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Polyelectrolyte Coacervate Composites

Philip Schlenoff
THE FLORIDA STATE UNIVERSITY
COLLEGE OF ARTS & SCIENCES

Polyelectrolyte Coacervate Composites

By

PHILIP SAMUEL SCHLENOFF

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The members of the Defense Committee approve the thesis of Philip Schlenoff defended on April 23rd, 2015.

______________________________
Dr. Kamal Tawfiq
Professor and Chair
Department of Civil Engineering
Thesis Director

______________________________
Dr. Mykhailo (Michael) Shatruk
Associate Professor
Department of Chemistry & Biochemistry
Committee Member

______________________________
Dr. Justin Kennemur
Assistant Professor
Department of Chemistry & Biochemistry
Committee Member
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I. Abstract

 Polyelectrolyte complex coacervates change their characteristics when mixed with aggregates. These aggregates can be inert, like sand, or react on interaction with material in the polymer complex. Poly(styrenesulfonate) and poly(diallyldimethylammonium) complex coacervate (saloplastic) was mixed with both sand and cement systems and their physical and mechanical properties characterized to investigate potential as a construction and repair material. Compressive strength, rheology, packing, and hardening of the coacervate and sand mixture shows potential as a replacement for current driveway-repair products. The same studies of coacervate with sand and cement unveiled a superplasticizing property of saloplastic, and an ability to allow concrete to be cured underwater. Air curing the cement/saloplastic mixture produced a material with a compressive strength more than double that of normal concrete.
II) Introduction

Concrete is the single most used material on earth.¹ With a material so important comes the need for innovation; the pursuit of a stronger, smarter material with less environmental impact and increased strength. Concrete is not just used industrially, it makes up a large portion of the average consumer’s home, from stairways to driveways. The need for repairing old concrete matches the need for new, smarter concretes. The aim here is to address both of these issues by bridging the sciences of Mechanical Engineering and Polymer Chemistry. Over the last year, a series of polymer based admixtures has been developed that can address each of these problems thanks to “saloplastic,” a new polymer with unique properties.

Saloplastic, literally “salt plastic,” was first introduced in 2009 at the Florida State University.² Its potential applications range from the biomedical field to adhesives.³–⁷ Structure and strength of dry admixtures, where saloplastic is the binding agent have yet to be investigated. Saloplastic gains its unique properties from its composition of positive and negative polyelectrolyte chains, which complex on mixing.⁸ Adding salt, in this case the nontoxic potassium bromide (KBr), breaks the complexation between the positive and negative chains and softens the material.⁹ By washing out the salt, the positive and negative polymers are free to complex again. This cycle is reversible.⁹ In this project the negatively charged poly(styrenesulfonate) [PSS] (Figure 1) and positively charged poly(diallyldimethylammonium chloride) [PDAD] (Figure 2) are used and the saloplastic complex is termed PSS/PDAD or PEC.
Figure 1: Poly(styrenesulfonate). PSS, with sodium counterion

Figure 2: Poly(diallyldimethylammonium) chloride, PDAD
Scheme 1: Doping and complexation of PSS/PDAD. Polyelectrolytes are complexed from aqueous solutions of NaCl (left) and form ion-free, glassy complex when ions are washed out with water (center). Doping with KBr solution (right) transforms the complex into liquid-like coacervates.

Similar to how water condenses and hardens saloplastic coavervate, cement also uses water to “set” or “cure”. Exposed to water, Portland cement base reacts as follows:

$$2\text{Ca}_3\text{SiO}_5 + 7\text{H}_2\text{O} \rightarrow 3(\text{CaO}) \cdot 2(\text{SiO}_2) \cdot 4(\text{H}_2\text{O})_{(\text{gel})} + 3\text{Ca(OH)}_2 \quad \text{[Equation 1]}$$

to form a gel-like structure that slowly nucleates into calcium silicate crystals, which fuse over time to form the rigid backbone. Since this reaction is water-mediated, the longer the cement is exposed to water, the longer it “cures” (hardens). Concrete continues to cure long after it is set, over a scale of decades. Because pure cement-based concrete has a very low viscosity, and therefore a low workability (the two are related, workability being determined in-field being subjective to the project at hand), it is normally mixed with substances such as silica fume (fly ash), sand, and course aggregates such as rocks.
ratio of these aggregates to cement influences viscosity/workability and the overall compressive strength of the final material. In this project, play sand was used as the base with cement forming the crystalline structure holding it together. Various aggregates (ash vs. course material) which dramatically change the final strength, were not investigated here.

![Figure 3: Scanning electron micrograph of cement showing crystalline structure (reproduced from Wan et al. 2007)](image)

In 1971, the American Concrete Institute formally recognized and instituted regulations on a new wave of “polymer concretes.” These admixtures are usually a mix of epoxy resin and traditional Portland cement with filler, and show many advantages in the field. There are, however, many disadvantages to modern polymer concretes. For businesses, their cost and difficulty to manufacture presents a problem. In terms of environmental impact, they contain a mix of proprietary, sometimes toxic, chemicals that make them unsuitable to
use in locations where it could affect the local environment. Due to the non-toxic nature of PSS/PDAD complex and KBr, the only three components besides water and cement, it is believed that the substitution of epoxy resin by saloplastic will have a reduced environmental impact.

To make a product, the process of small scale to large scale manufacturing would have to be considered, i.e. the difficulty of mass polymer synthesis. In this area, the PEC synthesis by Shamoun et al. (2012) was significantly simplified, reducing the number of steps from eight to two and formulating a reliable “one-pot” method. The water content, viscosity (as it relates to salt concentration) and percent of dry PSS/PDAD complex to overall weight can be precisely controlled at the delicate phase-separation line using an equation from Wang et al. (2014). Its viscosity was used to estimate the ratio of wet polyelectrolyte complex (PEC) to sand, or to sand and cement, to control the viscosity/workability of the final mixture.

To eliminate the cement portion of the admixture completely, in case high-performance concrete repairs or precasts are not needed, a durable sand-polymer complex was formed. This is optimal for simple consumer driveway-repair projects, and may be adapted in the future as a filter due to its high porosity and polarity. A ratio of polymer to sand that gives good workability, is more durable, and lower cost than current competitor products is a viable solution to the problem of poor concrete repair products. This solution may also be stored wet over long periods of time, or powdered and transported where water can be added. Once spread into a crack, spraying water across the polymer hardens it ("cures") to form a permanent seal by removing salt ions that soften the material.

The mechanism for the hardening of this saloplastic and sand mixture is exceedingly simple. Its main components are all non-toxic and can therefore be a viable alternative in cases where a material without the compressive strength of concrete is suitable. A lack of
compressive strength may be compensated by a higher flexural strength.

III) Experimental

a) Materials

Poly(styrenesulfonate) was supplied as a 18wt% solution in water at pH 7 by AkzoNobel as Versa TL130 with a molecular weight of 200,000g/mol. The PDAD was from Ondeo-Nalco as a 26wt% solution (SD 46104) with a molecular weight of 400,000g/mol. Potassium bromide was purchased from Sigma-Aldrich and was ACS reagent grade ≥ 99% purity. Deionized E-Pure water (Barnstead) was used for all solutions and when adding water. Filtered Arena Natural Play Sand produced by Sakrete (from Home Depot) was used as the filling agent. All traditional Portland cement came from the Department of Civil Engineering at the Florida State University, generously provided by Dr. Kamal Tawfiq. The molds used for 1”x1”x1” were cut out of a fiberglass square tube purchased from McMaster-Carr. Two aluminum bars were drilled out to form the molds used in conductivity tests.

b) One-pot synthesis

In the paper by Shamoun et al., the first saloplastic synthesis was detailed.\textsuperscript{14} The first PSS/PDAD complexes in this project followed this synthesis as well. PSS and PDAD were mixed at a 1:1 charge ratio based on the polymer repeat unit. PSS and PDAD at 0.125M were mixed at a 1:1 molar ratio in the presence of water with 0.25M NaCl. This solution was stirred for thirty minutes, yielding a solidified white complex. This gooey substance, colloquially termed “cheese” due to its appearance mimicking that of feta cheese, was then scooped by hand into a separate container.
The precipitate was washed with at least three batches of water over seven days to remove any traces of NaCl. The intermediate result was a “cheese” like complex, free of salt, which could then be tuned to the desired viscosity by adding the appropriate amount of potassium bromide (KBr). From the solidified form it could also be dried (accelerated by microwave or vacuum oven) and ground into a fine powder, ready to be stored and used again with the addition of water.

\[
\text{Polyelectrolye } A/B^+(\text{complex}) + \text{Salt}^{+/-(l)} \leftrightarrow \text{PolyA}^-/\text{Cation}^+(l) + \text{PolyB}^+/\text{Anion}^-(l) \quad \text{[Equation 2]}
\]
In the new synthesis, the production of bulk, non-phase separated viscous saloplastic with 20% by weight PEC content was greatly expedited by eliminating some purification steps. The end product contains small amounts of sodium and chloride ion residues from the
PSS-Na and PDAD-Cl precursors. While this may influence the use of saloplastic in or near some cement structures that have steel reinforced bars (the bars rust in presence of chloride ions), this disadvantage can be negated by using stainless steel rebar.\textsuperscript{16}

The new method relies heavily on Wang et al.’s study of the continuum of polyelectrolyte complexes to obtain the \textit{coacervate} (“elastic liquid”) version of saloplastic.\textsuperscript{9} The elastic-liquid state is in the region C-D in the phase diagram in Figure 7 and occurs when PSS/PDAD complex is doped with approximately 1.8M KBr. The coacervate is optimal for mixing with aggregate or filler. To mix PSS-Na and PDAD-Cl directly into the coacervate liquid form, without any phase separation or need to decant excess water, the phase separation equation, Equation 3, of PEC:salt:water was used.

\begin{equation}
\text{H}_2\text{O wt\%} = 2.38\text{KBr wt\%} + 32 \quad \text{H}_2\text{O wt\%} + \text{KBr wt\%} + \text{PEC wt\%} = 100
\end{equation}

\textit{Figure 7: Phase separation for workable gel PSS/PDAD complex (reproduced from Wang et al. 2014)}\textsuperscript{9}

By controlling the total amount of water present during synthesis, as well as adding KBr and PSS/PDAD in the proper proportions as described by Equation 3, the coacervate is formed in two steps, the first of which is preparation and the second is mixing. This offers
huge advantages in scaling up production of ready-to-mix saloplastic coacervate using only weight percents. The amount of pure, dry PEC in the complex was 20%, as it was simple to prepare. If the total amount of saloplastic desired is 100%, this equation states that for 20% PEC there must be 14% KBr and 65% water. The leftover 1% is lost as sodium and chloride ion residue impurities, since this method does not wash these ions out of solution (Equation 2).

Figure 8: Setup (left) and product (right) of bulk one-pot synthesis
Scheme 2: Comparison of old vs. new syntheses

Rabih et. al 2012

1M solution of PSS-Na in 0.25M salt pH 7
1M solution of PDAD-Cl in 0.25M salt pH 7

Mix in 0.25M salt solution, stir 30 minutes

Complex
Precipitates

Decant liquid
Replace with DI water

Add KBr ~1.8M

Wait for PEC to partially dissolve

New synthesis (bulk)

Prepare
10.3 wt% PSS-Na
9.7 wt% PDAD-Cl

Mix 14 wt% KBr into PDAD-Cl

Mix PSS and PDAD in 65 wt% water

PEC @ 1.8 M KBr

Soft PEC Ready to mix

20% PEC
14% KBr
65% Water

Decant liquid
Dry and store (optional)
Add water

Scheme 2: Comparison of old vs. new syntheses
c) Polymer:Sand complex

At first, the polymer itself was considered as a building or repair material. However, when this polymer is saturated with water it swells significantly, then shrinks when it dries.\(^{17}\) To apply saloplastic, it needs to be in a workable state, containing both water and salt. After the water dries, instead of forming a polymer scaffold, the size of the applied patch shrinks altogether. To decrease this shrinkage, sand was used as an aggregate filler. Mixing saloplastic and sand forms what is known as an “admixture” or “coacervate:sand,” a mix of particles in a gel-phase material. It also provides structural integrity which increases compressive strength.

i) Ratios/packing

Considering the large proportion of water needed to form a workable product, the shrinkage due to drying was the biggest problem. Also, the more sand added, the weaker the overall polymer bonding, given there is less polymer to hold the aggregate together. Density differences between the two materials led to excessive phase separation of sand at the bottom and a need to mix the product every time it was worked with. It further phase separated as it set, a problem which could lead to a gradient in strength as the polymer diffuses towards the upper portion and the sand sinks down.

At a certain ratio, however, the PEC coacervate (PECoA) reaches a balance of separation in which it is equally distributed throughout the sand phase and is just enough to fill the voids between packed sand particles. Ratios of 1:1 through 1:10 of dry polyelectrolyte complex (PEC) to sand were investigated. The pure polymer/sand admixture ratios are in terms of pure polyelectrolyte complex to sand weight:weight. Since the final method of one-pot synthesis produced a PEC coacervate with \(\sim20\%\) PSS/PDAD complex (the rest being
water and KBr), a “1:1” ratio of dry PEC to sand means that 50 grams of PEC coacervate was mixed with 10 grams of sand giving 10 grams “dry” PEC to 10 grams dry sand.

After mixing 1:0, 1:1, 1:2, 1:4, 1:6, 1:8, and 1:10 PEC:Sand samples in scintillation vials, they were placed vertically on a bench and allowed to settle over a period of three days. Pictures were taken of these samples after the three day period, and the proportion of phase separation (visible PEC separated from the sand) was calculated using ImageJ software (from http://imagej.nih.gov/ij/) analysis to plot height of the separated phase over height of the total sample.

![Figure 9: Solid and liquid-phase separation of PEC:Sand at different ratios](image)
ii) Conductivity

Just as traditional Portland cements cure with the addition of water to form crystal structures, the polymer-sand aggregate cures with the addition of water by washing out salt “doping” agents, in this case KBr. With the positive potassium and negative bromide ions washed out, the opposite charges on the polyelectrolytes PSS and PDAD form tight ionic bonds (seen in Scheme 1). Once all the doping agents have been washed out of the PEC, in theory there will be no more changes in the material and it is fully cured.

Small differences, however, do arise when the dry and hardened polymer-sand complex has not been fully washed with water. Any residual KBr or NaCl impurities will, when hydrated, overcome some of the charges in the crosslinked state and reduce the compressive strength because the PSS and PDAD separate in proportion to how many available counterions there are to “dope” the polymer.

Diffusion, or washing, of salt from the PEC:Sand material was probed by measuring...
the conductivity, which is proportional to salt concentration, of a known volume of water containing PEC:Sand complex in a mold of known depth. Only one side was exposed to the water (therefore allowing salt diffusion only out of this side), approximating the “one-sided plate model” of diffusion described in the Discussion section.

![Image of aluminum molds](image)

*Figure 11: Aluminum molds used for conductivity experiments*

The temperature was held constant and a conductivity probe (Thermo Scientific Orion 3-Star) was dipped into the apparatus containing 150 mL of nanopure water. At the same time, the aluminum mold of known depth, filled with a sample of known volume, was dropped into the apparatus and a stir bar placed inside to ensure good mixing. As the sample lost salt concentration, the probe recorded the changes in conductivity of the solution and output the reading every 15 seconds into a raw text file on a computer. Using Excel, the time vs. conductivity was plotted and manipulated to extrapolate diffusion data about the system.
The viscosity of the pure PEC, and PEC:Sand mixture with increasing amounts of sand, was studied at the Ramakrishnan lab at the National High Magnetic Field Laboratory using an Anton Paar MCR 302 Rheometer with a parallel plate head (model PP25/S). Tests were conducted by oscillating the parallel plate pressing down on the sample.

For pure PEC, only one measurement “sweep” was conducted, strain % vs. stress (MPa), in order to make sure that the fluid had viscoelastic (viscous and elastic) properties typical of polymer admixtures.\textsuperscript{18,19} For PEC:Sand mixture, the ratios 1:1, 1:3, 1:5, 1:8, and 1:10 all went through three different oscillating sweep intervals: the first keeping oscillation
frequency steady, the second increasing the oscillation speed from 0.1 to 10 Hz, and the third increasing the strain from 0.1 to 50% (increasing the distance the plate oscillates). The values output during sweeps were Storage Modulus ($G'$), Loss Modulus ($G''$), Strain (%), and Frequency (Hz). All were done at 25 Celsius.

![Rheometer setup (left) and parallel-plate geometry tip (right)](image)

*Figure 13: Rheometer setup (left) and parallel-plate geometry tip (right)*

**iv) Compressive Strength**

Arguably, the most important characteristic of this product is its final compressive strength. Something that will compete with current market products has to be able to withstand the weight of vehicles or pedestrian traffic over its repair area. Tensile strength will eventually play a factor in efficacy of the product, but the most important industry standard is compressive strength in MPa (Megapascals) or PSI (Pounds per Square Inch).

For the PEC:Sand mixture, two different sizes of molds were made. One was a
2”x2”x2” cube, the concrete industry standard\(^1\), and the others were 1”x1”x1” cubes cut from fiberglass and split down the middle. Because complete salt diffusion out of the 2x2” cube took so long, the majority (3/4) samples measured were in the 1”x1”x1” mold form. These molds were filled with 1:10 PEC:Sand mixture, and submerged in water. To prevent the bottom of the complex from sticking to the bottom of the container, the molds were first sprayed with water and then quickly flipped into the container; the spraying formed a skin that would not stick to the container bottom.

*Figure 14: 2”x2” molds used for compressive strength tests*
To ensure complete salt diffusion, the molds were left underwater for extended periods of time (1-2 weeks). After the top layer had solidified, each mold was flipped and left for another day, a process that was repeated until it felt hard to the touch. The molds were then removed from the water container and left to dry. Drying under the oven or in a vacuum led to the formation of air bubbles, so drying was done at room temperature.

Eventually, the molds solidified and the cube-shaped sample was separated by pulling
the sides of the mold apart. These samples were tested at the Department of Civil Engineering Materials Lab at Florida State University using a Forney compression machine to evaluate compressive strength, which is the “failing point” where the PEC:Sand cube loses structural integrity. The output in pounds was converted to PSI and then MPa.

![Figure 17: Setup (left) of compression tests with 2”x2”x2” cube of PEC:Sand and compression machine (right)](image)

d) Polymer:Sand:Cement complex

For industrial applications, including fracking pipes, buildings, or structures that need high-strength building material, the PEC:Sand mix alone was not believed to provide a sufficiently high compressive strength or sufficiently fast hardening time. The process of hardening while cement crystals form due to a reaction with water is known as “curing.” Cement, in bulk, has a faster curing time than saloplastic complex, reaching 75% strength within seven days and normally plateauing around 28 days.¹ This project evolved to have a
secondary focus on a saloplastic admixture due to the prevalence of polymer-modified
concretes in industry$^{13,19,20}$ and the ease of incorporating PEC coacervate into a Sand:Cement
mixture.

i) Ratios and Curing

The cement curing reaction (Equation 1) provides a product with the highest
compressive strength when the water:cement ratio is 0.35 to 0.45.$^1$ In mixing the polymer
complex with sand and cement powder, this same ratio was achieved. Since ~65% of the
polyelectrolyte complex solution is water-based (using the new synthesis method), Using a
0.66 ratio the of liquid PEC to cement powder (0.65*0.66) gives a 0.43 water:cement ratio,
the rest being the salt and pure PSS/PDAD. This falls comfortably within the 0.35-0.45 range
desired. A major question was whether the PEC would surrender the water to the cement as it
cured. Optimally, the PEC would be able to provide the exact amount of water required to
cure the concrete and minimal shrinkage would occur.

Because cement shrinks while curing$^1$, similar to saloplastic, adding a neutral
aggregate such as sand helps improve the overall structural integrity of concrete. The
aluminosilicate-based sand particles easily incorporate into the calcium silicate cement
crystal structure. Two versions of a cement building/repair material were prepared: a control
with a typical combination of cement, water, and sand (also known as mortar) and an
experimental combination with cement, sand, PEC coacervate. The water in the PEC
coacervate was the source for the cement curing reaction in Equation 1.

Most tests were done on a 1:2:1.5 weight ratio of PEC coacervate:Sand:Cement,
($\text{PECoA:Sand:Cement}$) providing the 0.43 water:cement ratio and containing sand to act as
the shrinkage-reducing filler. It is important to note that, unlike experiments on the PEC:Sand
product alone, the ratio of polymer described in the cement tests is in terms of total weight of
the liquid solution, not just dry PEC. Here, a 1:2 ratio of PECoA:Sand is similar to the 1:10 PEC(dry):Sand described in the previous sections. There were differences in curing procedure for different samples, including curing underwater, air-drying, sealed-molds, and mixtures of the three.

Two types of samples were air-cured, which means letting the mixture sit while cement formed crystals, with no enclosure or barrier preventing water from evaporating during the curing procedure. One type of sample was cured in an enclosed-mold, preventing evaporation of water, then split into two further categories of subsequent exposure to water or not. The most common types of samples were poured in 1”x1”x1” or 2”x2”x2” cube molds and placed under water for up to seven days to cure while losing salt to solution and “curing” the saloplastic in parallel. The last type of sample was kept underwater during its entire lifetime until tests were performed, to mimic this product if it were applied to, or used as, an underwater structure. Controls of all these samples used only sand, cement, and DI water in the initial mix as opposed to getting the water content from the liquid PEC solution.

Figure 18: PECoA:Sand:Cement 2”x2”x2” molds curing underwater
ii) Rheometry

The same rheometer at the National High Magnetic Field Laboratory was used to probe the properties of a 1:2:1.5 mixture PECoA:Sand:Cement compared to a control of 2:1.5 Sand:Cement with added water to complete the cement reaction. Only a time vs. storage modulus sweep is shown in the results because of the complexity in understanding the nature of this system’s viscoelastic properties while the cement is curing at the same time. First, the appropriate amounts of sand and polymer were mixed, then the cement powder was added and the material immediately tested.

iii) Compressive Strength

To measure the compressive strength of the PECoA:Sand:Cement product, both square and cylindrical molds were made with the 1:2:1.5 ratio mix. Because the compressive strength only relies on surface area, the shape of the mold did not matter as long as it would fit in the machine. Here, the same Forney compressor was used to measure PSI and MPa.
Figure 20: Cured disk-mold (left) and compression test on 1”x1”x1” cube (right)

Five different types of cement-polymer admixture samples were crushed and compared. The control was a literature-obtained average value for the compressive strength of industrial concrete. This was compared to several 1:2:1.5 mixes of PECoA:Sand:Cement, including:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nickname</th>
<th>Enclosed</th>
<th>Water Exposure</th>
<th>Cure Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PSC UW</td>
<td>No</td>
<td>Immediate</td>
<td>Underwater (7days) Air (30 days)</td>
</tr>
<tr>
<td>2</td>
<td>PSC, W</td>
<td>Yes</td>
<td>After 3 days</td>
<td>Enclosed (3 days) Underwater (7 days) Air (23 days)</td>
</tr>
<tr>
<td>3</td>
<td>PSC</td>
<td>Yes</td>
<td>None</td>
<td>Enclosed (3 days) Air (30 days)</td>
</tr>
</tbody>
</table>
Each cube or disk was allowed to cure for more than 28 days, the industry-standard time when the compressive strength is plateauing.\textsuperscript{1} For the disks, the compressive strength was translated into PSI using the surface area $\pi r^2$. Conversions to MPa used the factor 145 PSI = 1MPa. When the samples broke, they were collected and inspected to make sure that nothing out of the ordinary had occurred, and their fracture pattern evaluated by Mr. Squillacote in Civil Engineering to look for anomalies compared to traditional concrete fracture patterns.

**IV) Results and Discussion**

**a) One-Pot Synthesis**

This method provided a solution that had equivalent composition and properties to the more complex procedure. After drying, the water concentration was calculated to be 65%, and conductivity results indicate that it effused salt normally. The total PEC of 20%, KBr of 14%, and water of 65% indicated a sodium chloride impurity of approximately 1% by weight, a result of speeding up the bulk synthesis by eliminating the purification step.

**b) Polymer:Sand Complexes**
i) Ratios/Packing

**Figure 21: Phase separation vs ratio of PEC:Sand.**

It was important to study phase separation in the product to determine the tradeoff between workability (less sand makes it less viscous), compressive strength, and storage capabilities for different ratios of polyelectrolyte complex mixed with sand. The results for volume separation in Figure 21 were plotted against the ratio of PEC:Sand, and reached a qualitatively acceptable minimum (no phase separation) around a fraction PEC = 0.09, or 1:10 PEC:Sand in Figure 9 (using the dry weight of PSS/PDAD complex as convention).

The point of no phase separation was modeled with a manually fit trendline to be around 0.07 fraction PEC. This is closer to a 1:12 ratio, but 1:10 was used because of the tradeoff between increasing the amount of sand decreasing the workability of the final product. At 1:10, the ratio calculations are simple, and the volume percent separation is lower than 10%. It does, however, result in the need to stir the final product slightly to mix in the remaining < 10% PEC if stored for long periods of time where it has a chance to settle.
ii) Conductivity

Samples of 1:10 PEC:Sand packed into the molds in Figure 11 were immersed in water to allow the salt to diffuse out. A stir bar ensured that mass transfer of salt was limited by diffusion in the complex to the surface of the complex. Conductivity versus time for the various samples was recorded.

*Figure 22: Depths 1.79mm (red), 3.0mm (blue), 4.3mm (yellow), 6.91mm (green) and 9.09mm (brown) underwater conductivity over time*
Deeper samples containing more product (and inherently more KBr) took longer to plateau; the point where most of salt had diffused from the sample. Figure 22 shows the readings from the conductivity probe in 150 mL water with each sample, and a close-up of the first few minutes indicates that each sample has a linear (and similar) diffusion speed. At first, this is known as “semi-infinite diffusion,” where the diffusion front has not encountered a physical boundary. As each sample loses enough salt the diffusion front reaches the bottom of the sample (“finite diffusion”), less salt diffuses out, and the conductivity/concentration stabilizes. This is recognizable in Figure 22 and Figure 23 where the plateaus occur further and further away from \( t = 0 \).

Using a calibration curve of KBr concentration versus conductivity, the conductivity in \( \mu \text{S/cm} \) was translated into salt concentration. This gives a similar perspective on the amount and rate of salt diffusion, as well as allowing prediction of how much salt is left. To find this concentration of KBr, the measured conductivity was divided by the slope of the
calibration curve, 139,275. Because the volume of each sample (height of a cylinder), the
density of the 1:10 product, and the percentage of salt by weight are all known, the grams or
moles of KBr in the solution and remaining in the sample can be predicted given the solution
conductivity.

In addition to allowing the visualization of when the complex has been completely (or
nearly) crosslinked by losing salt, performing a study of depth vs. loss of salt concentration,
over a variety of depths, provided a **diffusion coefficient** that can be used as a predictor of
how long it will take for a 1:10 PEC:Sand mold or structure will take to completely wash out,
given the height or depth, “h” of the sample.

In these experiments, the “plate” model of diffusion was fitted against experimental
values. The plate model allows a generalized description of outward diffusion from a one-
sided area. This model was chosen because if the mixture were used as a driveway crack
repair material, washing the freshly covered crack only allows diffusion out of the top of the
repair spot.

The fraction \( f \) of material which has diffusion out of (or into) a plate from one side,
which includes the initial (semi-infinite) and later (finite) portions is given by:\(^{21}\)

\[
f = \frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ - \left( \frac{2n + 1}{h} \right)^2 DT \right]
\]

or
\[
f = 1 - \frac{8}{\pi^2} \left( \frac{1}{1} \exp \left[ -\frac{(1)\pi^2}{h^2}Dt \right] + \frac{1}{(2 + 1)^2} \exp \left[ -\frac{(2 + 1)\pi^2}{h^2}Dt \right] \right) \\
+ \frac{1}{(4 + 1)^2} \exp \left[ -\frac{(2n + 1)\pi^2}{h^2}Dt \right] \ldots \right)
\]

This was done for \( n = 1 \) through \( n = 6 \), at which point further summation of the series contributed little to the fit curve. The diffusion coefficient, \( D \), is the only adjustable fit parameter and is chosen to most closely match the data. The diffusion coefficient is the rate that salt transports out of the sample, and is given in \( \text{cm}^2/\text{s} \).
The fits above use $D = 1.5 \times 10^{-6}$ cm$^2$ s$^{-1}$. This diffusion coefficient was chosen because it matched the best when all five sample depths were compared. The observation that the fit matches well for all depths indicated that this diffusion coefficient can be extrapolated.

Figure 24: Diffusion from a plate fits with $D = 1.5 \times 10^{-6}$ (red). Experimental (blue)
to other depths and that the 1:10 PEC:Sand product acts as a nearly ideal diffusion controlled system. There is slight variation in the sample with depth \( h = 6.91 \text{mm} \), which is possibly due to the polymer portion of the product hardening as the salt effuses from the sample. This distances the ideal-fit diffusion value at shorter time, but all converge to the experimental value towards \( f = 1 \). At short time, for \( f < 0.7 \), the full equation above can be approximated by diffusion under semi-infinite boundary conditions:

\[
    f = \frac{4D\tau^{1/2}}{\pi h}
\]

The time for a slab of PEC:Sand of thickness \( h \) to harden to a 0.7 ratio can be approximated by:

\[
    t = \frac{h^2}{2D}
\]

Where \( D = 1.5 \times 10^{-6} \) and the only unknown is the height, \( h \), in cm of the applied area. This predictability is a key factor in understanding the cure time for industrial applications.

### iii) Rheometry

Workability in the field is largely determined by the viscosity of the concrete or polymer admixture, as analyzed by rheometry with a variable oscillation frequency.
In the first sweep for testing the rheometric properties of PEC:Sand (here, the PEC is still a liquid coacervate), the storage modulus $G'$ remained constant for all samples with time. It increased with an increasing amount of sand to coacervate, which is expected as the storage modulus is closely related to viscosity and elasticity (hence, a “viscoelastic” material which has both viscous and elastic properties). A higher storage modulus in the higher PEC:Sand ratios indicates that this material is much more difficult to deform. For all samples, $G'>G''$, indicating that the viscoelastic material “acted” more like a liquid than a solid. It is interesting to note here that there is a large gap between the 1:3 and the 1:5 samples, indicating a jump in modulus as the sand particles start to interact rather than being suspended separately in the coacervate.
Figure 26: Storage modulus versus frequency from 0.1Hz to 10Hz for PEC:Sand samples

As frequency was varied from 0.1Hz to 10Hz, the lower ratios showed a linear increase in storage modulus while the 1:5, 1:8, and 1:10 ratios remained steady. Frequency dependence is a common characteristic of viscoelastic materials, and this shows that the material loses its viscoelastic properties with an increased amount of sand.\(^\text{18}\)

Figure 27: Stress vs. Strain shows that, for the 1:5 - 1:10 samples, the linear viscoelastic response regime is less than about 5%
Figure 28: Strain vs Storage Modulus shows a failure of the linear viscoelasticity for some samples

The last sweep compared strain to stress and storage modulus. There was a loss of structure when the strain was above about 4%, indicating that this is the yield strain where the head plate is slipping on sand particles instead of smoothly rotating/stretching the PEC:Sand on the sample plate. Linear regions in the shear strain vs. G’ graph further identify this material as “viscoelastic.” The modulus of each sample, and through that the viscosity, is obtained by manipulating data in the stress vs. strain graph, but it provides a rough and probably inaccurate value.

iv) Compressive Strength
The sand-cement composite cubes were approximately 2:1.5 Sand:Cement, with 45wt% water added to cure the cement at optimal water:cement wt/wt ratio, stated to be 0.35-0.45 in the literature. A compressive strength of around 15 MPa (correlating to 2175 PSI) was achieved reproducibly as the control. The PEC:Sand cube in which a dry PEC 1:10 wt/wt ratio was used provided a reproducible ~5.8MPa of compressive strength (841 PSI).

It was already hypothesized that the ionic bonding in polymer when it hardens would be weaker than the crystalline cement structure when it cures. However, in the PEC:Sand cubes, 91% of the dried material is pure sand, a cost effective and available filling agent. Thus, adding only 9% dry PEC to sand as a binder can provide a compressive strength of over one-third that of its cement-based cousin. An average of 841 PSI is enough to prevent deformation if a car were to drive over a filled crack of normal width and depth. It is stronger than the most popular Sakrete polymer-based driveway repair product, which could not be tested due to its near-instantaneous deformation under low pressure, i.e. by squeezing it in...
one’s hand.

Figure 30: Interior structure of a dried PEC:Sand cube

Figure 31: Close-up of the interior of a dried PEC:Sand cube
Light microscopy indicated that the polyelectrolyte complex, when salt has been washed out and the PEC dried, forms a scaffolding between the sand particles that holds them together and give compressive strength. The interior and surface are both porous. No other binding mechanism was theorized or expected.

c) Polymer:Sand:Cement Complexes

To assess what saloplastic might have to offer to the technology of cement new polymer composites were made, where the PEC acts as a polymer viscosity-modifying admixtures (VMAs). Saloplastic acts as a superplasticizer for concrete; a material that decreases the viscosity of the cement composite to increase workability, and in some cases, improve compressive strength. Due to the wide prevalence of these compounds, particularly polymer-based materials with high toxicity and high costs, saloplastic was investigated as an admixture to traditional Portland cement.
i) Ratios and Curing

Regardless of ratio of PEC or sand to cement powder, the cement admixture starts to cure immediately due to the water content of the PEC in liquid form (Equation 1). After 7 days, the cured material should have about 75% of its total compressive strength, and within 28 days this value begins to plateau. The ratio of 1:2:1.5 was used because the polymer ratio provided an optimal water content (0.43) for the cement powder to react with. There is possibly an interplay between polymer and cement, i.e. the polymer could “feed” the cement water as the cement cures, while the PEC either retains salt (air-cured) or diffuses it to the surroundings (water-cured). This remains to be studied.

ii) Rheometry

![Figure 33: Storage modulus of 1:2:1.5 PECa:Sand:Cement (blue) and 2:1.5 Sand:Cement: with water added control (red)](image)

Due to the complexity of this system, much rheometric data was gathered (as it was for the PEC:Sand complex) but analysis proved to be more complex and most results are not included here. One important finding, however, was the average storage modulus of the PECa:Sand:Cement admixture, around 10,000 Pa upon mixing water with cement, and its
comparison to the same system without polymer. The control, a typical mix of sand, cement, and water, had a modulus $\sim 10^{2.5}$ higher than the system with PEC included (see Figure 33). This indicates that the polymer indeed acts as a plasticizing agent, or an admixture that lowers the viscosity of concrete in its workable state.

iii) Compressive Strength

![Figure 34: Concrete admixture compressive strengths, see TABLE 1 for details](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nickname</th>
<th>Enclosed</th>
<th>Water Exposure</th>
<th>Cure Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PSC UW</td>
<td>No</td>
<td>Immediate</td>
<td>Underwater (7 days) Air (30 days)</td>
</tr>
<tr>
<td>2</td>
<td>PSC, W</td>
<td>Yes</td>
<td>After 3 days</td>
<td>Enclosed (3 days) Underwater (7 days) Air (23 days)</td>
</tr>
<tr>
<td>3</td>
<td>PSC</td>
<td>Yes</td>
<td>None</td>
<td>Enclosed (3 days) Air (30 days)</td>
</tr>
<tr>
<td>4</td>
<td>PSC air cured</td>
<td>No</td>
<td>Immediate, For 1 minute</td>
<td>Air (lifetime)</td>
</tr>
<tr>
<td>5</td>
<td>PSCW</td>
<td>No</td>
<td>Immediate</td>
<td>Underwater (lifetime)</td>
</tr>
</tbody>
</table>

*Table 1: Samples used for PECoA:Sand:Cement compression tests*
The “concrete” label in Figure 34 is a literature value for the average compressive strength of Portland cement and fine/course admixture concretes.\textsuperscript{1} It is considered the “average” compressive strength of industrial concrete, and all samples were compared to this average value to determine their efficacy.

“PSC UW” indicates a PECoA:Sand:Cement mix immediately placed and cured underwater. This produced a material with a compressive strength nearly identical to traditional concrete. The benefit is that saloplastic acts as a superplasticizer so this mix is much more workable than normal wet cement with a similar amount of sand, but still retains the same compressive strength after application and curing. Also, for underwater curing, a cement powder and sand admixture would suffer from runoff and other decomposition problems, whereas the PECoA:Sand:Cement composite forms a “skin” as soon as it is submerged, containing all the concrete components.

The PSS/PDAD polyelectrolyte complex system does, however, swell on contact with water while the salt is leeching out. This swelling is minor when PEC is combined with sand, but may be the reason that PECoA:Sand:Cement admixtures cured underwater are not as tough as when they are cured in an enclosed environment or just in the air. The silicate-based crystals may have trouble forming as tight of a matrix around the swollen polymer.
This impediment to curing would explain the higher compressive strength of the next three samples, cured in an enclosed petri dish (to prevent evaporation) or in the air. Each was around 75MPa, or just under 11,000 PSI. Note that this is more than twice the average compressive strength of the traditional concrete admixture value. These high values are
expected to be from polymer losing water to the cement and drying whilst integrating itself within the cement-based calcium silicate crystal structure, providing additional support.

![Figure 37: Cement and sand (left) cured internal structure vs. PECoA:Sand:Cement (right) showing PEC integration](image)

After the cement has cured for 3 days, it was placed underwater, washed, and maintained its compressive strength as shown by sample “PSC, W” in Table 1. At this point, the cement has already reacted with enough water to form a crystalline structure and integrate the polyelectrolyte complex as an additional structural agent. Whether or not the salt diffuses out of a hardened cement sample has to be studied. This material was reflective and marble-like before placing underwater, and reverted to a dull concrete finish after washing, also theorized to be due to PEC content.
The sample labeled “PSC air cure” was cured in a petri dish with the top open, and sprayed with water for one minute. The skin visibly formed (as observed by a color change) and could help protect the concrete from losing water content as it dries, a common problem in industry in which the cement has to be covered or fed water while it cures to compensate for evaporation. There was some salt which leached out and dried on the surface, but after this salt was wiped off the compressive strength compared to the enclosed samples. A control admixture of sand and cement was air cured, but this sample cracked due to shrinkage from water evaporation. The curing behavior and high compressive strength of the enclosed PECoA:Sand:Cement mixture confirms that the polymer coacervate provides the water content for the cement reaction in Equation 1 to occur, and this combination also increases compressive strength to higher levels than the control.

Lastly, a sample was cured and kept underwater for more than 28 days, then crushed while still wet. It retained similar compressive strength to the sample cured underwater then dried, indicating that similar cement crystalline structures had formed, but were reduced in
integrity by the swollen polyelectrolyte portion of the mixture during the curing process.

Figure 39: Closeup of the surface of PECoA:Sand:Cement cube which spent its lifetime underwater, shows little to no surface defects for underwater curing.

V) Conclusion and Future Work

There is clear promise for both the PEC:Sand coacervate and PECoA:Sand:Cement admixture in industry. The compressive strength of the PEC:Sand mixture and workability could allow it to be effective as a repair product, and the saloplastic itself to be used as a binding product for other admixtures. Conductivity has shown that the PEC:Sand mixture acts and hardens in a predictable manner when exposed to water. As a test, this mixture was applied to a crack in a driveway and watched over a period of several months, in which it retained its integrity and showed no further cracking. Coloring agents have also been mixed in which change the shade of the product to suit the need of the consumer.

In a more demanding commercial application, the PECoA:Sand:Cement product has shown itself to be a formidable underwater concrete building material. In air, its compressive strength rivals that of some epoxy-based admixtures and may be useful as a replacement in certain scenarios. Industry experts should be given this material to use and their feedback is
equally important as the quantitative characteristic studies.

Future work will, in all likeliness, focus on the PECoA:Sand:Cement admixture, as there were several interesting properties discovered (some by accident) while working with the material. The skin that forms allows the admixture to retain its shape much better than normal after being poured, so application towards new cement that conforms to its position rapidly is possible. It also forms a non-stick putty when exposed to water and molded in the hands, which can then be shaped and squeezed into cracks or used as a toy. The shimmer of enclosed PECoA:Sand:Cement samples makes the cured concrete look like marble, towards use as a cheap indoor marble replacement. The self-curing, porosity, and diffusion coefficient of the material should also be investigated. Different ratios of PECoA:Sand:Cement should be used and their properties characterized, as this changes the viscosity of the workable form and, if successful, adds a whole range of applications to a commercial product. Once different forms for different uses are created, field application studies and application methods should be developed, and the synthesis further scaled up to meet the demands of a growing economy which requires a new generation of smart concrete.
Figure 40: Applying, washing, and drying product in the repairing a driveway crack with PEC:Sand

Figure 41: Viscosity determines how deep the product seeps into a crack, as well as nozzle size for application (shown is a prototype applicator)
Figure 42: PECoA:Sand:Cement applications. In order (from top left): crack repair, making molds, marble imitation, and workable non-stick putty
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VII. References


