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Contributions of Polyelectrolyte Complexes and Ionic Bonding to Performance of Barrier Films for Packaging: A Review

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Barrier films that are used on packages play an important role, especially in the protection of food products. Research is being carried out at an accelerating pace to replace petroleum-based plastic films, which do not biodegrade and are difficult to recycle. This review article considers publications related to the use of polyelectrolyte complexes (PECs) in barrier films as a strategy to decrease the permeation of oxygen and other substances into and out from packages. Research progress has been achieved in using combinations of positively and negatively charged polymers, sometimes together with platy mineral particles, as a way to restrict diffusion through packaging materials. In principle, the ionic bonds within PECs contribute to a relatively high cohesive energy density within such a barrier film, which can resist diffusion of various gases and greasy substances. Resistance to water vapor, as well as aqueous substances, represent important challenges for barrier concepts that depend on ionic bond contributions. Factors affecting barrier performance of PEC-based films are discussed in light of research findings.

Keywords: Polyelectrolyte complexes; Layer-by-layer (LbL); Water vapor; Oxygen; Self-assembly; Healing

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Contents

INTRODUCTION

Research is under way throughout the world to find eco-friendly ways to ship and store food and other products with less spoilage. Packaging systems for food products currently rely heavily upon the usage of petroleum-based plastics, as well as metal films and glass (Lange and Wyser 2003; Fang and Vitrac 2017). Plastic films such as low-density polyethylene (LDPE) persist for a long time in the environment (da Costa *et al.* 2016; Blasing and Amelung 2018). Plastic-containing litter and other waste that reach the ocean are creating serious harm to aquatic life and food chains (Derraik 2002).

Important progress has been achieved in the usage of bio-based, biodegradable materials in the preparation of barrier layers for packages. For example, nanocellulose can be formed into dense films having superior ability to block the diffusion of oxygen (Hubbe *et al.* 2017). Such films can be effective, especially under low humidity conditions, due to the high cohesive energy density provided by the hydrogen bonds (Lagarón *et al.* 2004). The present article reviews progress related to a parallel track of research in which ionic bonds provide strong bonding, thus limiting the ability of permeants to pass through a barrier layer. In particular, polyelectrolyte complexes (PECs) have been shown to be effective under favorable circumstances in reducing the passage of gases, vapors, and liquids (De Oliveira *et al.* 2008; Priolo *et al.* 2010a; Ibn Yaich *et al.* 2015; Haile *et al.* 2017; Smith *et al.* 2018).

Hypotheses

To provide focus in the course of reviewing literature related to ionic bonding contributions and PECs as barrier films, a series of hypotheses, as follows, will be considered in this article.

Hypothesis 1: Contribution to cohesive energy density

As a first hypothesis, it is proposed that ionic bonding can contribute substantially to the barrier performance of thin films prepared from ionically charged polymers, *i.e.* polyelectrolytes and related systems. The idea is that strong bonding between the polymer segments within the plastic material can prevent the random opening up of spaces within the polymeric material that are large enough for the passage of molecules (Lagarón *et al.* 2004). It is further proposed that ionic bonds linking surfaces of mineral particles or nanocellulose to oppositely charged polyelectrolytes within a PEC system also can contribute to barrier properties.

Hypothesis 2: Can be prepared as contiguous nanostructures

It is proposed that, by the use of suitable procedures, it is possible to achieve a sufficiently contiguous nanostructure within PECs and related film structures, as would be required for very high efficiency of barrier effects. To place this hypothesis in context, it is well known that interactions among oppositely charged polyelectrolytes often lead to strongly flocculated mixtures (Durandpiana *et al.* 1987; Hubbe 2007). In fact, even PECs themselves can used as effective flocculants (Korhonen *et al.* 2013; Petzold and Schwarz 2014). Accordingly, it is important to look for evidence in the published literature about ways to avoid such unintended nonuniformity in the structure of ionically bonded films.

Hypothesis 3: Nanofillers can enhance barrier performance of PEC films

It is proposed that the barrier performance of PEC films can be improved by incorporation of various solid fillers or reinforcing particles during their preparation. According to the principle of tortuosity, diffusion of molecules through a film will be slowed down by the presence of completely impermeable particles, such as minerals (Ghanbarian *et al.* 2013). In addition, one might propose that reinforcing particles, especially those that have a fibrillar shape, might in some cases help hold a film material more securely as a contiguous structure, thus contributing to barrier properties.

Hypothesis 4: Healing of PEC barrier films can be achieved

It is proposed that reliance upon ionic bonds is compatible with the preparation of self-healable barrier films. Self-healing means that, by manipulation of conditions such as temperature, moisture, or saline solution, a crack in a film will be able to close itself up. This hypothesis is important to consider in the context of evidence that PEC films can be brittle, especially when dry (Feng *et al.* 2006; Meka *et al.* 2017; Fares *et al.* 2019).

Hypothesis 5: Vulnerable to permeants

The first four hypothesis statements, as described above, all pertain to proposed favorable aspects of barrier films that rely upon ionic bonds. The final four consider negative aspects, *i.e.*, proposals that PECs and related films are likely to provide poor barrier capabilities, at least in some circumstances.

As the fifth hypothesis, it is proposed that PECs and related barrier films will tend to be permeable to various permeants. Such a hypothesis is important in light of the hydrophilic nature of polyelectrolytes, which can serve as a reason to doubt their ability to resist the permeation of water and water vapor. For example, PECs including the cationic polyelectrolyte chitosan are good barriers to oxygen, but that capability degrades when they are exposed to high humidity (Lazar *et al.* 2019). Also, PECs are known to swell in the presence of water (Ahmadiannamini *et al.* 2012).

Hypothesis 6: Susceptibility to mechanical failure

It is proposed that barrier layers based on PECs and similar systems tend to be prone to mechanical failure and that this is a significant issue. This susceptibility to failure can include a brittle nature, vulnerability to damage by scratching, and a typically low modulus of elasticity. A tendency toward brittle failure has been noted (Feng *et al.* 2006; Fares *et al.* 2019). Such studies indicate that even wet PEC films generally have little ability to stretch without failure, and dried PECs often can be described as brittle. Concerns about scratch resistance follows from the extremely thin nature of many PEC-based films.

Hypothesis 7: Susceptibility to non-equilibrium trapped states

It is proposed that PECs, during their formation, essentially become frozen into structures that are governed by kinetics, as well as by the flow conditions during initial mixing and preparation. Such structures, because of their inability later to rearrange themselves into an equilibrium structure, are proposed to trap nonuniformities, which may include pores. It is proposed that there is an inherent conflict between the desire for a high cohesive energy density and the desire for a high degree of uniformity within the nanostructure.

Hypothesis 8: Their fussy nature makes their implementation challenging

Finally, it is proposed that PEC-based films can be described as "fussy". In other words, it is proposed that various deviations from ideal conditions of preparation and composition will result in unfavorable barrier performance. Evidence of the fussy nature may consist of wide ranges in reported barrier performance, a propensity for the formation of porous structures rather than dense, continuous structures (Hariri and Schlenoff 2010), and stickiness of PECs, resulting in deposits on processing equipment that are hard to clean up (Heermann *et al.* 2006).

BACKGROUND

The purpose of this section is to lay groundwork for subsequent discussions of mechanistic aspects as well as factors affecting the barrier performance of PECs and related films. Topics in this section include historical notes related to PECs, materials that have been used to make PEC barrier films, permeability properties of typical PEC-based films, and physical properties of typical PEC-based films.

Historical Background

Evidence for ionic bonding contributions

Max Born, who published in the period of 1918 to 1920, appears to have been the first to give a modern account of the energies associated with contact between oppositely charged ions (Sherman 1932). Born's work focused on the crystal structure of sodium chloride, making use of emerging methods in X-ray diffraction. Clear evidence and quantitation of ionic bonds within organic materials did not become established until later. For instance, the presence of ionic bonds was proposed to account for the development of wet strength when the highly cationic polymer polyethyleneimine (PEI) was added to paper (Trout 1951). It was observed that, rather than fall apart upon complete wetting, the paper retained a modest faction of the strength that it had when it was dry. By contrast, ordinary paper, which relies on hydrogen bonding to establish strong inter-fiber bonding, loses almost all of its strength when it becomes completely soaked in water. Allan and Reif (1971) demonstrated the development of especially strong wet strength when PEI was sprayed onto paper prepared from cellulosic fibers that had been rendered more anionic by derivatization with an anionic dye. The likely mechanism is illustrated schematically in Fig. 1. Note that the cellulose itself, due to its content of surface carboxylate groups, can be regarded as a polyelectrolyte in terms of its interactions with the PEI. Delgado *et al.* (1997) achieved a more elegant demonstration of ionic bond participation by attaching zwitterionic groups to papermaking fibers; the subsequent development of wet strength was consistent with double ion-pair formation between such groups bound to adjacent fibers within the paper. Moeller (1966) showed that cationic starch was able to increase the strength of paper even when the water was removed from the sheet by freeze-drying. If one assumes that hydrogen bonds are effectively prevented from forming under such drying conditions, then one is left to conclude that the strength development must have been due to ionic bonds.

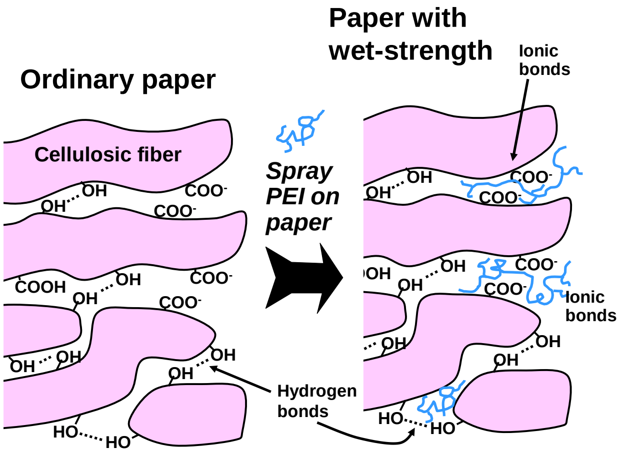

Fig. 1. Wet-strengthening effect of a high-charge cationic polyelectrolyte sprayed onto ordinary paper, providing early evidence of practical contributions of ionic bonding to material properties

The first reported observations of polyelectrolyte complex formation came even earlier. Kossel (1896) showed evidence of PEC formation in studies of the nuclei of biological cells. Willstätter and Rhodewald (1934) showed related effects when studying glycogens. Bungenberg de Jong and Kruyt (1929) carried out some of the first extensive research involving mixtures of oppositely charged polyelectrolytes. For instance, they showed that such mixtures could separate into two phases, each phase having a fixed polymer concentration and a distinct ratio of polyelectrolytes to water. The science of PEC formation and properties became well grounded by the 1960s (Michaels 1965). A key milestone, from the perspective of forming barrier films, was the discovery of layer-by-layer (LbL) multilayer formation of PECs (Decher and Hong 1991; Decher 1997). Though the preparation of such multilayers is time-consuming, the precision of layering has led to impressive results and a great increase in understanding.

Usage of PECs in charge titrations

PECs are formed in the course of titration methods that are widely used to determine the charge-equivalent concentrations of polyelectrolytes in solution. Terayama (1952) used a charge-sensitive dye, toluidine blue-O, to determine the titration endpoint. A key step in such a titration is illustrated in Fig. 2. As shown, the dye initially has a blue coloration when it is placed into pure water. Complexation between the dye and a high-charge-density anionic polymer such as the potassium salt of polyvinylsulfate (PVSK) causes the hue of the dye to shift from blue to pink. The color change can serve for detecting the endpoint of charge titrations due to the fact that the complexes formed with the dye are not as strong as the complexes formed between the two polyelectrolytes. The technique became widely used in the papermaking industry for monitoring and control of process conditions (Halabisky 1977; Hubbe 1979). Such titrations subsequently became quicker and more reliable with the advent of streaming current detectors, which can be used either in the laboratory or within the manufacturing process for online measurements (Hubbe and Waetzig 2018). Such measurements depend on the accuracy of forming 1:1 matching of charged groups between the titrant and the aqueous mixture. Increasing systematic deviations from 1:1 pairing, depending on which standard titrant is being added to which, have been found with increasing salt concentration (Chen *et al.* 2003).

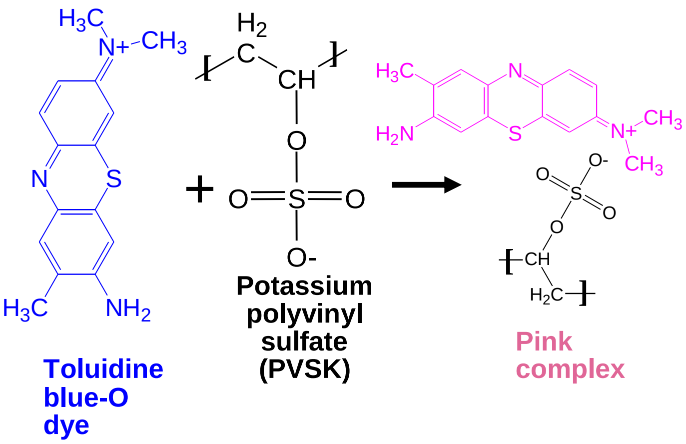

Fig. 2. Charge complexation giving rise to the characteristic color change when toluidine blue is used as an indicator of the endpoint for polyelectrolyte titrations

Usage of PECs as bonding agents

PECs can function as bonding agents to increase the strength properties of paper (Carr *et al.* 1974; Nagata 1991; Gärdlund *et al.* 2003, 2005; Lofton *et al.* 2005; Maximova *et al.* 2005; Torgnysdøtter and Wågberg 2006; Fatehi *et al.* 2009; Sang *et al.* 2010; Mocchiutti *et al.* 2016; Strand *et al.* 2017; Schnell *et al.* 2018). Superior performance has been found when forming the PECs *in-situ* within a briskly stirred suspension of fibers (Hubbe 2005; Heermann *et al.* 2006). By such treatment it is possible to adsorb much greater amounts of polyelectrolyte onto cellulosic fiber surfaces, compared to conventional treatments that involve single treatment with a polyelectrolyte solution. Paper-like sheets could be prepared even when using non-bonding glass microfibers (Hubbe 2005). Compared to treatment with PECs, higher paper strength sometimes has been achieved by the painstaking procedure of LbL assembly of multilayers (Eriksson *et al.* 2005; Ankerfors *et al.* 2009; Feng *et al.* 2009). However, direct addition of PECs, usually with a minor excess of positively charged polyelectrolyte, is very much faster than the LbL method and is almost as effective relative to the amounts of polyelectrolytes used. Key impediments to wider industrial use of PECs as a strategy for increasing paper strength include the high cost of chemicals and a propensity for the formation of tacky deposits on forming screens (Heermann *et al.* 2006).

Usage of PECs for barrier films

More recently, various researchers have been studying the preparation of PEC-based films, with evaluation of their barrier properties. Such studies are extensively listed in Table A, which due to its size is placed in the Appendix to this article. Review articles have appeared discussing various aspects of such research (Priolo *et al.* 2015; Lindström and Österberg 2020; Machado *et al.* 2020). In general it has been found that PEC-based films resist the permeation of oxygen, especially under dry conditions. However, PECs often contain about 20% water (Mende *et al.* 2002). Generally, PEC-based films become more permeable to oxygen, water vapor, and various liquids with increasing moisture content or relative humidity.

Materials Suitable for PEC Barrier Films

Polyelectrolytes

An attractive feature of PEC technology is the facility with which a broad range of substances can be included in a PEC-based barrier film. In principle, PECs are formed from a positively charged (cationic) polyelectrolyte and a negatively charged one (anionic). Each polyelectrolyte needs to be soluble in water. The charge density of each needs to be high enough to promote strong association. Petroleum-based polyelectrolytes that are often used in studies of PECs include acrylamide copolymers, polydiallyldimethylammonium chloride (poly-DADMAC), and polyvinylsulfate, potassium salt (PVSK). Bio-based polyelectrolytes often used in studies of PECs include cationic starch, chitosan, alginates, and carboxymethyl cellulose (CMC). In addition, various hemicellulose fractions and their derivatives are being studied as components of PECs (Ibn Yaich *et al.* 2015). The chemical structures of some of the mentioned polyelectrolytes are shown in Fig. 3.

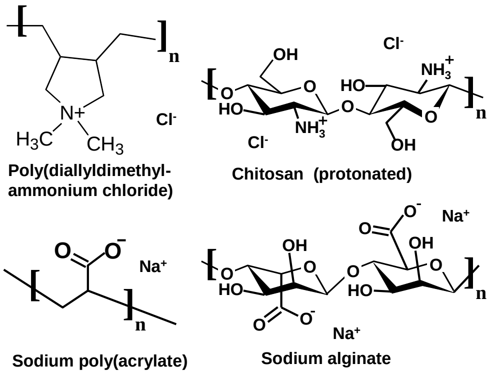

Fig. 3. Chemical structures of some polyelectrolytes that have been commonly used in forming polyelectrolyte complexes (PECs). Cationic polymers on top; anionic below. Synthetic polyelectrolytes on left; bio-based on right

Colloidal particles as components of PECs

Because a PEC is formed by combining positively and negatively charged colloidal-sized entities, it makes logical sense that one can substitute solid particles, having a suitable surface charge, in place of one of the polyelectrolytes. The recent review by Lindström and Österberg (2020) describes the increasing research attention being devoted to sodium montmorillonite (sometimes called bentonite or nanoclay) as a component in PECs prepared as barrier film. Such nanoclay has a highly platy shape and a negative surface charge, so the particles can be used in combination with cationic polyelectrolytes. Another option is to employ hydrotalcite, which is sometimes referred to as Mg Al double-hydroxide nanoplatelets (Dou *et al.* 2014; Lee *et al.* 2016). These have a positive surface charge. Figure 4, in its top section, presents drawings of two mineral products that have been employed in PEC barrier films.

Another widely researched solid component for PEC barrier films is nanocellulose. As shown in the bottom section of Fig. 4, two of the major classes of nanocellulose are cellulose nanocrystals (CNC) and nanofibrillated cellulose (NFC), which is sometimes called cellulose nanofibril. Though the fibrillar shape of the nanocellulose particles does not lend itself well to the physical blocking of substances from diffusing in a film, the material generally has a high content of crystalline regions, which are impermeable. Also, nanocellulose, if it is well bonded to the surrounding material in a film, has the potential to help maintain a defect-free film structure in ideal cases. Abdul Khalil *et al.* (2016) reviewed the usage of NFC in combination with chitosan to form composite films. The properties of different kinds of nanocellulose have been reviewed (Salas *et al.* 2014; Klemm *et al.* 2018).

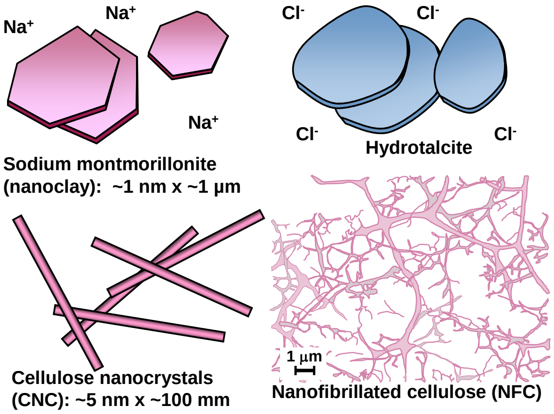

Fig. 4. Sketches of some particles that have been considered for the preparation of PEC barrier films. Platy minerals on top; fibrillar cellulosic particles on bottom

Permeability of Typical PEC Barrier Films

The ability of typical PEC materials to impede the diffusion of oxygen, water vapor, liquid water, and greasy substances, *etc.*, is of great interest to researchers who are considering PECs for barrier films. As stated in the first of the hypotheses at the start of this article, it is proposed that ionic bonding within thin films can contribute substantially to the barrier performance of thin films prepared from ionically charged polymers, *i.e.* polyelectrolytes and related systems. On the other hand, as illustrated in Fig. 5, the strong tendency of oppositely charged polymers to flocculate can be expected to be a cause of nonuniform structures in some cases.

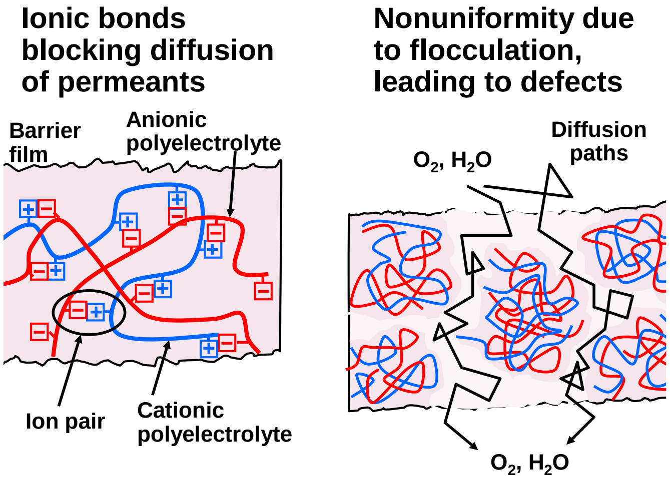

Fig. 5. Sketch illustrating two competing tendencies of the ionic bonds formed between oppositely charged polyelectrolytes. Left: Ionic bonds, by increasing the cohesive energy density, have potential to impede diffusion of permeants through the film. Right: Flocculation during preparation of some PECs can be expected to leave pores and defects, which may make the film more permeable.

Table A (see Appendix) includes a large number of studies in which PEC films were used in an effort to decrease permeation of various substances through films. Because Table A contains data that can be useful at several times in the discussion that follows, some key aspects will be noted. The first two columns list the positively charged (cationic) and negatively charged (anionic) components, which are usually polyelectrolytes but sometimes nanoparticles, where indicated. All abbreviations are defined in the first set of notes below the table. The third column indicates the nanoparticles, if used; items in parentheses indicate cases where the nanoparticles explicitly played the central role of complex formation with an oppositely charged ingredient, usually a polyelectrolyte. The fourth column indicates the preparation method, and it should be noted that the preparation methods will each be described in a later section. In preparing the list of the reported permeability values, some of the data have been converted to match the most commonly reported sets of units. Note that oxygen permeability is commonly reported using the units $cm^3/(m^2 \cdot day \cdot atm)$, whereas water vapor permeability is often reported as $g/(m^2 \cdot day \cdot atm)$. In a few cases, the cited authors did not report their results in a way that allowed such conversions to be made. In particular, some authors expressed rates of permeation based on a unit thickness of the barrier film but without disclosing the determined value of film thickness.

To briefly summarize the results in Table A, the term "highly variable" is maybe the best description. Various studies included in the table have shown decreases in permeation of gases when a PEC-based film was compared to either a layer of a single polyelectrolyte (De Oliveira *et al.* 2008) or a bare default plastic film without the PEC layer on it (Haile *et al.* 2017). By contrast, other studies not included in the table have reported the intentional preparation of permeable or porous membranes by use of PEC formulations (Lukas *et al.* 2002; Li *et al.* 2013; Molgaard *et al.* 2014; Zhao *et al.* 2014; Zhu *et al.* 2014; Ong *et al.* 2016). As mentioned earlier, some of the more promising barrier systems are those that include nanoclay or hydrotalcite within the PEC film structure (Jang *et al.* 2008; Priolo *et al.* 2010a,b, 2013; Tzeng *et al.* 2014). Permeability values below the detection limit of the instruments employed are listed in Table A with the "less than" sign (<).

Several studies, including the following, have documented effective resistance against the permeation of oxygen through PEC films (Jang *et al.* 2008; Priolo *et al.* 2010a,b; Li *et al.* 2013; Molgaard *et al.* 2014; Ibn Yaich *et al.* 2015; Shimizu *et al.* 2016; Haile *et al.* 2017; Schnell *et al.* 2017; Soltani *et al.* 2017; Satam *et al.* 2018; Smith *et al.* 2018). These favorable results possibly have a similar explanation as has been discussed in the case of pure nanocellulose films, which have a high hydrogen bond density. It has been proposed that the high resistance to oxygen in such nanocellulose films is due to a combination of defect-free structure and the fact that the hydrogen bonds hold the adjacent macromolecular chains tightly together. By arresting motions of the segments of the macromolecules, the hydrogen bonds effectively prevent permeant molecules from squeezing between the adjacent macromolecular chains within a film (Aulin *et al.* 2013; Hubbe *et al.* 2017; Lindström and Österberg 2020). It is reasonable to suppose that ionic bonds could play a similar role.

Significant resistance to grease and oil permeation has been reported for some typical PEC systems (Sirviö *et al.* 2014; Basu *et al.* 2017; Chi and Catchmark 2018a,b). Ahmadiannamini *et al.* (2012) noted that certain PECs did not swell in organic solvents, which is consistent with the presence of frequent hydrogen bond connections holding the molecules tightly together. The favorable barrier results achieved against the penetration of grease and oils probably has explanations that are parallel to those used to explain resistance to oxygen. Both types of permeant are non-polar and uncharged. Thus, the permeants do not have a tendency to become solubilized in the inherently polar PEC materials. Rather, the enhanced energy density contributed by the ionic bonding can be viewed as a means by which the polymer chains are held close together and relatively immobile. In addition, the organic solvents have a very different dielectric constant from that of water. The higher dielectric constant of water is an additional factor leading to higher swelling of PECs in aqueous systems. A simulation study has predicted a strong influence of local dielectric constant in the swelling of PECs (Qiao *et al.* 2010).

The presence of water appears to pose some of the greatest challenges to the PEC systems as potential barrier layers. The polyelectrolytes that are employed to make the PECs must be readily soluble in water in order to allow the needed processing, and that hydrophilic nature appears to be a point of inherent vulnerability of PEC barrier layers. Various articles have documented the tendency of PECs to swell in water (Fajardo *et al.* 2011; Ahmadiannamini *et al.* 2012; Zhu *et al.* 2014; Bajpai *et al.* 2016; Lv *et al.* 2018). In general, PECs can be expected to be less hydrophilic than either of their components. However, De Oliveira *et al.* (2008) reported an instance where the PEC was more hydrophilic than chitosan, which was one of its components. The hydrophobic nature of chitosan films, when used alone, is likely due to specific factors related to molecular conformation and orientation (Hubbe 2019). Farhat *et al.* (1999) found that polyelectrolyte multilayers contained about 10 to 20% of water. Even when dry, the ability of typical PECs to resist water vapor permeation can be described as intermediate, *i.e.* better than a polyelectrolyte layer alone, but not a superior barrier (Bajpai *et al.* 2016; Chi and Catchmark 2018b). Some PEC layers even can be described as “permselective,” *i.e.* having a much higher water vapor permeability in comparison to their permeability toward other substances (Meier-Haack and Muller 2002).

Even when dry, PEC films have variable ability to resist the permeation of water vapor (Li *et al.* 2011; Sirviö *et al.* 2014; Ibn Yaich *et al.* 2015; Soni *et al.* 2016; Basu *et al.* 2017; Schnell *et al.* 2017). The most promising PEC systems for restricting the passage of water appear to be those that incorporate highly platy mineral particles (Findenig *et al.* 2012; Chi and Catchmark 2018a; Wang *et al.* 2018).

Physical Properties of Typical PEC Barrier Films

Physical properties such as stretchability and modulus of elasticity can be important in determining whether or not a barrier film will be able to resist breakage during use. In general, PECs tend to be more rigid and less stretchable than films prepared from the corresponding separate polyelectrolytes (De Oliveira *et al.* 2008). Figure 6 provides a schematic plot to emphasize the generally weak nature of PECs and also the strong dependency of their properties on humidity and moisture content.

The drying of PECs tends to make them more brittle (Rhim and Lee 2004; Feng *et al.* 2006; Meka *et al.* 2017; Fares *et al.* 2019). Non-conventional strategies such as usage of non-ionic soluble polymers in PEC-like structures may be needed if high levels of stretching without breakage are required (Qin *et al.* 2017). The non-ionic polymers appear to function as plasticizers. On the other hand, evidence suggests that PECs are sufficiently flexible to greatly increase the toughness of paper, when they are used as a bonding agent (Vainio *et al.* 2006).

High scratch resistance is not expected for PECs in general, though it can be achieved in certain formulations that include highly platy minerals (Humood *et al.* 2016). Likewise, PECs are not generally expected to have high resistance to electrical conductance. Increasing electrical conductance of PECs can be expected with increasing moisture content and with increasingly non-stoichiometric charge composition (Zheng *et al.* 2006; Ghostine *et al.* 2013). As shown by De *et al.* (2011) and Cramer and Schonhoff (2014), sometimes the ionic conduction within a PEC is dominated by migration of ions having one charge rather than the other.

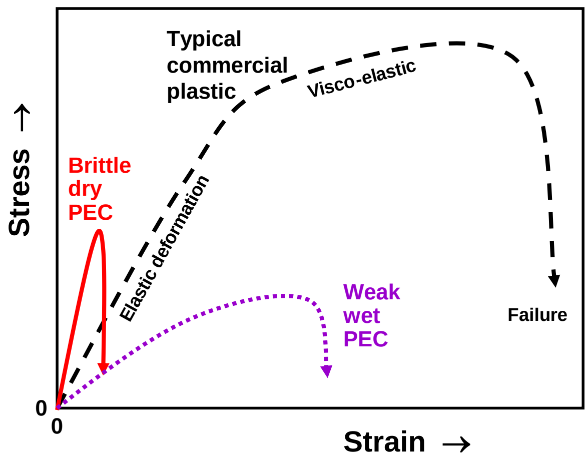

Fig. 6. Schematic plot contrasting the stress strain curves of typical dry and wet PEC material compared to a commercial plastic such as polyethylene

MECHANISMS OF PEC FORMATION AND BEHAVIOR

This section reviews the basics of what has been published about the mechanisms by which PECs form and stay together. Topics include thermodynamic considerations, self-assembly, trapped non-equilibrium states, and healing.

Thermodynamic Considerations

Free energy content

Thermodynamic principles ordinarily are based on starting assumptions that the processes being considered are reversible and that they are continually trending towards a state of equilibrium. Those assumptions are not necessarily true for many of the PEC systems considered in this article. Nevertheless, the main conclusions from thermodynamics continue to be quite useful for understanding the mechanisms relating to PEC formation and some of their properties. Key thermodynamic issues related to PECs have been described in various publications (Michaels 1965; Decher 1997; Park *et al.* 2002; Schneider 2012; Das and Tsianou 2017; Ji *et al.* 2017; Rathee *et al.* 2018).

The driving force for oppositely charged polyelectrolytes to associate with each other in aqueous systems is known to depend on the energy of formation of ionic bonds. Various authors have estimated the free energy involved in ionic bond formation to be in the range of about 1.2 or more kcal/mole (Allan *et al.* 1993; De Stefano *et al.* 1998; De Robertis *et al.* 2001; Schneider 2012; Spruijt *et al.* 2012; Askeland and Wright 2015). Higher values of ΔG for ionic bonding have been reported in some cases, which is consistent with the multivalent ionic species considered in some of these cited works. Notably, Spruijt *et al.* (2012) used an advanced atomic force microscopy method in which single chains of polyelectrolytes were pulled away from a surface coated with a brush copolymer having a sparse, but opposite charge. By that means it was possible to quantify the force and energy needed to break an individual ion-pair attachment. In the absence of salt, each ion pair accounted for about 3.6 kcal/mole of energy, but that quantity was reduced to about 0.6 kcal/mole when salt was added to the solution.

The amount of energy embodied within a single pair of oppositely charged ions is clearly not enough to cause oppositely charged entities to remain together in an aqueous mixture. Rather, just like a grain of sodium chloride tossed into a glass of water, the ions will immediately enter the bulk solution, spending only a very small fraction of their time as ion pairs. Glinel *et al.* (2002) estimated that a charge density of at least 0.36 elementary charges per nanometer is needed to induce effective complexation between polyelectrolytes of opposite charge in the absence of salt. When a critical concentration of neutral salt is present in an aqueous solution, the polyelectrolytes require between 53% and 75% of the units to be charged in order to maintain a stable PEC that does not dissolve back into the bulk solution (Schoeler *et al.* 2002). To place these values into context, the well-known high-charge cationic titrant poly-diallyldimethylammonium chloride (polyDADMAC) has 19.5 charges per nm of chain length, and 53% of that amount would give 10.3 charges per nm of chain length.

Self-assembly

Due to the inherent electrical attraction between positive and negative ionic groups, the term "self-assembly" is often employed when describing the preparation of PEC systems. When using such a term, it is important to keep in mind that many factors in addition to the electrical charges on the polyelectrolytes can contribute to the results. A high-performing PEC barrier layer is unlikely to be formed just by combining the materials under arbitrary conditions. To draw an analogy, even though plants are very capable of growing in the wild, they are not likely to form an organized garden that meets with the approval of a gardener without a lot of detailed effort by the gardener.

Michaels (1965), in an early review of PEC technology, laid out two limiting-case models to describe the conformation of PECs formed in aqueous solution. As illustrated in Fig. 7, the "scrambled egg" model envisions PECs as similar to random intertwined strands of cooked spaghetti. The "ladder" model envisions PECs as forming in zipper-like fashion between pairs of oppositely charged macromolecular chains.

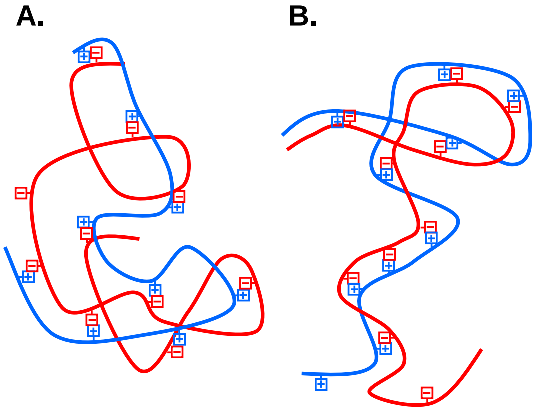

Fig. 7. Illustration of the (A) "scrambled egg" and (B) "ladder" models of polyelectrolyte complex nanostructure, as described by Michaels (1965)

The ladder model would be consistent with an orderly pairing between each set of oppositely charged ions along the two chains. In either model, the process is driven toward completion not only by the ionic attractions, but also by the fact that the pairing of ionic groups on the macromolecular chains allows the counter-ions to diffuse away from the polyelectrolytes into the bulk of solution. The greater degrees of freedom experienced by the released counter-ions makes a large contribution of entropy, which is part of the free energy discussed in the previous subsection. Michaels *et al.* (1965) concluded, based on changes in conductivity due to the release of ions, that the process happens quickly and that the ladder model was dominant under the dilute conditions used in their research. Lazutin *et al.* (2012), based on molecular dynamics simulations, predicted that a scrambled egg form of PECs will be predominant in systems comprised of highly flexible polyelectrolyte chains.

The reason for the entropy increase, upon formation of a PEC by combining solutions of oppositely charged polyelectrolytes (Michaels 1965; Veis 2011; Das and Tsianou 2017; Rathee *et al.* 2018), is illustrated in Fig. 9. At the left of the figure one can envision two beakers that contain polyelectrolyte solutions having opposite signs of charge. In addition to the charges bound to the chains, there also are counter-ions. Though the counter-ions are not fixed to the polyelectrolyte chains, their average positions are constrained based on double-layer theory (Debye and Hückel 1923; Tadmor *et al.* 2002; Muthukumar 2004; Landy *et al.* 2012; Chremos and Douglas 2016). The polyelectrolyte chains themselves have relatively few degrees of freedom, due to the fact that each monomeric group is constrained by covalent bonds. The situation is analogous to a chain-gang of prisoners, who still regard themselves as being locked up, even though collectively they are not attached to anything. When the two oppositely charged polyelectrolyte solutions are combined, as shown in the right side of the figure, the polyelectrolyte chains give up much of what little freedom they had when in separate solutions. Ion pairs form within the precipitated PEC material. Meanwhile, the monomeric ions such as sodium and chloride gain complete freedom as they diffuse away from the PEC and enter the bulk of solution, making a major contribution to the free energy of the system.

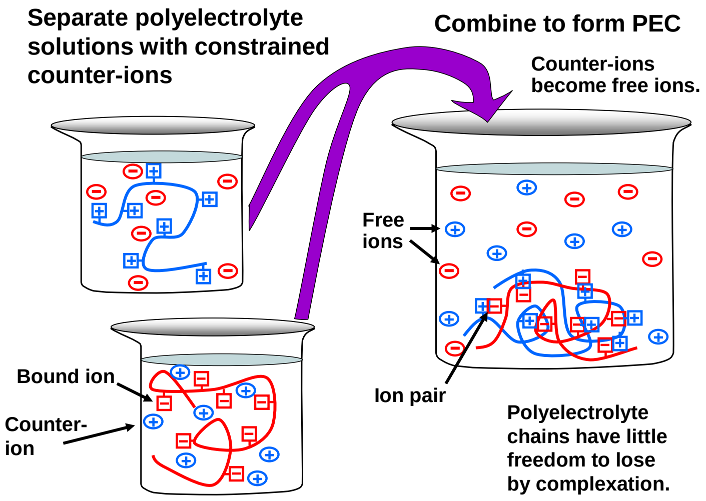

Fig. 8. Illustration of the changing situation and relative freedom of monomeric ions when two polyelectrolyte solutions are combined to form a polyelectrolyte complex

An approximately 1:1 stoichiometry of interactions between ionic groups on polyelectrolytes chains, as mentioned earlier in the context of polyelectrolyte titrations, has been widely reported as a predominant tendency of PECs (Michaels 1965; Philipp *et al.* 1982; Argüelles-Monal *et al.* 1990; Schneider 2012; Meka *et al.* 2017). Deviations from 1:1 stoichiometry generally have been observed to involve minor proportions the total charges (Michaels 1965). Sometimes deviations from stoichiometry are required by conformational requirements of the two respective polyelectrolytes (Tse *et al.* 1979; Advincula *et al.* 1996); in other words, an attempt to form a ladder-type of PEC results in the skipping of some ionic groups. Tse (1979) found that equal spacing of charged groups within different ionenes in comparison to polyvinylsulfate led to non-equilibrium interactions in which some charged groups were not included in the complexation. Haronska *et al.* (1989) predicted deviations from 1:1 stoichiometry due to differences in the tendencies of different counter-ions to dissociate from the polyelectrolyte-bound groups. Michaels *et al.* (1965) attributed deviations from 1:1 stoichiometry to the tight coiling of polyelectrolytes, which becomes increasingly important with increasing concentrations of salt in the solution. Han *et al.* (2016) proposed that un-paired bound ionic groups within PECs may be responsible for unusually high swelling and flexibility.

A special class of unpaired ionic groups associated with PECs are those at the ends of chains or on protruding loops, wherein the segments extend outwards into the bulk solution. Those charges have been called “extrinsic” (Schlenoff and Dubas 2001; Riegler and Essler 2002; Fares and Schlenoff 2017b). Such structures were proposed by Chen *et al.* (2003) to account for deviations from 1:1 stoichiometry when polyelectrolyte titrations were carried out with standard titrants at increasing levels of salinity. Nearly equal and opposite trends of deviation from 1:1 stoichiometry were observed depending on which of the two polyelectrolytes was used to titrate the other one. These results were in agreement with the findings of Pergushov *et al.* (1999) and Naderi *et al.* (2005). The findings are consistent with a model in which a core of PEC, having approximately 1:1 stoichiometry, is surrounded by tails of the one of the polyelectrolytes extending into the solution phase. When a titration is carried out to a neutral endpoint, based on streaming current output, there will be an excess of the second gradually added polyelectrolyte (*i.e.* the titrant) at the surfaces of the PEC entities, allowing them to be charge-stabilized in the resulting suspension that is present at the titration endpoint.

Results reported by Basu *et al.* (2017) suggest that an unbalanced ratio of polyelectrolytes sometimes can give more favorable results in PEC film preparation. The researchers selected a ratio that would provide cationically stabilized PECs in suspension. These were allowed to adsorb onto paperboard surfaces by a dipping method. Oil-resistant properties were achieved after drying of the paper.

There has been some debate about what happens when an existing layer of polyelectrolyte (which might consist of the outer-most polyelectrolyte layer on a multi-layer film structure) comes into contact with a solution of an oppositely charged polyelectrolyte. It has been proposed, for instance, that the latest adsorbing polymers interact in a three-dimensional manner with those already at the surface, leading to a fuzzy layered structure (Decher 1997; Arys *et al.* 2001). Other authors have emphasized a high degree of recognizability of the layered structure after multilayer formation (Kotov *et al.* 1995; Radeva *et al.* 2001; Cho *et al.* 2008; Kiel *et al.* 2010).

Trapped Non-equilibrium States

Binding by multiple charge interactions

When oppositely charged polyelectrolytes interact with each other in an aqueous solution, their patterns of attachments are governed primarily by kinetics. Once contact has been established in which a local grouping of several ion pairs connects the two polyelectrolytes, the pattern can become essentially frozen. The term trapped non-equilibrium states has been used to describe such situations (Claesson *et al.* 2005; Naderi *et al.* 2005; Wu *et al.* 2018; Potaufeux *et al.* 2020). Michaels (1965) mentioned the "entrapment" of polyelectrolyte segments that had failed to form ion pairs within a PEC during its formation. Spruijt *et al.* (2012) estimated that a group of about five ionic bonds, working together, would be enough to trap oppositely charged polyelectrolytes into an essentially irreversible association. This rule is illustrated schematically in Fig. 9. Even though each of the individual ionic bonds is in a continual process of equilibration, it is extremely unlikely that all of them will disengage at the same time. Wang (2009) demonstrated the development of trapped non-equilibrium states in the course of numerical simulations. Trapped non-equilibrium states within PECs are of particular concern with respect to PEC-based barrier films due to an expectation that they will lead to nonuniformities, and maybe even to the presence of open channels, within the films. Also, such considerations help to explain why the details of mixing and orders of addition can make a large difference in PEC film properties (Naderi *et al.* 2005).

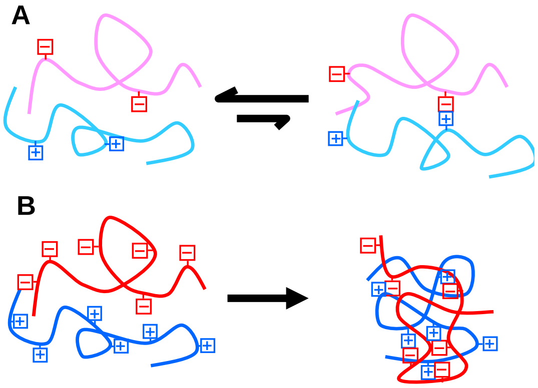

Fig. 9. Illustration of the principle that groups of five or more simultaneous ion pairs can be sufficient to establish an essentially irreversible attachment between oppositely charged polyelectrolytes

The concept of trapped non-equilibrium states helps to explain the performance advantage that was achieved when forming PECs in the presence of a stirred fiber suspension, for the purpose of increasing the strength of a resulting sheet of paper (Hubbe 2005; Heermann *et al.* 2006). When the polyelectrolytes were instead mixed with each other prior to their addition to the fiber suspension, the strength contributions were much lower, and the PECs showed a much greater tendency to contaminate the forming screen that was used to prepare sheets of paper. The results suggest that PEC formation *in-situ* within a stirred fiber suspension involves concurrent adsorption and complexation, thus taking advantage of some extra degrees of freedom before the PECs become fully entrapped together (Hubbe 2006). Another potential advantage of forming the PECs *in situ* within a cellulosic fiber suspension just before forming a paper sheet is that such PECs are likely to be more highly swollen with water. Strand *et al.* (2017) found that PECs coupled with relatively large amounts of water tended to contribute greater strength to paper after the drying process.

Entanglements of polyelectrolyte chains

The preceding discussion has been based on an assumption that ionic charge interactions serve as the main or only factor holding PECs together as durable structures. Polymer chain entanglements also can be considered, in light of their wide importance in the behavior of polymers in general (Seguela 2005). Such contributions have been considered in the case of PECs (Yeo *et al.* 2012; Akkaoui *et al.* 2020). Yeo *et al.* (2012) reported that the degree of entanglement during layer-by-layer preparation could be manipulated by adjusting the pH. The polybase employed in the research was poly(allylamine hydrochloride) (PAH), which has weak base groups. The degree of chain entanglement was found to increase with increasing charge density of the PAH with decreasing pH. Akkaoui *et al.* (2020) noted a strong dependency of PEC suspension viscosity on molecular weight. On the basis of the cited work, chain entanglement can be regarded as a significant contribution to the quasi-irreversible (*i.e.* "sticky") interactions involved in the formation of PECs. Future studies might be conducted to reveal implications of entanglement with respect to the barrier properties of PEC films.

Healing

Self-assembly tendency

The term healing has been used to describe a process by which cuts or cracks within a film structure can come together in such a way that the cut or crack essentially disappears. Such a process has been shown dramatically in the case of relatively large hydrogel blocks that had been prepared with bright coloration (Yuan *et al.* 2019). The cited authors were able to cut the hydrogel specimens with a razor and then reassemble differently colored blocks. The initial properties were restored as the material remained together. South and Lyon (2010) reported the rapid healing of LbL PEC hydrogel films formed with poly(diallyldimethylammonium chloride), N-isopropyl polyacrylamide, acrylic acid, and a poly(ethylene glycol) diacrylate crosslinker. Ren *et al.* (2016) proposed that an endothermic process of reversible ionic bonding was responsible for an observed healing of PEC hydrogels prepared from a chitosan derivative and alginate.

Strength is another important criterion of self-healing. Thus, Luo *et al.* (2106) observed a return to the starting strength and toughness levels after disruption and healing of certain PECs. Notably, the favorable healing and other properties were achieved even in some cases where there were deviations from 1:1 stoichiometry of the mixture. Nie *et al.* (2019) reported favorable self-healing results for PECs prepared from polymerized ionic liquids. In all of these cases, the mechanism appears to involve an ability of various bonds or associations to self-assemble after their breakage. Reif (1972), in aiming to understand the wet-strength capability of polyethyleneimine (PEI), proposed the self-assembly of ionic bonds by their "realignment" after disruption.

It has been proposed that the movements of macromolecular segments, rather than diffusion of complete macromolecular chains, is a likely explanation of self-healing tendencies of various PECs (Fares and Schlenoff 2017b). Those authors focused on the diffusion of "sites" rather than the diffusion of whole polyelectrolytes. By locally detaching and then reconnecting with an adjacent pairing between oppositely charged groups, net changes can take place at a speed that is about two orders of magnitude faster than that of diffusion of whole macromolecular chains. Figure 10 presents a pictorial concept of how the continual and random opening up of ion pairs, in concert with Brownian motions of the polymer segments, may permit reassembly of a PEC in ways that might repair mechanical damage or rupture.

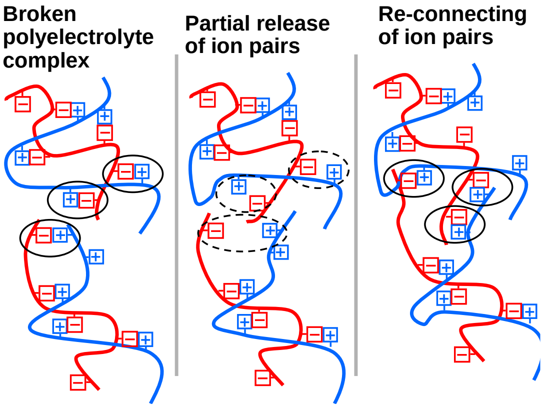

Fig. 10. Illustration of a mechanism by which a PEC film, when in a suitable environment, might be subject to processes of random release and reconnection, which may result in repair of ruptures

Weakening of the interaction

The mechanism by which PECs sometimes are able to heal themselves may be related to the reversibility of individual ionic cross-links (Han *et al.* 2016). Accordingly, a promising approach to bring about self-healing involves the intentional weakening of ionic associations. This can be done, for instance, by adding salt (Fares and Schlenoff 2017b). Another approach is to change the pH to favor less expression of ionic charge on one of the polyelectrolytes (Smith *et al.* 2018). Sometimes all that may be needed to sufficiently weaken ion pairs within a PEC is to apply moisture so that the PEC can heal itself while in a swollen condition (Yan *et al.* 2000).

Ren *et al.* (2016) intentionally weakened ionic attachments within a PEC by replacing ordinary chitosan with a derivatized version of chitosan having quaternary ammonium groups. Because of the bulky nature of such groups, the positive and negative ions within the resulting PEC cannot come as close together, and the energy of interaction is lower. The healing capability of the specialized PEC was attributed to this difference.

An inherent drawback of various healing-promotion strategies involving a weakening of ionic interactions is that they tend to reduce the cohesive energy density within the resulting PEC. As was discussed earlier, a high cohesive energy density is generally regarded as a required attribute of non-crystalline films that need to inhibit the passage of oxygen, oils, or greases (Lagarón *et al.* 2004; Aulin *et al.* 2013). It follows that some self-healing strategies may require a two-step process, such as increasing the salt concentration, followed by rinsing. Alternatively, the pH could be reduced enough to allow the PEC linkages to disengage, and this could be followed by a return to neutral pH (maybe with buffer solution) to allow the PEC's ionic connections to form again, hopefully with a more uniform nanostructure structure within the film. Another challenge that faces processing strategies based on the use of salts to promote healing is a general observation that PEC structures, once formed, may remained trapped with respect to their molecular arrangements. In other words, even though the number of remaining ionic interactions is reduced by the salt addition, the decrease in connectedness is still not sufficient to permit timely rearrangements of long-chain polyelectrolytes comprising the PEC film. Future research is recommended in this topic area.

Hydrophobic association of alkyl tails

The importance of hydrophobic associations between the alkyl groups of fatty acids and triglyceride esters was highlighted in a recent review article in this journal related to pitch deposition and hydrophobic sizing in paper manufacturing systems (Hubbe *et al.* 2020). As explained further in that work, the effect can be attributed to the change in free energy when hydrophobic groups self-associate, thereby allowing a greater amount of hydrogen bonding within the system as a whole. A net negative change in free energy leads to spontaneous association. For such associations to be influential, the hydrophobic entities need to be large enough, *e.g.* alkyl chains having at least ten and ideally 16 or more carbons in the chain.

In the work of Nie *et al.* (2019), a reported self-healing ability within structures formed from polymerized ionic liquids appeared to be related to a partial reliance on hydrophobic associations between groups attached to polymer chains. The allowable "slippage" between such groups and the ability of such associations to form again were given as explanations for the self-healing tendencies. Kotov (1999) proposed that such interactions can operate in concert with ionic bonding when the macromolecules contain a suitable combination of ionic groups and hydrophobic groups. Stevens *et al.* (2014) employed a hydrophobically modified polyelectrolyte in an effort to improve the self-healing ability of a PEC system that incorporated nanoclay particles with the highly cationic polyelectrolyte PEI. Wickramasinhage *et al.* (2020) prepared PEC hydrogels that could be stretched by relative amounts as high as 4000% without breakage. This was done by formulating PEC systems with extensive associations among hydrophobic groups.

PREPARATION METHODS FOR PEC FILMS

Various approaches have been employed in published research related to the preparation of PEC-based films. In this article, emphasis is placed on approaches aiming to achieve both a relatively uniform, dense film, and a high density of ionic interactions, as needed to effectively inhibit diffusion of gases and oils or greases through the film. Topics within this section include layer-by-layer (LbL) assembly of PECs, Langmuir-Blodgett options, mixing and casting options, procedures based on the preparation of charge-stabilized PEC colloids, and various post-treatments to improve the barrier properties of PEC films.

Layer-by-Layer

Exposing, rinsing, and drying

In studies where the emphasis is placed on exact control and on maximization of performance, above other considerations, the layer-by-layer (LbL) method offers advantages. As long as the successive layers to be added to the film have sufficiently high and opposite ionic charge, along with some other suitable properties, that approach can encompass a huge range of options, including the incorporation of minerals in place of one of the polyelectrolytes in the pair. Studies have emphasized the fact that the layered nature of LbL-applied PEC films can be clearly distinguished by means of such methods as X-ray diffraction (Decher *et al.* 1992, 1994; Tarabia *et al.* 1998; Arys *et al.* 2001). Such layered structures are a consequence of the LbL application method, since they are not found when, for instance, the bulk solution contains a mixture of positively and negatively charged polyelectrolytes (Wang 2009).

The most successful early studies of the LbL method tended to use a specific sequence of steps, as follows: (A) dipping an ionically charged substrate into a solution of oppositely charged polyelectrolyte, (B) rinsing away excess polyelectrolyte, usually using pure water, and (C) drying the film. As indicated in Fig. 11, the cycle then repeats, starting with a solution of the oppositely charged polyelectrolyte. Thereafter, the whole process of steps A through F can be continued, often allowing the accumulation of multiple layers.

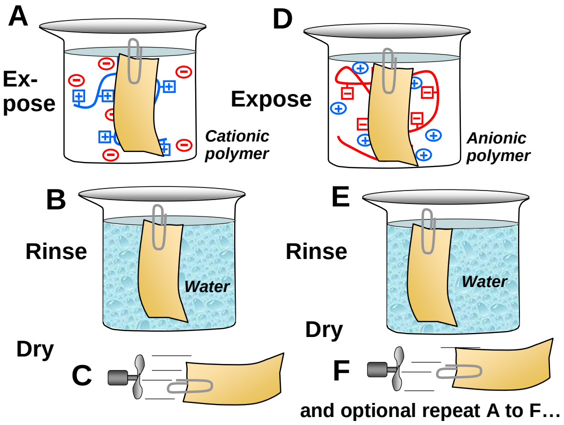

Fig. 11. Depiction of the sequence of steps for the most careful and traditional preparation of layer-by-layer PEC films. Note that parts A and D show polyelectrolytes with their charged groups (attached in squares) and counter-ions (in circles).

In addition to removing excess polyelectrolyte, beyond what is needed to interact with the preceding layer (or a bare surface at the start of the process), the rinsing step also seems to play an important role in removal of salt ions (Das and Tsianou 2017). The counter-ions, such as sodium and chloride ions, which are initially associated with a pair of polyelectrolytes, become released when the PEC is formed. By rinsing those ions away, one tends to lock the PEC together in an irreversible manner. Recent findings by Fares *et al.* (2019) suggest that better results can be achieved when an optimized relatively low concentration of salts is present in the rinse solution. It appears that such an approach allows for a more gentle assembly of the PEC structures, leading to greater uniformity and better barrier performance. By contrast, usage of ion-free rinse water was said to result in defects and pores. Machado *et al.* (2020) similarly found that they could achieve superior resistance to oxygen permeation when skipping the rinsing step, *i.e.* forming “unwashed” PEC films.

Gamboa *et al.* (2010) found that the sequencing of rinsing and drying steps could make a very large difference in the barrier performance of PEC films. They used a “high speed” robotic method in which the rinsing was carried out with a gentle spray. The fact that each cycle of this “high speed” procedure took six minutes helps to dramatize the fact that the LbL method is generally much too slow to be considered for manufacture of most commodity items, including packaging films.

Even in a very early article by the inventors of the LbL method (Decher *et al.* 1994), the drying step was regarded as optional. Since drying is likely to be a time-consuming step in the process, there is motivation to skip it. On the other hand, the drying step can play a role in dehydrating the PEC, allowing it to become dense, nonporous, and insoluble (Basu *et al.* 2017).

Overcompensation

With each subsequent exposure of a surface to the next solution of oppositely charged polyelectrolyte, an excess of polyelectrolyte charge is left on the surface. In other words, the surface charge is overcompensated (Schlenoff and Dubas 2001; Fares and Schlenoff 2017a). This over-charging appears to be an essential feature of the LbL process. One indication of this overcompensation is a switching back and forth between positive and negative zeta potentials during deposition of successive layers of polyelectrolytes (Ladam *et al.* 2000; Lin *et al.* 2008; Li *et al.* 2019a). Further evidence of overcompensation can be provided by studies utilizing charged fluorescent probes (Caruso *et al.* 1999). Such probes were found to adsorb onto LbL multilayer only when the outermost layer had a charge opposite to that of the probe.

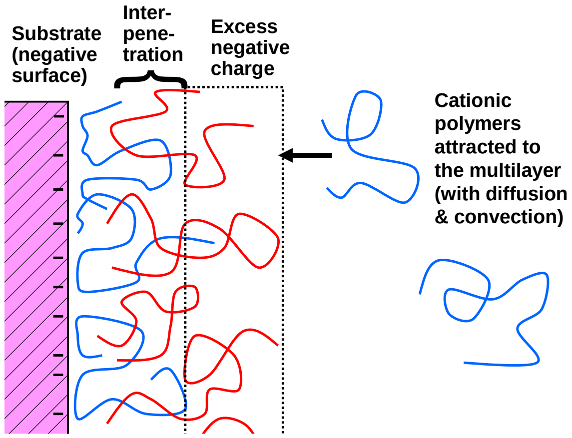

Fig. 12. Illustration of the over-compensation effect, wherein each subsequent layer of polyelectrolyte interpenetrates as complexes mainly with the preceding layer and presents an excess of charge in the outer tails and loops

Langmuir-Blodgett Options

The Langmuir-Blodgett method is analogous to formation of LbL PEC multilayer films, except that the layers are comprised of surfactants rather than polyelectrolytes (Ariga *et al.* 2013). To start the deposition process, a monolayer of a selected insoluble surfactant is spread on the surface of an aqueous solution in a shallow trough. A barrier is moved with precise control to compress the monolayer film. While using the barrier to control the two-dimensional pressure within the film, a solid object, such as a glass slide, is very slowly dipped into and just as slowly withdrawn from the trough. During each downstroke, an oriented molecular layer of surfactant is transferred to the substrate. During each upstroke, another molecular layer is deposited, such that all of the molecules are in a head-to-head and tail-to-tail arrangement in different layers. Lvov *et al.* (1993) showed that the LbL method and the Langmuir-Blodgett method can be combined. Though the cited work did not consider either healing capabilities or barrier properties, the approach appears to merit research attention to explore these aspects.

Mixing and Casting

Given the inherently very slow nature of the LbL process just discussed, it is worth considering whether a high-performing PEC barrier layer can be formed by just mixing solutions of two oppositely charged polyelectrolytes together. Such an approach is bolstered by the highly favorable results achieved when forming PECs *in situ* during the agitation of a fiber suspension that is subsequently formed into a sheet or paper (Hubbe 2005). Superior inter-fiber bonding strength was achieved. In the papermaking process, the use of PECs, whether prepared *in-situ* or prepared ahead of time, makes it possible to incorporate the treatment into a current-generation commercial manufacturing process with no sacrifice in production speed. However, the goal of achieving increased paper strength is very different from serving as an effective barrier layer. The strong flocculation that occurs when oppositely charged polyelectrolytes are directly mixed together raises concerns regarded an expected non-uniformity of the resulting material and whether or not it can be formed into a coherent layer.

In principle, solutions of two oppositely charged polyelectrolytes can be mixed together, followed by spreading or extruding the mixture as a layer, and then drying. Haile *et al.* (2017) were able to prepare a PEC film by first allowing the complexed polyelectrolytes to settle after mixing solutions of PEI and polyacrylic acid. The relatively concentrated PECs, along with some water, were spread as a film using a wire-wound steel rod (Mayer rod). Oxygen barrier performance was achieved after thermal treatment (150 °C for 2 hours at high humidity) of the resulting layer.

Blending of a PEC suspension and casting it

In the interest of achieving a more uniform layer, Basu *et al.* (2017) agitated the PEC mixtures in a blender before spreading the mixture. The approach is illustrated in Fig. 13.

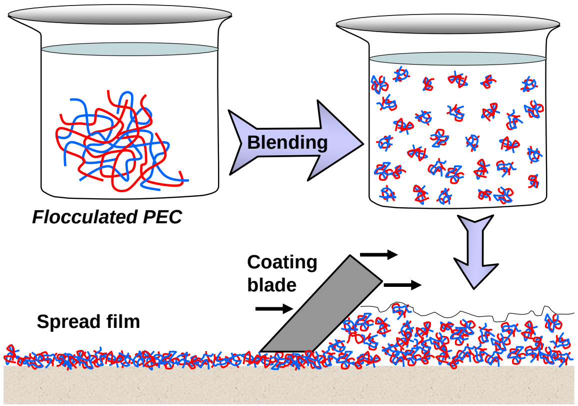

Fig. 13. Schematic description of possible steps in the preparation of a PEC film by combining the polyelectrolytes as a flocculated mixture, applying high hydrodynamic shear to convert the mixture into small PEC particles, and then spreading the mixture on a surface

Basu *et al.* (2017) speculated that the high shear conditions would cause the PECs to form elongated, fiber-like nanostructures that might be beneficial for the film properties. Dehydration of the PECs that had been formed from carboxymethylcellulose (CMC) and chitosan yielded dense, nonporous, and insoluble films that resisted both water and oil. Similarly promising results were obtained by Chi and Catchmark (2018b) and Chi *et al.* (2020), who used high-shear homogenization to create nanostructured PEC particles.

These were said to electrostatically coalesce in the course of dehydration. The films prepared by Chi and Catchmark (2018b) had homogeneous properties, which indicated that any pores and voids had been successfully removed.

Preparing and Using Charge-stabilized PEC Colloids

Concept of barrier layers from PEC Colloids

In principle, it would be possible to create a barrier layer by exposing an ionically charged surface to a suspension of charge-stabilized PECs. For example, Kekkonen *et al.* (2002) showed that a colloidal suspension of charge-stabilized PECs could be adsorbed onto silica. Studies related to papermaking technology provide evidence that such an approach has the potential to deposit relatively large amounts of polyelectrolyte in a single exposure step (Hubbe 2005; Lofton *et al.* 2005; Heermann *et al.* 2006). The question that needs to be determined is whether such layers could be effective barriers against oxygen and other substances. Evidence presented in the previous subsection suggests that favorable results are possible, especially after drying of the films. It is not known whether the intersections between adjacent charge-stabilized PEC particles, after they have been formed together as a film, will serve as defects that permit greater diffusion of various substances through the film. Figure 14 illustrates how such a process could work, involving the three steps of preparing a polyelectrolyte solution, adding a second polyelectrolyte solution with stirring, and allowing the charge-stabilized PEC colloids to be attracted to a substrate, leading to their deposition as a contiguous layer.

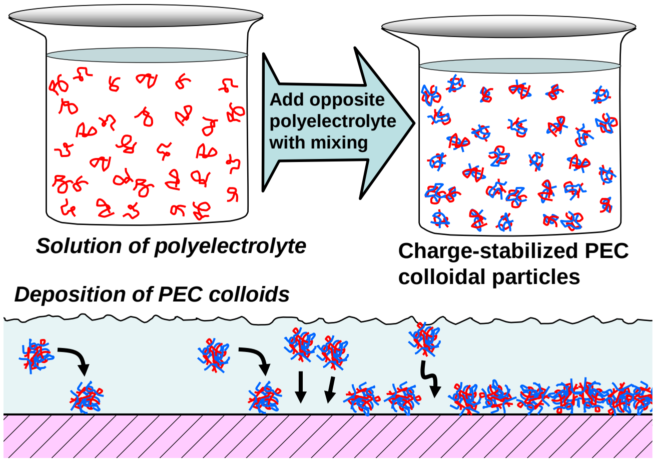

Fig. 14. Steps in the preparation of a PEC film by combining the polyelectrolytes as a flocculated mixture, applying hydrodynamic shear, and then allowing the suspended PEC particles to adsorb onto a substrate having an opposite net charge

Forming Charge-stabilized PECs

To be able to prepare a PEC layer from PEC colloids, the first step involves forming the charge-stabilized colloidal particles. When a dilute solution of a polyelectrolyte is being gradually added to a stirred solution of an oppositely charged polyelectrolyte, most of the time one of the two polyelectrolytes will be in excess. At those points in the titration, the mixture is likely to consist of roughly spherical PEC particles that are each electrostatically stabilized due to an outer layer that is composed of whichever polyelectrolyte is in the excess (Dautzenberg *et al.* 1996). When that outer charged layer of the PEC particles is opposite to that of a suspended solid, such as cellulosic fibers or a packaging material such as paper, strong adsorption can be expected (Hubbe *et al.* 2005). To achieve such goals, the amount of the second polyelectrolyte may need to be adjusted so that the resulting PEC particles are charge-stabilized to a favorable degree.

Conditions during PEC preparation

The aqueous conditions of the mixture in which the PEC is being prepared can be expected to affect the polyelectrolyte ratio and other properties. As was noted earlier, increasing concentrations of salt cause increases in the relative amounts of excess polyelectrolyte in the stabilizing layers on the PEC colloids (Chen *et al.* 2003). Salt also tends to weaken the interaction between the bound positive and negative ionic groups of the polyelectrolytes (Han *et al.* 2016). A promising strategy involves finding an optimum (relatively low) concentration of salt that gives a good balance between colloidal stability (so that massive precipitation does not occur), while also avoiding overly energetic interaction between the polyelectrolytes. Overly energetic interaction would be expected to result in trapped non-equilibrium states (Lagarón *et al.* 2004), leading to non-uniformity of films prepared from the PEC material. This explanation is also consistent with the findings of Gamboa *et al.* (2010) and Machado *et al.* (2020), who found the best barrier performance of PEC layers when rinsing steps were skipped during LbL deposition, thus moderating the strength of interaction during the formation of the PECs. Smith *et al.* (2018) likewise found the best resistance to oxygen permeation when PEC films, which were prepared in a single step by mixing, were made in the presence of an optimized salt concentration. Wu *et al.* (2018) found that an optimum level of salt allowed the formed PEC films to readjust themselves so that they achieved more stable structures rather than kinetically trapped structures.

Higher levels of salt also have been found useful for the preparation for PECs, but for uses other than for barrier films (McAloney *et al.* 2001; Lindhoud and Stuart 2014; Lalwani *et al.* 2020). For instance, membranes with well-defined permeability properties can be prepared by mixing polyelectrolytes under “saloplastic” conditions (Porcel and Schlenoff 2009; Harari and Schlenoff 2010; Shamoun *et al.* 2012). In other words, there was enough salt so that the PEC material could be formed into a porous film even after it was precipitated from solution.

Adjustment of the pH can be a powerful tool by means to direct polyelectrolyte behavior during PEC formation, especially when either weak acid or weak base groups are present on the polyelectrolytes (Philipp *et al.* 1982). In such cases, changes in pH can change the charge density of the respective polyelectrolytes. Accordingly, some researchers have manipulated the pH back and forth between different levels as a means to increase the amounts of polyelectrolyte deposited during each step in an LbL assembly process (Eriksson *et al.* 2005; Priolo *et al.* 2010a; Yang *et al.* 2011). Likewise, Fajardo *et al.* (2011) studied changes to PEC structure, as well as the release of polyelectrolyte molecules from PECs following changes in pH. Such strategies need to be considered with caution, however, since the charged nature of some PEC films adjacent to an aqueous solution will tend to shift the value of pH within the film so that it does not match the pH of the bulk solution (Rmaile and Schlenoff 2002).

Post-treatments

Crosslinking effects

After a PEC film has been formed, some researchers have applied a final procedural step or steps to modify the resulting film properties. Some such treatments can be described as crosslinking. For example, the initial procedure may consist of forming a layer of nanofibrillated cellulose (NFC) that has been oxidized under specialized conditions to achieve a high density of carboxylate groups, and then those films are treated with a solution with calcium ions (Sirviö *et al.* 2014; Shimizu *et al.* 2016). The calcium ions can be expected to form complexes with carboxylate groups, thus bonding the material together with ionic crosslinks. This scenario is illustrated in Fig. 15. Shimizu *et al.* (2016) reported very low oxygen permeabilities when such films had been treated with divalent or trivalent metal cations. Sirviö *et al.* (2014) reported that the water vapor permeability was decreased following treatment of the NFC film with calcium chloride. If one considers the NFC as functioning as a polyelectrolyte in such interactions, the resulting cross-linked film can be regarded as being analogous to a PEC. A related result was achieved by Rhim and Lee (2004), who used calcium chloride to post-treat barrier films that had been prepared with sodium alginate.

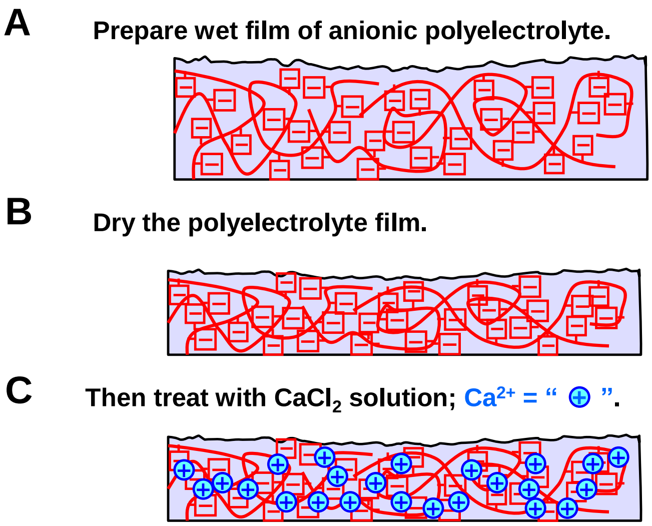

Fig. 15. Procedure for forming a barrier film by preparing a solution of anionic polyelectrolyte (*e.g.* alginate or polyacrylate), drying the layer to form a film, then crosslinking the film by treated it with calcium chloride solution

Covalent reactions can be used as a more permanent way to accomplish crosslinking within a PEC film. For example, Ben Dhieb *et al.* (2019) achieved much more effective resistance to diffusion of oxygen through films comprised of polyvinyl alcohol and nanoclay following crosslinking with either glyoxal or glutaraldehyde. Lazar *et al.* (2019) used a free-radical initiator to induce crosslinking in a PEC film comprised of chitosan and polyacrylic acid. A 36-fold reduction in oxygen transmission was observed due to the crosslinking. Likewise, Yang *et al.* (2012) achieved large decreases in oxygen permeability through a PEC film comprised of PEI and polyacrylic acid following crosslinking with either glutaraldehyde, 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC), or thermal crosslinking. Peng *et al.* (2018) achieved crosslinking by means of Diels-Alder reactions within a copolymer formulation that included both positively and negatively charged monomers, *i.e.* a polyampholyte having reversible covalent crosslinking capabilities.

Heating after PEC film formation

Heat treatments can be regarded as a way to permit the final self-assembly of polyelectrolyte segments, with the aim of achieving a relatively dense, impermeable film. A recent review article mentions such "thermal annealing" as an emerging trend in PEC technology (Lalwani *et al.* 2020). Based on reviewed literature, the authors concluded that the heat treatment tended to give denser and better-organized PEC films. Lvov *et al.* (1993) reported an improvement in the ordering of multilayer PEC films after heating to 70 °C and gradual cooling. Schnell *et al.* (2017) achieved promising results after heating PEC films comprising xylan and chitosan to 75 °C for 10 min, followed by gradual evaporation at 40 °C. Yang *et al.* (2012) noted reduced water vapor transmission after thermal crosslinking of PEI-poly(acrylic acid) PEC films at 180 °C for 5 h. Small positive effects relative to resisting oxygen permeability were observed. Haile *et al.* (2017) heated PEC-type films for 2 h at 150 °C. The thermal treatment was found to be much more effective in comparison to exposing the film to a high humidity condition.

Healing

Self-healing strategies and procedures can be regarded as another category of potential post-treatment of PEC barrier films. Ideally, one might hope such repair to happen automatically due to the inherent nature of the components of the film. Alternatively, the aim might be for the repair to take place when the film is exposed to certain conditions. Although there have been a variety of approaches used to achieve self-healing characteristics of films, all of them share a central requirement: Some aspect of the bonding needs to be reversible. For example, McKee *et al.* (2014) designed a system in which a composite was held together, in part by the interdigitation of polymer chains having 2-ureido-4[1H]-pyrimidone (UPy) pendant groups. The association among such groups falls into a range allowing them to (a) come apart at a stress low enough so that breakage can occur before the polymer chains are damaged, and (b) once the stress has been removed, the associations can form again rapidly. As mentioned earlier, certain relatively labile covalent bonds, such as Diels-Alder crosslinks (Peng *et al.* 2018) also appear to fall in that range.

Potaufeux *et al.* (2020) make the case that ionic bonds also can fall into the same category. They noted that increased temperature, which makes it easier to locally exceed the activation energy related to ionic bonding, can promote self-healing. However, that view can be challenged. As was noted during the discussion of trapped non-equilibrium states, ionic bonds tend to work in groups. Whereas an individual ionic bond may be envisioned as forming, coming apart, and forming reversibly many times per second, a bunch of five or more such bonds acting together can be expected to act in an irreversible manner (Spruijt *et al.* 2012), thus conferring a brittle nature to the PEC. It follows that a promising strategy to achieve greater healing tendency may involve an intentional weakening of the ionic pairing forces and energies.

Moisture-mediated healing

As a first step towards rendering PECs more self-healable, one can increase the moisture content, either by direct addition of water or by exposure to a very high relative humidity (Zhang *et al.* 2016). This can be viewed as a reversal of the final drying step that is included in many procedures for preparation of PEC films (Decher 1997). Swelling with water can be expected to increase the mobility of polymer segments (Chen *et al.* 2018). South and Lyon (2010) found that they could heal damaged PEC structures by exposing them to water. The PECs had been prepared by combining negatively charged hydrogels with poly(diallyldimethylammonium chloride) solution. Likewise, Zhang *et al.* (2016) were able to repair PEC films made from PEI and poly(acrylic acid) by exposing them to distilled water.

Some researchers have found that it is sufficient just to place a damaged PEC structure in the presence of high humidity to bring about self-healing. Dou *et al.* (2014) studied the barrier properties of PEC films prepared with the negatively charged polyelectrolyte poly(sodium styrene-4-sulfonate) and positively charged hydrotalcite particles. The oxygen barrier ability was found to deteriorate gradually when the film was flexed (between 200 and 500 times bending). When the PEC films were post-treated with a poly(vinyl alcohol) solution, the resulting film achieved a remarkable self-healing ability that was triggered by exposure to air with 85% relative humidity. Song *et al.* (2017) were able to repair cracks in a PEC film comprised for PEI and polyacrylic acid by exposing it for 10 minutes at 97% relative humidity.

Salt-mediated healing

As noted by Meka *et al.* (2017) and O'Neal *et al.* (2018), increasing ionic strength of the aqueous environment is an effective way to weaken the ionic bond interactions within a PEC. This is evidenced, for instance, by increased swelling in the presence of a salty solution (Dubas and Schlenoff 2001). Under such conditions, the pattern of ionic bonding within the structure is more easily rearranged, and this can contribute to self-healing. Zhang *et al.* (2016) found that superior healing results could be achieved by first using a NaCl solution, and this was followed by rinsing with distilled water. Presumably the saline solution allowed relaxation of the structure, and then a tight, well-bonded structure was restored upon removal of the salt.

O'Neal *et al.* (2018) and Guo *et al.* (2018) found that the self-healing capability of poly(ionic liquid) materials could be profoundly affected by the size of the counter-ion. The ability of LbL-formed PEC films to self-anneal and self-heal could be increased by replacing Cl^- ions in the film with the larger Br^- ions (O'Neal *et al.* 2018). Replacing the Br^- counter ion with bis(trifluoromethanesulfonyl)imide (TFSI-) counter-ion rendered the poly(ionic liquid) yet more self-healable. Because ionic liquids fall into a specialized class of materials, it is not yet known whether the same principles can be applied to more typical PEC materials.

FACTORS AFFECTING PEC BARRIER PROPERTIES

Overview of Factors Affecting Barrier Properties

This section will focus on factors that govern the effectiveness of various PEC films in preventing the transmission, through an intact film, of oxygen, greases and oils, water vapor, or aqueous solutions. Topics within this section include polyelectrolyte charge and mass, the stoichiometry within the PEC, effects of different kinds of ionic groups, structural fitting between the respective polyelectrolytes, cross-linking within a PEC, plasticizers, salinity, hydrogen bonding contributions, the hydrophobic effect, layer attributes, defects, fillers, and the use of other barrier layers in combination with PECs.

Polyelectrolyte Charge and Mass

Charge density

The likely importance of charge density, relative to the development of barrier properties, can be considered in the light of the first hypothesis proposed at the start of this article. That is, it was proposed that ionic bonding can contribute to a higher cohesive energy barrier and thereby impede passage of substances through the film. Oxygen is a nonpolar molecule, so it makes sense to expect that PEC films, which contain highly polar bonds, to be effective barriers. By extension, one might expect a higher charge density on the polyelectrolyte to yield a higher density of ionic bonds and thereby higher barrier performance. Such a concept is supported, in part by a lesser swelling in water of PECs formed from polyelectrolytes having a higher charge density (Ahmadiannamini *et al.* 2012; Das and Tsianou 2017). However, Kurihara and Isogai (2015) found only a weak dependency on charge density when evaluating the moisture content of films formed with oxidized cellulose nanofibers and acrylamide copolymers. The cited authors observed large agglomerates when combining the cationic PAM copolymers with the anionic nanofibers. Such evidence of flocculation is not consistent with forming an effective barrier film. Notably, in none of the cases just cited was there a clear relationship drawn between polyelectrolyte charge density and the resulting barrier performance of PEC films. Accordingly, there is an opportunity for important future research.

Blockiness

It has been proposed that a blocky structure of polyelectrolytes has the potential to form stronger ionic associations within PECs (Potaufeux *et al.* 2020). Denser and more salt-resistant structures can be expected (Rumyantsev *et al.* 2019). Again, however, the present search of the literature did not find any published research demonstrating whether or not blockiness of the polyelectrolytes is correlated with PEC film barrier properties.

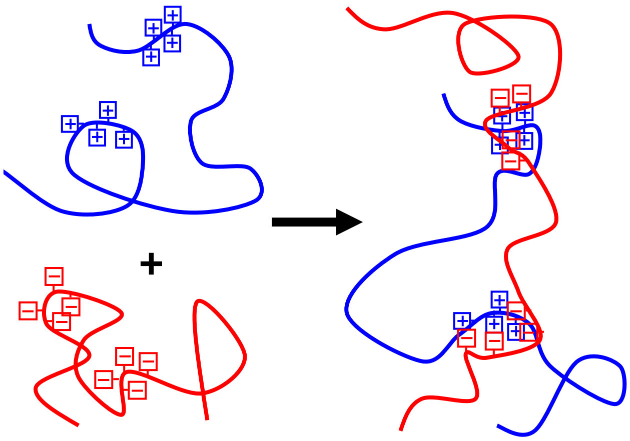

Fig. 16. Illustration of the expected propensity of “blocky” polyelectrolytes to form complexes that are hard to reverse, but loose in structure

As illustrated in Fig. 16, a blocky distribution of charges on the polyelectrolyte chains can be expected, on the one hand, to give strong and hard-to-reverse connections between the chains. On the other hand, the structure is likely to be relatively loose. The loose structure might be expected to favor transmission of permeants through the film.

Molecular mass

Though molecular mass of polyelectrolytes can be important with respect to many applications, for instance in flocculation of wastewater, the search of the literature did not reveal a clear trend of effects of molecular mass on PEC barrier properties. One might suspect that higher-mass polyelectrolytes would be more prone to problems with formation of large agglomerate structures, leading to nonuniformity of the resulting films. Surprisingly, Fares and Schlenoff (2017b) found no dependency on molecular weight with respect to the diffusion of polyelectrolytes within PECs. By contrast, Chi *et al.* (2020) observed that larger molecular mass of starch-based PEC components led to stiff and entangled structures and a densely packed film structure with favorable barrier properties.

Solubility of the permeant in the barrier phase

It has been proposed that a low solubility between the permeant and the material composing the film layer can be a major contributor to barrier performance (Lagarón *et al.* 2004). This expectation is borne out in the great effectiveness of polyolefin films, *e.g.* polyethylene (Doong *et al.* 1995), in resisting water and water vapor (Dury-Brun *et al.* 2007). The polyethylene is non-polar and lacking in hydrogen bonding ability, thus offering very low solubility to water. To a large extent, the relative solubilities of various low-mass substances can be predicted based on the polarizabilities of electrons, by the content of polar groups, and by hydrogen bonding capability (Hansen 2004). These concepts appear to have been applied only to a limited extent with respect to the barrier properties of PEC films (Doong *et al.* 1995; Basu *et al.* 2017).

Stoichiometry within the PEC

There is reason to expect that barrier performance of PEC films will be favored by 1:1 stoichiometry of interactions among the polyelectrolyte ionic groups. Un-matched ions that remain in a PEC film can be expected to encourage adsorption of water molecules, which likely would lead to swelling and consequent greater permeability to all low-mass substances. In support of this concept, Lv *et al.* (2018) were able to “tune” the swelling ratio of hydrogels by adjusting the mass ratio of carboxymethylchitosan and alginate.

An inherent flaw in the proposition being considered is the fact that the self-assembly process tends to favor formation of PEC domains with 1:1 matching or ionic charges on the polymer chains, with any excess of charged groups either acting as a stabilizing layer (Chen *et al.* 2003) or remaining in the adjacent solution phase (Michaels *et al.* 1965; Dautzenberg *et al.* 1996). Depending on the details of procedures, a charge-stabilizing layer may be expected to play an essential role in the assembly of a PEC film. In light of such complications, it is perhaps not surprising that the present review of the literature did not find any clear evidence regarding whether or not the charge-stoichiometry within a PEC film is correlated with barrier performance.

Polyelectrolytes with Different Types of Ionic Groups

As was noted earlier, certain pairs of positive and negative ions bound to polyelectrolytes are known to interact with each other more strongly than some others

(Sukhishvili *et al.* 2006). Relatively strong ionic bonds are expected when primary amine groups interact with either sulfite or sulfate groups, whereas weaker bonds are formed when quaternary ammonium groups interact with carboxylate groups. There has been no published work in which such differences were rigorously studied in relation to barrier performance. As illustrated in Fig. 17, the protonated primary amine group (left top) is physically much smaller than the trimethylalkyl amine group (right top). Thus, the center of charge of the primary amine group is able to approach much closer to an adjacent negative ion. The strong ability of the sulfate ion to engage in ionic bonds is possibly due to the strong electronegativity of the oxygen atom, which causes the negative charge to be expressed on the external part of the ionic group.

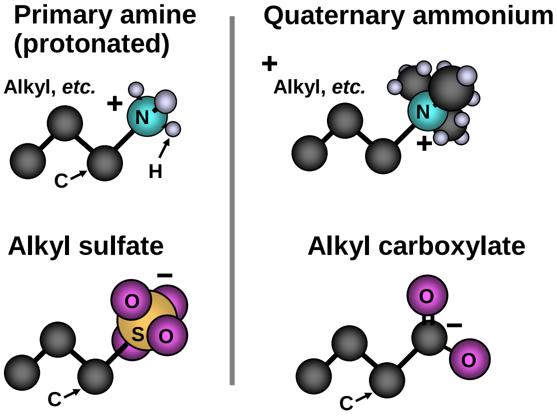

Fig. 17. Ionic groups having differing ability to form high-energy ion pairs. Left: Ionic groups of organic compounds providing stronger ion pairs; Right: Ionic groups of organic compounds providing weaker ion pairs

Structural Fitting between the Polyelectrolytes

Different polyelectrolytes can have widely different structures, some of which would appear to preclude efficient pairing with certain oppositely charged polyelectrolytes, especially if one assumes that a ladder structure must be involved. For example, Fig. 18 considers the case of interaction between a stiff polyelectrolyte chain and another polyelectrolyte of opposite charge having a different spacing of ionic groups.

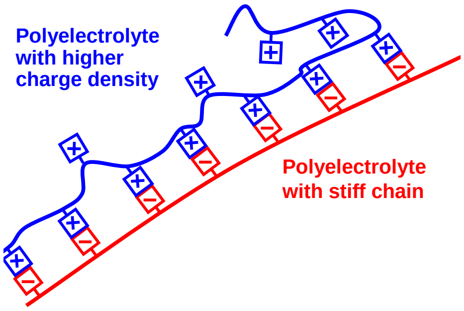

Fig. 18. Illustration explaining how there can be incompatibility in the spacing of ionic groups of two polyelectrolytes, resulting in incomplete pairing, especially if at least one of the chains is stiff

Such contrasts in the spacing of ionic groups have been predicted to affect the nature of resulting PECs (Lytle *et al.* 2019). The cited work developed this concept based on a simple model based on placing hypothetical beads – some representing positive or negative sites – along straight strings lying parallel to each other in two dimensions. The model appears to imply that, by careful pre-arrangement of such beads, highly contrasting behavior can be achieved, even in two dimensions. If such a mechanism remains valid for real materials in three-dimensional space, it follows that complex charged polymers, such as proteins, can be pre-programmed with a propensity to form complex structures that allow them to display contrasting characteristics, even including such things as enzymatic abilities. In that context, one can appreciate that there might be potential to design sets of positively and negatively charged polyelectrolytes having an inherent ability to self-assemble themselves into effective barrier layers. However, when one is considering three-dimensional space, multiple macromolecular conformations, and many different possible distributions of ionic groups, the results of self-assembly may be very difficult to predict.

When considering strategies that might be more likely to achieve success in the medium term, one can take simple steps such as choosing polyelectrolytes having different stiffness of their chains. Molecular dynamics simulations showed that PECs formed from polyelectrolytes having highly flexible chains tended to form scrambled egg-type PECs, whereas stiffer chains favored ladder-type PECs (Lazutin *et al.* 2012). Since there does not appear to have been any focused work attempting to connect polyelectrolyte chain stiffness to barrier properties, this can be regarded as a needed area of future research.

Cross-links and Barrier Properties

The establishment of cross-links within a barrier film can be regarded as a way to restrict the motion of polymer segments, thereby possibly decreasing the diffusion rates of low-mass substances through the films. By analogy to hydrogel preparation, covalent crosslinks can be expected to permanently insolubilize polyelectrolyte material and restrict its ability to swell when wetted (Wang *et al.* 2009; Hubbe *et al.* 2013). Ben Dhieb *et al.* (2019) found that crosslinking of a barrier film comprised of polyvinyl alcohol and nanoclay, using either glyoxal or glutaraldehyde, increased the resistance to oxygen permeation under high humidity conditions. Yang *et al.* (2012) reported that crosslinking with either glutaraldehyde, 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC), or thermal crosslinking decreased oxygen permeation through a PEC film with PEI and poly(acrylic acid). In addition, the water vapor transmission was reduced following thermal crosslinking. Lazar *et al.* (2019) reported that free-radical crosslinking of a PEC film including chitosan and poly(acrylic acid) achieved a large reduction of oxygen transmission when evaluated at 90% relative humidity.

When multivalent ions are added to a solution of anionic polyelectrolyte, two kinds of results can be obtained, depending on the concentration of polyelectrolyte (Ermoshkin and de la Cruz 2003). In a favorable range of concentration, the cited authors proposed that the mixing would result in a gel-like structure, encompassing all of the material in one phase. Under dilute conditions, the mixture is expected to separate, resulting in precipitation of complexed material.

The addition of divalent metal cations to a film that contains carboxylate groups can be regarded as a form of crosslinking. Rhim and Lee (2004) found that treatment of soy protein films with calcium chloride solution decreased water vapor permeability and swelling. Surprisingly, however, only a small decrease in water vapor permeability was found when sodium alginate films were similarly immersed in calcium chloride solution.

More promising results were obtained by Shimizu *et al.* (2016), who prepared films by drying suspensions of oxidized nanofibrillated cellulose (NFC). Extremely low values of oxygen permeability were obtained after such films had been exposed to either calcium chloride or aluminum chloride solutions. In the latter examples, one can envision the highly anionic nanocellulose playing the role of an anionic polyelectrolyte. Sirviö *et al.* (2014) achieved related results by treating NFC with calcium ions. The ionically crosslinked NFC films showed very strong resistance to turpentine. The treatment also decreased the water vapor permeability.

Plasticizers and Barrier Properties

In light of the role of plasticizers in allowing greater mobility of polymer segments within a film, it is reasonable to expect the presence of plasticizers to have a negative effect on PEC film barrier properties. Plasticizers also tend to decrease the cohesive energy density, thereby favoring permeation (Lagarón *et al.* 2004). On the other hand, certain films may be so brittle that they have no practical use in the absence of plasticizers (Rhim and Lee 2004). Figure 19 illustrates a concept in which the plasticizer compounds in a PEC film can promote the permeability of the film in two ways. First, the plasticizer may allow for greater mobility of polymer segments, making it more likely that permeant molecules will be able to find an opportunity to squeeze through. Second, the permeant molecules may find a path of least resistance by passing through the plasticizer-rich domains of the film. Diffusion may be favored in such domains due to the absence of ionic bonding and possibly due to a lower molecular mass and/or higher solubility of the diffusing substance.

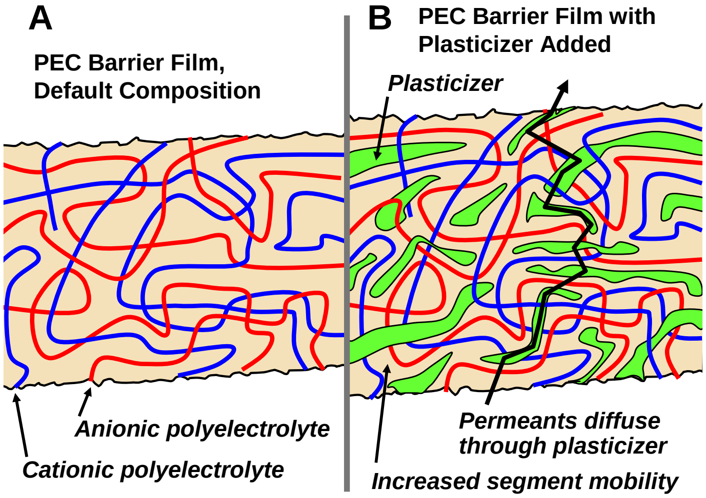

Fig. 19. Pictorial description of a PEC film formed in the (A) absence or (B) presence of a plasticizer

When a PEC film is exposed to aqueous solution or high humidity, the water molecules can function as plasticizing agents (Lysaght 1976). Farhat *et al.* (1999) and Mende *et al.* (2002) estimated that typical polyelectrolyte multilayers contain about 10 to 20% moisture under ambient conditions.

The plasticizing role of water is evident from a change in the properties of dry PEC films from brittle nature to a rubbery state upon treatment with water (Feng *et al.* 2006; Meka *et al.* 2017). Meanwhile, the oxygen barrier performance degrades with increasing moisture content in the case of typical PECs (Holder *et al.* 2012; Lazar *et al.* 2019).

Nonionic substances such as polyethylene glycol (PEG or PEO) and glycerol are often considered to control the brittle nature of biopolymer films. Schnell *et al.* (2017) obtained moderate resistance against oxygen permeation when 10% of glycerol was present in PEC films comprised of xylan and chitosan. Likewise, Machado *et al.* (2020) had 40% glycerol present in PEC films comprised of pectin and chitosan. Good resistance to water vapor and oxygen were obtained. Cho *et al.* (2015) demonstrated promising barrier performance of multilayer films prepared by successive layering with PEI, PAA, PEO, and PAA. In such “quad-layer” construction, the non-ionic polymer essentially takes the place of one of the cationic polymer layers. Such structures were highly effective barriers to oxygen diffusion. Thus, despite the expectation that plasticizers are likely to hurt barrier properties, they still need to be considered as important potential components in PEC barrier films.

Although brittleness is an important issue with respect to various potential applications of PECs, it needs to be emphasized that brittleness is a common feature of a wide range of polymers. For example, starch films show brittle behavior (Ghanbarzadeh *et al.* 2011). In comparison, PEC films prepared from starch derivatives have been reported to have a suitable range of properties (Chi *et al.* 2020). An important topic for future research will be to determine whether the generally non-crystalline nature of PECs can be advantageous with respect to avoiding high levels of brittleness under various conditions of usage.

Salinity and Barrier Properties

Effects of salt were considered earlier in the context of preparing or bringing about self-healing PEC films. In general, the presence of salts tends to weaken the ionic bonding (Dautzenberg 1997; Fu *et al.* 2017), which is generally unfavorable for achieving strong resistance to permeation. On the other hand, a small amount of salt has been found to provide a substantial decrease in aggregation within PEC films (Dautzenberg 1997), and that is likely to favorably affect barrier performance. Findenig *et al.* (2012) found that barrier performance of PECs formed from PEI and 2-hydroxy-3-trimethylammonium propyl chloride starch, together with nanoclay, were improved after treatment with water. Such effects will be considered in more detail in a later subsection dealing with platy minerals. In summary, though there is a general expectation that exposure to salinity is likely to be harmful for PEC barrier properties, the present review of the literature did not find specific evidence to support such an expectation.

Figure 20 presents a sequence of steps that might be considered as a strategy to improve the uniformity of an existing PEC, based on the cited research.

The first frame shows a PEC having areas that are lacking in the amount of polymeric material. The central part suggests a loosening of ion parts in the presence of salt (as indicated by a light purple background). The right-hand part envisions the final situation after a final rinsing of the film with water, to remove the salt ions and re-establish the ion pairs within the PEC film.

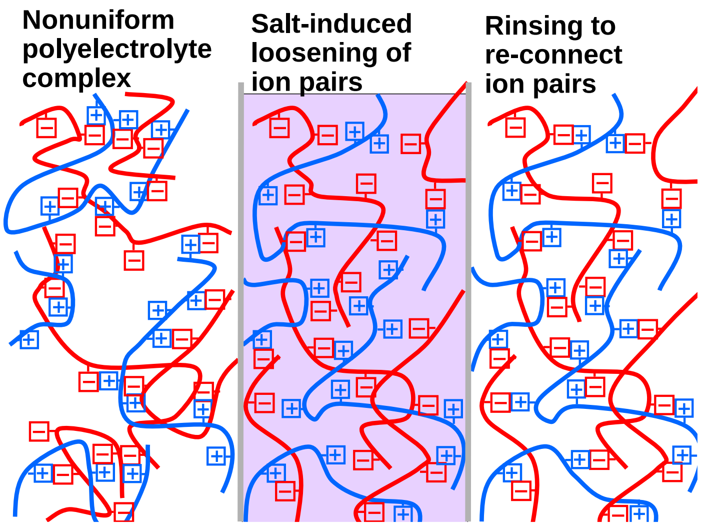

Fig. 20. Concept of a strategy to improve the uniformity of density within an existing PEC film by immersing it in a salt solution to loosen the ion pairs, allowing the polymer segments to diffuse to other positions, then re-establishing the ion pairs in the PEC by rinsing away the salt ions

Hydrogen Bonding Contribution

When barrier films are prepared by the drying of nanocellulose, it is clear that the resulting barrier properties are highly dependent on a dense pattern of hydrogen bonding between and within the cellulosic phases (Aulin *et al.* 2013; Hubbe *et al.* 2017; Lindström and Österberg 2020). A combination of ionic bonding and hydrogen bonding results when such films are treated with divalent metal ions (Li *et al.* 2019b). The cited authors found that such treatment increased the physical strength of the NFC films; however there were no tests of barrier performance. Feng *et al.* (2006) proposed that both ionic bonding and hydrogen bonding were working in concert in PEC films comprised of poly(vinylamine-co-vinylformamide) and carboxymethyl cellulose (CMC), prepared in an aqueous solution of formic acid. McKee *et al.* (2014) enhanced the bonding of cellulose nanocrystal (CNC) films by derivatizing the CNC with 2-ureido-4[1H]-pyrimidone (UPy) pendant groups. The resulting films were described as being bonded by both ionic bonds and hydrogen bonds. Cho *et al.* (2015) credited the presence of hydrogen bonding to explain the favorable performance of multi-component films that contained poly(ethylene oxide) (PEO). Since PEO is non-ionic, the authors attributed its contribution to film performance to hydrogen bonding. Though this seems a reasonable assumption, there was no detailed accounting of the hydrogen bonding contribution, nor any spectroscopic evidence presented. The work cited in this paragraph suggests that hydrogen bonds formed during the drying of cellulosic materials or related polymers clearly can be important for achieving barrier performance against oxygen. Such effects can be shown by PEC films that contain such materials.

Contributions of Hydrophobic Effect to PEC Barrier Properties

The hydrophobic effect was mentioned earlier when discussing self-healing. The idea is that associations among pendant hydrophobic groups may contribute, in a reversible way, to cohesion within a film. Kotov (1999) considered the thermodynamics related to hydrophobic interactions within a PEC. It was noted that such associations may tend to exclude water molecules, which are sometimes a negative factor with respect to achieving a dense film with immobilized polymer segments. Kotov (1999) estimated that the hydrophobic effect might contribute to cohesive energy in the range of 7.5 or 60 kJ/mol based on a chain of poly-(diallyldimethylammonium chloride). Figure 21 conceptualizes how hydrophobic association within an aqueous system might work within a PEC system where such pendant groups are present. In the figure, the purple lines represent chains of polyelectrolytes, and the green zig-zags represent long-chain alkyl groups or other hydrophobic groups. During the first instants after placing such materials in solution, one can expect formation of micelles in which hydrophobic groups are clustered together, in a reversible process. Though, for simplicity, the figure represents the hydrophobic groups as being absolutely straight, in reality such groups are flexible, and some may contain double bonds, *etc.*, which entail kinks in such chains.

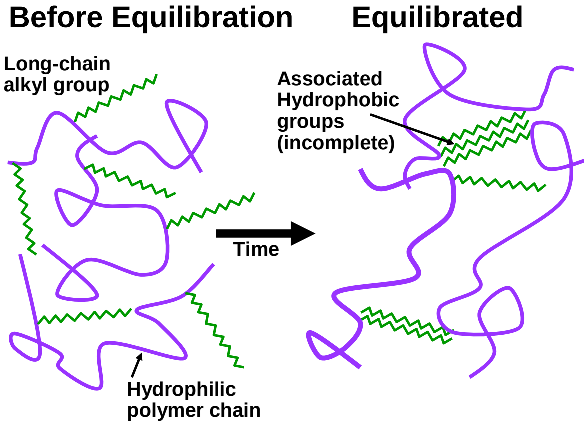

Fig. 21. Illustration of the way in which hydrophobic association among pendant hydrophobic groups might contribute to the structure and properties of PEC films

The best example showing an apparent contribution of hydrophobic associations to barrier performance appears to be that of Stevens *et al.* (2014). Pyrene side groups were used to modify poly(ethyleneimine), which was used sequentially with poly(acrylic acid) and montmorillonite clay. The resulting PEC barrier films showed excellent resistance to oxygen transmission, in addition to the self-healing effects that were discussed earlier.

Layer Attributes

The layer-by-layer (LbL) approach to preparing PEC films, as discussed earlier, clearly has the potential to produce a layered film structure. Such a structure can remain detectable even after building up large numbers of layers (Decher *et al.* 1992, 1994; Caruso *et al.* 1999; Ladam *et al.* 2000; Klitzing and Steitz 2002; Ben Dhieb *et al.* 2019). A question can be asked, however, whether the persistence of distinguishable layers within a PEC film makes a significant difference with respect to barrier properties. The inventor of the LbL approach (Decher 1997) described the layers as being "fuzzy," due to a tendency of polyelectrolytes within successive layers to inter-mingle. Arys *et al.* (2001) described a process in which each step in an LbL assembly process involves a sequence of adsorption of oppositely charge polyelectrolyte, a blurring step in which that polyelectrolyte diffuses into the previous layer, and a surface-constrained complexation. It is generally believed that the electrostatic effects tend to be short in range, such that any electrical charge on the underlying material will play no further role after application of a couple of layers of polyelectrolyte (Radeva *et al.* 2001).

The concept of relative fuzziness of PEC layers in an LbL film is illustrated in Fig. 22. Part A shows a hypothetical example that is drawn with minimum interpenetration, such that layered nature remains obvious in this type of depiction. Part B shows that the inherent layered nature can become obscured when each layer penetrates by about 50% into the adjacent layers. A structure with substantial overlap, as represented by Part B, is expected to be more likely, since it allows more efficient ion pairing throughout the structure.

If layered structures were very important for purposes of achieving barrier performance, then one ought to expect to find large differences when comparing LbL and direct mixing methods for preparation of PEC barrier films. Ankerfors *et al.* (2009) made such a comparison for two different chemical combinations, but no barrier properties were evaluated. Rather, the two systems of PECs gave about the same contribution to adhesion, which was the focus of the work. Thus, the present literature search did not find any direct analysis of whether or not there is a relationship between a layered nature of the PEC film and barrier properties.

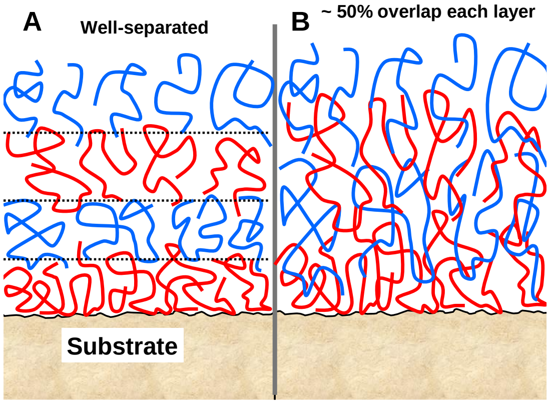

Fig. 22. Different degrees of fuzziness of PEC layers in a multilayer film. A: Well-separated layers with a minimum of inter-diffusion; B: The same polyelectrolyte chains, but each shown with about 50% of inter-penetration of the adjacent layers

Fillers and Barrier Performance

Nanocellulose

It is well known that the properties of some film materials can be improved for various applications by formulating them with well-selected particles, *i.e.* by preparing some kind of composite or nanocomposite. Because nanocellulose films, when dry, can provide superior resistance to the passage of oxygen (Lindström and Österberg 2020), and due to their polar nature, nanocellulose may seem like an ideal choice of filler to enhance the barrier properties of PEC-based films. As discussed in the review article by Klemm *et al.* (2018), one of the main classes of nanocellulose is cellulose nanocrystals (CNC). The lengths of CNC particles are often about 50 to 300 nm, and the widths are often about 4 to 10 nm. When incorporated into PEC-based films, such nanoparticles have the potential to provide reinforcement. Some researchers have reported improved water vapor barrier properties when CNC particles were incorporated into PEC-type films (Chi and Catchmark 2018a,b). Resistance to water vapor was also reported by Satam *et al.* (2018), who formed PECs with anionic CNC and cationic chitosan nanofibers. In some other work, only minor effects of CNC on barrier properties of PEC films were observed (Halasz *et al.* 2015).

Nanofibrillated cellulose (NFC) is generally at least an order of magnitude longer than CNC and somewhat thicker, and the material also can have a branched or network structure (Klemm *et al.* 2018). Partly due to its content of non-crystalline regions, and partly due to its great length to width ratio, NFC material can be envisioned as highly flexible in aqueous suspension. High gas barrier performance has been achieved with formulations including NFC and oppositely charged polyelectrolyte (Aulin *et al.* 2013; Molgaard *et al.* 2014). Sirviö *et al.* (2014) achieved a type of PEC with very high grease resistance by first preparing a NFC film with sodium alginate; after drying, the films were crosslinked by exposing them to calcium chloride. In addition to these examples, NFC appears to work very well in combination with highly platy mineral products, which will be discussed next (Qin *et al.* 2019a). Figure 23 depicts a hypothetical PEC film that has been reinforced with a combination of CNC and NFC. The figure is drawn to suggest the possibility that the reinforcing particles can contribute to holding the film together, especially if the distribution is quite uniform. Note that sometimes, especially in LbL-type films, the nanocellulose may be used in place of an anionic polyelectrolyte layer (Aulin *et al.* 2013; Li *et al.* 2013; Halasz *et al.* 2015; Li *et al.* 2019b).

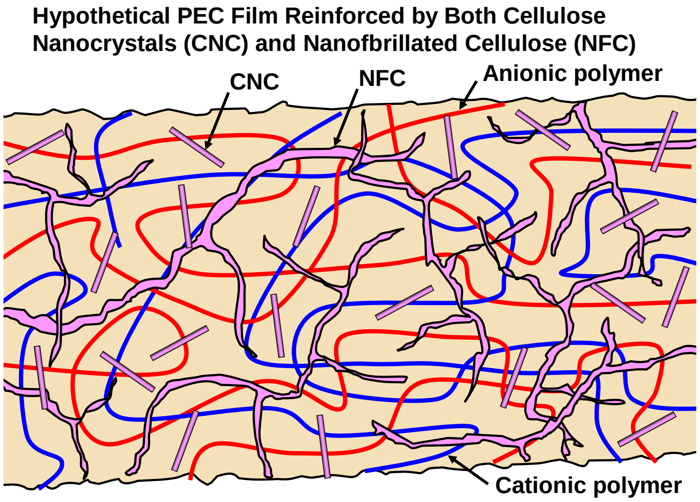

Fig. 23. Illustration of a hypothetical PEC film that has been prepared with both CNC (rod-shaped) and NFC (long and irregular) nanocellulose

Platy minerals

Some of the most promising barrier properties of PEC-based films have involved systems that included highly platy minerals such as sodium montmorillonite (nanoclay). As shown by results listed in Table A, such systems have been reported to have some of the lowest rates of transmission of oxygen and water vapor. Table 1 shows a subset of general findings, limited to PEC-based films that contained sodium montmorillonite. A notable feature of some of these reports is the fact that high resistance to oxygen and other gas transmission was achieved even at high levels of relative humidity (Holder *et al.* 2012; Song *et al.* 2016; Wang *et al.* 2018). In fact, the study by Dou *et al.* (2014) employed high humidity conditions in a step aimed at improving the barrier performance. Another highly platy material that has been receiving increasing attention for PEC-based barrier layers is graphene. Studies involving such films are listed in Table 2.

Table 1. Studies of Polyelectrolyte Barrier Films Incorporating Highly Platy Mineral Particles

Mineral Type	Polymers	Effects on barrier properties	Citation
Kaolin	PEI & PAA	OTR reduced.	Chiang *et al.* 2020
HT	PSS	OTR reduced.	Dou *et al.* 2014
MMT	PEI or HPMAS	WVTR reduced, especially at high salt.	Findenig *et al.* 2012
MMT	PAA & PEI	OTR reduced.	Hagen *et al.* 2014a
MMT	PEI	OTR reduced.	Hagen *et al.* 2014b
MMT	PAA & PEI	OTR reduced.	Hagen *et al.* 2016
MMT	PVP	OTR reduced even at high humidity	Holder *et al.* 2012
MMT	PEI	Durability and scratch resistance	Humood *et al.* 2016
MMT	cPAM	OTR reduced.	Jang *et al.* 2008
NHA	CS & CMC	WVTR reduced.	Jiang *et al.* 2009
MMT	CS & CR	OTR reduced.	Laufer *et al.* 2013a
MMT	CS & PAA	OTR reduced.	Laufer *et al.* 2013b
MMT	CS & wax	OTR reduced, WVTR reduced.	Li *et al.* 2019a
MMT	PEI	OTR reduced to very low values.	Priolo *et al.* 2010a
MMT	PEI & PAA	OTR reduced (with NFC).	Priolo *et al.* 2010b
MMT	PAAm & PAA	OTR reduced.	Priolo *et al.* 2013
VMT	Cat. CNF	OTR reduced.	Qin *et al.* 2019a
MMT	PEI	OTR & CO_2 transmission reduced.	Soltani *et al.* 2017
VMT	PEI & PAA	OTR reduced even at high humidity.	Song *et al.* 2016
MMT	PEI & PAA	OTR reduced.	Tzeng *et al.* 2014
HT	CMC	CO_2, N_2, CH_4 vapor transmissions reduced.	Wang *et al.* 2018

Key: Minerals: HAP = hydroxyapatite; HT = hydrotalcite; MMT = montmorillonite; VMT = vermiculite; **Cationic polymers:** CS = chitosan; HPMAS = 2-hydroxy-3-trimethyl-ammonium propyl chloride starch; PAAm = poly(allylamine); PEI = polyethyleneimine; PVP = poly(vinylpyrrolidone); **Anionic polymers:** CMC = carboxymethyl cellulose; CR = carrageenan; PAA = poly(acrylic acid); PSS = poly(sodium styrene-4-sulfonate); **Barrier properties:** OTR = oxygen transmission rate; WVTR = water vapor transmission rate

Table 2. Studies of Polyelectrolyte Barrier Films Incorporating Graphene

Particle Type	Polymers	Effects on barrier properties	Citation
GNP	PAA	OTR reduced.	Gokhale *et al.* 2013
GNP	PVOH	OTR reduced.	Mun *et al.* 2017
GO	PU+ & PU-	OTR reduced.	Noh *et al.* 2018
GO	PEI	OTR & CO_2 transmission reduced.	Yang *et al.* 2013
GO	PEI	OTR reduced.	Yu *et al.* 2012

Key: Particles: GNP = graphene nanoplatelets; GO = graphene oxide; **Polymers:** PAA = poly(acrylic acid); PEI = poly(ethyleneimine); PU+ = polyurethane with positive charge; PU- = polyurethane with negative charge ; PVOH = poly(vinyl alcohol)

Figure 24 illustrates a concept presented by Stevens *et al.* (2014), who employed a system called "nanobrick wall multilayer". The cited authors reported the lowest oxygen permeability when constructing "quad-layers" of the type illustrated in the figure. In the LbL assembly of these films, the negatively charged nanoclay was preceded and followed each time by layers of the highly cationic, branched polymer poly(ethylene imine) (PEI). However, the negatively charged layers alternated between the nanoclay and poly(acrylic acid) (PAA). One can envision such a construction as providing "mortar" to hold the nanoclay "bricks". The nanoclay, due to its shape, orientation, and impermeable nature, is an excellent component of a barrier film. However, it appears that PECs can serve as an excellent mortar for such barriers due to the good barrier properties of the PECs themselves.

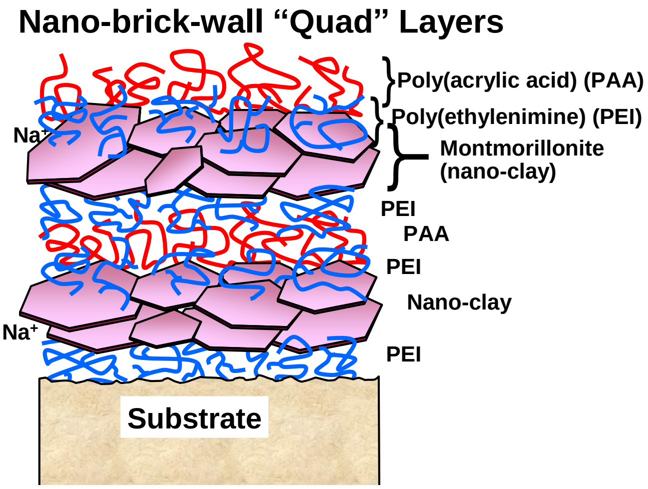

Fig. 24. The "quad"-layer structure benefits from the principle of tortuosity, by which diffusing molecules are forced to take a longer path, thus decreasing the overall rate of diffusion through a material

Tortuosity issues

To start to explain the strong gas barrier effects that have been achieved with platy minerals or graphene to PEC-based films, one needs to consider the paths that gas molecules need to take when diffusing through a barrier film (Zid *et al.* 2018). As shown in Fig. 25, if the film contains platy particles, then the required distance of diffusion can be considerably increased, especially if the platy particles have a high aspect ratio and a favorable concentration. In theory, the time required for a molecule to diffuse all the way through a film ought to be proportional to that distance (Belbekhouche *et al.* 2011; Ghanbarian *et al.* 2013; Tan and Thomas 2017). Various researchers have mentioned tortuosity as a means to explain superior barrier performance of PEC films that contained platy minerals or graphene, often as layers in a multi-layer structure (Gokhale *et al.* 2013; Min *et al.* 2017; Wang *et al.* 2018).

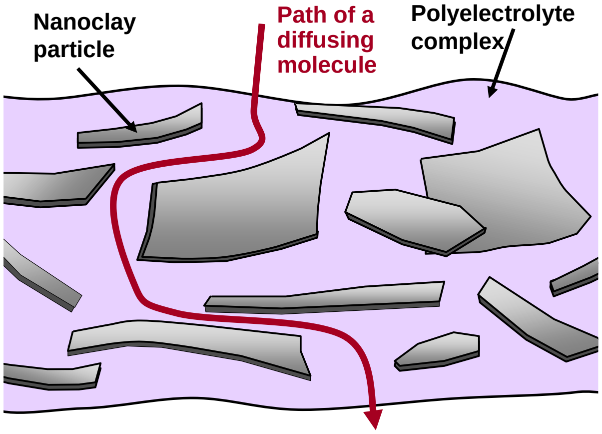

Fig. 25. Schematic for diffusion of a gas molecule through a film with or without the presence of platy impervious particles (figure adapted from a version used earlier by the author)

In principle, the effectiveness of an impermeable filler material to resist diffusion through a film will be determined by is shape (ideally platy), aspect ratio (*e.g.* width over thickness of a plate), orientation, and uniformity of distribution within the film (Tan and Thomas 2017). Several groups of researchers have described the nanoclay within their PEC-based barrier layers has being “oriented”, thereby providing more efficient blocking of oxygen or water vapor (Priolo *et al.* 2010a; Holder *et al.* 2012; Hagen *et al.* 2014a,b; Tzeng *et al.* 2014; Wang *et al.* 2018; Ben Dhieb *et al.* 2019a). It should be noted, however, that due to the tiny size of the mineral or graphene particles, such reports are very difficult to verify by microscopy. Accordingly, there is a continuing need for new methods and research to better characterize relationships between barrier properties and orientation of particles within a composite film.

Defects

A key uncertainty, when considering theories related to diffusion and tortuosity, is whether the barrier film being considered is indeed free from significant defects such as cracks and pores. Published articles in which barrier properties were evaluated are generally silent on the issue of whether such defects were present. The issue is challenging because sometimes the best way to detect such defects may be the leakage of oxygen or other substance through the film. Then it becomes really hard to know whether such transport was due to leakage or just due to diffusion through the film in general.

One approach to demonstrating the role of defects with respect to barrier properties is to take steps to plug up the defects. Such an approach was used, for instance, by Spence *et al.* (2011) to enhance the barrier properties of nanocellulose films. Those authors showed that a layer of beeswax greatly increased resistance to transmission of water vapor through NFC-type films. Because wax by itself is not a particularly good barrier film (Hagenmaier and Shaw 1992; Donhowe and Fennema 1993), the results suggest a plugging mechanism, in which wax is able to plug cracks or pores. Li *et al.* (2019a) showed reductions in water vapor passage through PEC films comprised of chitosan and montmorillonite following their treatment with carnauba wax.

Other Layers in Combination with PECs

When problems in the performance of barrier layers are due to defects such as cracks, another reasonable way to approach the problem is to rely upon a support layer, which ideally may prevent cracks from forming. For example, it is known that very high resistance to moisture can be achieved by deposition of thin SiOx films, but such films easily form cracks (Qin *et al.* 2019b). The cited authors showed that the problem could be solved by pairing the SiOx film with a PEC multilayer film. The combination of layers overcame the brittleness of the SiOx moisture barrier and also helped protect the PEC multilayer from moisture. PEC-based films also can be combined with bioplastic films, such as poly(lactic acid), which likewise provides moisture protection (Aulin *et al.* 2013; Laufer *et al.* 2013a,b; Halasz *et al.* 2015; Satam *et al.* 2018). Such a system is illustrated in Fig. 26.

An important question regarding the structure depicted in Fig. 26 is whether there might be problems related to the ability of water vapor to diffuse through the bioplastic film, thus affecting the oxygen-barrier contribution of the PEC-based layer within the sandwich.

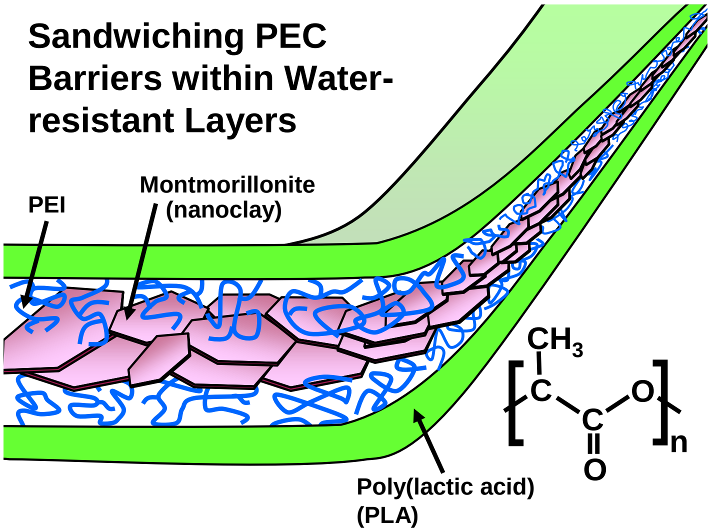

Fig. 26. Sandwich type barrier film in which the PEC film, this time including montmorillonite clay as a component, is protected by upper and lower films of the highly water-resistant bioplastic poly(lactic acid) (PLA)

An effective way to prevent a brittle sheet of paper from developing cracks in the course of folding is to encase that sheet in a close-fitting plastic envelope (Baty *et al.* 2010). It appears that the layers on each side of the brittle sheet are effective because they increase the minimum radius of bending if the material is creased. A similar approach can be used, in principle, when a brittle barrier layer is supported by other layers. Those layers might, for instance, serve also to protect a brittle layer from moisture.

PATHS FORWARD FOR PEC BARRIER FILMS

Likely Key Contributions of the PEC Layer

Based on the published work cited in this article, it is clear that a great deal of progress has been made, at an increasing pace, in understanding and developing effective PEC-based barrier films. It is proposed that important future progress can be achieved by focusing on specific attributes of films that may be desirable in certain applications. For example, there appears to be a demand for research related to the preparation of barrier films under mild conditions, thus allowing direct coating onto perishable objects, such as food. There is an accelerating interest in developing resistance to grease, in response to concerns and regulations about perfluorocarbon grease-proofing agents (Hubbe and Pruszinski 2020). There may be opportunities related to finding ways to achieve better alignment of highly platy mineral particles or graphene flakes within PEC-based barrier layers. In addition, there may be opportunities related to development of more highly stretchable PEC-based films that still retain barrier properties.

PEC Layers Applied Directly to Items

In several respects, the PEC formation process offers potential advantages for the direct application to fresh foods as a protective layer. To avoid damaging the food, it is possible to carry out the whole process of PEC film deposition, including the drying step, at room temperature. One has the option to employ only food-grade ingredients such as chitosan and alginates, *etc.* (Molgaard *et al.* 2014). The whole process can be carried out with water as the suspending medium. Meat poses particular challenges due to its propensity to spoil (Kulig *et al.* 2017). The cited article showed that a PEC film comprising sodium alginate, chitosan, and PEC hydrosols was effective in reducing the rate of spoilage of the meat. Likewise, Younis and Zhao (2019) prepared and evaluated edible PEC films comprised of chitosan and pectin. In such applications, even modest improvements in shelf-life can be beneficial. In principle, a PEC-based film could be applied to a wide variety of sensitive objects of different shapes, with the only requirements being their tolerance to a brief exposure to aqueous solution and a realization that certain hard-to-wet interior pore spaces may remain uncovered.

Pair with Other Layers in Packaging

Another category of application that seems to hold promise for PEC-type barrier films involves their usage in combination with different layers. Contrasting layers have potential to work together in synergistic ways. Due to the inherent properties of typical PECs, it makes sense to focus on applications where the PEC layer can provide resistance to permeation by greases and oxygen. The PEC-based layer can be paired with other layers having more promise to protect against the effects of water and water vapor (Lagarón *et al.* 2004). Due to the inherent weakness of typical PEC layers, it also makes sense to pair them with mechanically robust protective layers, which could include nanocellulose-based films.

Some of the most promising PEC-based barrier systems, based on the present review of the literature, are those that involve highly platy mineral products or graphene flakes (Priolo *et al.* 2010a, 2015; Hagen *et al.* 2016). Sodium montmorillonite (MMT) particles are generally nontoxic, very highly platy, and endowed with a high density of negative charge, allowing them to serve as the anionic partner in a PEC system. Alternatively, if one wants to pair a negatively charged polyelectrolyte with a positively charged platy material, one can use hydrotalcite (Dou *et al.* 2014; Lee *et al.* 2016; Wang *et al.* 2018). The platy particles in the film structure, especially if they are well aligned and uniformity arranged, can provide a high level of tortuosity, as well as outright blocking of diffusion paths through the film. There appear to be great opportunities to further optimize procedures of PEC film preparation in order to maximize alignment of the impervious mineral or graphene platelets or flakes. The relatively good ability of typical PECs to impede the permeation of oxygen and grease implies that the PEC can serve as an effective “mortar” in the “brick wall” that can be formed with platy mineral particles (Jang *et al.* 2008; Priolo *et al.* 2015; Cho *et al.* 2018; Qin *et al.* 2019a). In addition, the presence of the minerals has the potential to provide scratch resistance to the PEC films (Humood *et al.* 2016).

Assessment of the Hypotheses

Eight hypotheses were proposed at the beginning of this article. The idea was to help focus the discussion and plant the seeds of thinking about important issues. At this point, based on consideration of the published findings, some comments can be made regarding the validity of various hypotheses in the list. These judgments are encapsulated in Table 3.

Table 3. Judgements about the Hypothesis Statements Based on the Reviewed Literature

Hypothesis Statement	Judgement	Discussion
1. It is proposed that ionic bonding within thin films can contribute substantially to the barrier performance of thin films prepared from ionically charged polymers, *i.e.* polyelectrolytes and related systems.	Yes	Ionic bonds clearly embody sufficient energy to be able to contribute to effective resistance to permeation by oxygen and grease. Thus, PEC-based films can be regarded as a serious option for preparing barrier films.
2. It is proposed that it is possible to achieve a sufficiently contiguous nanostructure within PECs are related film structures, as would be required for very high efficiency of barrier effects.	Yes	Contiguous, relatively uniform PEC films can be prepared either by layer-by-layer (LbL) deposition, by forming the film at very low pH and then rinsing the film later, or by exposing a formed PEC film to divalent metal ions, for instance.
3. It is proposed that the barrier performance of PEC films can be improved by incorporation of various solid fillers or reinforcing particles during their preparation.	Yes	It is clear from many recent publications that highly platy particles such as nanoclay can be very effective to develop resistance to permeation by oxygen and even by water vapor.
4. It is proposed that reliance on ionic bonds is compatible with the preparation of self-healable barrier films.	Maybe	Though some self-healing capabilities have been demonstrated for PEC-based films, the conditions needed to bring about self-healing are not the same as the conditions required to achieve barrier performance.
5. It is proposed that PECs and related barrier films will tend to be permeable to various permeants.	No	Although some PECs show permeability, such characteristics can be avoided by use of platy particles and layered structures.
6. It is proposed that barrier layer based on PECs and similar systems tend to be prone to mechanical failure.	Yes & No	PEC systems that have high cohesive energy density do tend to be stiff when dry, so they tend to be prone to cracks. But this issue will not be a concern for all PECs and all applications.
7. It is proposed that PECs essentially become frozen into structures that are governed by kinetics, as well as by the flow conditions during initial mixing and preparation.	Yes	The irreversible nature of formation of PEC films, plus the rigid nature of most such films under dry conditions, implies that non-uniformity can be expected.
8. It is proposed that PEC-based films can be described as “fussy”. In other words, it is proposed that various deviations from ideal conditions of preparation and composition will result in unfavorable barrier performance.	Yes & No	Though careful attention to detail is needed to prepare good PEC-based barrier films, the technology appears to be quite forgiving, allowing usage of a wide range of materials and procedures.

Some of the most exciting research findings, from the perspective of considering the hypothesis statements, has involved strategies to avoid strong agglomeration of the oppositely charged polyelectrolytes in the course of forming PEC films at high speeds. Though the answer to the second hypothesis listed in Table 3 emphasizes the tried-and-true method of layer-by-layer deposition, such procedures are inherently very slow relative to the needs of typical industrial operations. Thus, it is encouraging to note that progress has been made in implementing procedures that are orders of magnitude faster. Such options include high-shear treatment of freshly prepared PEC mixtures, followed by film preparation (Basu *et al.* 2017), and forming a film with an anionic polymer, then exposing that film to a solution with calcium ions (Sirviö *et al.* 2014; Shimizu *et al.* 2016). There also seems to be a lot of potential to apply charge-stabilized PEC colloids onto surfaces (Hubbe 2005), followed by their consolidation using such strategies as treatment with calcium ions or variations in drying procedures (Decher *et al.* 1994; Gamboa *et al.* 2010). The simplicity and highly promising results obtained by such methods suggest that additional ways might be found in the coming years to prepare highly effective PEC-based barrier layers at industrial speeds. There will be opportunities to utilize sustainable, bio-based polyelectrolytes such as starch derivatives (Chi *et al.* 2020). In addition, there appear to be many opportunities for researchers to pursue some of the yet-unanswered questions that were noted in the course of this article.

ACKNOWLEDGMENTS

The work of Martin A. Hubbe is supported by an endowment from the Buckman Foundation for the support of research and teaching related to papermaking technology. The following volunteers provided critical comments and suggested changes based on an earlier draft of this article: Stefano Farris, University of Milan, Department of Food, Environmental, and Nutritional Sciences; Jeffrey M. Catchmark, Penn State University, Department of Agricultural and Biological Engineering (PSU-ABE); Wei-Shu Lin, PSU-ABE; and Parisa Nazemi, PSU-ABE. Their help is much appreciated.

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APPENDIX

Table A. Polyelectrolyte Films and Reported Barrier Properties

Cationic polyelec-trolyte	**Anionic polyelec-trolyte**	**Part-icle (filler)**	**Prep-aration method**	**General findings**	**Perm-eant**	**Permeability (and units)**	**Citation**
PEI	NFC	(NFC)	LbL 50	Flexible and transparent	Oxygen	9 cm^3/(m^2·day·atm)	Aulin *et al.* 2013
PEI	CMC	-	LbL 50	Tunable props by PE ratios	Oxygen	11 cm^3/(m^2·day·atm)	Aulin *et al.* 2013
PEI	NFC	(NFC)	LbL 50	Flexible and transparent	H_2O vap.	2.3 g/(m^2·day·atm)	Aulin *et al.* 2013
PEI	CMC	-	LbL 50	Tunable props by PE ratios	H_2O vap.	2.3 g/(m^2·day·atm)	Aulin *et al.* 2013
Chitosan	PAM-Itaconic	-	Mix	Neutral pH best performance	H_2O vap.	6300 g/(m^2·day·atm)	Bajpai *et al.* 2016
Chitosan	CMC	-	Shear	Fiber-like nanostructures	H_2O vap.	1000 to 1214 g/(day·m^2)	Basu *et al.* 2017
Chitosan	MMT	(MMT)	LbL 12	Orientation is important	Oxygen	1.5 cm^3/(m^2·day·atm)	Ben Dhieb *et al.* 2019a
(PVOH)	MMT	(MMT)	LbL 15	Coating methods	Oxygen	0.6 cm^3/(m^2·day·atm)	Ben Dhieb *et al.* 2019b
Chitosan	CMC	-	Shear	High-shear blending; kit tests	H_2O vap.	200 g/(m^2·day·atm)	Chi & Catchm. 2018a
Chitosan	CMC	-	Shear	High-shear blending, kit tests	H_2O vap.	160 g/(m^2·day·atm)	Chi & Catchm. 2018b
PEI	PAA	MMT	Bar coat	Mix, allow to settle, spread	Oxygen	1 cm^3/(m^2·day·atm)	Chiang *et al.* 2020
(PVOH)	PAA	GO	LbL 40t	Strain increased transmission	Oxygen	0.7 cm^3/(m^2·day·atm)	Cho *et al.* 2018
PEI	PAA (PEO)	-	LbL 20q	Strain increased transmission	Oxygen	5 cm^3/(m^2·day·atm)	Cho *et al.* 2015
Cat. guar	NFC	(NFC)	LbL 8	Resists multiple fluid	O_2, H_2O	Minor effects	Dai *et al.* 2017
Chitosan	PAA	-	Mix	Formic acid at two levels	A drug	2 to 10x less permeable	De Oliveira *et al.* 2008
Chitosan	PAA	-	Wetted	Chitosan film wetted by PAA	H_2O vap.	Minor effects	De Lima *et al.* 2009
Hyd-talcite	PSS	(HT)	LbL 20	Layers & humidity levels	Oxygen	10,000 cm^3/(m^2·day·atm)	Dou *et al.* 2014
PEI	MMT	(MMT)	LbL 20	Salts enhanced barrier	H_2O vap.	150 g m^2/day	Findenig *et al.* 2012
PEI	MMT	(MMT)	LbL 20	Rinse down, dry up sequence	Oxygen	0.1 cm^3/(m^2·day·atm)	Gamboa *et al.* 2010
PEI	PAA	-	LbL 10	Adjustment of the pH & rinse	Oxygen	0.4 cm^3/(m^2·day·atm)	Gokhale *et al.* 2013
PEI	PAA	MMT	LbL 20	Alternating with/without PAA	Oxygen	0.007 cm^3/(m^2·day·atm)	Hagen *et al.* 2014a
PEI	MMT	(MMT)	LbL 15	Adjustments of pH	Oxygen	0.1 cm^3/(m^2·day·atm)	Hagen *et al.* 2014b
PEI	PAA	-	Mix	Spread with Mayer rod	Oxygen	0.08 cm^3/(m^2·day·atm)	Haile *et al.* 2017
Chitosan	CNC	(CNC)	LbL 4	Ultrasonic dispersion of CNC	H_2O vap.	Up to 29% reduction	Halasz *et al.* 2015
PVP	MMT	(MMT)	LbL 40	Highly aligned nanobrick wall	Oxygen	3.5 cm^3/m^2 atm day	Holder *et al.* 2012
PEI	MMT or GO	(MMT)	LbL 10	Scratch resistance	Oxygen	0.15 cm^3/(m^2·day·atm)	Humood *et al.* 2016
Cat. NFC	Xylan	-	LbL 40	50% or 80% rel. humidity	Oxygen	100-6000 g/(m^2·day·atm)	Ibn Yaich *et al.* 2015
cPAM	MMT	(MMT)	LbL 30	Brick wall construction	Oxygen	0.015 cm^3/(m^2·day·atm)	Jang *et al.* 2008
Chitosan	Gum	MMT	LbL 10q	Quadlayers	Oxygen	5x10^{-5} cm^3/(m^2·day·atm)	Laufer *et al.* 2013a
Chitosan	PAA	MMT	LbL 10q	Ten quad-layers, 90% r.h.	Oxygen	4.6 cm^3/(m^2·day·atm)	Laufer *et al.* 2013b
Chitosan	PAA	-	LbL 15	Cross-linking, 90% r.h.	Oxygen	0.08 cm^3/(m^2·day·atm)	Lazar *et al.* 2019

Cationic polyelec-trolyte	Anionic polyelec-trolyte	Part-icle (filler)	Prep-aration method	General findings	Perm-eant	Permeability (and units)	Citation
Chitosan	CNC	(CNC)	LbL 30	Cellulose nanocrystals	Oxygen	1.52 cm^3/(m^2·day·atm)	Li *et al.* 2013
Chitosan	Pectin	-	Mix	Glycerol content, washing	Oxygen	0.7-1.8 cm^3/(m^2·day·atm)	Machado *et al.* 2020
PEI	MMT	(MMT)	LbL 20	Spraying as an option	Oxygen	1x10^{-7} cm^3/(m^2·day·atm)	Min *et al.* 2017
Cat. NFC	Pectin	(NFC)	LbL 10	20% relative humidity	Oxygen	1100 cm^3/(m^2·day·atm)	Molgaard *et al.* 2014
PVOH	PSS	GO	LbL 10	PSS & GO added together	Oxygen	<2.5 cm^3/(m^2·day·atm)	Mun *et al.* 2017
Cat. PU	Anionic PU	(GO)	Spin ct.	Spin-coat order; 15% strain	Oxygen	20 cm^3/(m^2·day·atm)	Noh *et al.* 2018
PEI	MMT	-	LbL 70	pH-tailoring	Oxygen	<0.005 cm^3/(m^2·day·atm)	Priolo *et al.* 2010a
PEI	PAA	MMT	LbL 20	Quad: PEI/PAA/PEI/MMT	Oxygen	<0.005 cm^3/(m^2·day·atm)	Priolo *et al.* 2010b
PAAm	PAA	MMT	LbL 4	Different spacing of MMT	Oxygen	0.02 cm^3/(m^2·day·atm)	Priolo *et al.* 2013
Cat. NFC	VMT	(VMT)	LbL 20	Strong & flame-resistant	Oxygen	0.013 cm^3/(m^2·day·atm)	Qin *et al.* 2019a
-	PAA/PEO	MMT	LbL 10	High stretchability	Oxygen	1.7 cm^3/(m^2·day·atm)	Qin *et al.* 2017
PEI	PAA	SiO_2	LbL 16	PEC to protect brittle SiO_2	H_2O vap.	0.4 g/(m^2·day·atm)	Qin *et al.* 2019b
$CaCl_2$	Soy protein	-	Cast	Crosslink by $CaCl_2$ rinse	H_2O vap.	Minor decrease	Rhim & Lee 2004
$CaCl_2$	Alginate	-	Cast	Crosslink by $CaCl_2$ rinse	H_2O vap.	Minor changes	Rhim & Lee 2004
Chitin NPs	CNC	Dual	LbL 5	Cat. & anionic nanoparticles	Oxygen	400 cm^3/(m^2·day·atm)	Satam *et al.* 2018
Chitosan	Xylan	-	Mix	Glycerol plasticizer content	Oxygen	<0.36 cm^3/(m^2·day·atm)	Schnell *et al.* 2017
TO-NFC	Metal ions	(NFC)	Cast	NFC film soaked with cations	Oxygen	0.1 cm^3 μm/m^2 kPa day	Shimizu *et al.* 2016
$CaCl_2$	MFC	(NFC)	Cast	MFC decreased permeability	H_2O vap.	6200 g/(m^2·day·atm)	Sirviö *et al.* 2014
pDADMAC	PAA	-	Mix	Mix at pH 2, neutralize film	Oxygen	0.02 cm^3/(m^2·day·atm)	Smith *et al.* 2018
PEI, PETi	MMT	(MMT)	Expose	PEI, then MMT suspension	O_2, CO_2	1200 cm^3/(m^2·day·atm)	Sontani *et al.* 2017
PEI	PAA	-	LbL 8	Self-healing	Oxygen	<0.005 cm^3/(m^2·day·atm)	Song *et al.* 2017
PEI	PAA	VMT	LbL 30	Layer thickness, humidity	Oxygen	15-57 cm^3/(m^2·day·atm)	Song *et al.* 2016
PEI	PAA	VMT	LbL 30	Layer thickness, humidity	H_2O vap.	1.4 g/(m^2·day·atm)	Song *et al.* 2016
Chitosan	TO-NFC	(NFC)	Cast	Sorbitol plasticizer	Oxygen	0.3 cm^3/(m^2·day·atm)	Soni *et al.* 2016
Chitosan	TO-NFC	(NFC)	Cast	Sorbitol plasticizer	H_2O vap.	4.7x10^{10} g/(m^2·day·atm)	Soni *et al.* 2016
PEI	PAA	MMT	LbL 4q	Pyrene-labeled PEI, quads	Oxygen	0.3 cm^3/(m^2·day·atm)	Stevens *et al.* 2014
PVAm,PEI	PAA	MMT	LbL 10q	Various sequences	Oxygen	4x10^{-8} cm^3/(m^2·day·atm)	Tzeng *et al.* 2014
Hyd-talcite	CMC	(HT)	LbL 30	Also CO_2 and methane	Nitrogen	0.012 cm^3/(m^2·day·atm)	Wang *et al.* 2018
Chitosan	Alginate	-	LbL 3	High permeability to water	H_2O vap.	2.6 g μm/(m^2·day·atm)	Yan *et al.* 2000
PEI	PAA	-	LbL 8	Glutaraldehyde crosslinking	Oxygen	0.0077cm^3/(m^2·day·atm)	Yang *et al.* 2012
PEI	GO	(GO)	LbL 30	Also tested CO_2 transmission	Oxygen	0.2 cm^3/(m^2·day·atm)	Yang *et al.* 2013
PEI	PAA	-	LbL 8	Glutaraldehyde crosslinking	Oxygen	<0.005 cm^3/(m^2·day·atm)	Yang *et al.* 2011
Chitosan	Pectin	-	Blend	Edible films	H_2O vap.	Similar to components	Younis & Zhao 2019
PEI	GO	(GO)	LbL 5	Post-treatments	Oxygen	0.25 cm^3/(m^2·day·atm)	Yu *et al.* 2012
pDADMAC	CMC	(GO)	LbL	CMC & GO added together	Oxygen	Greatly reduced trans.	Zhao *et al.* 2013

Notes for Table A

Labeling: CNC = cellulose nanocrystals; cPAM = cationic copolymer of poly(acrylamide); GO = graphene oxide; Hyd-talcite (HT) = double hydroxide, hydrotalcite; LbL = layer-by-layer; The number following "LbL" indicates the number of repeating sequences, were "t" indicates trilayers and "q" indicates quadlayers; MFC = microfibrillated cellulose; NFC = nanofibrillated cellulose; MMT = montmorillonite (nanoclay)**;** PAAm = poly(allyl amine); pDADMAC = poly(diallyldimethylammonium chloride); PEI = poly(ethyleneimine; PETi = poly(ethylene terephthalate) ionomer; PSS = poly(sodium styrene-4-sulfonate; PU = polyurethane; PVP = poly(vinylpyrrolidone; TO-NFC = TEMPO-oxidized nanofibrillated cellulose; VMT = vermiculite; the term "mix" means that the ingredients were combined; the term "shear" means that significant shear stress was applied; and "blend" implies use of a blender device.

Unit conversions: 1 kPa = 0.009869 atmospheres; 24h / day; 1.145E-5 days/s; Certain authors expressed their results based on film thickness.
Ben Dhieb *et al.* 2019a; reported 0.5 cm^3·μm/(m^2·day); thickness = 0.33 μm; assume 1 atm. → 1.5 cm^3/(m^2·day·atm)
Ben Dhieb *et al.* 2019b; reported 0.5 cm^3·μm/(m^2·day); thickness = 0.9 μm; assume 1 atm. → 0.6 cm^3/(m^2·day·atm)
Chi & Catchm. 2018a; reported 10 kg·μm/(m^2·day); thickness = 50 μm; assume 1 atm. → 0.2 kg/(m^2·day·atm) = 200 g/(m^2·day·atm)
Chi & Catchm. 2018b; reported 8 kg·μm/(m^2·day); thickness = 50 μm; assume 1 atm. → 0.2 kg/(m^2·day·atm) = 160 g/(m^2·day·atm)
Dou *et al.* 2014; reported 1 cm^3/cm^2 atm day; → 10,000 cm^3/(m^2·day·atm)
Humood *et al.* 2016; reported 10^{-19} cm^3 cm/(cm^{2}sPa); 1s = 1.145E-5 days; thickness = 0.6 μm; →
10^{-19} cm^3 cm/(cm^{2}sPa) x (10^{4}μm/0.6 μm) /[(10^{-4} m^2/cm^2) x (1.145E-5 days/s) x (0.000009869 atmospheres/Pa) = 0.15 cm^3/(m^2·day·atm)
Ibn Yaich *et al.* 2015; reported 0.1-6 cm^{3}μm/m^{2}daykPa); Assume a 40-layer film is about 100 nm, based on Molgaard *et al.* 2014; →
0.1-6 cm^{3}μm/m^{2}daykPa) x (1 μm/0.1 μm) x (kPa/0.009869 atm) = 100-6000 cm^3/(m^2·day·atm)
Laufer *et al.* 2013a; reported 3x10^{-20} cm^3 cm/cm^2 s Pa; film thickness = 55 nm;
3x10^{-20} cm^3 cm/cm^2 s Pa x [1/(55 x 10^{-7} cm)] /[(1.145E-5 days/s) x (0.000009869 atm/Pa)] = 5x10^{-5} cm^3/(m^2·day·atm)
Li *et al.* 2013; reported 0.015 cm^3/m^2 kPa day → 1.52 cm^3/(m^2·day·atm)
Molgaard *et al.* 2014; reported 0.03 cm^3 mm/m^{2}atm day; film thickness 27 nm; →
0.03 cm^3 mm/m^{2}atm day / 27E-6 mm = 1100 cm^3/(m^2·day·atm)
Satam *et al.* 2018; reported 20 cm^3 μm/m^2 kPa day; thickness *ca.* 5 μm; →
20 cm^3 μm/(m^2 kPa day) x (1/5 μm) x (kPa/0.009869 atm) = 405 cm^3/(m^2·day·atm)
Schnell *et al.* 2017; reported <0.3 cm^3 μm/m^2 kPa day; thickness = 50 to 120 μm, take average = 85 μm; →
<0.3 cm^3 μm/m^2 kPa day x (1/85 μm) x (kPa/0.009869 atm) = 0.36 cm^3/(m^2·day·atm)
Shimizu *et al.* 2016; reported 0.1 cm^3 μm/m^2 kPa day; thickness = not stated and no way to estimate thickness.
Sirviö *et al.* 2014; 7x10^{-7} g/(Pa.s.m^2); → 7x10^{-7} g/(Pa.s.m^2) x (Pa/0.000009869 atm) x (s/1.145E-5 days) = 6200 g/(m^2·day·atm)
Soltani *et al.* 2017; reported 6x10^{-3} cm^3 m/m^2 atm day; thickness = 500 nm; →
6x10^{-3} cm^3 m/m^2 atm day x (1/500E-9 m) = 1200 cm^3/(m^2·day·atm)
Soni *et al.* 2016; reported 2.6 g/(Pa h m); thickness = 0.1346 mm; →
2.6 g/(Pa h m) x (Pa/0.000009869 atm) x (24 h / day) x (1/ 0.1346E-3 m) = 4.7E10 g/(m^2·day·atm)
Tzeng *et al.* 2014; reported 5x10^{-22} cm^2 cm/(cm^{2}Pas); {thickness = 50.9 nm, term not needed} →
5x10^{-22} cm^2 cm/(cm^{2}Pas) x (10000 cm^2/m^2) x (Pa/0.000009869 atm) x (s/1.145E-5 days) = 4.4 x 10^{-8} 1200 cm^3/(m^2·day·atm)
Yan *et al.* 2000; reported 2 g mm/(m^2 day mmHg); thickness = not reported and no way to estimate.
2 g mm/(m^2 day mmHg) * 760 mmHg/atm = 0.0026 g mm/(m^2·day·atm) = 2.6 g μm/(m^2·day·atm)
Yang *et al.* 2012; reported 5.9x10^{-21}cm^{3}cm/cm^{2}sPa); thickness = 551 nm; →
5.9x10^{-21}cm^{3}cm/cm^{2}sPa) x 1/551E-7cm x (10000 cm^2/m^2) x (Pa/0.000009869 atm) x (s/1.145E-5 days) = 0.0077cm^3/(m^2·day·atm)