A comparison of complexation induced brittleness in PEI/PSS and PEI/NaPSS single-step coatings

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In the field of coatings, there is a major trend towards the reduction of volatile organic compounds by developing water-based alternatives for traditional solvent-based paints. Complexes of oppositely charged polyelectrolytes have recently emerged as a promising candidate for such coatings. Recently, we developed an ammonia-evaporation induced complexation approach to form polyelectrolyte complex films of two weak polyelectrolytes in a single step. Here, we extend this method by applying it to a combination of PEI/PSS, a weak polycation and a strong polyanion. Homogenous solutions at different ratios were successfully prepared. After casting and drying, dense and optically transparent layers were formed. As a comparison, PEI/NaPSS was also studied. Contrary to PEI/PSS, the pH in PEI/NaPSS films remains high during drying and NH\textsubscript{3} evaporation, so PEI does not acquire a positive charge, thereby preventing complexation. We show that this leads to large differences in the properties of the films, with the PEI/NaPSS films being more sensitive to water, more ductile, and more prone to phase separation. We also found that the mechanical properties of the films depend strongly on the charge ratio: films made at a PEI/PSS ratio between 2:1 and 1:1 formed the strongest complexes, resulting in films that swell relatively little in water, but that are also brittle and prone to cracking during drying. In this work, we report a systematic study into this promising system and show its potential and tunability.

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1. Introduction

Polyelectrolyte complexes (PECs) have been widely applied in the pharmaceutical and biomedical fields [1–3]. Single polyelectrolytes are usually water-soluble, but when two or more oppositely charged polyelectrolytes meet, they can form water-insoluble complexes [4]. This unique transition of a PEC makes it a promising water-based material for making dense polymer coatings. The most commonly used method to construct PEC coatings is layer-by-layer (LbL) assembly. By simply repeated dipping or spraying two oppositely charged polyelectrolytes, a well-defined nanometer-thick polyelectrolyte multilayer (PEM) structure can be fabricated [5,6]. However, this method is time-consuming, which limits practical use especially when macroscopic coatings are required. Researchers have therefore been working on rapid LbL assembly [7] or new methods with fewer deposition steps [8–12]. Among others, previous work [13], following Pietsch et al. [14], has demonstrated an evaporation-based method to form polyethyleneimine (PEI) and poly(acrylic acid) (PAA) complex films. Ammonia, as a volatile base, was used to gradually change the pH during drying, thereby charging up the PEI and inducing complexation. This approach also allowed us to cast PEC films in one step with precise control over composition and thickness.

One of the interesting features of PECs is their reversibility and responsiveness to the environment. While this behavior is often desired for applications like drug delivery [1] and anti-reflecting coatings [15], it can be problematic to other applications that require mechanical stability. The mechanical properties of PECs are not only defined by the blending of single polyelectrolytes but also by the ionic interactions. It is well established that several key factors influence the mechanical properties, for example, water content, temperature, pH, stoichiometry, and salt concentration [16–25]. Water, for example, is known to be a strong plasticizer for PECs, having a pronounced effect on the mechanical properties and allowing PECs to be processed as plastics [16]. Another significant factor is the morphology and structure of PECs which varies from application to application. Thus, the mechanical properties of PECs are studied in versatile forms, including PEM [16, 26–31], nanoparticles [32], nanotubes [33], capsules [34–37], hydrogels [38–40], fibers [22], scaffolds, [41,42] extruded rods or tubes [43], and flat membranes [44–46]. Except for standard mechanical measurements, other indirect techniques were utilized such as atomic force microscopy (AFM) [30,31,47].

However, limited by the preparation methods, most of the previous studies mentioned above only focused on one specific composition or charge ratio. With our preparation method, which can control the final composition of the film, it is possible to study the influences of the presence/absence of complexation and charge ratio on the mechanical properties. Since our method is evaporation-based, the cracking of the film at different thicknesses can also be an indicator of the mechanical properties. Similar to other polymers, the evaporation of solvents can build up stress in the film that can eventually lead to shrinkage, cracking, or delamination. This phenomenon worsens with increasing thickness [48]. The maximum thickness beyond which films begin to crack is defined as the critical cracking thickness.

In this work, we apply the ammonia-evaporation induced complexation approach to a new polyelectrolyte combination, branched PEI and poly (4-styrenesulfonic acid) (PSS), to fabricate micrometer thick films. As a comparison, PEI and polyelectrolyte complexation (NaPSS) films were also prepared by a similar evaporation method. Both free-standing PEI/PSS and PEI/NaPSS films were prepared at various charge ratios. By comparing their phase behavior, water uptake, and mechanical properties, the importance of pH and the different levels of complexation for the final mechanical properties is clearly demonstrated. Finally, dense PEI/PSS films were prepared on biaxially oriented propylene sheets to examine whether it can work as an oxygen barrier coating.

2. Experimental section

2.1. Materials

Branched polyethylenimine with two different molecular weights (PEI, average Mw = 25 kg mol$^{-1}$, ≤1% water and average Mw = 750 kg mol$^{-1}$, 50 wt% in water), poly (4-styrenesulfonic acid) (PSS, average Mw = 75 kg mol$^{-1}$, 18 wt% in water), poly(sodium 4-styrenesulfonate) (NaPSS, average Mw = 70 kg mol$^{-1}$, 30 wt% in water), ammonia aqueous solution (NH$_3$, for analysis EMSURE® ISO, Reng. Ph Eur, 25% in water), hydrochloric acid (HCl, ACS reagent, 37%), sodium hydroxide (NaOH, >98% pellets), sodium sulfate (Na$_2$SO$_4$, ACS reagent, >99.0%, anhydrous, powder), and thymol blue (ACS reagent) were all purchased from Sigma-Aldrich (The Netherlands). According to Sigma-Aldrich, both branched PEI have a high polydispersity (PDI$~$75k ~ 2.5 and PDI$~$750k ~ 12.5). All water used was deionized water (Milli-Q®, Merck, The Netherlands). All chemicals were used without further purification. Biaxially oriented polypropylene (BOPP) sheets were purchased by BASF from Hapece B.V., The Netherlands. Acetate sheets (250 μm thick) were purchased from JEJE produktd, The Netherlands.

2.2. Preparation of PEI/PSS phase diagrams

2.2.1. Varying NH$_3$ concentration

PEI (Mw = 25 kg mol$^{-1}$) was used for all phase diagrams. It was diluted to 20 wt% using deionized water. PSS 18 wt% aqueous solution was first dried in the oven at 80 °C overnight and stored under vacuum at 30 °C. A 35 wt% stock solution of PSS was prepared from this dried solid. Then it was diluted with 25 wt% NH$_3$ solution to 30, 25, and 20 wt%. These solutions were further diluted to 20 wt% with deionized water, resulting in four different levels of NH$_3$ concentrations. Different charge ratios of PEI/PSS were prepared from 3:1–1:3. The monomeric mixing ratio was based on the ratio of charged monomers considering every amine group of PEI (M$_{NH_3}$ = 43.04 g mol$^{-1}$) and one charge per monomer for PSS (M$_{SS}$ = 184.23 g mol$^{-1}$).

The turbidity of samples at a ratio of 1:3 were measured using a portable turbidity meter (Turbtur® 430 IR–WTW). The samples were prepared (~ 20 g) following the same procedures in a transparent glass bottle. The measurements were conducted after at least 8 h to ensure no bubbles were present. The unit was FNU (Formazin Nephelometric Units).

2.2.2. Varying polyelectrolyte concentration

Both PEI and PSS were diluted with deionized water to 35, 20, 10, and 5 wt%. Four sets of samples (35, 20, 10, and 5 wt%) with different ratios of PEI/PSS were prepared.

2.2.3. Adjusting pH before mixing

Five sets of different pH (2, 4, 6, 8, and 10) samples were prepared. The pH of 20 wt% PEI and PSS solutions were first adjusted to the desired pH value by adding HCl or NaOH. After that, they were further diluted with deionized water to 10 wt%. The pH was adjusted again if required. Different ratios of mixtures were prepared for each pH value.

All phase diagram samples were prepared by adding PSS-NH$_3$/PSS solution into the PEI solution. The mixtures were stirred vigorously with a stirring bar overnight. Photographs of these samples were taken after at least 48 h. Depending on the appearance of the mixtures, they were identified as a solid complex (visible solid in solution), a colloidal dispersion (one turbid phase), or a solution (one transparent phase). Then the pH was measured using pH strips (pH 0–14 Universal indicator, Merck, The Netherlands). Proper measurements with a pH meter were not possible since the viscosity of mixtures was high and it might cause damage to the probe. The eye dropper tool from Adobe Illustrator was used to identify the final pH (Fig. S1).
2.3. Preparation of PEI/NaPSS solutions

Different charge ratios of 20 wt% PEI25k:NaPSS solutions were prepared from 3:1–1:3. As before, the ratios of charged monomers were used for calculation (\( M_{\text{eq}} = 43.04 \, \text{g} \, \text{mol}^{-1} \) and \( M_{\text{NaPSS}} = 206.21 \, \text{g} \, \text{mol}^{-1} \)). NaPSS solution was diluted from the stock 30–20 wt%, then added into 20 wt% PEI solution. The mixtures were stirred vigorously overnight.

To observe and compare the pH changes, thymol blue was used as an indicator. Thymol blue was added into the solutions (PEI:PSS 3:1/1:3 and PEI NaPSS 1:3) and mixed homogenously until a uniform blue color appeared. Then, they were brushed onto white paper to observe the color changes. Comparison photos of these samples were taken before and after they were completely dried.

2.4. Preparation of free-standing films

Free-standing films were prepared for water content/uptake and tensile measurements. To prepare films with homogenous thicknesses, an acetate sheet was chosen as the substrate. Polyelectrolyte solutions were able to spread on this acetate sheet, and can also be removed after drying. For PEI/PSS film casting, the solutions maintaining PSS:NH\(_2\) wt % ratio of 1:0.53 were used. It was noticed that 20 wt% polyelectrolyte solutions were too diluted to remain as a film during drying, especially for ratios with excess PSS. The total polyelectrolyte concentration for making blank samples was adjusted to 30 wt% while maintaining a PSS:NH\(_2\) wt % ratio of 1:0.53. For PEI/NaPSS films, also 30 wt% solutions were used. PEI with two different Mw (25k or 750k \( \text{g} \, \text{mol}^{-1} \)) was used for comparison and the samples were differentiated by stating PEI25k or PEI750k. With the same 30 wt% concentration, all ratios of mixtures were prepared with three different thicknesses (wet 300, 500, and 800 \( \mu \text{m} \) casting bars). The compositions of these solutions are summarized in Fig. 1. After casting, films were dried inside the fume hood under ambient conditions. NaPSS 30 wt% solution was dried in the oven at 80 °C overnight and stored under vacuum at 30 °C. For pure PSS and NaPSS films, 35 wt% solutions were prepared for casting to increase the viscosity. Free-standing films of pure PEI could not be prepared due to their strong adhesion. All films (pure PSS, pure NaPSS, PEI25k:PSS 3:1–1:3, and PEI25k:NaPSS 3:1–1:3) were investigated with a scanning electron microscope SEM (JSM-6010LA, JEOL, Japan). The samples were stored under vacuum overnight at 30 °C to remove excess water and coated with a Pt/Pd 5 nm coating (Quorum Q150T ES, Quorum Technologies, Ltd., UK).

Fourier transform infrared spectroscopy (FTIR, Spectrum two, PerkinElmer, USA) was used to examine pure polyelectrolytes (PEI, PSS-NH\(_2\), PSS, and NaPSS) and all the mixed films. To check whether PSS-NH\(_2\) sample contains residual NH\(_2\) after proper drying, it was dried under vacuum at 30 °C for 24 h. All the other samples were measured without this extra drying step. All measurements were conducted in the reflectance mode at a spectral resolution of 4 cm\(^{-1}\) from wavenumber 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). For each measurement, 16 scans were performed. Ion chromatography (Metrohm® Eco IC analyzer, Switzerland) was performed to help identify the unknown white powder from PEI/NaPSS. A 10 mg/L solution was prepared for the test.

2.5. Water content and water uptake

The water content (%) of all free-standing samples under ambient conditions (pure PEI 25k/750k, pure PSS, pure NaPSS, PEI 25k/750k: PSS 3:1–1:3, and PEI 25k/750k:NaPSS 3:1–1:3) were recorded. It was calculated based on Eq. (1), where the masses before (\( m_{\text{ambient}} \)) and after drying (\( m_{\text{dry}} \)) were measured.

\[
\text{Water content} \quad (\%) = \frac{m_{\text{ambient}} - m_{\text{dry}}}{m_{\text{ambient}}} \quad (1)
\]

For the swelling test, all samples (0.5 g) were soaked in deionized water (50 mL) and stirred by a stirring bar for 1 h. After 24 h, extra surface water of the sample was removed carefully with dust-free tissues and the weight was measured as the wet weight. The pH of the final mixture was checked using a pH strip. The water uptake (%) was calculated according to Eq. (2), with dry weight (\( m_{\text{dry}} \)) and wet weight (\( m_{\text{wet}} \)).

\[
\text{Water uptake} \quad (\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (2)
\]

The related humidity (RH) was ranging from 40% to 49%. The room temperature was fluctuating from 19.4 °C to 19.7 °C. For drying, the samples were first dried in the oven at 80 °C for 4 h and stored under vacuum at 30 °C overnight. The dry weight was measured immediately after taking the samples out of the oven. For each value, three different samples were measured and the average result was reported. It should be mentioned that pure PEI remained sticky after drying, and therefore could not be measured alone. Thus, the difference between total weights including the container was considered as the weight loss.

2.6. Thermogravimetric analysis

Thermogravimetric analysis (TGA, PerkinElmer TGA 400, USA) was used to further examine the water content and the decomposition behavior. Pure PEI 25k/750k solutions were first dried at 80 °C for 4 h in the oven to remove the initial water. For the complex samples, PEI25k was used. Then all samples (pure PEI, pure PSS, pure NaPSS, PEI:PSS 3:1–1:3, and PEI:NaPSS 3:1–1:3) were stored under ambient conditions at 19.3–20.1 °C and RH 38–43%. TGA measurements were conducted under nitrogen environment and the temperature range was set to 30–800 °C with a ramp of 10 °C/min. Heating was maintained for 5 min after reaching 800 °C then followed by cooling. For measuring the water content, the program was set to 30–120 °C (10 °C/min) and maintained...
for 10 min. For each reported value, 2 measurements were conducted.

2.7. Tensile measurements

After the free-standing films were dried and stabilized under ambient conditions (>72 h), samples for measuring tensile strength were prepared by cutting the films into 5 cm × 0.5 cm (height × width) strips. The thickness of each sample was measured by a micrometer at 4 random points and the average result was reported. The measurements were conducted by using an electromechanical testing system (Instron 5942, USA). For each data point, at least 3 samples from different films were measured. The ambient conditions were RH 38–42% and 21.3–21.5 °C.

2.8. PEI/PSS film formation on BOPP and oxygen permeation

To find the minimum thickness where the film starts to crack, 20 wt % PEI25k:PSS solutions (PSS:NH$_3$ wt% ratio 1:0.53) at various ratios (3:1–3) were cast on biaxially orientated polypropylene (BOPP) sheets. This experiment was conducted under ambient conditions. The RH was around 56–60% and the temperature was 21.2–22.0 °C. To introduce hydrophilicity to BOPP, an oxygen plasma cleaning was performed (Femto plasma cleaner, Diener electronic GmbH, Ebhausen, Germany). The film thickness was controlled by using different casting bars with thicknesses of 10, 25, 50, and 100 µm. After complete drying, the film appearance was judged visually. Due to the cracking of films, the thickness could not always be directly measured. According to the 20 wt% solution we used, we assumed the dry thickness was approximately one-fifth of the casting thickness. The critical cracking thickness of each film was recorded. The thinnest films were first examined with SEM. After confirming the density, the oxygen permeation of the thinnest films of each ratio was measured at 0% RH, and cracked films were checked with an optical microscope (Leitz Ortholux, Germany).

3. Results and discussion

3.1. Phase diagrams of PEI/PSS

To find the conditions under which PEI and PSS form solutions and complexes, we studied the phase behavior of the mixtures at different NH$_3$ concentrations, polyelectrolyte concentrations, and mixing ratios. Different from our previously studied PEI/PAA system, PSS is a strong polyanion whose degree of ionization is independent of pH. Thus, a stronger complexation between PEI and PSS is expected. Furthermore, PEI and PAA are both weak polyelectrolytes so the final PEC remains sensitive to both acid and base, while PEI/PSS-based PECs should be only base-sensitive.

First, the effect of varying NH$_3$ concentration on the phase behavior of PEI/PSS mixtures was studied (Fig. 2a). Pictures of these samples are shown in Fig. S2. Fig. 2a shows that a homogenous solution phase can be achieved for each ratio when the NH$_3$ concentration is sufficiently high. The concentration required is slightly higher than for the PEI/PAA system, probably because PSS is a stronger acid than PAA. Considering the drying process, a decrease in NH$_3$ concentration eventually leads to a phase transition from solution to solid complex. This solid complex is a macroscopic precipitate that cannot be cast, but it is the state that is desired in the final dry film for applications. This transition can be achieved for all ratios, which was not possible for PEI/PAA. It is also noticeable that the intermediate phase for ratios 1:1–1:3 resembles a colloidal dispersion instead of a coacervate phase shown in Fig. 2c. This finding is consistent with literature that reports that PEI/PSS formed small aggregates instead of a coacervate phase [49]. To confirm this pseudo-colloidal phase, dynamic light scattering (DLS) measurements were conducted. The Z-average diameter was 1.376 µm with a high PDI = 0.84 (Fig. S3a), while for the solution phase, no particles could be detected with DLS. However, because the particle concentration was probably too high for reliable DLS measurements, we also observed the particles in the wet state using an optical microscope. By using ImageJ particle analyzer, the average diameter was found to be 1.603 ± 0.314 µm (Fig. S4). For our samples, these aggregates eventually sedimented after a few months (>3). The origin of this slow sedimentation is probably the high viscosity of the mixtures and a small difference in density. The turbidity of samples with PEI/PSS at a monomeric ratio of 1:3 was measured for different NH$_3$ concentrations (Table 1). This ratio was chosen because it contains the most PSS and requires the most NH$_3$ to be neutralized. Once we ensured that ratio 1:3 can form a homogenous solution, all other ratios should also be able to achieve this state. To make a homogeneous solution, the wt% ratio of PSS:NH$_3$...
Table 1

| Three phases | Complex | “Colloid” | Solution | 20 wt% PSS solution |
|--------------|---------|-----------|----------|---------------------|
| PSS/NH₃ ratio | 1:0.12  | 1:0.29    | 1:0.53   |                     |
| SS/NH₃ mol ratio | 1:3.30  | 1:3.14    | 1:5.73   |                     |
| Turbidity (FNU) | 269.0   | 12.6      | 7.0      | ± 3.5              |

The turbidity data of PEI/PSS at a ratio of 1:3 and the corresponding wt% and molar ratios.

should be 1:0.53, at which the turbidity of the resulting solution is close to a pure 20 wt% PSS solution. When increasing PSS to 1:0.29, particles start to form and a turbid phase appears, which should be avoided for casting. For the film application, this “dispersion” can also be cast, but instead of solution drying, particle coalescence would probably happen which may induce heterogeneity. When converting to molar ratio, 1 mol of PSS monomer requires around 5.73 mol of NH₃ to form a homogenous solution with PEI. It should be noted that the exact PSS:NH₃ ratio can have small errors due to the fast evaporation of NH₃ during measurements; in the final mixture, the NH₃ content could be slightly lower. We also verified that homogeneous solutions can always be obtained at high enough NH₃ concentration, regardless of the order of addition: when NH₃ was added after PEI and PSS had already formed a complex, it could redissolve the complex after stirring for some time.

The pH values of different samples (Fig. 2b) were determined using pH indicator paper instead of a pH meter. The accuracy is, however, limited to 1 pH unit. For our system, only the charge density of PEI is influenced by pH. To avoid direct complexation, the pH has to be around pH 2 or higher (Fig. S7b), which was sufficient to keep PEI uncharged. The turbidity of PEI/NaPSS at a ratio of 1:3 (30 wt%) was 7.4 ± 0.3, also indicating that solutions were formed.

After drying, PEI/PSS films appeared homogenous and transparent (Fig. S9). Films at ratios 2:1, 1:1, and 1:2 showed different degrees of cracking, which could be a result of different degrees of ionic cross-linking: ionic cross-links make the film more rigid and less stretchable, thereby increasing the likeliness to crack during drying. This trend was not observed for PEI/NaPSS (Fig. S10), suggesting the absence of ionic cross-linking in these films. Moreover, the films of PEI/NaPSS, in general, appeared inhomogeneous with white patterns that resemble crystalline domains. For both PEI/PSS and PEI/NaPSS films, there was no clear influence of the Mₙ value.

SEM was utilized to further examine the film morphology and structure. Here, we use PEI/PSS and PEI/NaPSS at a ratio of 1:3 as an example for comparison. SEM images of the other samples are shown in Fig. S11. As shown in Fig. 5a and c, the surface of PEI/PSS films appeared smooth and dense. However, the surface of PEI/NaPSS films were very heterogeneous, which suggests that PEI is acting as a binder for NaPSS crystals (Fig. 5b and d). The cross-section image (Fig. 5e) also shows that this phase separation happened not only on the surface but throughout the whole film.

To further examine the composition of the dried films, FTIR was utilized. When comparing PSS and PSS-NH₃, there was a trace of NH₄⁺ (Fig. S12a). However, it was unclear whether NH₄⁺ fully evaporated from the mixed films due to peak overlap with the amine group from PEI (Fig. S12b). For both PEI/PSS and PEI/NaPSS (Fig. S12b and c), IR
spectra show indeed mixtures of both polyelectrolytes, however, the exact composition and the state of ionic cross-linking remain unknown. IR spectra of the white powder-like regions in the PEI/NaPSS films suggest that these regions may consist of Na$_2$SO$_4$ crystals, which may have been present as a salt impurity in the NaPSS samples, although there may also be NaPSS in these domains (Fig. S12d). The presence of Na$_2$SO$_4$ in the mixture was confirmed by ion chromatography (0.299 mmol/L Na$^+$ and 0.141 mmol/L SO$_4^{2-}$). After 2 weeks, similar crystallization was obtained when 35 wt% NaPSS was dried in a beaker (Fig. S13a). Also, the thin films of pure NaPSS that were cast turned opaque with time (Fig. S13b). These confirm the crystal domains observed in PEI/NaPSS films were caused by NaPSS. Since PEI is not charged in these films, there are no attractive interactions between the chains of the two polymers for these films to undergo segregative phase separation during drying which accelerated the crystallization of NaPSS.

At this point, it is important to note the distinction between two methods, one where polyelectrolyte complexation is induced by drying, and another where complexation happens in an aqueous environment. In the former, the counterions remain in the product, unlike in the latter where they are discharged into the supernatant after phase separation. Hence, crystallization of counterions needs to be considered while designing a system where drying induces complexation.

3.3. Water content and water uptake

Since water plays an important role in the mechanical properties of the films, the water content (ambient vs dry) and water uptake (dry vs wet) of each film were measured. It can be seen from Fig. 6a that the PEI/PSS films in general contained less water than pure PEI and PSS films. Polyelectrolytes are known to be hygroscopic and the complexation between them reduces the available free charge that can effectively lower the water content. The PEI/NaPSS films showed similar water content as the pure NaPSS films, but lower than the PEI films (Fig. 6b). Apparently, the addition of PEI did not make these films more sensitive to water. For both PEI/PSS and PEI/NaPSS, the $M_w$ of PEI showed no influence on the water content. We also checked whether the water content depends on the thickness for films with PEI (750k):PSS 3:1 and PSS only. As shown in Table S2, the water content is independent of thickness.

Swelling tests of all samples were then conducted. When encountering water, inorganic salts often dissolve, while PECs usually swell and turn white indicating the formation of pores within the films. As shown in Fig. S14, films with PEI:PSS at ratios of 3:1, 1:2, and 1:3 were unstable in water and could not be weighed. The pH values of these samples showed a gradual decrease from ratio 3:1 to ratio 1:3, indicating that excess PEI might be leached into the water. The water uptake results for PEI/PSS films at 2:1 and 1:1 ratios are shown in Fig. 7. For both PEI $M_w$, films at a ratio 2:1 show the least swelling, which indicates that the ideal complexation ratio is close to 2:1. Compared to multilayered PEI:PSS films (swelling $\sim$ 75 v/v%) [52], the water uptake is much higher. With our method, the charge ratio is fixed, and any rearrangement or exchange with the aqueous phase to find the ideal ratio is not possible. If the ideal ratio is not exactly at 2:1, then any extra charge may cause enhanced swelling. There is no significant difference when using a different $M_w$ of PEI. This indicates that the resistance to swelling is mostly determined by the ionic cross-links and the charge in the film, rather than by entanglements. In contrast to the PEI/PSS films, all PEI/NaPSS films dissolved completely in water and showed a basic pH as in the initial solution phase (Fig. S15), which again indicates that an ionic network did not form in PEI/NaPSS films.
3.4. Thermogravimetric analysis

As shown in Fig. 8a, the TGA results of pure polyelectrolytes are consistent with literature [53,54]. Both PEI 25k and 750k showed a sharp decrease from 300 °C and decomposed completely at around 400 °C. The trends were almost identical so that only mixture samples with PEI25k were measured. Sulfonate groups are much more thermally stable [55,56]. PSS started to decompose around 300 °C and showed ~ 40 wt% residue at 800 °C, while for NaPSS, the Na⁺ ions resulted in a delay in decomposition to around 430 °C and ~ 50 wt% residue after heating to 800 °C.

For PEI:PSS complexes, all ratios showed a higher onset temperature for decomposition when compared to pure PEI (Fig. 8b). This finding is consistent with observations of Krishna B et al. for PDADMAC-NaPSS complexes [46]. The possible reason is that the ionic interaction stabilized both amine and sulfonate groups, so that a higher temperature is needed for degradation. Furthermore, the ratios 2:1 and 1:1 which are close to the ideal complexation ratio showed higher decomposition temperatures than the other ratios. After reaching temperatures above 400 °C, the decomposition behavior of each sample resembled pure PSS, and PEI:PSS from 3:1–1:3 gradually had more residue. By contrast, for PEI:NaPSS, there was no delay of the decomposition temperature and all ratios followed the same trend: PEI degradation was first observed for temperatures below 400 °C, and then NaPSS started to degrade; hence each polymer degraded at approximately the same temperature as for the pure polymer. Similarly, PEI:NaPSS from 3:1–1:3 showed a gradual increase in the amount of residue since more NaPSS was present.

The water content of films can also be calculated basing on the weight loss from 30 °C to 120 °C. Similar results are observed in Fig. 8c when compared to Fig. 6. In general, less water was found by using TGA than we calculated based on the wet and dry weights. The possible reasons can be that the RH was lower when conducting TGA and for TGA measurements, less than 10 mg was used for each sample which may not be representative for the whole film, especially for inhomogeneous PEI/NaPSS films.

3.5. Tensile strength of free-standing films

All the samples were cut into the standard shape for the tensile tests (Fig. S16 and S17). Here, we focused on varying the charge ratio, instead of humidity and temperature. Thus, all samples were measured under the same conditions. As discussed in Section 3.2, all samples have similar water contents. All samples were prepared with three different thicknesses and here the average results for each composition are shown (Tables S3 and S4). PEI:PSS films at ratios of 2:1 and 1:1 all cracked and could not be further cut into the standard shape for tensile tests.

Uniaxial extension of the films showed an initially linear stress-strain curve for all PEI/PSS films, followed by strain softening and rupture of the films (Fig. 9a). All complexed PEI/PSS films showed a higher Young’s modulus (Fig. 10a), a higher yield stress and lower yield strain
than pure PSS, which is expected since the ionic cross-links make the materials more rigid and less extensible, consistent with other dry PECs \[8,44,46\]. It can be concluded that PEI:PSS complex films are rather brittle and break already at low strains. This finding is in agreement with studies in the Schlenoff group which showed that PECs containing PSS tend to give “glassy” complexes with relatively high \(T_g\) \[29,55,57\]. We do not observe a significant difference between the samples with high and low \(M_w\) of PEI. This indicates that the mechanical properties are dominated by ionic cross-links and not by entanglements. The same was observed by Krishna B. et al., who found that varying the \(M_w\) of poly(diallyldimethylammonium chloride) (PDADMAC) and NaPSS had little effect on the Young’s modulus \[46\].

The PEI/NaPSS films at ratios of 3:1 and 2:1 showed completely different mechanical behavior than the PEI/PSS films, with a much more ductile response, a lower yield stress, and a higher yield strain (Fig. 9b and c). This agrees with our finding that PEI/NaPSS films act like a polymer blend rather than an ionically cross-linked complex. This ductile response was most pronounced for the films with excess PEI, which were also much softer than the films with excess NaPSS (Fig. 10b). Films with excess NaPSS first tend to become more brittle as the amount of PEI increases. This may be related to the phase-separated structure and the presence of crystalline domains in these films as shown in the SEM images (Fig. 5 and Fig. S11), which may act as nuclei for crack initiation. We also note that the heterogeneities made it difficult to accurately determine the Young’s moduli of these films, leading to large error bars. Several samples with large crystalline domains were too fragile to be prepared (Fig. S18) and were omitted from the analysis, which may bias the results.

Combining the results from the swelling and tensile tests of free-standing films, it is clear that complexation has a large effect on the properties of the films, leading to a higher resistance to swelling and more brittle films for PEI/PSS. PEI/NaPSS films behave more like polymer blends, without any interchain ionic cross-linking. The unexpected crystallization in these films still needs to be investigated, but our results suggest that it is related to phase separation in these films.

### 3.6. Critical cracking thickness of PEI/PSS films on BOPP

As shown in Fig. S9, some of the PEI/PSS films cracked during drying. This cracking is a consequence of mechanical stresses in the film that develop as the film shrinks during solvent evaporation and solidification, and it is known to occur especially for relatively thick films \[48\]. To investigate the stability of our films, we cast PEI/PSS films of different thicknesses on biaxially oriented polypropylene (BOPP) sheets. As shown in Fig. S19 and summarized in Fig. 11, films prepared at a PEI/PSS ratio of 3:1 were stable at all thicknesses produced, but at other ratios, different degrees of cracking were observed when the estimated dry thickness exceeded 10 \(\mu m\). Cracks were generated when trying to flatten the curled films. The cracking increased when the film thickness increased and eventually delamination occurred. Samples at ratios of PEI/PSS 2:1 and 1:1 are the most brittle, and cracks were observed already for films of 5 \(\mu m\). This trend was consistent with the swelling and mechanical results. It is noticeable that after changing the substrate from acetate sheets to BOPP, PEI/PSS at ratios of 1:2 and 1:3 showed cracking in lower thicknesses. A possible reason for this may be that the acetate sheet is less hydrophilic than plasma-treated BOPP which may lead to weaker adhesion forces and therefore less shrinkage stress. BOPP was chosen because it was the support of choice for further gas permeation tests; however, the critical cracking thickness can vary significantly depending on the substrate on which the films were formed.

For the thinnest films (Fig. S20), PEI/PSS films at a ratio of 3:1 remained relatively flat, while the other films curled up. The maximum curling was observed at ratios of 2:1 and 1:1, again indicating that these films carried the highest degree of mechanical stress. From all SEM images, these thinnest films (~ 2 \(\mu m\)) all showed a dense structure (Fig. S21).
Fig. 8. TGA results of a. Pure polyelectrolytes. b. PEI25k/PSS and PEI25k/NaPSS. c. Water content extracted from TGA data (weight loss from 30 to 120 °C).
We then tested whether these films showed oxygen barrier properties, motivated by our earlier work on PEI/PAA films. However, samples prepared at ratios of 3:1, 2:1, and 1:1 all showed cracks directly after the oxygen permeation measurements (Fig. S22). Probably, the low humidity used during oxygen flushing removed all the water from the films. Since water is known to be a plasticizer for these films, the removal of water leads to a further increase in brittleness. The OTR results for the different films (including pure PSS) are given in Table S5.

The PEI/PSS films do reduce the oxygen permeation, even after cracking. However, compared to LbL [58], other one-step methods [59, 60], and our previous study [13] on films with PAA instead of PSS, the present films showed much higher OTR. The possible explanation is that PSS is less polar than PEI and PAA, thus the solubility of oxygen may be increased.

4. Conclusions

In previous work, we proposed the evaporation of a volatile base as a way to trigger complexation during drying, which allowed the one-step formation of micrometer thick PEC films. Here, this one-step method was extended by applying it to a PEI/PSS system to form a solid complex film with one weak and one strong polyelectrolyte. Moreover, by comparing PEI/PSS and PEI/NaPSS, we could conclude that the properties of PECs depend strongly on the degree of ionic cross-linking. With the ideal complexation ratios (PEI:PSS 2:1 and 1:1), they showed the most cracking, least swelling, delayed decomposition temperatures, and they were independent of the M_\text{w} of PEI. These results all suggest that ionic cross-linking is the dominating factor instead of chain entanglements.

To reduce the brittleness of the PEC films, different kinds of plasticizers can be studied in future work. For example, salt is well-known to be a plasticizer for polyelectrolyte complexes. Another solution can be
replacing PSS with softer polyelectrolytes or copolymers that can dilute the charge density and therefore weaken the complexation. Furthermore, we found that swelling of the films in water can be reduced by finding the ideal complexation ratio, which can be learned from other PEC systems, such as LbL. Moreover, the water sensitivity of these films should be systematically studied with changing humidity. Finally, long-term studies can be conducted to track how ageing affects the mechanical properties.

Supporting Information

The document contains: method to determine pH values, original pictures of phase diagrams and their pH values of PEI/PSS, DLS and optical microscope images of the “colloidal” sample, salt-induced phase transition, PEI/NaPSS solution mix and their pH values, tracking pH changes with pH indicators, dried PEI/PSS, PEI/NaPSS, pure PSS, and pure NaPSS films on acetate sheets, SEM images of free-standing films, IR spectra of different samples, crystallization of NaPSS, water contents of same films with different thicknesses, swelling behavior of PEI/PSS and PEI/NaPSS films, tensile samples and tensile results of all samples with different thicknesses, inhomogeneity of PEI/NaPSS films, critical thicknesses of PEI/PSS complexed films on BOPP, different curling levels of PEI/PSS films, SEM images of PEI/PSS films on BOPP, attempted oxygen permeation tests, and cracked films after oxygen permeation tests. The Supporting Information is available free of charge.

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CRediT authorship contribution statement

Jiaying Li: Investigation, Validation, Data curation, Writing – original draft. Ameya Krishna B: Investigation, Validation, Data curation, Writing – review & editing. Gerard van Ewijk: Conceptualization, Writing – review & editing. Derk Jan van Dijken: Conceptualization, Writing – review & editing. Wiebe M. de Vos: Conceptualization, Project administration, Funding acquisition, Supervision, Writing – review & editing. Jasper van der Gucht: Conceptualization, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.129143.

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Fig. 11. Film appearances of PEI/PSS at different ratios and various thicknesses.
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