Relaxation Dynamics at Different Time Scales in Electrostatic Complexes: Time-Salt Superposition

Evan Spruijt, Joris Sprakel, Marc Lemmers, Martien A. Cohen Stuart, and Jasper van der Gucht

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

School of Engineering and Applied Sciences, Harvard University, 9 Oxford Street, Cambridge, 02138 Massachusetts, USA

(Received 15 June 2010; published 8 November 2010)

In this Letter we show that in the rheology of electrostatically assembled soft materials, salt concentration plays a similar role as temperature for polymer melts, and as strain rate for soft solids. We rescale linear and nonlinear rheological data of a set of model electrostatic complexes at different salt concentrations to access a range of time scales that is otherwise inaccessible. This provides new insights into the relaxation mechanisms of electrostatic complexes, which we rationalize in terms of a microscopic mechanism underlying salt-enhanced activated processes.

DOI: 10.1103/PhysRevLett.105.208301 PACS numbers: 83.80.Rs, 41.20.Cv, 82.35.Rs, 83.60.Bc

Electrostatically driven assemblies are ubiquitous in natural and man-made soft materials. In nature, attractive electrostatic forces play an important role in the condensation of DNA with histones [1], in the binding of peripheral proteins to membranes [2] and in the exceptional thermal stability of enzymes in thermophilic bacteria [3]. Nature’s approaches for electrostatic assembly have been mimicked using synthetic building blocks to create photonic materials [4], self-healing gels [5], and multilayered capsules of various sizes and possible cargos [6]. Despite the plethora of phenomena where electrostatic attractions are relevant, it remains poorly understood how environmental factors, such as ionic strength, influence the dynamics of these complexes. Moreover, there are no clear methods available to experimentally analyze these effects.

In this Letter, we propose a new approach to study the dynamics of electrostatic complexes. We show that probing the rheological behavior of a model electrostatic complex at different ionic strengths is equivalent to probing the behavior at different time scales. This allows for superimposing rheological data at different salt concentrations, which together with the proposed model leads to a new way to systematically investigate the effects of temperature and salt concentration on relaxation behavior and mechanical properties of these complexes.

Superposition is used as a tool in rheology to probe dynamical processes in a wide variety of soft materials, thereby extending our understanding of their dynamics. For example, time-temperature superposition [7] relies on the acceleration of all activated processes at high temperatures, enabling probing of longer effective time scales at high temperatures. Analogously, strain-rate-frequency superposition allows one to probe low-frequency structural relaxation of soft solids, such as concentrated suspensions and foams, by enhancement of activated processes by external force [8]. In this Letter, we apply a similar approach to study the dynamics of a yet underrepresented class of soft materials: electrostatic complexes. In addition to the model materials presented here, our approach could easily be extended to other electrostatic complexes, both natural and man made, to help elucidate unresolved issues in the dynamics of electrostatic complexes.

We use complexes of two equally long and oppositely charged polyelectrolytes, namely, poly(acrylic acid), a polyanion (effective $pK_a = 5.0–5.5$ for $c_{salt} = 2.0–0.10$ M), and poly(N,N-dimethylaminoethyl methacrylate), a polycation (effective $pK_a = 8.0–7.5$). The phase behavior of these complexes in aqueous monovalent electrolyte solutions has been worked out experimentally [9]. We use polyelectrolytes with a degree of polymerization of 20, 50, 150, or 510 (PDI < 1.2) at pH 6.5 where the polycation and polyanion have equal charge densities. When mixed together, the mixture phase separates into a dilute phase and a dense, viscoelastic phase that contains about 70 wt % water. Our polyelectrolyte complexes are prepared at different salt concentrations but always at 1:1 stoichiometry of polymeric charges. In addition, another set of polyelectrolytes, synthesized by atom transfer radical polymerization, with a degree of polymerization of 100 (PDI < 1.1) is used [10]. These polyelectrolytes contain no pH-dependent charges, but permanently charged sulfonate and quaternary ammonium groups. Complexes with these polyelectrolytes are made in the same way as described above. All rheological measurements are carried out on an Anton Paar MCR501 series stress-controlled rheometer using a cone-plate geometry.

The frequency sweeps shown in Fig. 1 are typical examples for our model polyelectrolyte complexes in a regime of linear deformation. The rheological response of polyelectrolyte complexes to an oscillatory strain depends strongly on salt concentration. At low salt concentration the response is similar to that of soft solids [8], whereas the response is liquidlike at high salt concentration. These observations are in line with results on biological electrostatic complexes [11].
Salt is known to accelerate dynamic processes in polyelectrolyte complexes. This leads to faster equilibration and eventually to hysteresis-free cycles of compression and disruption of polyelectrolyte complexes, as was shown using atomic force microscopy [12]. In well-known superposition methods in rheology, like time-temperature superposition and strain-rate-frequency superposition, such acceleration of dynamic processes provides the basis for probing dynamic processes on a range of time scales that is otherwise experimentally inaccessible. Could we use analogous rescaling of measurements shown in Fig. 1 in order to get more insight into the dynamics of these polyelectrolyte complexes as well? Figure 2(a) shows that the frequency sweeps for different salt concentrations can indeed be rescaled onto a single mastercurve using salt concentration dependent shift factors for the frequency, such that \( \omega_{\text{scaled}} = \omega \tau_c \), and for the moduli, such that \( G'_{\text{scaled}} = G'/G_c \) and \( G''_{\text{scaled}} = G''/G_c \). Shift factors \( \tau_c \) and \( G_c \) are chosen such that the crossover between storage and loss modulus, which is related to a typical relaxation time in many rheological models, occurs at a rescaled frequency and modulus of unity. Figure 2(a) shows that the relevant dynamic processes in these polyelectrolyte complexes respond similarly to salt concentration, which enables us to probe these complexes over seven decades in frequency.

The limits of the accessible dynamic range are dictated by a combination of instrumental and thermodynamic factors. The upper limit is given by the maximum accessible frequency of the rheometer and a theoretical minimum salt concentration close to zero. The lower limit is given by the critical salt concentration, beyond which polyelectrolyte complexes no longer form. In this case, we use a creep test to probe the lowest frequencies and hence longest time scales. Data of creep compliance as a function of strain rate are converted into frequency-dependent storage and loss moduli using a direct mathematical procedure [13].

If the apparent relaxation times, \( \tau_c \), and moduli, \( G_c \), are to provide a meaningful measure for the relevant dynamic processes in electrostatic complexes, we expect that they can be used to rescale nonlinear flow experiments as well. Indeed, Fig. 2(b) shows that both linear and nonlinear regimes of strain rate sweeps at various salt concentrations can be rescaled using the same shift factors as for Fig. 2(a). The inset shows rescaled flow curves for \( N = 20 \) (\( \triangle \)), \( 50 \) (\( \times \)), \( 100 \) (\( \diamond \)), \( 150 \) (\( \square \)), and \( 510 \) (\( \bigcirc \)) polyelectrolyte complexes. For reasons of clarity, one per five data points is shown in the inset.

As shown in the inset of Fig. 2(b), a similar rescaling can also be applied to polyelectrolytes of different chain

---

**Fig. 1** (color online). Frequency sweeps of a \( N = 510 \) polyelectrolyte complex at \( \gamma = 2\% \) and salt concentrations as indicated in the figure, showing storage (\( \bigcirc \)) and loss (\( \triangle \)) moduli.

**Fig. 2** (color online). (a) Rescaled frequency sweep of a \( N = 510 \) polyelectrolyte complex at \( \gamma = 2\% \). Storage moduli are shown using circles and crosses, loss moduli using triangles and pluses. Filled symbols are converted from a creep test. Solid lines are drawn to guide the eye. (b) Rescaled flow curves for \( N = 510 \) polyelectrolyte complexes. The inset shows rescaled flow curves for \( N = 20 \) (\( \triangle \)), \( 50 \) (\( \times \)), \( 100 \) (\( \diamond \)), \( 150 \) (\( \square \)), and \( 510 \) (\( \bigcirc \)) polyelectrolyte complexes. For reasons of clarity, one per five data points is shown in the inset.
ical data can be superimposed by using two salt-dependent
completely independent of chain length [9], and entanglements
the onset of the nonlinear regime is not exactly the same for
all chain lengths. This can be explained by the fact that
polymer concentrations in these complexes are not com-
pletely dependent on chain length [9], and entanglements
become important for longer polymers.

Our observation that both linear and nonlinear rheolog-
ical data can be superimposed by using two salt-dependent
shift factors, \( \tau_c \) and \( G_c \), suggests that a simple mechanism
underlies the dynamics of electrostatic complexes. Figure 3
shows that there is a strong dependence of the apparent
relaxation time, \( \tau_c \) and a much weaker dependence of the
modulus, \( G_c \), on salt concentration for all chain lengths.

The depicted dependences of \( \tau_c \) and \( G_c \) are closely
related to the stress relaxation mechanism inside poly-
electrolyte complexes. These complexes can be seen as
concentrated two-component polymer solutions. Stress
relaxation occurs by movement of chains, which is hin-
dered by associations in the form of ion-ion pairs between
two oppositely charged polyelectrolytes (sticky points).
This suggests that the dynamics of chains with “sticky
points” should apply, for which [15]

\[
\tau_c = N^a \phi_p^b \zeta_0(c_{\text{salt}})
\]

where \( N \) is the polymer chain length, \( \phi_p \) is the polymer
volume fraction and \( \zeta_0 \) is an effective friction coefficient,
which depends on salt concentration. The magnitude of \( a \)
depends on the regime of relaxation: for Rouse-like relaxa-
tion \( \alpha = 2 \), for reptation \( \alpha = 3.4 \). The magnitude of \( b \)
depends somewhat on solvent quality, but is typically close
to unity [15]. The breaking of association points is related
to the dissociation rate of ion-ion pairs. We assume this is
an activated process, governed by an energy barrier, \( E_a \)

\[
\zeta_0(c_{\text{salt}}) = \frac{1}{\omega_0} \exp \left[ \frac{E_a(c_{\text{salt}})}{k_B T} \right]
\]

Reorganization of associations encompasses the break-
ing of polymeric ion-ion-pairs, separating each two ionic
groups, thereby surrounding them with monovalent coun-
terions, and reforming polymeric ion-ion pairs at different
positions. This route contains an energy barrier that can be
estimated as the difference between the electrical free
energy of four separated ionic groups of charge \( \pm e \) in
an electrolyte solution, and the Coulombic energy of
two ion-ion pairs in contact: \( E_a = E_{\text{corr}} - E_{\text{Coul}} \). The elec-
tric correlation energy is approximated as \( E_{\text{corr}} =
-2\kappa e^2/4\pi\varepsilon e_0 \propto \sqrt{c_{\text{salt}}} \) [16], where \( \kappa \) is
the inverse Debye length. The Coulombic energy can be written as
\( E_{\text{Coul}} = -e^2/2\pi\varepsilon e_0 d \), where \( d \) is the contact distance
of charged groups in an ion-ion pair. Combining this with
Eqs. (1) and (2), we find

\[
\tau_c \approx \frac{1}{\omega_0} N^a \phi_p^b \exp[-a(T)c_{\text{salt}} + b(T)]
\]

Equation (3) predicts that the activation barrier depends
on the square root of salt concentration, leading to a
stretched exponential dependence of \( \tau_c \) on \( c_{\text{salt}} \). We have
previously found that also \( \phi_p \) depends weakly on \( c_{\text{salt}} \) [9].
This dependence is, however, significantly weaker than
the variations in \( \tau_c \) shown in Fig. 3. The relaxation times
presented in Fig. 3(a) have therefore been fitted to
Eq. (3), using only an adjustable prefactor \( A = \omega_0^{-1} N^a
\phi_p^b \exp[b(T)] \), and a fixed value of 11 for \( a(T) \). We find an
good agreement between our data and the presented
model. Moreover, the value of \( a(T) \) we find is quantita-
tively in agreement with the theoretical prediction of
11.3 for \( \varepsilon = 45 \) and \( T = 293 \) K, which is a reasonable
assumption for concentrated polyelectrolyte complexes
[17]. Finally, the prefactors, \( A \), scale according to \( N^a \),
with \( \alpha = 2.5 \), as expected.

A key assumption in our conceptual picture is that an
activated dissociation of ion-ion pairs governs the relaxa-
tion dynamics of electrostatic complexes. Consequently, \( \tau_c \)
should be a function of temperature as well. This is verified
in a time-temperature superposition experiment, where we
determine relaxation times as a function of temperature
[Fig. 3(a), inset]. Assuming that \( \varepsilon \) is independent of \( T \) [17],
we expect \( \tau_c \) to scale with \( \exp(T^{-1}) \) or \( \exp(T^{-1.5}) \)
as the two limiting cases [Eq. (3)]. The fits in the inset of
Fig. 3(a) for \( \exp(T^{-1}) \) (solid lines) and \( \exp(T^{-1.5}) \) (dashed
lines), show that it is experimentally not possible to dis-
tinguish between these limiting cases for aqueous systems.
In contrast to the relaxation times, the moduli are found to depend only weakly on $c_{\text{salt}}$. This is simply due to the coupling between salt concentration and overall polymer density, as was shown in [9]. We find a linear relation between the modulus and $\phi_p/N$ (data not shown), as expected for unentangled polymer solutions in which each chain contributes $k_B T$ to the modulus [15].

The presented analysis of the dynamics in polyelectrolyte complexes provides a general tool to study dynamics in other soft materials that are assembled by electrostatic complexation. To verify this generality, we carry out the same approach on a transient network formed by telechelic complexes: for example, those concerning the formation mechanism of electrostatic complexes [18] and those concerning the dynamics of biological complexes, such as the DNA-histone complex, at rest or under mechanical and chemical stresses during cell division [19].

The authors gratefully acknowledge Frans Leermakers for fruitful discussions. E.S. and J.S. acknowledge the Netherlands Organisation for Scientific Research (NWO) for financial support.

*evan.spruijt@wur.nl