On the Benefits of Rubbing Salt in the Cut: Self-Healing of Saloplastic PAA/PAH Compact Polyelectrolyte Complexes

Andreas Reisch, Emilie Roger, Thida Phoeung, Cyril Antheaume, Camille Orthlieb, Fouzia Boulmedais, Philippe Lavalle, Joseph B. Schlenoff, Benoît Frisch, and Pierre Schaaf**

The ability to heal, a major advantage, extends the lifetime of natural over synthetic materials. In the case of natural systems healing usually relies on the production of new material from sun, CO_2 and food, a concept still difficult to implement in man-made materials. To circumvent this problem alternative pathways have been developed to create self-healing materials.[1–11] Self-healing generally consists of two major challenges: bringing the separated parts together and reforming broken bonds.[11] It was realized early on that the latter is easiest when non-covalent bonds have been broken and need to be reformed, where no activation energy is needed (or the thermal energy is sufficient).[1,4,10,12] Achieving resistant materials in the absence of covalent bonds requires cooperativity of many weaker non-covalent bonds.[13–16] Hence, polymeric systems are of great interest as they potentially provide a large number of interactions, such as physical entanglements, between molecules. In the aqueous environments found in biological applications, interactions between oppositely charged ionic groups are particularly desirable. Thus polyelectrolyte complexes have drawn enormous interest over the last two decades especially in the form of thin films deposited layer-by-layer: so-called polyelectrolyte multilayers.[17] Complexes in the form of exponentially growing multilayers, which behave as highly viscous liquids,[18] have shown the capacity to self-heal by microscopic flow.[19] More recently, a new processing method provides resilient macroscopic polyelectrolyte complexes through ultracentrifugation[20] or extrusion[21] in the presence of salt. This processing leads to compact polyelectrolyte complexes (CoPECs) which have proven to be attractive materials for biomedical applications due to their mechanical properties,[22] porosity,[23] and easy integration of biologically active compounds.[24] For these applications self-healing of the bulk material, as opposed to a thin polyelectrolyte film, would be an attractive property, mimicking another biologically related feature and providing added versatility. Furthermore, the underlying auto-adhesion is of particular interest for such materials as it would allow the combination of different biologically functionalized building blocks in complex devices.

In the present work, we investigate the inherent mending properties (in the sense of repair requiring external intervention) of poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) CoPECs and how these are facilitated by salt and result in actual self-healing (i.e., entirely autonomous repair).

While working with PAA/PAH CoPECs, especially with samples cut for imaging purposes and conditioned in high concentrations of salt, we realized that these materials tended to stick together without a change in temperature and that they sometimes became very difficult or even impossible to separate

Dr. A. Reisch,[+] Dr. E. Roger, Dr. T. Phoeung, C. Orthlieb
Laboratoire de Conception et Application de Molécules Bioactives
UMR 7199, CNRS/Université de Strasbourg
Faculté de Pharmacie
74 Route du Rhin, 67401 Illkirch Cedex, France

Dr. A. Reisch, Dr. E. Roger, Dr. T. Phoeung,
C. Orthlieb, Dr. F. Boulmedais, Dr. B. Frisch, Dr. P. Schaaf
International Center for Frontier Research in Chemistry
8 Allée Gaspard Monge, 67083 Strasbourg, France
E-mail: frisch@unistra.fr

C. Antheaume
Service Commun d'Analyse
Université de Strasbourg, Faculté de Pharmacie
74 Route du Rhin, 67401 Illkirch Cedex, France

Dr. F. Boulmedais
Centre National de la Recherche Scientifique
Institut Charles Sadron
UPR 22, 23 Rue du Loess, 67034 Strasbourg Cedex, France

Dr. P. Lavalle
Institut National de la Santé et de la Recherche Médicale
INSERM Unité
1121, 11 Rue Humann, 67085 Strasbourg Cedex, France

Prof. J. B. Schlenoff
Department of Chemistry and Biochemistry
The Florida State University
Tallahassee, FL, 32306, USA

Dr. B. Frisch
Laboratoire de Conception et Application
de Molécules Bioactives
UMR 7199, CNRS/Université de Strasbourg
Faculté de Pharmacie
74 Route du Rhin, 67401 Illkirch Cedex, France

Dr. P. Schaaf
Institut National de la Santé et de la Recherche Médicale
INSERM Unité 1121, 11 Rue Humann 67085
Strasbourg Cedex, France
E-mail: schaaf@unistra.fr

Dr. P. Schaaf
Centre National de la Recherche Scientifique
Institut Charles Sadron, UPR 22
23 Rue du Loess, 67034 Strasbourg Cedex, France

[+]Present address: CNRS UMR 7213, Laboratoire de Biophotonique et Pharmacologie, Université de Strasbourg, Faculté de Pharmacie, 74 Route du Rhin, F-67401 Illkirch Cedex, France

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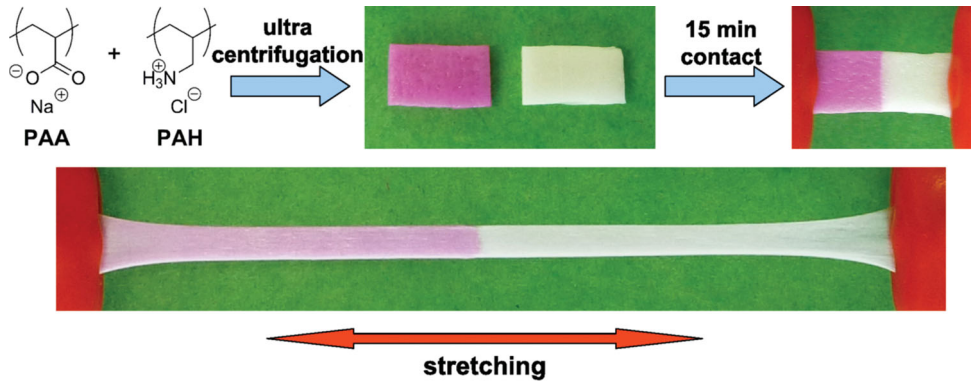

Figure 1. General procedure of making, cutting, mending, and stretching of the compact polyelectrolyte complexes (all at room temperature): CoPECs were made by mixing solutions of PAA and PAH then compacting by ultracentrifugation in the presence of salt. CoPECs were compressed to obtain thin sheets and cut into the desired shapes (here, the PAH in the left-hand piece of complex is labeled with rhodamine). For mending they were brought into contact for the desired time period (here 15 min) in a specific salt concentration (here 2.5 M NaCl). After reconditioning the samples were stretched until they broke.

again. Two parameters influencing the strength with which pieces stuck together (**Figure 1**) were the time the samples were in contact and the NaCl concentration under which this occurred. We studied the resistance to stretching for samples cut and then brought together for different time intervals in 2.5 and 1 M NaCl (**Figure 2**). (Unless otherwise noted, the samples were conditioned in 0.15 M NaCl before stress-strain experiments were performed.)

Strain to break experiments on uncut samples showed that they have excellent stretchability with an ultimate tensile strain above 500 % and an ultimate tensile strength of about 3.2 MPa (Figure 2). An analysis of the initial part of the curves gave a Young's modulus of about 300 kPa corresponding to soft rubbers and of the same order of magnitude as the modulus of skin.[25] Using the area under the stress strain curve (using the true stress and strain) yields a toughness of 1. 7 (±0.6) MJ m^{-3} about half that found for PSS/PDADMA CoPECs under the same conditions.[21] This toughness may be compared to that of poly(methyl methacrylate) which is about 2 MJ m^{-3}, to that of nanocomposite layer-by-layer formed films made of montmorillonite and chitosan (0.5 MJ m^{-3}) or poly(diallyldimethylammonium chloride) (0.9 MJ m^{-3}).[26] Using the area under the stress-strain curves recorded after cutting and mending did not show a significant influence of the mending procedure on the form of the curve, except for the difference in ultimate tensile strengths (Figure 2a). As can be seen in Figure 2b the ultimate tensile strain of the samples increased with the contact time. For more than 1 h of contact in 2.5 M NaCl the mended samples fully regained their original stretch resistance, though the rupture still occurred at the cut because of the residual weakness.

Mending in 1 M NaCl always yielded a lower ultimate tensile strain for a given contact time than mending in 2.5 M NaCl. Furthermore, at 1 M NaCl the samples did not completely recover their initial ultimate tensile strain, even after mending times close to 6 h. We hence investigated the influence of the salt concentration on mending in more detail. For this we chose a contact-time of 20 min, as this corresponded to the time after which samples in 2.5 M NaCl recovered most (about 80%) of their initial ultimate tensile strain. Mending was performed in different salt concentrations and the samples were stretched to break (Figure 2c). The resulting ultimate tensile strain depended strongly on the salt concentration of the "mending solutions": In the case of 0.15 M NaCl mending practically did not occur and only about a third of the samples were healed well enough to allow testing by the stretching device, while the others broke prematurely during handling. Increasing the salt concentration of the solution in which the samples were brought into contact led to an increase of the ultimate tensile strain especially for mending in more than 1 M NaCl, and above 2.5 M NaCl at least part of the samples were recovered nearly entirely their mechanical resistance. Interestingly, this mending was still possible after more than 5 days of separation of the samples (Supporting Information, Figure S1).

Together, these results indicate that mending of these materials did not simply involve direct interaction of chains on the surfaces, that is the complexation of partially free chains situated on opposite surfaces. Such a mechanism should be practically independent of the contact time and it should work whatever the salt concentration (or even become more difficult at higher salt concentration due to screening of the attraction between different charges). To better understand the mending, the structure giving mechanical resistance to CoPECs should be considered.[20,22,27] These are actually physical gels in which cross-links are formed by ion pairs between charged groups located on different chains on the one hand and entanglements of the chains on the other hand. As no covalent cross-links exist, the chains are in principal able to move relative to each other. However, this has to involve the cooperative separation of several ion pair cross-links and the reformation of new ones. To evaluate the influence of the salt concentration on the movement of chain segments, we employed ^{13}C NMR relaxation measurements. NMR relaxation times are known to correlate with the mobility of the corresponding groups.[28–33] Over the range of NaCl concentrations tested here, the T_2 relaxation times of the backbone carbons increased roughly by a factor

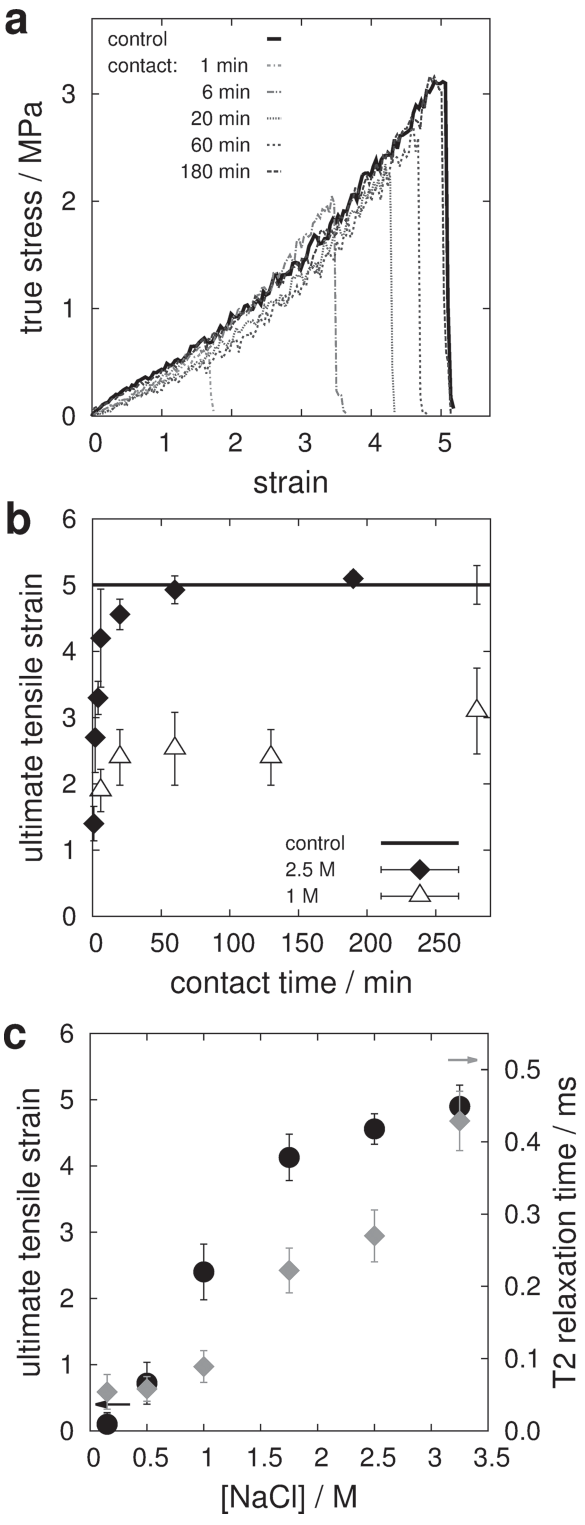

Figure 2. Stretching of CoPECs and the influence of time and NaCl concentration on mending: a) Typical stretch to break curves for CoPECs as prepared (control) and after cutting and mending for different times in 2.5 M NaCl. All samples were conditioned in 0.15 M NaCl before straining at a rate of 2 mm s^{-1}, or 15% s^{-1} b) Ultimate tensile strain as a function of contact time for mending in 1 and 2.5 M NaCl. c) Influence of the salt concentration on ultimate tensile strain for a contact time of 20 min (black circles) and on the ^{13}C T_2 relaxation time of the peak at 46 ppm corresponding to the PAA and PAH backbone carbons (grey diamonds).

of 8 (Figure 2c), which is accompanied by a corresponding decrease of the peak width (Supporting Information, Figure S2). At the same time the T1 relaxation times only decreased slightly (Supporting Information, Figure S3). This indicates that the corresponding chain segments became increasingly mobile. This could be explained by considering the equilibria of complex precipitation (Equation 1) and salt-doping (Equation 2):

$$Pol^+Cl^-_{aq} + Pol^-Na^+_{aq} \rightarrow Pol^+Pol^-_s + Na^+_{aq} + Cl^-_{aq} \quad (1)$$

$$Pol^+Pol^-_s + Na^+_{aq} + Cl^-_{aq} \rightarrow Pol^+Cl^-_s + Pol^-Na^+_s \quad (2)$$

where "aq" is the aqueous phase and "s" is the solid PEC phase.

An increase of the NaCl concentration shifts the equilibrium 2 to the right and thus leads to the breaking of cross-links.[27,34] The decrease of the concentration of cross-links would then lead to the observed higher mobility of the chains relative to each other. Breaking of crosslinks is manifested as decreased bulk modulus and plasticization of the bulk CoPEC.[34]

The assumed mechanism of mending is as follows: cutting the CoPEC leads to breaking of chains and to extraction of parts of chains from one side under the action of the blade. Once the different sides are brought together again, polyelectrolyte chains can interdiffuse across the cut and engage in new bonds between charged groups, finally recovering the same amount of bonds across the cut as before. With time this interdiffusion will "heal" the cut. With increasing salt concentration, the mobility of the chain segments increases, and the more mobile the segments, the faster the chains diffuse and thus "heal" the cut. However, if the mobility of the segments is very low as in the case of 0.15 M NaCl, the cooperative movement of the chains is hindered so that even after long times mending is not achieved.

What is described above is actually not self-healing of the CoPECs as it always required manually placing the samples in contact. True, autonomous self-healing, on the other hand, requires that, once the force that caused the samples to break is removed, the samples can regain their initial shape and reconstruct the break plane in the absence of external manipulations. To test this we worked in 1 M NaCl (**Figure 3**), where the samples remained elastic yet mending was clearly observed. Strips of complexes conditioned in 1 M NaCl were slightly stretched, cut halfway through, then left to relax in 1 M NaCl, recovering their initial shape. After 2 h, slight stretching of the samples showed that healing of the cut indeed started. Leaving them for another 8 h in 1 M NaCl then led to a practically complete healing of the cut, which also survived stretching.

In summary the inherent room temperature mending and self-healing properties of saloplastic PAA/PAH CoPECs were studied. Mending in these non-covalent materials is due to interdiffusion of the polyelectrolyte chains across the cut. One can assume that full adhesion of the plane of fracture only requires interdiffusion on the order of a few times the dimensions of the polymer chains, a few nm, to complete re-entanglement. As the mobility of chain segments increases with increasing salt concentrations, mending becomes faster and more complete. At intermediate salt concentrations the CoPECs remain elastic enough to recover their original shape while the chains are mobile enough to repair the cut, leading to

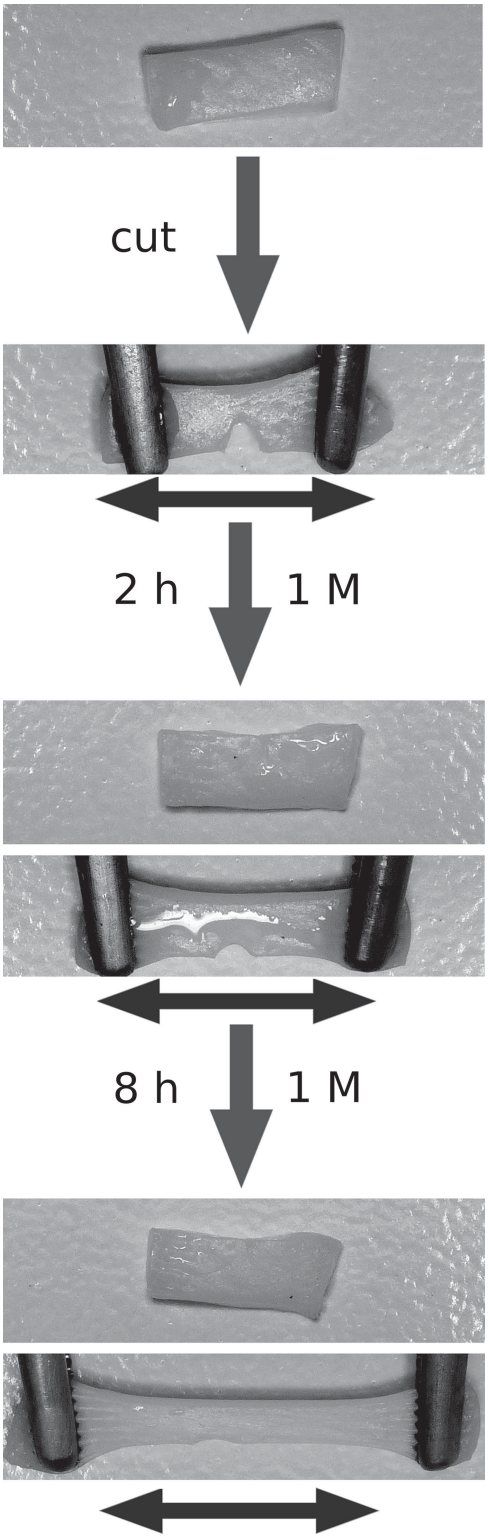

Figure 3. Autonomous self-healing and elasticity of a strip of CoPEC in 1 M NaCl. From top to bottom: the strip of CoPEC was conditioned in 1 M NaCl and cut halfway through while being stretched; when the force was removed the strip returned to its initial shape and after leaving the strip for 2 h in 1 M NaCl the cut had already partly disappeared; after a further 8 h the cut had healed nearly completely and the strip could be stretched further again.

actual self-healing behavior. These properties are of particular importance in view of the high potential of these materials for biomedical applications, as they could not only allow for their auto-repair in situ, but also lead to the assembly of complex materials through the combination of CoPECs containing different types of cells or biomolecules. Because it is based on the interdiffusion of polyelectrolytes, self-healing in CoPECs does not require any polymer modification or additional chemical compound, in contrast to many other self-healing polymeric materials.

Experimental Section

CoPEC and Sample Preparation: PAA/PAH CoPECs were obtained as described previously:[23] equal volumes of PAA (Sigma–Aldrich, M_w = 250 000 g mol^{-1}) and PAH (AlfaAesar, M_w = 104 000 g mol^{-1}) 0.1 M solutions (2.5 M NaCl, Tris buffer) were added simultaneously to a beaker under stirring. Complexes were then transferred into polycarbonate thick-wall centrifuge tubes (Beckman Coulter Inc.) and ultracentrifuged in a Beckman Coulter Ultracentrifuge using a Ti90 rotor at 188 000g for 4 h at 23 °C. The PAA/PAH ratio of these CoPECs was 1.00 ± 0.03.[23]

For mending and mechanical experiments, the CoPECs were compressed to yield 1 mm-thick flat sheets. Samples were then cut using a dogbone-shaped cutter (linear part 2 mm × 6 mm, Pappadeck-Formadeck, France). For the NMR experiments ultracentrifugation was performed in tubes having an internal diameter of 4 mm placed inside the centrifuge tubes.

Mechanical Testing: Stretching was performed using a rheometer (Haake Rheowin Rheometer, Fisher Scientific) equipped with clamps that allowed vertical stretching at room temperature (22 ± 2 °C) on samples conditioned in 0.15 M NaCl. The sample was stretched at a speed of 2 mm s^{-1} while recording the normal force. All the mechanical measurements were performed while the CoPEC was wetted by 0.15 M NaCl. For each condition three samples were tested in at least two independent series. Videos of the stretching together with the normal force as a function of displacement were used to obtain the strain on the linear part ε and the true stress σ_{true} (see Supporting Information).

Mending: The samples were cut using histological blades and left separated for a given time in 0.15 M NaCl. They were then immersed for 1 min into a solution of a given NaCl concentration. Immediately afterwards they were placed on a glass slide and held in contact by hand for 1 min. Then they were put back in the salt solution for a given time. Finally they were reimmersed in 0.15 M NaCl (for at least twice the time they have been in other salt concentrations).

NMR Spectroscopy: NMR spectroscopy experiments were conducted on a Bruker Avance III operating system at 500 MHz for ^{1}H and 125 MHz for ^{13}C. The ^{13}C T_1 relaxation time was determined using the standard pulse sequences from Bruker. The ^{13}C T_2 relaxation time was measured using a Carr, Purcell, Meiboom and Gill (CPMG) pulse sequence with inverse gated decoupling. Analysis of the results is described in more detail in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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