Hot-pressing polyelectrolyte complexes into tunable dense saloplastics

Ameya Krishna B\textsuperscript{a,b}, Joshua D. Willott\textsuperscript{c}, Saskia Lindhoud\textsuperscript{b,*}, Wiebe M. de Vos\textsuperscript{a}

\textsuperscript{a} Membrane Surface Science, Membrane Science and Technology, MESA+ Institute of Nanotechnology, University of Twente, Enschede, the Netherlands
\textsuperscript{b} Department of Molecules & Materials, University of Twente, Enschede, the Netherlands
\textsuperscript{c} ARC Centre of Excellence for Enabling Eco-Efficient Beneficiation of Minerals, University of Newcastle, Callaghan, NSW, 2308, Australia

\begin{abstract}
Salt-plasticized polyelectrolyte complexes of sodium polystyrenesulfonate (Na-PSS) and polydiallyldimethylammonium chloride (PDADMAC) were found to be fully dense (non-porous) when hot-pressed under optimal conditions. The quality of these saloplastics is determined by the molecular weights of polyelectrolytes, the salt type and concentration, as well as processing conditions like pressure and temperature. Higher molecular weights give more compact precipitates that are easy to process while decreasing the molecular weight led to particulate ones. Both the type and concentration of salt on complex formation and doping are explored and are found to play an equally important role. The effects of individual hot-pressing parameters, namely, pressure and temperature are studied thoroughly, facilitating the formation of uniform free-standing films over a wide range of thicknesses from 8 \textmu m to 1 mm. For the first time, saloplastics were studied as free-standing films that are dense even at the nanometer scale. In their dry states, they were brittle and strong, showing a uniform Young’s modulus over a range of relevant thicknesses, while the wet states were rubbery and elastic, showing a decreasing trend with thickness. In the wet state, the inverse trend is due to the quicker drying of thin films. Within a single hot-pressing step, protruding shapes and structures from the surface were efficiently made at different length scales. Moreover, saloplastics were also successfully reinforced with thin woven and nonwoven fibers for enhanced tensile strengths, higher than conventional thermoplastics. Overall, this work demonstrates an easy approach to fabricate dense saloplastics and their unique mechanical properties.
\end{abstract}

\section{Introduction}

The quest for dense, cheap, and easily recyclable transparent materials has been a long-drawn one. From packaging materials to self-healing plastics, they are used in a wide array of applications \cite{1}. Flexible transparent materials, such as low-density polyethylene (LDPE), are cheap and allow us to visually examine products without having to open the packaging, but their disposal is of growing concern. Microplastics seep into our waterways \cite{2} causing a whole new cycle of problems \cite{3}. Polycarbonate plastics contain BPA, which is a “chemical of concern”, endocrine-disrupting, and interacts with hormone receptors \cite{4}. Alternatives and many biodegradable materials such as PLA (Polylactic Acid) and cellulose acetate have been processed into plastics. However, different properties are desirable for different applications. Some applications demand properties such as biocompatibility, barrier for gases, or the ability to permeate a specific gas or ion. This necessitates the further development and exploration of suitable materials for particular applications.

Plastics are categorized in different ways depending on the context, one of which is the method of processing. In this regard, thermoplastics and baroplastics are the basis of popular moulding methods. Here, \textit{thermos} (heat) or \textit{baros} (weight/pressure) are the drivers of plasticity. A thermoplastic, such as polyethersulfone (PES), softens at an elevated temperature due to weakened intermolecular forces and is mouldable, while it hardens when cooled \cite{5}. Similarly, a baroplastic, such as PS-b-PBMA \cite{6}, demonstrates melt-like behaviour when pressure is applied at temperatures much lower than the \textit{T}_g \cite{7}. In either case, this happens without changing the inherent chemical or mechanical properties of the plastic. Thermosets are polymers that strengthen at elevated temperatures and cannot be remoulded after forming, unlike thermoplastics. This is due to extensive crosslinking, resulting in an infusible polymer network.

Polyelectrolytes fall into a special category. Charges confer a degree of hydrophilicity to polyelectrolytes \cite{8}. Tweaking this property in water-soluble polyelectrolytes allows them to be used as flocculants, coatings, and PEC nanoparticles to be used as vehicles for drug delivery.
In this work, we introduce and study the material properties of novel dense saloplastics in terms of their tensile strengths in both dry and wet states, and thermal properties with TGA and DSC. The hot-pressing approach is described in detail wherein several parameters are investigated. Systematic research on the influence of polymer chain length, salt type, and ionic strength on one hand, and the hot-pressing parameters like temperature and pressure on the other were performed. After much process optimisation, dense saloplastics are formed with uniform thicknesses in a narrow window of operating conditions. This work also showcases the possible flaws, their causes, and methods to eliminate them while processing such materials. The mechanical properties of the formed dense plastics are studied and compared to conventional plastics, showing the key role of water. It is also demonstrated that plastics with advanced structures and reinforcements can easily be prepared via hot-pressing.

### 2. Experimental

#### 2.1. Polyelectrolyte complexation

NaBr (>99%), NaCl (EMPROVE® ESSENTIAL), KCl (>99%), and KBr (EMPROVE® ESSENTIAL), Sodium salt of Poly(sodium 4-styrene sulfo-nate) (Na-PSS) in three molecular weights: 1000 kg mol⁻¹ 25 wt%, 200 kg mol⁻1 30 wt%, and 70 kg mol⁻1 30 wt% in H₂O. Poly(diallyldimethylammonium) chloride (PDADMAC) in three molecular weights: 400–500 kg mol⁻¹ 20 wt%, 200–300 kg mol⁻1 20 wt% g·mol⁻¹, <100 kg mol⁻1 35 wt% in H₂O were purchased from Sigma Aldrich and used as received. Milli-Q water was used from a Millipore Synergy® Water Purification System.

Individual 125 mM Na-PSS and PDADMAC solutions were prepared with respect to their repeating monomer unit, at varying salt concentrations. Both solutions were poured into a third beaker under stirring for 30 min to form a PEC precipitate. Each precipitate was washed and stored in a 250 mM solution of the salt used for preparation.

#### 2.2. Hot-press moulds

Various metal and polymer slabs with dimensions 177 × 127 mm² (equal to the length and breadth of the hot-press plates) were cut from sheets. The metallic slabs were 7 mm thick while those of PVC, Teflon, and Delrin were 9 mm thick. PTFE Coated Fiberglass sheets with adhesive on one side (Lubriglas®-CHAP-1540) of thicknesses 0.122 mm and 0.225 mm were purchased from Reichelt Chemietechnik GmbH + Co (Heidelberg, Germany). They were cut to make spacers and glued to a slab (Fig. 1). Adequate outlets were provided for extra PEC and water to leave when pressurised. An aluminium mould, for example, consists of two 177 × 127 × 7 mm³ slabs of aluminium placed one on top of the other with the spacer glued to the lower slab.

#### 2.3. Hot-pressing

PECs were hot-pressed using an FVR ROLLIE 20 ton Desktop Rosin Press, (FVR, Canada). A schematic of the hot-press is shown in Fig. S1. 1. The anodized aluminium plates of the hot-press measure 177 × 127 × 38 mm³. To form a saloplast, the PEC precipitate was placed on the lower plate of a mould and covered with the top plate. This sandwich was inserted between the aluminium plates of the hot-press. The two plates of the hot-press were then closed using the hydraulic system and no pressure was applied. A predetermined temperature was set for each plate using the respective temperature controller and allowed to heat. When the set temperature was reached, a predetermined pressure was applied and the PEC was allowed to plasticize under these conditions for 5 min. The temperature was set to 25 °C and allowed to cool under pressure. When this temperature was reached (typically 30 min from 80 °C to 25 °C), the mould was taken out of the hot-press and opened.

### Table 1

A review of methods used in literature for processing polyelectrolyte complexes.

| Method          | Polyelectrolytes (Molecular weight) | Relevant properties                                      |
|-----------------|-------------------------------------|---------------------------------------------------------|
|                 | Polyanion                           | Polycation                                              |
| Extrusion       | PSS (200)                           | PDADMAC (400)                                          | Extruded into various geometries, pores up to 10 μm²        |
| Spin coating    | PSS (200)                           | PDADMAC (400)                                          | Micropores [21]                                               |
|                 | PSS (200)                           | PDADMAC (400)                                          | Complex formation, ground and converted to coacervate followed by spin coating, rinsed and dried [20] |
|                 | PSS (70)                            | PDADMAC (400)                                          | Coacervate spin coated, rinsed and annealed [23]             |
| Solvent evaporation | Alginate acid sodium salt (PSS (200)) | Chitosan (PDADMAC (100–200))               | Centrifugation, complexation, pellet formation, resuspension in coacervate, dried and freeze dried [24] |
| Coated layer    | Gellan gum (200–300)                | Chitosan (190–310)                                     | Complexed, settled in tube, dried in petri dish.             |
| Patterned       | PSS (70)                            | PDADMAC (200–350)                                      | Single biopolymer film immersed in oppositely charged film on both sides, dried [26] |
|                 |                                     |                                                         | Mould PEC gel with small applied pressure [27]               |
|                 |                                     |                                                         | Porous structure, non-transparent                             |
2.4. Water uptake

Plastic pieces of $1 \times 1$ cm$^2$ were stored in MilliQ water for 24 h. The wet mass of each was recorded after removing surface water using a tissue. The samples were dried in an oven at 50 °C for 24 h and the dry masses were recorded. Water uptake is obtained from the following equation wherein $m_{\text{wet}}$ and $m_{\text{dry}}$ are the wet and dry masses respectively:

$$\text{Water uptake} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}$$

2.5. Thermal Gravimetric Analysis (TGA)

A Perkin Elmer TGA 4000 instrument was used to perform TGA to measure the water content of the film. A small piece of the saloplastic was soaked in MilliQ water for 15 h (overnight). Extra water was soaked up by a Whatman® filter paper on each side. The saloplastic was then quickly inserted in the TGA holder to minimize the loss of moisture by evaporation. The temperature was swept from 30 °C to 120 °C while heating at 10 °C/min in the presence of N$_2$, following which the temperature was maintained at 120 °C for 30 min to ensure complete drying of the saloplastic. The ratio of the difference in wet and dry weights to the dry weight gives the relative water content.

$$\text{Relative water content (RWC)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100$$

In addition to this, the decomposition temperature of the saloplastic was determined by raising the temperature to 800 °C from room temperature at 10 °C/min.

2.6. Differential Scanning Calorimetry (DSC)

A DSC 6000 equipment was used to carry out DSC measurements at a heating rate of 10 °C/min from room temperature to 350 °C and cooled back to room temperature.

2.7. Tensile strength

An electromechanical testing system, Instron 5800, was used to measure the mechanical strength of the hot-pressed PECs. The size and shape of the samples were prepared according to the ASTM D882 [29, 30] standard valid for polymer films with a thickness of less than 1 mm. The samples had a length of 50 mm and a width of 5 mm, and different thicknesses. The method is similar to measurements reported in literature with the same procedure [31,32]. The reported values are an average of at least three specimens measured at room temperature at a speed of 2 mm min$^{-1}$.

3. Results and discussion

The process of pressing PECs to plastics involves two stages: Fabrication of processible PECs, and a procedure to press the PECs to plastics. Firstly, the influence of important parameters, such as the type and concentration of salt, as well as the molecular weight, on the formation of polyelectrolyte complexes is discussed. Subsequently, the fabrication of moulds for the hot-press is explained, followed by the processing of appropriate complexes, tuning parameters such as pressure and temperature. We will conclude by giving an overview of the different materials that were obtained and their characteristics.

3.1. Preparation of polyelectrolyte complexes

Equimolar solutions of the polyelectrolytes Na-PSS and PDADMAC were prepared according to their monomer ratio. Making two separate polyelectrolyte solutions and then combining them in a third bigger vessel under stirring was performed as this led to a better controlled and faster precipitation when compared to adding the Na-PSS solution into the beaker containing PDADMAC or vice versa. Optimal processable complexes were obtained by simultaneous pouring while stirring.

The effect of the molecular weight of the two polyelectrolytes was studied by considering three molecular weights of each. The molecular weights of Na-PSS were 70 kg mol$^{-1}$, 200 kg mol$^{-1}$, and 1000 kg mol$^{-1}$, while those of PDADMAC were 100 kg mol$^{-1}$, 200–350 kg mol$^{-1}$, and 400–500 kg mol$^{-1}$. All the 9 possible combinations at the fixed 1:1 monomer ratio led to complex formation (Fig. SI 2). The complex formed with the lowest molecular weights (PSS 70 kg mol$^{-1}$, PDADMAC 100 kg mol$^{-1}$) had very fine aggregates. With PDADMAC 100 kg mol$^{-1}$, the size of the complex aggregates was small irrespective of the size of Na-PSS. With an increase in the molecular weight of PSS, the size of the aggregates marginally increased. On the other hand, an increase in the molecular weight of PDADMAC led to an increase in the aggregate size, especially for the 400–500 kg mol$^{-1}$ variant. The size marginally increased with PDADMAC of 200–350 kg mol$^{-1}$, while at 400–500 kg mol$^{-1}$ big and mechanically stronger aggregates were formed. It was possible to hot-press all of them but the precipitates formed with the highest molecular weight polymers were the easiest to handle and process.

To get a suitable precipitate, not only the polymer lengths but also the salt concentration and type of salt added are important, which have been studied by several groups for specific systems [33–35]. In Fig. 2(a), the series was made with a fixed polyelectrolyte concentration but...
progressively increasing salt (NaCl) concentration from 0 mM to 400 mM. Visually good complexes and clear supernatants were repeatedly obtained between 125 mM and 250 mM NaCl. In our study to form saloplastics via hot-pressing we discovered that ideal precipitates have a natural viscoelasticity to them for optimal processibility. Such precipitates appear like a chunk of mozzarella cheese, as for example shown for the KBr vial of Fig. 2(c), as opposed to discrete tiny particles in the first three vials of Fig. 2(c).

To choose the type of salt best suited for our system, we started with common salt, NaCl. The PEC obtained consisted of small disperse granules that settled at the bottom when stirring was stopped. Next KBr was used, as it is used to prepare saloplastics in literature [17]. This salt is referred to as a good dopant [36], which means it effectively softens the complex by externally compensating the charges on the polymer chains, allowing mobility. The PEC obtained with KBr was more compact with some few disconnected granules. This was easy to handle for further processing. Since this used K⁺ and Br⁻ ions, NaBr and KCl were also tested to see which ion was making the difference and to understand the effective transition between the two salts. In Fig. 2, it can be seen that both K⁺ and Br⁻ ions appear to play a role in visual appearance of the PEC and we observed that the clump of PEC as seen in Fig. 2(c), vial 4. Hence, complexes were made using both 125 mM and 250 mM with all 4 salts. From this exercise, it was apparent that 250 mM was better and more compact complexes where formed when mixed in KBr. Further, with 250 mM KBr, complexation began instantly, indicated by a milky white solution followed by precipitation. After less than 5 min, there was a tough white ball of PEC at the bottom of the beaker making it difficult for the stirrer bar to move anymore (Video 1 in Supplementary information). When allowed to stir for at least 15 min, the supernatant gradually became clear, leaving behind a strong precipitate shown in vial 4 of Fig. 2(b). Such complex may be stored in the hydrated state for immediate use, or dried to form sugar-like particles (Fig. SI 3) for convenient storage, transport, and later use.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.polymer.2022.124583

3.2. Pressing PECs to plastics

When the precipitates were pressed in between the anodized aluminium plates of the hot-press, the material would mostly flow out from all edges and some of the trapped material would have non-homogenous transparent patches with the rest remaining translucent or white. It was also difficult to open the plates as the precipitate behaved as adhesive to form a strong sandwich and by opening it the plastic sheet deformed.

Therefore, a set of removable plates was considered. Several materials were experimented with to be used as plates (Table SI 1, Fig. SI 4 and 5), and Delrin® (purchased from DuPont) was found to be low-friction and non-sticky. Also, unlike Teflon®, it was not entirely hydrophobic facilitating easy movement and plasticization of the polymer. It was stable at least until 130 °C, which is well above the intended hot-pressing temperature. Delrin® made the best plastic sheets in combination with glass fiber reinforced Teflon spacers.

The effects of temperature and pressure were studied. A preliminary experiment (Fig. SI 6) was conducted on the flat hot surface. Further, the effect of temperature was studied using the hot-press from 17 °C to 110 °C at a constant pressure of 200 bar (Fig. SI 7). At 17 °C, the PEC only flattened out and there was no hint of plasticization. There were lots of holes and the plastic was rubbery. Every increase of 5 °C until 40 °C led to an increased degree of plasticization. At 50 °C, the saloplastic occupied the entire space between the moulds but still contained holes and white patches. Between 60 °C and 80 °C, the thickness of the plastic film became uniform. 90 °C was found to be the right temperature to obtain reproducible films with uniform thicknesses. Temperatures over 95 °C were tricky due to their proximity to the boiling point of water. Temperatures >100 °C led to the film sticking to the mould, or becoming brittle when left for longer durations. Plasticization was difficult at these conditions and a host of new issues emerged, including the loss of all water leading to pressing dried hard complexes at high pressures, thereby denting the Delrin plates. In some cases the dried complex became embedded in the dents of the plates.

A similar study was performed to optimize the amount of pressure applied during hot-pressing. The temperature was kept constant at 90 °C and the pressure was varied between 0 bar and 200 bar (see Fig. SI 8). Due to the high temperature, the PEC already became transparent at 0 bar when the upper plate of the hot-press was just touching the mould. A gradual increases in pressure decreased the thickness of the saloplastic while also making it more even. This data is shown in Fig. 3. At ~1 bar, the thickness is high and the error is very big. As we increase the pressure, the thickness, as well as error in thickness, reduces. A fairly uniform thickness close to the intended thickness of 150 μm is reached at pressures above ~100 bar. The value at 200 bar and 90 °C was 149 ± 3
Each point is an average of 10 values measured at different points of the μ salo-plastic.

Fig. 3. Variation of thickness with respect to pressure applied by the hot-press. Each point is an average of 10 values measured at different points of the salo-plastic.

The optimum quantity of PEC needed to obtain a compact film was also determined. 2.0 g of fully hydrated precipitate was found to give a compact plastic of ~1.4 cm², and thickness 100 μm weighing ~0.4 g, using a 122 μm deep mould. The loss in weight is due to the removal of water (60–80% of the mass of the precipitate) from the channels provided. There is no loss of material because any extra polymer pushed out of the channels can be reused for the next pressing. Hence, this process of making saloplastics is very efficient.

When the hydrated PEC weighed >2.5 g, the precipitate spilled out of the edges onto the spacer impacting thickness control. Below 2.0 g, the applied pressure is not uniformly distributed, resulting in an inhomogeneous plastic not in its most compact state. When far too little PEC was used (<1.6 g), a film still formed, but only around the centre where the precipitate was placed, not touching the edges of the mould. The correct amount of PEC resulted in uniformly pressed sheets of plastic with the same thickness throughout, with a little excess material pushed out of the little channels provided for this purpose (see Fig. 1). Therefore, the quantity of PEC not only influences the compactness of the film to form, but may also lead to inhomogeneity and non-uniform thicknesses as it impacts the spacer width. Hence, this aspect was found to be extremely important.

Glass fiber reinforced Teflon spacers were used to enable the production of saloplastics with different thicknesses. Pressure was a tool to facilitate this, and different thicknesses were made possible by altering the pressure as well as the thickness of the spacer (Table SI 2). Further, to avoid wastage of material, spacers were cut to the right shapes to get the right size and shape of the plastic piece as in Fig. 2. Such films were sturdy, flexible, and homogeneous. The films were transparent, indicating that they were dense with no pores to reflect light. Shamoun et al. fabricated saloplastics using extrusion and ultracentrifugation. Their films are dense to the micro-scale. The microscopy images showed their largest pores to be 10 μm and the smallest ones were about 100 nm [17]. We have shown that our hot-pressed plastics are completely dense even at the nanometer scale (Fig. 4) [22]. These hot-pressed plastics took up 40 ± 5% of water, and the transparency was not affected by this.

Inaccuracies may be observed in a hot-pressed plastic if the right conditions are not adhered to. As shown in Fig. SI 9, when a large excess of precipitate is used, the volume in between the plates is insufficient and the material overflows and gets pressed in between the spacer and the top plate. This leads to a plastic that is thicker than the desired thickness, mostly inhomogeneous, and loss of material. When sufficient time is not given for the material to be plasticized after reaching 90 °C, the trapped air and water do not have a chance to escape leading to bubbles in the plastic. On the other hand, when they are pressed after being left for too long at a high temperature, patterns are formed. This is due to the loss of most water, thus lowering the plasticity of the complex. The formation of white patches may have different reasons if the temperatures of the two plates differ by > 10 °C while pressing, if the complex is not allowed sufficient time to plasticize, if there is insufficient water, if there is too little or no salt, or if the plates are not heating properly. Clearly, the preparation of salo-plastics through hot-pressing is a sensitive process, where successful dense films are only obtained in a narrow region of parameters.

3.3. Mechanical behaviour of hot-pressed plastics

Thickness is an important parameter for characterisation as well as comparison of polymer films. It is known for thermoplastics that thickness influences the cooling rate, and hence, the characteristics of the resultant films [37]. The tensile strength was measured in order to quantify the effects of thickness on the mechanical properties of the hot-pressed plastics. From the stress strain curves of dry plastics (examples in Fig. 5 (b)), it can be observed that the strain at break is very small, 0.01–0.02 mm/mm amounting to 1–2%, showing that the material is brittle in this state, as expected for a crosslinked material in the absence of a plasticizer [38]. Elongation at break was measured to be 0.76 ± 0.11 mm while the tensile strength was 22.75 ± 1.79 MPa. It is known that hard materials are generally brittle [39], which is in line with the high values of Young’s modulus (4–6 GPa) observed with an average standard deviation of < ±8%. Indeed, a comparison to traditional plastics (Table 2) shows that this material is strong. It is important to highlight that while saloplastics are held together by ionic crosslinks, thermoplastics like polyethylene, polystyrene, acrylic, and polyvinyl chloride owe their mechanical properties to their crystalline structures [40].

![Fig. 4](image-url). (a) Fully transparent hot-pressed plastic (b) SEM image of the hot-pressed plastic.
Table 2
Values of Young’s modulus for common plastics compared to hot-pressed saloplastics in their dry states.

| Material                        | Young’s modulus [32,41,42,44] (MPa) |
|---------------------------------|-----------------------------------|
| Polycarbonate, moulded          | 2390                               |
| HDPE, moulded                   | 980                                |
| LDPE, moulded                   | 230                                |
| PVC, moulded                    | 2160                               |
| Polystyrene, moulded            | 2750                               |
| Acrylic, moulded                | 2940                               |
| Cellulose acetate, moulded      | 2080                               |
| PSS-PDADMA plastic, 150 µm, moulded | 5200                            |
| PSS-PDADMA plastic, reinforced, 150 µm, moulded | 6552                            |

Also, when thickness was increased, the Young’s modulus did not vary significantly (Fig. 5a and b), indicating that the stiffness of such material remains constant as the thickness is increased. This is in line with the fact that Young’s modulus is a material property independent of the dimensions [45]. This is also observed in common thermoplastics such as PVC and PE [37,39].

Although these hot-pressed plastics were not very sensitive to humidity changes in the environment, equilibration in MilliQ water led to them being more flexible. They were allowed to equilibrate in the water for 24 h after which tensile tests were conducted again to quantify the effect of water plasticization. The extensions were 1–2 orders of magnitude higher (40–80%) compared to the dry state (1–2%), thus completely changing the material properties (Fig. 5c). The wet materials showed smaller Young’s modulus values compared to the dry state as reported in Fig. 5(c). Wet plastics were much weaker and showed high elasticities in a linear regime (Video SI 2 and 3). However, to perform tensile tests, the plastics were naturally taken out of water and measured in room conditions. Due to this, there was a gradual decrease in water content leading to an increase in stiffness. The linear elastic region seen by the initial steep increase in tensile stress is followed by a yielding region with a dip and/or a gradual slope instead of a linear regime due to drying of the plastic. For 350 µm thick plastics, the strain hardening was distinct before necking, with this becoming less distinct as the thickness decreased. It was observed that at <100 µm, the curves and moduli were similar to those before wetting. This is due to the measurement in room conditions where a thin film dries fastest during fitting and measurement, and most of the water taken up is lost. The thicker plastics retain water and show much lower moduli of tens or few hundred MPa. Clearly, water plays an enormous role in the material properties of these saloplastics, setting the hot-pressed dense saloplastic apart from other commonly used plastics [17]. This is advantageous for their application as membrane materials which are used in the aqueous phase.

Although complexes formed using high molecular weights of the polyelectrolytes were easier to process, the precipitates from all the nine combinations of molecular weights (Fig. SI 2) were processed as well. As long as at least one of the two molecular weights in a pair was larger than 100 kg mol\(^{-1}\), processibility was straightforward by tuning the conditions. For lower molecular weight combinations, the precipitate was strained using filter paper and the filtrate was allowed to dry in air for a day to lose much water. It was then hot-pressed. From Fig. 6 it can be observed that the Young’s moduli of most of the resulting nine films were not very different from each other and their error bars overlap. The ones made from the lowest molecular weight of PSS (70 kg mol\(^{-1}\)) seemed to be the most brittle, also confirmed by a slightly higher value of Young’s modulus for each of the three PDADMAC molecular weight pairings. In hindsight, their precipitates were also the most fragile and formed powdery aggregates, and had shown the least elasticity (Fig. SI 2). The small effect of Mw on the measured Youngs modulus is in line with the expected ionically crosslinked structure of the saloplastics. Because of the already high crosslinking density, additional effects that would be expected for higher Mw, such as entanglements, have a negligible effect on the material properties.

The thermal properties of the plastic were measured by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry. Also, when thickness was increased, the Young’s modulus did not vary significantly (Fig. 5a and b), indicating that the stiffness of such material remains constant as the thickness is increased. This is in line with the fact that Young’s modulus is a material property independent of the dimensions [45]. This is also observed in common thermoplastics such as PVC and PE [37,39].

Although these hot-pressed plastics were not very sensitive to humidity changes in the environment, equilibration in MilliQ water led to them being more flexible. They were allowed to equilibrate in the water for 24 h after which tensile tests were conducted again to quantify the effect of water plasticization. The extensions were 1–2 orders of magnitude higher (40–80%) compared to the dry state (1–2%), thus completely changing the material properties (Fig. 5c). The wet materials showed smaller Young’s modulus values compared to the dry state as reported in Fig. 5(c). Wet plastics were much weaker and showed high elasticities in a linear regime (Video SI 2 and 3). However, to perform tensile tests, the plastics were naturally taken out of water and measured in room conditions. Due to this, there was a gradual decrease in water content leading to an increase in stiffness. The linear elastic region seen by the initial steep increase in tensile stress is followed by a yielding region with a dip and/or a gradual slope instead of a linear regime due to drying of the plastic. For 350 µm thick plastics, the strain hardening was distinct before necking, with this becoming less distinct as the thickness decreased. It was observed that at <100 µm, the curves and moduli were similar to those before wetting. This is due to the measurement in room conditions where a thin film dries fastest during fitting and measurement, and most of the water taken up is lost. The thicker plastics retain water and show much lower moduli of tens or few hundred MPa. Clearly, water plays an enormous role in the material properties of these saloplastics, setting the hot-pressed dense saloplastic apart from other commonly used plastics [17]. This is advantageous for their application as membrane materials which are used in the aqueous phase.

Although complexes formed using high molecular weights of the polyelectrolytes were easier to process, the precipitates from all the nine combinations of molecular weights (Fig. SI 2) were processed as well. As long as at least one of the two molecular weights in a pair was larger than 100 kg mol\(^{-1}\), processibility was straightforward by tuning the conditions. For lower molecular weight combinations, the precipitate was strained using filter paper and the filtrate was allowed to dry in air for a day to lose much water. It was then hot-pressed. From Fig. 6 it can be observed that the Young’s moduli of most of the resulting nine films were not very different from each other and their error bars overlap. The ones made from the lowest molecular weight of PSS (70 kg mol\(^{-1}\)) seemed to be the most brittle, also confirmed by a slightly higher value of Young’s modulus for each of the three PDADMAC molecular weight pairings. In hindsight, their precipitates were also the most fragile and formed powdery aggregates, and had shown the least elasticity (Fig. SI 2). The small effect of Mw on the measured Youngs modulus is in line with the expected ionically crosslinked structure of the saloplastics. Because of the already high crosslinking density, additional effects that would be expected for higher Mw, such as entanglements, have a negligible effect on the material properties.

The thermal properties of the plastic were measured by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry. Also, when thickness was increased, the Young’s modulus did not vary significantly (Fig. 5a and b), indicating that the stiffness of such material remains constant as the thickness is increased. This is in line with the fact that Young’s modulus is a material property independent of the dimensions [45]. This is also observed in common thermoplastics such as PVC and PE [37,39].

Although these hot-pressed plastics were not very sensitive to humidity changes in the environment, equilibration in MilliQ water led to them being more flexible. They were allowed to equilibrate in the water for 24 h after which tensile tests were conducted again to quantify the effect of water plasticization. The extensions were 1–2 orders of magnitude higher (40–80%) compared to the dry state (1–2%), thus completely changing the material properties (Fig. 5c). The wet materials showed smaller Young’s modulus values compared to the dry state as reported in Fig. 5(c). Wet plastics were much weaker and showed high elasticities in a linear regime (Video SI 2 and 3). However, to perform tensile tests, the plastics were naturally taken out of water and measured in room conditions. Due to this, there was a gradual decrease in water content leading to an increase in stiffness. The linear elastic region seen by the initial steep increase in tensile stress is followed by a yielding region with a dip and/or a gradual slope instead of a linear regime due to drying of the plastic. For 350 µm thick plastics, the strain hardening was distinct before necking, with this becoming less distinct as the thickness decreased. It was observed that at <100 µm, the curves and moduli were similar to those before wetting. This is due to the measurement in room conditions where a thin film dries fastest during fitting and measurement, and most of the water taken up is lost. The thicker plastics retain water and show much lower moduli of tens or few hundred MPa. Clearly, water plays an enormous role in the material properties of these saloplastics, setting the hot-pressed dense saloplastic apart from other commonly used plastics [17]. This is advantageous for their application as membrane materials which are used in the aqueous phase.

Although complexes formed using high molecular weights of the polyelectrolytes were easier to process, the precipitates from all the nine combinations of molecular weights (Fig. SI 2) were processed as well. As long as at least one of the two molecular weights in a pair was larger than 100 kg mol\(^{-1}\), processibility was straightforward by tuning the conditions. For lower molecular weight combinations, the precipitate was strained using filter paper and the filtrate was allowed to dry in air for a day to lose much water. It was then hot-pressed. From Fig. 6 it can be observed that the Young’s moduli of most of the resulting nine films were not very different from each other and their error bars overlap. The ones made from the lowest molecular weight of PSS (70 kg mol\(^{-1}\)) seemed to be the most brittle, also confirmed by a slightly higher value of Young’s modulus for each of the three PDADMAC molecular weight pairings. In hindsight, their precipitates were also the most fragile and formed powdery aggregates, and had shown the least elasticity (Fig. SI 2). The small effect of Mw on the measured Youngs modulus is in line with the expected ionically crosslinked structure of the saloplastics. Because of the already high crosslinking density, additional effects that would be expected for higher Mw, such as entanglements, have a negligible effect on the material properties. The thermal properties of the plastic were measured by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry.
modulus of the respective hot-pressed plastics. Each point represents an average position occurs between 370 °C (DSC) (Fig. SI 10). In Fig. SI 11, the TGA profile suggests that decomposition occurs between 370 °C and 500 °C, similar to extruded saloplastics in literature [22]. First, in order to evaporate water, the sample was heated from room temperature (18.3 °C) to 120 °C and cooled. The films were found to contain 10–12% water. It was then heated to 800 °C to observe decomposition. From literature and Fig. SI 11 and 12, it can be derived that the first peak ‘a’ (~400 °C) corresponds to the combustion of nitrogen, while the second peak ‘b’ (~450 °C) is that of sulphur, while a smaller peak ‘c’ at ~490 °C represents carbon [46,47]. The DSC experiment showed only one peak at ~107 °C, which is due to trapped water. The degradation of this saloplastic corresponds to the temperatures at which traditional plastics such as LDPE (~240 °C), cellulose acetate (~250 °C), and PET (~400 °C) begin to decompose [48].

Further, it is interesting to note from Fig. 7 that the decomposition of the PEC plastic begins at 370 °C, lying in between that of pure individual polymers Na-PSS (~270 °C) and PDADMAC (~440 °C). Likely the sulfonic group of PSS becomes more stabilized against decomposition, by the ionic bond with PDADMAC. The onset of decomposition of the plastic begins after that of Na-PSS, but has a steeper slope, and close to the latter until ~500 °C. At ~550 °C the Na-PSS is completely decomposed, but the components of PDADMA in the film are still present which continue to decompose [49].

The DSC profile of the PSS-PDADMA saloplastic is represented by (DSC) (Fig. SI 10). In Fig. SI 11, the TGA profile suggests that decomposition occurs between 370 °C and 500 °C, similar to extruded saloplastics in literature [22]. First, in order to evaporate water, the sample was heated from room temperature (18.3 °C) to 120 °C and cooled. The films were found to contain 10–12% water. It was then heated to 800 °C to observe decomposition. From literature and Fig. SI 11 and 12, it can be derived that the first peak ‘a’ (~400 °C) corresponds to the combustion of nitrogen, while the second peak ‘b’ (~450 °C) is that of sulphur, while a smaller peak ‘c’ at ~490 °C represents carbon [46,47]. The DSC experiment showed only one peak at ~107 °C, which is due to trapped water. The degradation of this saloplastic corresponds to the temperatures at which traditional plastics such as LDPE (~240 °C), cellulose acetate (~250 °C), and PET (~400 °C) begin to decompose [48].

Further, it is interesting to note from Fig. 7 that the decomposition of the PEC plastic begins at 370 °C, lying in between that of pure individual polymers Na-PSS (~270 °C) and PDADMAC (~440 °C). Likely the sulfonic group of PSS becomes more stabilized against decomposition, by the ionic bond with PDADMAC. The onset of decomposition of the plastic begins after that of Na-PSS, but has a steeper slope, and close to the latter until ~500 °C. At ~550 °C the Na-PSS is completely decomposed, but the components of PDADMA in the film are still present which continue to decompose [49].

The DSC profile of the PSS-PDADMA saloplastic is represented by

Fig. 6. The effect of molecular weight of Na-PSS and PDADMAC on Young’s modulus of the respective hot-pressed plastics. Each point represents an average of at least three independent measurements.

In addition to being completely dense, hot-pressed saloplastics offer several other advantages. This method has allowed the fabrication of free-standing dense films as thin as 8 μm and as thick as 1 mm. Hence, depending on the application, film thickness can be adjusted by over a factor of 100. Furthermore, this method of processing enables us to fabricate patterned plastics without an extra process step. Different projected shapes such as cylindrical pillars and chevrons were successfully made in different dimensions. A hot-press mould with 250 μm deep macroscopic cylindrical patterns were made, which got precisely replicated in the hot-pressed film as shown in Fig. 8 (a) and (b). Scanning Electron Microscopy images, such as in Fig. 8 (c–d), show that these structures seamlessly protrude from the surfaces without causing cracks or folds.

In industry, polymers are required in several forms and strengths. When thin sheets of polymer are not strong enough for a specific purpose, they need to be reinforced by being embedded in a mesh of woven or non-woven fibres. Along with strength, advantages include lower cost, wear resistance, custom thermal, and electrical properties [50]. PECs were conveniently hot-pressed into such meshes to form a uniform plastics of 100 μm each (Fig. 9). In one case, a plastic woven mesh was used, which showed up to 26% increase in elasticity modulus (6552 ± 340 MPa) in comparison to a hot-pressed saloplastic of the same thickness (5200 ± 280 MPa). In another case, a non-woven paper mesh was used, which showed up to 31% increase (6812 ± 433 MPa). All these films maintained their density and no pores were seen after pressing.

Such advanced structures and reinforcements were made repeatedly and did not have any noticeable defects. Overall, the hot-pressing method demonstrates a reproducible approach with plastics being dense and thickness controlled with reduced swelling. The parameters presented have been arrived at after trying various permutations, as well as possible errors and irregularities. The simple and straightforward procedure with relatively short processing times allows it to be scaled up. Indeed, large scale hot-press devices are available, with surface areas up to 5 m². Overall, it is a novel method with a potential to be applied in different fields allowing easy modification.

3.4. Advanced hot-pressing approaches

Saloplastics have been a breakthrough in the view of processability of polyelectrolyte complexes. However, the presence of pores and holes make them less useful in any practical applications. In this work, we have showcased for the first time, a novel hot-pressing method to make free-standing completely dense plastics and have also studied their properties. Key parameters for effective complexation, such as the molecular weight and concentrations of individual polyelectrolytes, type, and quantity of salt have been studied qualitatively and quantitatively in this work. K+ and Br− ions are shown to better aid complexation by extrinsic compensation compared to Na+ and Cl− ions. Hot-pressing parameters including temperature, pressure, and time have been studied in detail and their effects on film thickness and uniformity have been discussed. This dedicated study exposes a small window of opportunity for effectively process them in plastics. Hence their mechanical properties were also studied for the first time. The Young’s modulus was observed to be independent of film thickness when dry, but decreased with an increase in wet thickness. For the wet state, the inverse relation stems from the quicker drying of thinner films during the experiments. The nature of the complex is shown to strongly affect the quality of the

Fig. 7. Thermal Gravimetric analysis comparison of the PSS-PDADMA plastic along with those of pure Na-PSS and PDADMAC.

Fig. 8. Electronic microcopy images of the hot-pressed film.
hot-pressed saloplastic, in important parameters such as the water uptake. PECs have been effectively hot-pressed into woven and nonwoven meshes to make reinforced plastics with increased tensile strength, without the need for an extra process step. This method can be scaled up, and also allows the creation of profiles such as pillars, chevrons, or other protruding structures on the film surface in the micro and macro scale. Hot-pressing PECs to plastics overcomes challenges and opens doors to applications in many fields including biomedicine, ion-exchange membranes, and contact lenses. Overall, this work demonstrates a simple, effective hot-pressing method to make dense plastics, that are dense even on the nanometer scale.

**Funding sources**

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (ERC StG 714744 SAMBA). W.M.d.V. and J.D.W acknowledge funding support from the “Vernieuwingsimpuls” programme through project number VIDI 723.015.003 (financed by the Netherlands Organization for Scientific Research, NWO).

**CRediT authorship contribution statement**

Ameya Krishna B: Visualization, Investigation, Validation, Writing – original draft. Joshua D. Willott: Methodology, Visualization, Data curation, Supervision. Saskia Lindhoud: Conceptualization, Methodology, Supervision, Writing – review & editing. Wiebe M. de Vos: Conceptualization, Funding acquisition, Supervision, Writing – review & editing, Project administration.

**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.

**Acknowledgements**

The authors would like to thank the European Research Council and NWO for the grants. We would like to acknowledge Bob Siemerink, Jiaying Li, Wouter Nielen, Cindy Huiskes, and Frank Morssinkhof for their support in performing experiments.
