lifetime as a function of temperature for ionomers with varying cobalt content.

where ‘a’ is a constant depending on the polymer architecture, J_e^0 is the shear compliance and η_0 is zero shear viscosity. ‘a’ is $10/\pi^2$ (i.e. ≈ 1) for monodisperse entangled linear polymers, while it can range from 2.0 to 3.2 for monodisperse star polymers [28]. In this study, ‘a’ is taken as unity due to lack of information on its actual value. As long as ‘a’ remains constant and does not change with temperature or degree of neutralization, the assumed value for ‘a’ does not affect the trend in the calculated t_d . At low shear rates, these ionomers show a Newtonian behavior and exhibit a zero shear viscosity (η_0). The zero shear viscosity is typically obtained by rheological frequency sweep measurements. However for the higher ionic content ionomers, η_0 is beyond the experimentally accessible frequency range. In this case, time temperature superposition (TTS) can be used to extend the experimentally accessible frequency range as previously validated for low levels of ionic content [30,31]. Below a critical ionic content the ionic clusters do not have a significant effect on the relaxation of the polymer backbone. Fig. 3(a) and (b) show TTS plots for Co-3% and Co-7% ionomers shifted to 20 °C. Both the ionomers with 3% and 7% cobalt show consistent results after TTS, indicating that 7% cobalt content is still below the critical concentration limit at which TTS fails. However, as seen in Fig. 3, even the extended range of frequency does not capture the low frequency plateau. Therefore, creep-recovery tests were used to determine the zero shear viscosity values.

Zero shear viscosity values were obtained from this stationary flow region at the end of the creep plateau (see Fig. 4) using

$$\eta_0 = \frac{\tau_0}{\dot{\gamma}} \quad (2)$$

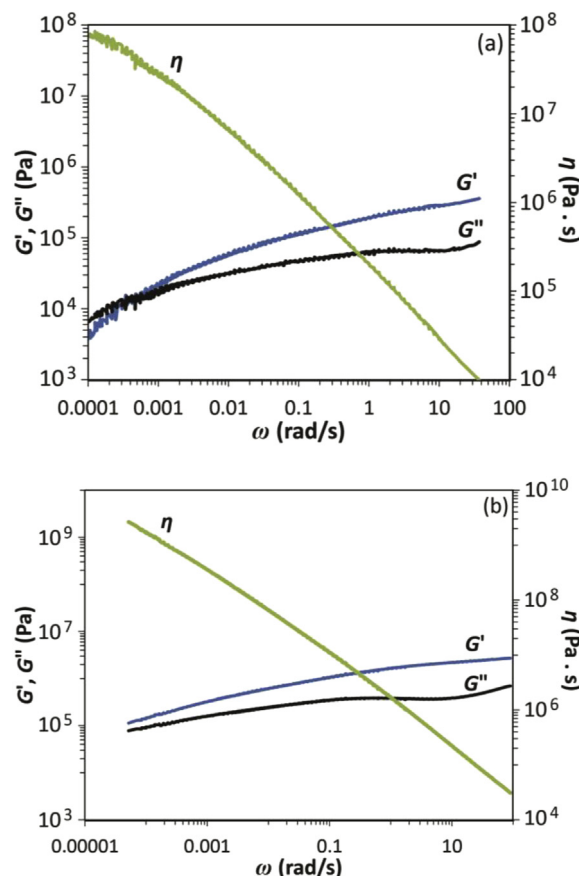


Fig. 3. Time-temperature superposition of (a) Co-3%, and (b) Co-7% ionomers.

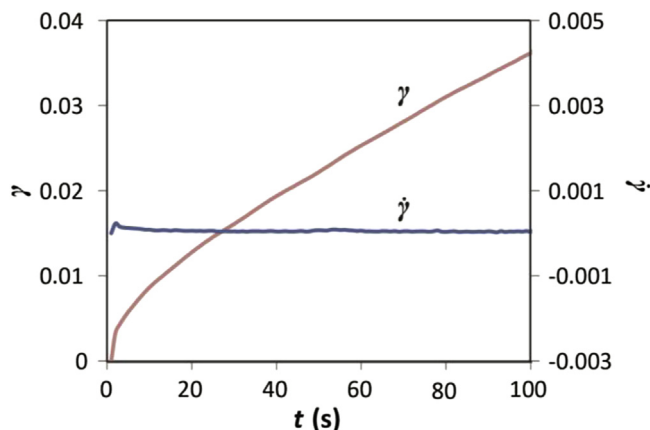


Fig. 4. Creep curve of Co-5% ionomer at 100 °C.

where τ_0 is the constant applied rotational stress and $\dot{\gamma}$ is the value of shear rate in the stationary flow region.

The values of the terminal relaxation time (t_d) as calculated from equation (1) and the supramolecular relaxation lifetime (τ) from the frequency sweep measurements are shown in Fig. 5 for Co-5% ionomer. For this Co content, the ionic transition temperature (T_i) is at around 80 °C [7]. Above 80 °C, the formation of ionic clusters is thermodynamically unfavorable. Consequently the supramolecular relaxation timescale τ determined rheologically at temperatures higher than T_i contains primarily contributions from other physical crosslinks in the network such as chain entanglements. However, interestingly, further below the ionic transition temperature, t_d and τ become closer in magnitude, as seen in Fig. 5 and the net contribution of both factors on the network relaxation kinetics becomes equal.

In order to relate the relaxation times to macroscopic phenomena, self-healing tests were performed and the results are shown in Fig. 6. Healing across the interface is achieved in two steps, each at a different temperature. Firstly, dissociation of the clusters and initial intimate contact of the two interfaces was established for varying times at 100 °C. Subsequently, in the second step, cluster formation and additional chain interdiffusion was established at 25 °C. Fig. 6(a) shows that the force required to separate the samples does not increase after an initial holding time of 15 min at 100 °C. This suggests that the timescale of cluster dissociation is 15 min or less at this temperature. For these

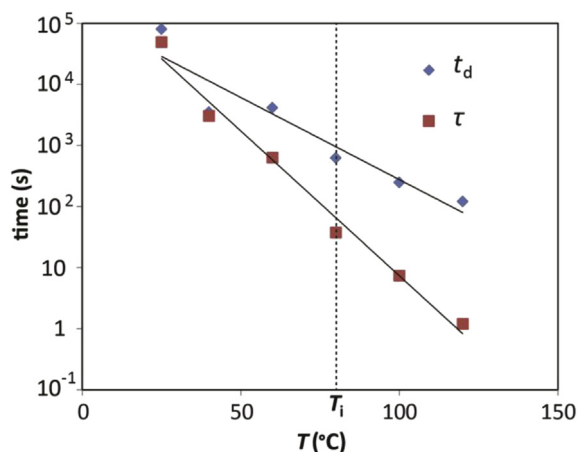


Fig. 5. Terminal relaxation time (t_d) and supramolecular cluster timescale as a function of temperature for Co-5% ionomer. The lines are a guide to the eye.

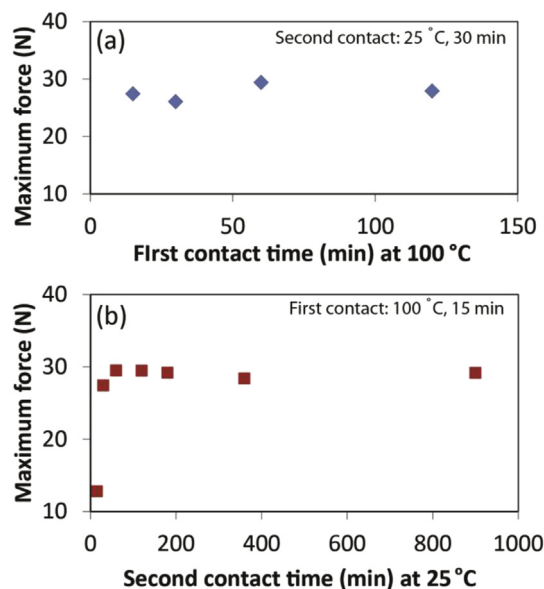


Fig. 6. Two-step axial healing at 100 °C ($T > T_i$) and 25 °C ($T < T_i$) for two-piece specimens of Co-5% ionomer. (a) Varying initial contact time at 100 °C, and 30 min at 25 °C, and (b) keeping initial contact time of 15 min at 100 °C constant, and varying second contact time at 25 °C.

experiments, the samples were cooled to 25 °C and held isothermally for 30 min. For the next set of experiments, based on the onset of plateau of Fig 6(a) the samples were heated to 100 °C for a constant time of 15 min, and then cooled to 25 °C for different times. Fig. 6(b) shows that upon increasing the time of contact at room temperature, the load required to separate the samples linearly increases up to 60 min of contact time and then saturates. This second phenomenon is attributed to the terminal relaxation of the polymer backbone. These results are in good agreement with the literature reporting that the two mechanisms involved in self-healing, namely initial sticker association and subsequent chain interdiffusion take place at time scales that are one or two orders of magnitude apart [21]. We assume that the times required for the onset of the plateaus of force in Fig. 6(a) and (b) correspond to the terminal and supramolecular relaxation timescales. Previous studies on UPy based supramolecular networks have shown that the relaxation time as determined by fitting to a first-order Maxwell model was in good agreement with the lifetime measured using NMR spectroscopy [32]. However, relaxation times from dielectric spectroscopy were several orders of magnitude faster, indicating that multiple hydrogen bonds along a single molecule need to relax before macroscopic flow sets in [33]. Our observations also show that care must be taken when comparing macroscopic flow phenomena such as interfacial healing to molecular scale motions.

In order to obtain a quantitative understanding of the thermally activated reversibility of the present Co-based ionomer, the temperature dependence of the various timescales was examined assuming an Arrhenius dependence equation. (3).

$$t = A_0 \cdot e^{\frac{E_a}{RT}} \quad (3)$$

The various timescales are plotted in Fig. 7 against the inverse of the absolute temperature. The time required to reach the plateau in debonding force at various temperatures $T > T_i$ is taken as the healing timescale. The network timescale (t_d) and the cluster lifetime (τ) are also plotted in this figure. All three datasets show a linear dependence of the logarithm of the characteristic time

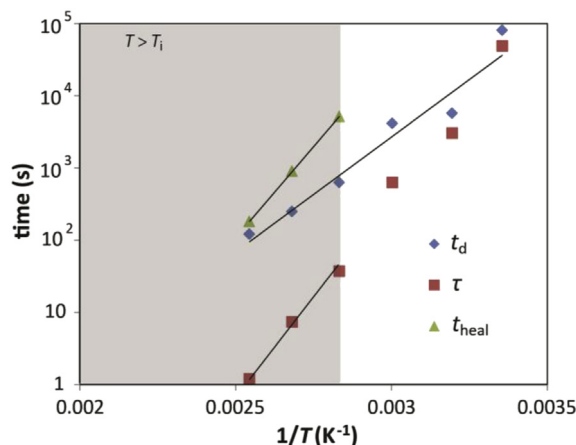


Fig. 7. Arrhenius plot of various timescales for Co-5% ionomer. The gray zone in the plot indicates the region of cluster instability (when $T > T_i$).

Table 1

E_a for different thermally activated process, in kJ mol^{-1} .

E_a (network)	E_a (supra-molecular cluster)	E_a (healing)
60.9	98.9	96.5

against the inverse of the absolute temperature. The activation energy values were determined from the slope of the lines and the values are listed in Table 1.

Different values for the activation energies for network relaxation and cluster formation have been reported by others as well [12], but this is the first time the activation energies for healing, network relaxation and cluster formation have been measured on a single system. The data of Table 1 suggest that the cluster activation is the limiting step of the healing kinetics.

4. Conclusions

In this work two polymer network timescales (chain dynamics and relaxation lifetime) have been correlated to the macroscale healing of model ionomers based on poly(butyl acrylate-co-acrylic acid) with varying fractions of cobalt counter ions. From the timescales of the two relaxation phenomena and the self-healing timescale, the activation energies were calculated. It was found that the activation energies for the macro-scale autonomous healing process and that of the ionic cluster are comparable and higher than the activation energy related to the network mobility.

This suggests that the cluster activation is the limiting step of the healing kinetics.

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