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Dynamic Viscoelasticity in Polyelectrolyte Multilayers: Nanodamping

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We report on the time-dependent viscoelastic response of nanoblended films of a polyelectrolyte complex prepared by the multilayering method. The ion-pairing interactions within polyelectrolyte multilayers (PEMUs) are reversibly broken by adding salt to the electrolyte in which the PEMU is immersed. Thus, the bulk modulus of these ultrathin films may be regulated without changing temperature. We have measured surprisingly effective mechanical damping exhibited by PEMUs. Compared to other hydrogel damping materials such as articular bovine cartilage and polyethyleneoxide−terephtalate/polybutylene−terephtalate networks, PEMUs provided enhancement in damping properties over the frequency range of 0.3−10 Hz. This was obtained when the multilayer dry thickness was orders of magnitude less than that of the hydrogels. The mechanism for enhanced damping may be related to the high proportion of ladder-like ion pairing between complexed polyelectrolytes.

Introduction

Vibrations in mechanical systems can have adverse consequences, such as fatigue, failure, and noise.[1] Vibration suppression is achieved by passive or active methods. Whereas active methods reduce vibrations in real time by making use of sensors and actuators,[2,3] passive methods exploit the inherent ability of viscoelastic materials such as polymers to absorb and dissipate (damp) vibrational energy.[4] The Maxwell model,[5] which comprises an elastic element (spring) and a viscous element (dashpot) in series, illustrates damping: for high-frequency vibrations, the Maxwell model predicts almost perfect elastic behavior, i.e., minimal energy dissipation, as the motion of the dashpot becomes negligible. For low or moderate frequencies, the time scales of the viscoelastic relaxation and vibration are comparable and they interfere destructively with one another,[6] allowing for more efficient energy dissipation and damping.

A polymeric system shows efficient damping when the polymer chains possess enough freedom to reorient to a state of lower free energy following the application of a stress.[7] It follows that in a compact network, as a result of cross-linking, crystallinity, the presence of thermodynamically incompatible solvents, etc., coordinated long-range chain molecular motion is restricted and damping capacity is decreased.[8] A structural transition similar to the one occurring near the glass-transition temperature, T_g, enhances chain mobility.[9] However, the width of this region does not exceed 30 °C in most homopolymers,[10] which limits any practical application of the polymeric material as a mechanical dampener. Multicomponent systems such as interpenetrating polymer networks, IPNs,[11] were found to be effective in widening the range of frequency and temperature over which damping is maximized.[12] Two polymers with two different glass-transition temperatures were mixed, and the resulting network had a broad T_g covering the range between the two polymers. However, if the polymers are either completely miscible or immiscible, damping will occur at one or two separate temperature or frequency ranges instead of a single broad one.[11]

Alternatively, a change in the free volume,[13] which defines the space available for polymer chain motions, can be triggered by modifying (decreasing) the degree of cross-linking. Obviously, this will allow the chains to slide past each other more easily and boost the efficacy of the damping material. Polyelectrolyte multilayers (PEMUs) are nano-blended networks of polymer,[14,15] held together by multiple ion-pairing interactions that can be broken by ionic strength variations.[14] Because they are typically 10−100 nm thick,

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PEMUs can damp vibrations with amplitudes on the nanometer scale. Thicker forms or slabs of complexed polyelectrolyte can obviously damp greater amplitudes. The efficiency of PEMUs as a potential mechanical dampener can be investigated using dynamic mechanical analysis or DMA.[6] This technique allows for direct measurement of the storage modulus (E'), loss modulus (E''), and loss factor (tan δ), which are important parameters that reveal the unique chemical and physical aspects of polymeric networks.[16] Isofrequency or isothermal dynamic tests have been used to probe glass transitions and secondary transitions in polymer composites, especially in relation to crystallinity, plasticization, copolymerization, cross-linking density, and molecular weight.[6,16]

The mechanical properties of PEMUs have been evaluated using nanoindentation of films on planar solid substrates,[17−19] strain-induced elastic buckling instabilities in both the dry and wet states,[20] and deformation of PEMU-based microcapsules using atomic force microscopy[21−25] or osmotic swelling.[26−28] These studies revealed a material with an elastic modulus in the range of 0.001−1 GPa.[18,29] Although DMA has been widely used to evaluate fundamental property changes in a variety of polymeric materials,[6,16] dynamic testing of PEMUs over a wide frequency range has been fairly limited, mainly because the size of PEMU samples (typically in the submicrometer range) is incompatible with traditional mechanical testing equipment. An example of dynamic mechanical characterization reported in the literature describes the use of quartz crystal microbalance techniques.[30] Further recent work has described the use of DMA in studying the morphology and mechanical characteristics of hydrogen-bonded poly(ethylene oxide) and poly(acrylic acid) multilayers.[31]

We have recently reported, using micromechanical testing, evidence of the viscous behavior within PEMUs[32] soaked in saline media. Here, we carry out direct dynamic tensile testing of PEMUs made from poly(diallyldimethylammonium), PDADMA, and poly(styrene sulfonate), PSS. Techniques used to study the mechanical properties of a single muscle fiber having widths in the range of micrometers were adapted to characterize the complex modulus and loss factor of the film.[33−35]

Experimental Section

PDADMA ($M_w = 3.7 \times 10^5$ g mol^{-1}, $M_w/M_n = 2.09$) and PSS ($M_w = 6.4 \times 10^4$ g mol^{-1}, $M_w/M_n = 1.4$) were used as received from Sigma-Aldrich. A robotic platform (StratoSequence, nanoStrata Inc.) was used to prepare a 250 layer-pair multilayer of PDADMA and PSS, (PDADMA/PSS)$_{250}$@1.0 M,[36] on an ethanol-cleaned poly(tetrafluoroethylene) (Teflon) substrate[31] ($50 \times 24 \times 1.6$ mm^3). The substrate was dipped alternately, for 5 min each, in the polyelectrolyte solutions (0.01 M concentration, quoted with respect to the monomer repeat unit) with three rinses (1 min each) of deionized water (Barnstead, E-pure, Milli-Q). The multilayer was then annealed at room temperature in 1.0 M NaCl for one week.[37]

The Teflon sheet was removed from the 1 M NaCl solution and a section of the PEMU was peeled off using flat-tipped tweezers. It was then transferred to a Petri dish (placed on the base of an inverted microscope) containing 1 M NaCl solution, where a razor blade was used to cut PEMU microcoupons (length 2.0 mm, width 150 μm, dry thickness 9.0 μm). The microcoupons were more pliable and easy to manipulate when bathed in 1 M NaCl. The ends were wrapped in aluminum foil clips and secured by applying a drop of silicone rubber before closing the clips. The microcoupons were mounted on a moving iron galvanometer motor (step time $\leq$ 300 μs; Aurora Scientific, Ontario Canada) and a capacitance-type force transducer (3.3 kHz resonance frequency; Aurora Scientific, Ontario, Canada, calibrated with small weights) designed for monitoring contractile behavior of single muscle fibers.[33−35] The motor and force transducer were located on the base of a Leitz Diavert (Wetzlar, Germany) inverted microscope. The position was monitored by a capacitance-type transducer in the motor and was calibrated with respect to the motor arm. Microcoupons were maintained in 200 μL anodized aluminum wells containing salt solutions and conditioned in these solutions for 10 min prior to testing. The temperature was maintained at 28 ± 1 °C with an ATR-4 regulator (Quest Scientific, North Vancouver, BC, Canada). Experimental control, data collection, and analysis of raw data were carried out using a PC-based system with a DT2831-G board (Data Translation, Marlboro, MA) and custom software.[38]

In DMA, the mechanical characteristics of a material are measured while a dynamic load whose rate varies sinusoidally is applied. Typically, the deformation amplitude does not exceed 1% to ensure that the sample maintains a linear stress−strain relationship. The applied deformation can be expressed by

$$e = e_0 \sin wt \tag{1}$$

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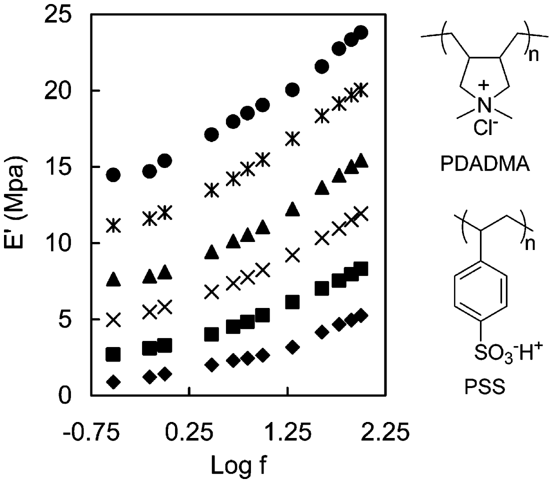

Figure 1. Storage modulus of PDADMA/PSS multilayer as a function of frequency (Hz). ●, *, ▲, ×, ■, and ◆ correspond to salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively. Strain amplitude was 1%. The stress was based on the actual cross-sectional area of the microcoupons.[32]

Where e_o, e, and w are the maximum strain at the peak of the sine wave, strain at time t, and the angular frequency of oscillation, respectively.

At any time, the resulting stress is given by

$$\sigma = \sigma_0 \sin wt \tag{2}$$

Where σ and σ_0 are the stress at time t and the stress at maximum strain given by $\sigma = Ee$, where E is Young's modulus.

For a viscoelastic material, the stress will be out of phase with the applied strain, and

$$\sigma = \sigma \sin(wt + \delta) \tag{3}$$

or

$$\sigma = \sigma_0 \sin wt \cos \delta + \sigma_0 \cos wt \sin \delta \tag{4}$$

where δ is the phase angle or phase lag between stress and strain.

Equation 4 can be resolved into two parts that are either in phase (elastic) or out of phase (viscous) with the strain. The former is the dynamic storage modulus and the latter is the dynamic loss modulus, respectively given by $E' = (\sigma_0/e_0) \cos \delta$ and $E'' = (\sigma_0/e_0) \sin \delta$.

Damping is related to the phase lag and is represented by

$$\tan \delta = \frac{E''}{E'} \tag{5}$$

The cross-sectional area of the multilayer microcoupon (calculated from the wet thickness at different swelling levels) was used to normalize the measured force (see ref 32 for more details).

Results and Discussion

Dynamic Storage Modulus of PEMU. Figure 1 depicts the influence of solution ion strength on the dynamic mechanical properties of PEMU. The microcoupons were subjected to a series of uniaxial sinusoidal strains, e, elongating the PEMU by 1% of their original length. The applied strain is within the region of linear viscoelastic behavior in which the measured stress is directly proportional to the strain.[32] The experiment was carried out in situ with microcoupons immersed in salt solutions of different ionic strength, and the ensuing dynamic stress, σ, was recorded.

When the PEMU microcoupon was oscillated sinusoidally (frequency, $f = 0.1-100$ Hz) at constant ionic strength, the relationship between E' and f showed two distinct regions (Figure 1). At low frequency (0.1−1.0 Hz), the PEMU has enough time to reorient to a new lower free-energy state before the next deformation cycle and the material is rubber like. At high frequency ($f > 1.0$ Hz) or at short time, the polymer chains do not have enough time to relax, reminiscent of glassy behavior.

At 0.0 M NaCl, the elastic modulus in the rubbery plateau region was 15 MPa, which agrees with the elastic modulus previously reported for a film of similar composition using mechanical testing[32] and is comparable to the value of 24 ± 15 MPa (assuming $G = E/3$) deduced from quartz crystal microbalance studies on planar PDADMA/PSS thin films.[30] However, it falls short of the reported elastic modulus of polyelectrolyte multilayer capsules, PEMC, of similar composition that is on the order of 45.5−140 MPa.[28,39] We have analyzed this difference and attribute it to nonequilibrium distribution of ladder vs network cross-link types (see below) and possibly residual orientation in nonannealed samples.[32] Annealing by salt is an effective way of promoting interdiffusion and long-term relaxation of the polyelectrolyte complex.[40]

As the ionic strength of the bathing solution increased, the whole curve shifted toward a lower value of E_1. This indicates that PEMU is storing less energy as it becomes less efficient at resisting the applied deformation. Other multilayer systems, such as poly(allylamine hydrochloride) (PAH)/PSS,[24,41] in contact with salt-containing solutions[42] showed a similar reduction in stiffness as a function of ionic strength. In contrast, multilayer films held together by hydrogen-bonding interactions in addition to electrostatic interactions, such as those made from PAH and DNA, are stiffer at elevated solution ionic strength, as hydrogen bonds are not broken by salt.[21,22,25,43]

Dynamic Loss Modulus of PEMUs. Figure 2 depicts the isothermal loss modulus spectra of PEMU immersed in salt solutions of various ionic strength. Again, a series of 1% sinusoidal uniaxial strains, e, were applied to the PEMU microcoupon, and the resulting stress, σ, was recorded.

E'' was also found to be a function of the rate of the applied strain and the salt concentration of the bathing medium (Figure 2).

In contrast to the low-frequency region, where E'' increased with frequency, regardless of solution ionic strength, the loss modulus deteriorated toward the high-frequency end of the spectrum. However, as the salt concentration decreased below 1.0 M, the loss modulus peak broadened progressively. Because E'' is directly proportional to E' ($E'' = E' \tan \delta$),

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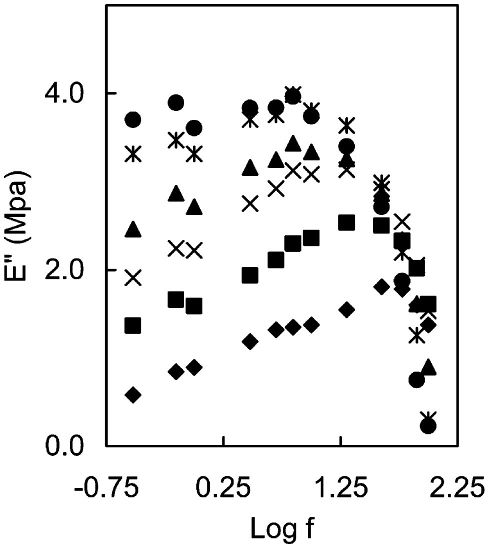

Figure 2. Loss modulus of PDADMA/PSS multilayer as a function of frequency (Hz). ●, *, ▲, ×, ■, and ◆ correspond to salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively. Strain amplitude was 1%. The stress was corrected for actual cross-sectional area of the microcoupons, with consideration of water volume fraction.

the whole curve shifted toward a lower value of E'' when the ionic strength of the medium increased.

The isothermal or isofrequency loss modulus spectrum of polymers would, if ideally resolved, show several maxima,[6] each attributable to the onset of some distinct large-scale cooperative displacement of polymer chains in the macromolecular network (α-transition), or to other secondary transitions such as the β and γ transitions.[13] The latter arise from side group motions (rotation and/or wagging) around the bond joining it to the chain backbone and backbone chain or short segment motions.[44] These have high natural torsional or rotational frequencies that will only show up in the moderate-to-high range of applied frequency. The presence of plasticizers or diluents may also contribute to secondary transitions. If the PEMU were viewed as a 100% cross-linked form of a salt, α-transitions would not be expected because of limited chain mobility. However, the system contains ladder cross-link types in addition to network cross-links (see below), which endows the complex with a certain degree of configurational freedom necessary for the onset of α-type transitions (the maxima observed in Figure 2).

When different systems are compared at the same strain amplitude, E'' serves as a measure of the energy dissipated per cycle.[13] Typically, viscoelastic polymers show E'' values in the range of 0.03−0.05 MPa at 1−10 Hz.[45] At the same frequency range, PEMU has a loss modulus of 0.5−1.5 MPa and 3.5−4.0 MPa at 1.0 and 0.0 M NaCl, respectively. Therefore, PEMUs may offer a significant increase in energy dissipation over typical viscoelastic materials.

Loss Factor of PEMUs. In DMA, the strain will be out of phase with the stress because of the time necessary for molecular rearrangements.[6] Thus, probing the extent of damping in PEMUs is accessible via the phase angle δ.

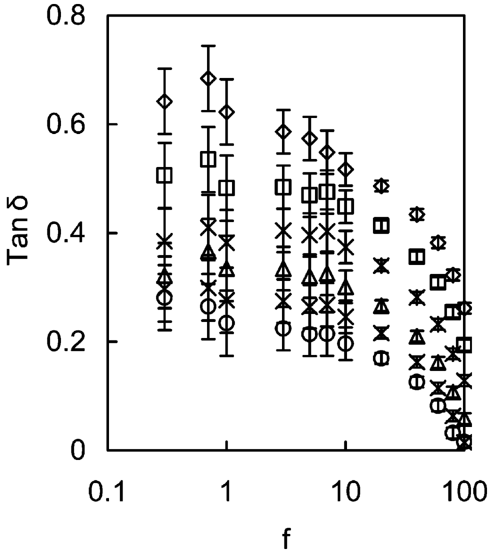

Figure 3. Damping vs frequency (logarithmic scale). ○, *, △, ×, □, and ◇ correspond to salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively.

Figure 3 shows quantitatively that the PEMU is able to dissipate a larger fraction of energy at higher ionic strength.

The effect of ionic strength and applied frequency on the damping ability of the multilayer can be summarized as follows: In the low-frequency region (0.3−10 Hz), tan Δ remained fairly constant, especially at salt concentrations above 0.2 M. It started to decline at ca. 20 Hz and progressively deteriorated as the multilayer response became more glassy-like ($f > 20$ Hz). As the salt concentration decreased, damping was observed to diminish.

Compared to other hydrogel damping materials such as articular bovine cartilage[46] (tan δ of 0.164, phosphate buffer saline, frequency test 1 Hz) and polyethyleneoxide−terephthalate/polybutylene−terephthalate IPN, PEOT/PBT,[46] (275 μm thick; tan δ of 0.155, phosphate buffer silane, frequency test 1 Hz), PEMU (0.2M NaCl; 9.0 μm dry thickness; tan δ of 0.27) showed up to 175% enhancement in damping properties over the range of 0.3−10 Hz. Damping on such a small length scale might have utility in microelectromechanical systems, MEMS.

Mechanism for Enhanced Damping. The relative density of cross-links within a polymeric network is a key factor that determines the response of the network to dynamic loads and affects its utility in vibration isolation composites. For example, damping peaks associated with the glass transition broaden and shift to higher temperatures as the cross-link density is increased.[47] This would limit the temperature or frequency ranges over which the proposed dampener can be efficiently utilized. The presence of a plasticizer is also of considerable importance and its ultimate effect on the mechanical properties of the network depends on whether the mixing between polymer chains and solvent molecules is thermodynamically favorable or not.[48] In contrast to solvent free networks that more or less resemble compact three-

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dimensional solids with highly restricted chains, a network in contact with good solvent swells.[49] The latter causes a change in the free volume, which defines the space available for polymer chain motion[13] and the slight loosening of the local environment enhances damping.[13] On the other hand, a network in contact with a theta or poor solvent is relatively compact.

The multiple "electrostatic" ion pairs holding polyelectrolytes together in PEMUs can be broken by the addition of salt ions. For example, when NaCl is added to the bathing solution of a PEMU, it swells as it sorbs both water and salt ions. Swelling is rapid, reversible, and roughly proportional to the salt concentration in solution.[50] Swelling takes place because some of the polymer−polymer ion pairs (intrinsic compensation) are replaced by salt ion−polymer pairs (extrinsic compensation),[51] as described by the following equilibrium

$$\mathrm{Pol^+Pol^-_m} + \mathrm{Na^+_{aq}} + \mathrm{Cl^-_{aq}} \rightleftharpoons \mathrm{Pol^+Pol^-_m} + \mathrm{Pol^+Cl^-_m} + \mathrm{Pol^-Na^+_m} \quad (6)$$

where $\mathrm{Pol^+}$ and $\mathrm{Pol^-}$ are positive and negative polyelectrolyte repeat units, respectively. The subscript m refers to components in the multilayer phase.

The doping illustrated in eq 6 also brings water into the multilayer.[51] Doping and hydration of counterions act synergystically to plasticize PEMUs. The question arises as to which effect, doping or hydration, is chiefly in control of damping properties. This question can be addressed by evaluating the transient stress-relaxation behavior of PEMU in contact with salt solutions, on which we have reported recently.[32] In this experiment, a 0.4% uniaxial strain was applied to the PEMU microcoupon immersed in salt solutions of various ionic strength, and the stress was recorded over a period of 100 ms.

Stress relaxation in solvent free networks, such as rubber vulcanizates, can be described in terms of the following power law[52]

$$\sigma_{\mathrm{t}} = \sigma_{\mathrm{eq}}\left[1 + \left(\frac{t}{\tau}\right)^{-\gamma}\right] \quad (7)$$

where σ_{t} and σ_{eq} are the uniaxial stress and equilibrium stress at constant elongation, and the parameters γ and τ depend on the cross-link density. The log−log plot of eq 7 (Figure 4), with values adapted from ref 32, is almost linear, indicating that the power law is a valid approximation of the stress relaxation behavior in PEMU. Thus, a PDADMA/PSS multilayer behaves more like a compact solid even in the presence of water of hydration.

In contrast to highly swollen hydrogels in which the swelling-induced uniaxial stretching contributes to stress relaxation, the cross-sectional area of solvated compact solids is constant after stretching[49] and the observed stress relaxation is a reflection of a polymeric network responding to an applied strain by readjusting its chain conformations to minimize the free energy of the molecular segments (viscouslike flow).[36] We have shown, using ATR-FTIR measurements, that a PDADMA/PSS multilayer contains around 9 and 11 water molecules per ion pair at 0.0 and 1.0 M NaCl, respectively.[53] Thus, the enhanced damping observed in Figure 3 at 1 M NaCl, in comparison to 0 M NaCl, is not due to the water of hydration but rather due to decreased cross-link density.

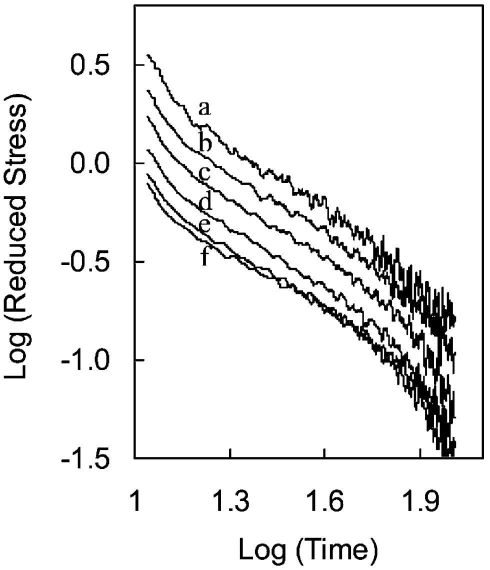

Figure 4. A log−log plot (eq 7, time in seconds) of the stress relaxation of a (PDADMA/PSS)$_{250}$@1.0 M NaCl multilayer at different salt concentrations with an applied strain of 0.4%. a−f correspond to salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively.

Although eq 6 summarizes individual electrostatic interactions, it does not describe the bulk morphology of the complexed polyelectrolyte that makes up the PEMU. Polyelectrolytes may be complexed as ladders, in which two oppositely charged polymers associate along their entire contours, or as networks, in which chains associate with many other chains. It is generally accepted that polyelectrolyte complexes are a random, amorphous combination of ladder and network, a so-called "scrambled salt" (Figure 5).[54,55] In recent studies of the PDADMA/PSS system, we have deduced that the PEMU contains about 70% ladder character, as the ladder ion pairs are slightly more energetically favorable than network pairs.[32]

The picture of PEMU being a tightly cross-linked system comprising an electrostatic cross-link per monomer repeat unit with relatively short molecular chains of reduced flexibility is not correct, and the ladder character imparts complexes with some flexibility crucial for damping. In the absence of salt, all polymers are ion paired and the polyelectrolyte ladders (and individual polymer segments within the ladder complexes) are essentially frozen. Salt works as a lubricating agent, freeing up frozen polyelectrolyte ladders, similar to the observed softening of brittle glassy

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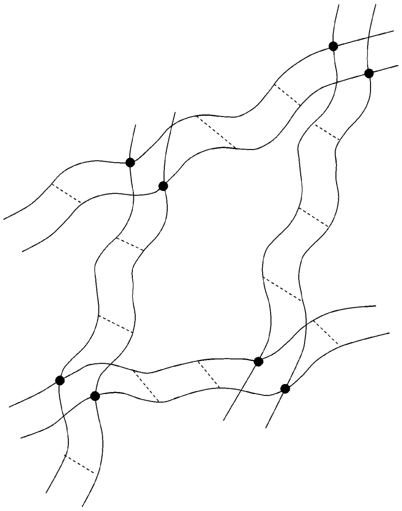

Figure 5. Scrambled salt morphology of PEMU. Solid lines represent PSS and PDADMA chains. Dashed lines are ladder-type ion pairs. Solid circles represent a network cross-link.

polymers when the temperature is raised beyond their glass-transition temperature (T_g),[6,13] an analogy we have termed “counterion-induced plasticization”.

A run of ladder-type ion pairs (as seen in Figure 5) is like a length of high-mass polymer (the mass is the sum of the two polyelectrolytes involved) that does not interact with its surroundings. Waters of hydration around this run provide opportunities for enhanced molecular motion, further absorbing energy. As ion pairs are broken by the addition of salt, the effective mass of the free runs of paired polyelectrolyte increases, as does the damping effectiveness, as seen in Figure 3. The fact that damping is constant over a range of (lower) frequencies is a further advantage of the PEMU system. This behavior is likely due to the statistical distribution of ladder lengths in complexes, with each length of ladder run able to absorb a specific frequency of mechanical energy. Direct information on molecular motions of PDADMA and PSS chains in PEMU, such as those provided by NMR, reveal relaxation times on the order of 10 s.[56] This finding is roughly consistent with our observations, because only frequencies applied at less than the relaxation time would be efficiently damped. Inspection of Figures 2 and 3, for example, indicate that energy loss and damping fall off at the 10 s time domain.

Conclusions

This study has shown that if a PEMU is applied to a vibrating surface, energy will be dissipated with conversion capabilities significantly higher than those normally observed for viscoelastic polymers. This will result in considerable mechanical damping, which, when coupled with the advantages of PEMU in terms of compactness, reliability, and resistance to thermal fluctuations, may translate into a superior passive damping material, especially for application in MEMS devices.[57] Larger dimensions of polyelectrolyte complex will be able to damp larger scale vibrations.

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