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**Paper**

# Tough Strained Fibers of Polyelectrolyte Complex: Pretensioned Polymers

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Polyelectrolyte complexes, PECs, are formed spontaneously by the interaction of oppositely charged polyelectrolytes. When hydrated, PECs are tough, elastic, biocompatible materials, but when dry they are hard and brittle. In either form, PECs have long been considered "unprocessible." Here, we show that PECs are transformed from brittle to tough (when dry) by extrusion into highly strained fibers. Partial molecular strain in dry fibers may be relaxed by exposure to solutions of salt or hot water under a salt/temperature equivalence. Efficient shape memory of complex strained in hot water is possible by cooling and recovering the original shape later in hot water.

## Introduction

Polyelectrolyte complexes, PECs, are precipitated either in bulk when two solutions of oppositely-charged polymers are mixed in reactors,[1-4] or as ultrathin films in the layer-by-layer ("multilayer") method of assembly.[5,6] Hydrated PECs offer an interesting range of soft matter, ranging from tough complexes to viscous, liquid-like coacervates, depending on the balance of polymer, water and salt within the material.[7] For PECs containing a 1:1 stoichiometry of positive and negative repeat units, modulus is reversibly controlled by salt content. Increasing salt progressively breaks ion pair crosslinks, rendering the material softer. Because these crosslinks are physical, and therefore reversible, significant viscoelasticity is seen over the full range of composition, in contrast to many classical hydrogels with chemical crosslinks.

While PECs have a long history of proposed uses, the recent slate of applications has focused on multilayers as active or passive coatings.[8] A key issue limiting the more widespread use of PECs is their acknowledged brittleness when dry.[9,10] Brittleness translates to inferior toughness when PEC solids are put forward for engineering applications,[9,11] and fragility when using PECs in their multilayer film morphology.[12-15] Because water is known to plasticize PECs[9,11,16] with efficiencies surpassing typical small-molecule polymer plasticizers,[17] many of the demonstrated applications are limited to those where the PEC remains in contact with water, such as (ultra)filtration membranes,[18-21] biomechanical materials[22,23] and biocompatible coatings for cell adhesion or nonadhesion.[24-27]

We have recently demonstrated that PECs, when fully plasticized by water and softened with a salt, may be extruded using classical laboratory extruders.[28] In these "saloplastics," water and salt, a highly non-traditional additive for polymer extrusion, decrease the PEC glass transition temperature. The polyelectrolytes employed were poly(diallyldimethyl ammonium), PDADMA, as polycation and poly(styrene sulfonate), PSS, as polyanion. In the present work, we have discovered that extrusion of fully hydrated PSS/PDADMA complex in the absence of salt yields fibers with markedly improved mechanical properties.

## Experimental Section

### Materials

Poly(4-styrenesulfonic acid, sodium salt) (AkzoNobel, VERSA TL130, molar mass *ca.* 200,000 g mol$^{-1}$) and poly(diallyldimethylammonium chloride) (Ondeo-Nalco, SD 46104, molar mass *ca.* 400,000 g mol$^{-1}$) were used as received. All salt solutions were prepared using deionized water (18 MΩ Barnstead, E-pure).

### Stored strain extruded complex

PSSNa and PDADMAC solutions in 0.25M NaCl were prepared at a concentration of 0.125 M with respect to their monomer units and precipitated to yield PECs as described previously.[28] Briefly, fully hydrated (i.e. wet with water) PEC was introduced into the hopper of an extruder (Model LE-075 from Custom Scientific Instruments) with a round exit nozzle of diameter 1.95 mm. The extruder parameters were: rotor temperature, 98 °C; header temperature, 102 °C; gap space, 3.8 mm; and rotor speed 110 rpm. The extruded complex was collected on a Model CSI-194T takeup reel with a 3 cm diameter drum at 10 rpm. These parameters allowed the extrusion of 0.9 ± 0.2 mm fiber at approximately 1 g min$^{-1}$. The as-prepared fibers were stored at ambient environment and have an equilibrated water content of about 13% (relative humidity: 40-60 % at 23 ± 2 °C), which means about 2.7 water molecules per PSS/PDADMA pair.

### Strength of strained exPEC

Strain to break measurements were carried out on both extruded and annealed exPECs using a TH2730 (Thümler GmbH) tensile testing unit equipped with a 100N load cell. Annealed exPECs were prepared by relaxing the stored strain with 1.5 M NaCl for 24 h, removing the NaCl with water, and drying at room temperature. Samples of length 20 mm were stretched at a speed of 10 mm min$^{-1}$ (50% strain min$^{-1}$).The toughness was calculated by integrating the area under the stress-strain (to failure) curve.

### Stored strain release

The strain stored by exPECs was released by NaCl solutions as follows: three exPECs with length 3 to 4 cm were put into solutions with [NaCl] = 0, 0.15, 0.3, 0.45, 0.6, 0.75, 0.9, 1.05, 1.2, 1.35, 1.5, 1.65, 1.8, and 2.0 M. Photos of the exPECs were taken as a function of time and measured by *ImageJ*. The normalized length of the three exPEC samples in each [NaCl] was averaged at each time point. Stored strain release by hot water was carried out by replacing the NaCl solution with distilled water at different temperatures: 23 (room temperature), 30, 40, 50, 60, 70, 77, and 88 °C. The change in weight of the exPEC was also measured as the stored strain was released in NaCl solutions of concentrations 0, 0.15, 0.45, 0.75, 1.2, and 1.5 M.

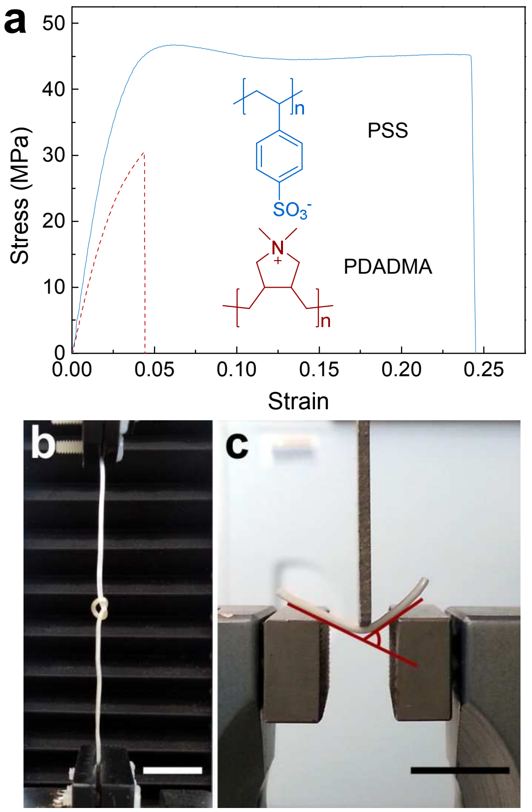

**Fig. 1** Strain-to-break test for stored strain (solid line) and annealed (dashed line) PEC fibers (a). Stretching speed: 10 mm min$^{-1}$ (50% strain min$^{-1}$). Photos of stored strain fibers in a tight knot (b) and the maximum degree (~58°) the annealed sample can be bent (c). The scales bars are 1 cm. Inset of (a) shows the structures of PSS and PDADMA.

## Results and Discussion

Starting materials for the extrusion were made by coprecipitation of equimolar solutions of PSS ($M_w$ ~ 200,000) and PDADMAC ($M_w$ ~ 400,000). After rinsing all the salt out, the precipitated PEC was chopped into pieces and extruded, still wet, at just under 100 °C to yield fiber of diameter about 1 mm. Annealing in salt solutions, or in hot water, allowed polyelectrolyte molecules to approach an anisotropic, compact random coil configuration in the bulk.[29] The properties of dry, as-extruded and dry, annealed fibers are compared in the stress-stain response (Fig. 1a).

The modulus of extruded PEC, exPEC, is higher and the

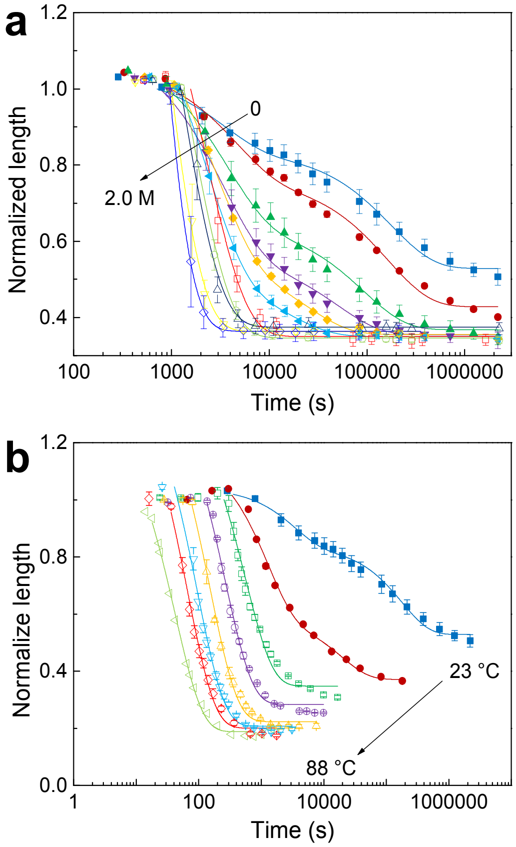

**Fig. 2** Length change (contraction) vs. time of extruded polyelectrolyte complex samples in (a) NaCl solutions 0 (■), 0.15 (●), 0.3 (▲), 0.45 (▼), 0.6 (♦), 0.75 (◄), 0.9 (□), 1.2 (○), 1.5 (△), 1.8 (▽) and 2.0 M (◇); and (b) water at 23 (■), 30 (●), 40 (□), 50 (○), 60 (△), 70 (▽), 77 (◇) and 88 °C (◁). The data with solid symbols were fitted with two rate constants and the data with open symbols were fitted with single rate constant.

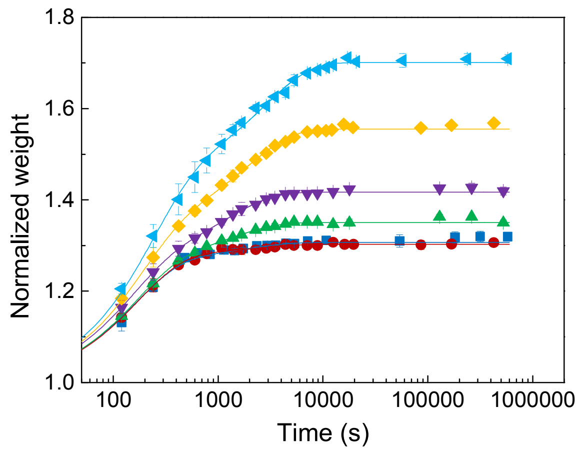

**Fig. 3** Weight change of stored strain polyelectrolyte complex samples in NaCl solutions 0 (■), 0.15 (●), 0.45 (▲), 0.75 (▼), 1.2 (♦), and 1.5 M (◀) with time at room temperature.

material is far tougher than the annealed, anisotropic PEC. For example, in Fig. 1a, the as-extruded samples show a higher modulus (1500 ± 200 MPa) than the annealed samples (1100 ± 40 MPa). The anisotropic PEC breaks at a strain of about 4% with no yield behavior whereas exPEC ruptured at about 24% elongation with a well-developed yield plateau. The toughness of exPEC and annealed PEC are 9.1 ± 2.0 MJ m$^{-3}$ and 0.7 ± 0.2 MJ m$^{-3}$, respectively. The increased toughness is immediately apparent in the properties of the fiber. The strained fiber could be tied into a knot without breaking (Fig. 1b) whereas the annealed material could be bent only about 60 degrees before snapping (Fig. 1c).

Extrusion of a polyelectrolyte complex presents an interesting contradiction in materials properties. On the one hand, each ion pair between positive and negative polyelectrolytes acts as a physical crosslink; thus, the effective crosslink density for materials not doped with salt is extremely high.[7,30] On the other hand, materials with dense, persistent crosslinks are not normally considered good candidates for extrusion.[10,11,28] In our prior work on extruded PEC salt was added during extrusion, with the reasoning that some degree of decoupling between chains was required. We were thus somewhat surprised that extrusion was still feasible with no doping. Because PEC crosslinks are physical it is probable that they can be reversibly broken with sufficient mechanical stress[31] which allows excessively strained chains to relax, rather than break, when the bulk material is sheared.

Under the shear forces of the extrusion individual polymer molecules partially orient, which imparts greater strength and toughness to the bulk material. There was insufficient contrast to use x-ray diffraction measurements to establish molecular alignment,[29] but the strain in the fibers could be relieved by either soaking in salt solutions at room temperature or in hot water. Figs. 2a and b illustrate the release of strain stored in exPEC fibers as a function of time in isothermal solutions of various salt concentrations or in water at various temperatures. The eventual length at long times is independent of salt concentration beyond about 0.3 M NaCl or 60 °C. The shrinkage rate may be fit over most NaCl concentrations with a single first order rate constant

$$l_t = l_f + (1 - l_f)\, e^{-k(t-t_h)} \qquad (1)$$

where $l_t$ is the normalized length of the PEC fibers at time $t$, $l_f$ is the final length (ie. at infinite time), $t_h$ is the time taken for the fiber to be swollen by water before it starts to shrink, and $k$ is the rate constant. When samples are immersed in solution they take up water and salt and swell. Fig. 3 shows the kinetics of swelling for dry exPECs dropped into aqueous NaCl. The time taken to swell to equilibrium in pure water is defined as the hydration time, $t_h$, which is on the order of 1000 sec at room temperature. An additional fit process of rate constant $k_2$ is needed for samples in [NaCl] ≤ 0.75 M or for samples at $T \leq 30$ °C (see Supporting Information for fitting details). For salt concentrations of less than 0.75 M $T_g$ is estimated to be lower than room temperature, thus the material is in its glassy state with slower, and possibly additional, relaxation mechanisms.

If the ratio of initial to final length is defined as the stored strain and related to the molecular anisotropy within the complex, it can be concluded from the salt relaxation measurements that the aspect ratio of the polyelectrolyte

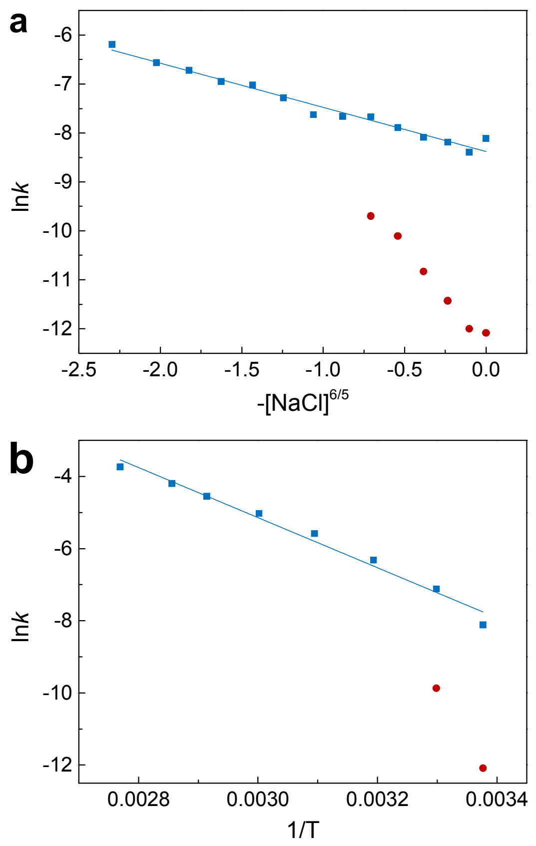

**Fig. 4** Rate constant (s$^{-1}$) $k_1$ (■) and $k_2$ (●) in (a) [NaCl]; and (b) water at different temperatures. The temperature data are depicted as an Arrhenius plot (ln*k* vs. 1/*T*).

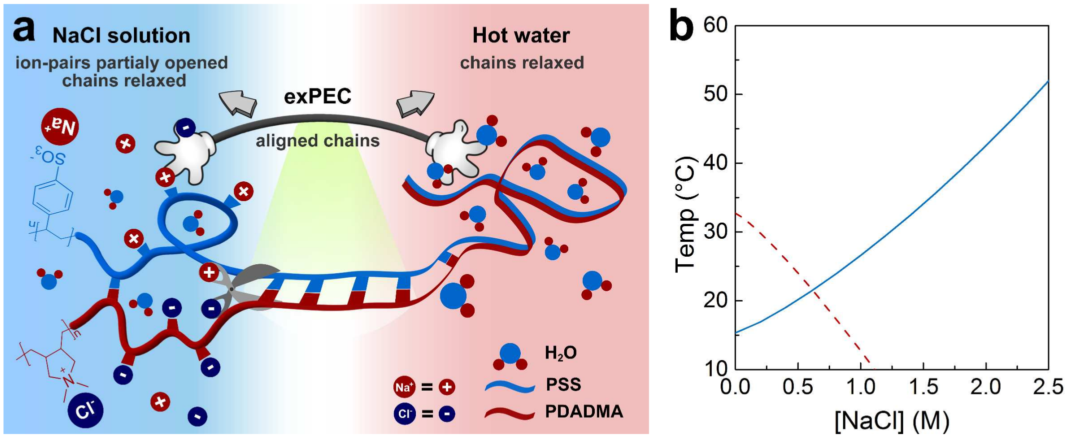

**Fig. 5** Schematic of relaxation of PSS/PDADMA chains in exPEC by NaCl solution and hot water (a); the equivalence between temperature and [NaCl] (solid line) when they yield the same rate constant $k$ (b). d also shows the $T_g$ of PEC(dashed line) at 0.1 Hz from prior work[32].

molecules in the exPEC is about 3. Somewhat higher orientation is deduced if hot water is used to relax the strained PEC, as seen in Fig. 5a. In this case, the molecular strain is about 5.5. We believe that salt allows slippage of some of the ion pairs, whereas in the absence of salt the crosslinks within the fibers are non labile. For proper comparison the material must be maintained in its fully hydrated state (i.e. immersed in aqueous solutions).The slope of an Arrhenius plot of ln$k_1$ vs. $1/T$ (Fig. 4) gives an activation energy of about 58 kJ mol$^{-1}$.

We have previously analyzed the relaxation dynamics of these PECs using a principle of time/temperature/salt superposition.[32] For example, a higher salt concentration can be substituted for a higher temperature in accelerating relaxation (salt/temperature superposition[33]). $T_g$ shifts to lower temperatures with increasing salt content, confirming the plasticizing effect of salt.[32] When the relaxation kinetics in Fig. 2 were fit to first-order decay (Equation 1), the data at higher [salt] or temperatures could be modeled using one process (see Supporting Information). Data below the $T_g$ required at least one additional decay process for good fitting.

Salt/temperature equivalence is illustrated in Fig. 5b, which compares the salt concentration or temperature needed to obtain the same relaxation kinetics (the same $k_1$). The equation relating the two is

$$T\ (^{\circ}\mathrm{C}) = \frac{7290}{25.4 - [\mathrm{NaCl}]^{6/5}} - 273 \qquad (2)$$

where the empirical [NaCl]$^{6/5}$ dependence is the same as determined previously for PSS/PDADMA in NaCl.[32] For example, from Fig. 5b, a change from 1M to 2M NaCl accelerates the relaxation equivalent to an increase of about 16 °C (from 27 to 43 °C). The dashed line shows $T_g$ at 0.1 Hz determined previously. Roughly speaking, to the left of this boundary the system is below $T_g$ and at least one additional relaxation process was needed for acceptable fitting.

The stored strain in exPECs translates to shape memory properties.[34-36] For example, Figs. 6a and b show a PEC sample that was stretched in water at 80 °C using tweezers, removed and allowed to cool. The deformed sample, including tweezer compression marks (Fig. 6b), was stable, even when hydrated. When dried then re-immersed in water at 80 °C for about 10 minutes the sample completely recovered its relaxed dimensions and lost all evidence of having been forcefully gripped by tweezers (Fig. 6c). If the hydrated sample was not allowed to dry, shape recovery took only about 5 seconds. This example of shape memory relies on a 3000-fold difference in relaxation speed between room temperature and 80 °C, although exPEC gradually relaxes in water at room temperature (Fig. 2b).

The shape memory persists for much longer if the sample is dried, a consequence of highly efficient water plasticization. Fig. 6d shows an example of how strain stored

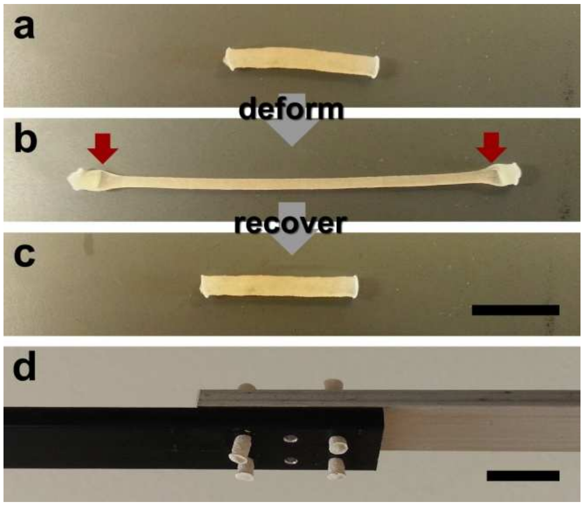

**Fig. 6** Shape memory of hydrated exPEC relaxed by 80 °C water (a); deformed by tweezers at 80 °C and cooled (b); and recovered in 80 °C water to original shape (c). The red arrows in (b) show the compression marks made by the tweezers, which disappear after recovering in hot water. (d) Demonstration of exPEC as "rivets" relaxed by hot water (80 °C) fixing two aluminum bars. The holes in the bars are 1.55 mm in diameter. Scale bars are 1 cm.

in exPECs may be exploited. Aluminum bars with holes of 1.55 mm diameter were threaded with small pieces of dry stored-strain exPEC that had been stored for one year in ambient conditions before use. When exposed to hot water these saloplastic "rivets" pulled the Al bars together and fastened them tightly.

The rivets from Figure 6d were extracted from the Al bars (see SI for images) and subjected to tensile testing (SI). The toughness was 5.5 ± 0.4 MJ $m^{-3}$, a value intermediate between fully relaxed and fully strained, as expected for material that has been partially relaxed.

## Conclusions

Macroscopic samples of polyelectrolyte complex should no longer be discounted as brittle and impractical for use when dry. Partial molecular alignment significantly increases the toughness of the material. The strain stored in PECs may be released with salt water or hot water (or a combination of both). Strain may be re-introduced into the complexes by deforming them in hot water and cooling. The original shape is fully recovered in hot water.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: figures for final length of relaxation in NaCl solution and hot water; details for the fittings. See DOI: 10.1039/b000000x/

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