

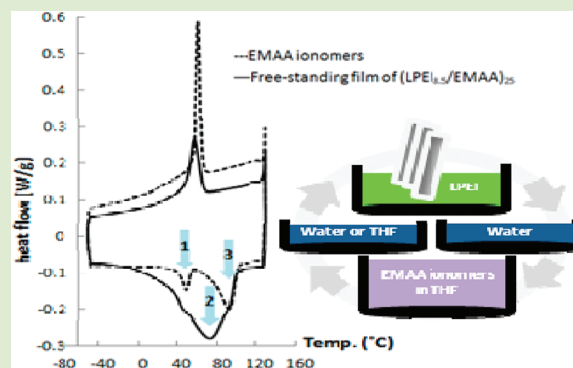
Polyelectrolyte Multilayers and Complexes to Modify Secondary Interactions in Ethylene-co-methacrylic Acid Ionomers

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Supporting Information

ABSTRACT: Ethylene-co-methacrylic acid (EMAA) ionomers are incorporated into polyelectrolyte complexes and thin films fabricated with the layer-by-layer technique using mixed solvent systems of THF and water. EMAA ionomers have been reported to have self-healing properties. The thin films were optically clear and can be made as a coating or freestanding. Their composition was determined with elemental analysis. DSC showed these polymer blend materials to have suppressed polyethylene crystallinity compared to bulk EMAA and an increased amount of energy required to create the order-to-disorder transition of disrupting the associations between the ionic groups of the ionomer.



Polyelectrolyte complexation and the layer-by-layer (LbL) method can be used to incorporate polyelectrolytes into useful materials.^{1,2} The LbL technique for fabrication of polyelectrolyte multilayers (PEMs) is to expose a substrate sequentially to oppositely charged solutions of polyions, directing their complexation onto a substrate. PEMs fabricated by the LbL technique have shown promise for a range of applications.² In addition to polyelectrolytes, these materials can be made with many different types of building blocks, including micelles, nanoparticles, and biological materials. Despite this wide range of functionality, incorporation of ionomers into PEMs and polyelectrolyte complexes (PECs) is thus far limited.^{3–6} Although ionomers carry charge, they are primarily composed of neutral, hydrophobic monomers and are not water-soluble. LbL assemblies are usually made from aqueous solutions. Use of organic solvents for electrostatic assembly is a less understood process.⁷

Ethylene-co-methacrylic acid (EMAA) ionomers are commonly used in different types of packaging, but are also reported to show promise for self-healing. Initial work has shown EMAA ionomers to heal upon impact from a projectile, with healing being activated by the temperature increase after impact.⁸ The impact disorders the associations between ionic groups, called multiplets, which are driven thermodynamically to reform. Heat created by impact allows for the reordering of the multiplets, healing the material. These materials are also potentially useful for energy dissipation or damage resistance. Upon impact, materials can use secondary interactions, such as the associations of multiplets, to dissipate energy from the damage event and prevent failure. Breaking and reforming reversible bonds is one way to initiate self-healing or to dissipate energy, and these bonds can respond on extremely short time scales.⁹ There are many such examples in biological

systems.¹⁰ The ability to control the presence of secondary interactions in polymer materials may provide a new route to materials with enhanced capability for energy dissipation. The LbL technique is well suited for the manipulation of secondary interactions. Individual polymer chains are held together in these assemblies with hydrogen bonds, electrostatic cross-links, and even metal-to-ligand complexes. The strength of these interactions can be finely tuned with different assembly conditions.

This work represents the first report of EMAA incorporated into polyelectrolyte multilayers and complexes and characterization of these materials.

Copolymers of ethylene and methacrylic acid were used, sold by Dupont as Surlyn 8940. These ionomers have 5.4 mol % methacrylic acid groups that are partially neutralized (30% of the acid groups) with sodium ions, and their morphology has three types of regions: crystalline polyethylene, amorphous regions, and regions of ionic clusters distributed in the amorphous regions.^{11,12} Poly(ethylene-co-methacrylic acid) (EMMA) ionomers were successfully incorporated into PEMs, polyelectrolyte complexes and free-standing films. A THF dispersion of EMAA was used with linear poly(ethyleneimine) (LPEI, over a range of pH values). A range of conditions were tried, including THF–water dispersions for the EMAA and a range of pH values for LPEI. Optimal deposition conditions were found to occur for EMAA dispersed in THF and LPEI ranging from about pH 4–9. When both ionomer and polyelectrolyte dipping steps were followed by water rinses, the films grew more thickly and were hazy. When

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the ionomer step was followed by a THF rinse, the film growth was thinner. Solid complexes are formed by mixing solutions of the polymers, and PEMs formed by sequential exposure of substrates to the solutions. Free-standing films were formed by heating the PEMs and then soaking in 1 molar NaOH. More detail can be found in Supporting Information.

Elemental analysis (Table S1) gives the wt% of LPEI as roughly 7% for all materials assembled with LPEI at pH 8.5. These results are close to a one-to-one balance of opposite charges expected in PEMs. Surlyn 8940 is 10.4 wt % methacrylic acid groups and 5.5 wt % Na⁺ neutralized acid groups. The ratio of weight of one methacrylic acid repeat unit to one LPEI repeat unit is about 2.2:1. The Na⁺ ion content of the LbL films and complexes is unknown, but estimating that 15% of the EMAA content of the LbL film or complex is from neutralized or un-neutralized methacrylic acid group containing repeat units and gives a weight ratio of acid bearing repeat units to LPEI repeat units of approximately 2:1. To verify that the films are PEMs and not just coatings of EMAA, glass slides were dipped multiple times in EMAA only as a control. Such a film did not grow (Figure 1a) further than an initial dip-coated layer of EMAA because of the interaction of the ionic groups.

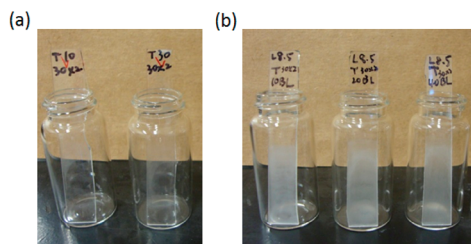


Figure 1. (a) Manually dipped films at 10 and 30 dipping steps in THF solution of EMAA, respectively, with subsequent rinsing steps in THF after a first dip in LPEI pH8.5 solution. This control experiment shows that without the LPEI the EMAA does not build up a thick film on its own. (b) LbL films assembled by LPEI and EMAA for 10, 20, and 40 bilayers and rinsed in THF baths.

Figure 2a shows a growth curve of linear poly-(ethyleneimine) (LPEI) and EMAA assembled at various pH

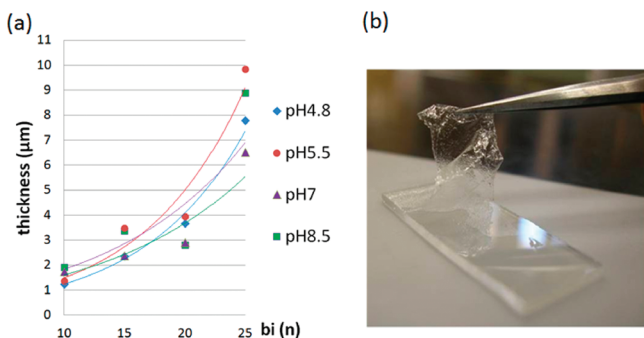


Figure 2. (a) Growth curve of the buildup of LPEI/EMAA multilayers as a function of bilayer number for a range of LPEI pH values. (b) LPEI/EMAA multilayer being pulled off of the substrate.

values of LPEI and with water rinses for both materials. The thick, superlinear, growth (25 bilayers are between 6 and 10 μm thick) results in part from EMAA being a dispersion. Film growth is seen at every step, and the assembly is truly a multilayered blend between the two polymers. Figure 2b shows

the free-standing film being pulled off of the substrate on which it was assembled and heated. The NaOH immersion process deprotonates the charge groups, swelling the film and causing delamination, but not dissolution. This is evidenced by the fact that elemental analysis shows the same LPEI composition for free-standing films and as assembled films. Although the PEMs are hazy as assembled, the free-standing films are clear. These films are hydrophobic, with contact angle of 125°.

FTIR analysis is shown in Figure 3 and spectra are normalized by min–max normalization method. Figure 3a is the typical spectra for 1 EMAA and 2 LPEI. The EMAA peaks of free and dimer COOH are at around 1740 and 1698 cm⁻¹, respectively, and carbonate asymmetric stretches at 1500–1590 cm⁻¹ can be seen. The broadness of the carbonate peaks stems from the association of ionic groups.^{13–15} In the LPEI curve, free secondary amine groups are shown by two peaks of ~3260 and ~1115 cm⁻¹.¹³ Figure 3b shows FTIR spectra of LPEI/EMAA LbL films made with LPEI at different pH values. With the increase of pH value, the carbonate peak increases and COOH depresses. At high pH (Figure 3b, line 4, pH 12), the characteristics of LPEI emerge as the appearance of the free amine group peaks (~3260 and ~1120 cm⁻¹), consistent with Figure 3a.

In Figure 3c, LPEI/EMAA complex, LbL film, heated film, and free-standing film of (LPEI_{8.5}/EMAA)₂₅ are shown. In the complex, a peak at ~1615 cm⁻¹, characteristic of charged secondary amine groups, and a weak peak at ~3300 cm⁻¹ for free amine groups emerge.^{16,17} The carboxylic acid groups are deprotonated in the heated and free-standing films. Although amidation might be expected, the FTIR spectra of the heated films (Figure 3c, line 3) do not show clear evidence of amide formation. Figure 3c, line 4, is spectra for free-standing films and shows two peak at ~3280 and ~1120 cm⁻¹, attributed to uncharged amine groups.

Modulated DSC (MDSC), a technique that has been applied to ionomers,^{18,19} data for pure EMAA (Surlyn8940) and pure LPEI are shown in Figure 4a. Materials were equilibrated in a desiccator before measurement, and although there may still be some residual solvent, the DSC curves shown here match closely to samples that were dried at elevated temperature before measurement. There are two endothermic peaks shown in the first heating of EMAA. The peak at ~92 °C is due to the melting of ethylene crystallites; for pure LPEI, there is also an endothermic melting peak at ~81 °C. The EMAA peak at ~50 °C is the subject of some discussion in the literature but is most likely the melting of secondary, thinner polyethylene crystallites.^{20,21} This peak is also sometimes assigned to the presence of an order to disorder peak for disordering ionic multiplets,^{12,22} but these ionic aggregates are known to persist up to temperatures of 300 °C. Without further study, we consider this endotherm to represent the disruption of certain secondary interactions in the material. Crystallization can be seen when EMAA is cooled. During the second heating, the lower temperature peak has shifted to slightly higher temperature and is smaller. LPEI does not recrystallize during the cooling process.

Figure 4b shows the total heat flow from MDSC of a PEM and a free-standing (LPEI_{8.5}/EMAA)₂₅ film. DSC for the complex is shown in the Supporting Information. Both of these assemblies show three overlapping endothermic peaks (marked by arrows 1, 2, and 3). The temperatures of arrows 1–3 of the PEM are ~46/48, 62/74, and 91/92 °C. Arrows 1 and 3 correspond to the melting peaks previously observed for pure

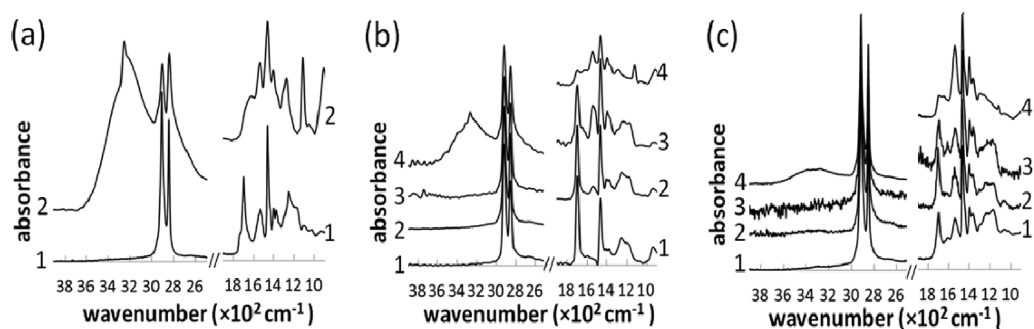


Figure 3. (a) Line 1 is FTIR spectra of pure EMAA and 2 is LPEI crystalline hydrates. (b) FTIR spectra of LbL films assembled by EMAA and 0.02 M LPEI solutions at different pH values: 1, pH 3; 2, pH 5; 3, pH 8; 4, pH 12 (crystalline hydrates remain in the LPEI solution). (c) FTIR spectra of 1, LPEI_{8.5}/EMAA (1:1) complexes; 2, LbL film of (LPEI_{8.5}/Surlyn8940)₂₅; 3, heated film of (LPEI_{8.5}/Surlyn8940)₂₅; 4, free-standing film of (LPEI_{8.5}/EMAA)₂₅.

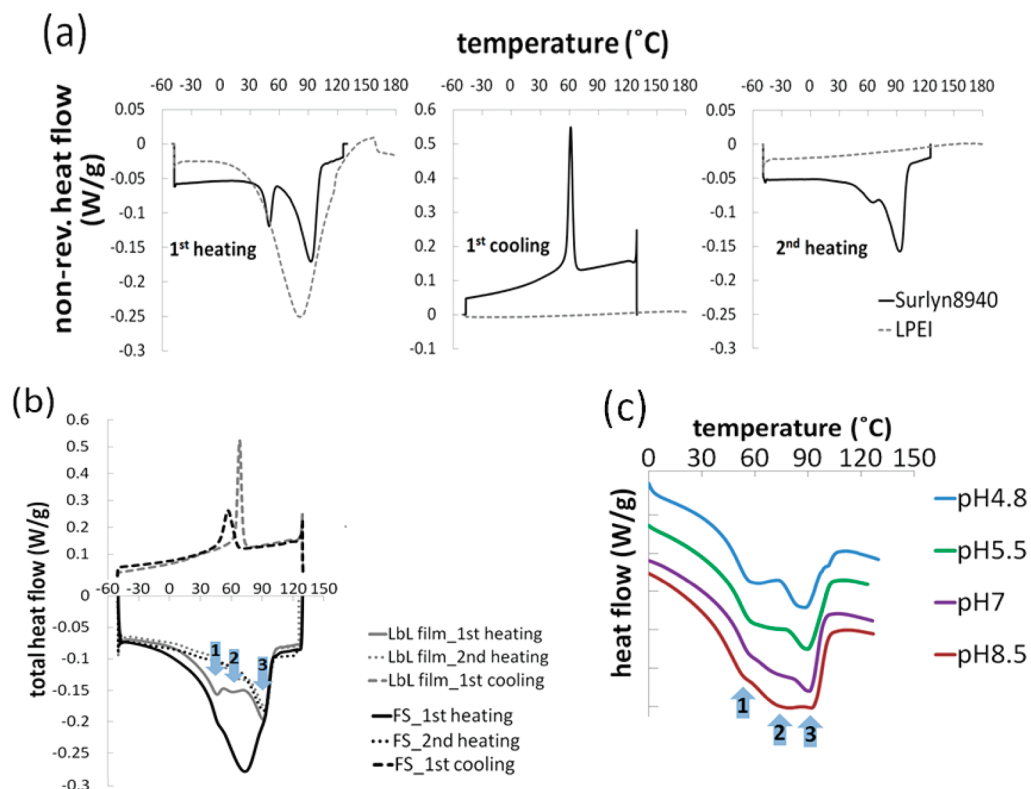


Figure 4. (a) Modulated DSC data, nonreversible heat flow of the first heating, first cooling, and second heating for EMAA and LPEI. (b) Modulated DSC, total heat flow for LbL and free-standing films of (LPEI_{8.5}/EMAA)₂₅. (c) DSC data for free-standing films of 25-bilayer of EMAA and 0.01 M LPEI at different pH values.

EMAA. The higher temperature peak for melting has not appreciably changed, but the lower temperature peak has shifted to a lower temperature and broadened. This has also been observed in blends of lithium salts of EMAA copolymers and different weight % of poly(ethyleneimine).²³ PEI inserted into the ionic domains of EMAA has also been shown to depress the lower temperature endotherm. The peak denoted by arrow 2 becomes larger in the free-standing LbL film. The exact origin of this new peak is not fully understood. The melting of LPEI occurs over this temperature range, but given that LPEI is 7 wt % of the film, this cannot fully explain the size of the peak. The NaOH treatment changes the degree of ionization and creates new associations between LPEI and EMAA, perhaps resulting in this new peak. Peaks 1 and 2 are not seen in the second heating curve, implying that they are

associated with interactions between polymer chains that are not able to reform during the cooling cycle. Figure 4c shows total heat flow for the first heating for LPEI/EMAA multilayers assembled over a range of pH values for the LPEI. This “new” peak is not seen for the film assembled with LPEI at lower pH values. There is a broadening of the lower temperature peak over the range of pH values, indicating that the formation of smaller crystallites is disrupted. This shows that LPEI charge density can influence the thermal properties of the assembly. The higher the pH of LPEI, the more energy is absorbed by the material, indicating that interactions between polymers are stronger. These initial results show that LbL can be used to tune the secondary interactions within ionomer assemblies.

We have demonstrated that by using a mixed solvent THF–water system it is possible to make polyelectrolyte complexes

and LbL assemblies of EMAA and LPEI. In addition to the first reported LbL assembly with ethylene-*co*-methacrylic acid ionomers, thermal characterization shows that the blending of ionomer and polyelectrolyte changes secondary interactions within the material, including degree of crystallization, changing based on fabrication conditions. These materials have possible application as energy dissipating or damping materials that can act as a protective barrier to mechanical damage. Modulating the secondary interactions found within the ionomer morphology will be an important step forward in realizing this.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and additional analytical information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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