Alicia Tosdal

There was no big moment for me – the epiphanic one that screams science is the future. My parents had one for me. According to my mother, it was one Christmas many years ago when I essentially stole my father's Christmas present: a deluxe building set. That was when they knew. To be quite honest, I don't even remember the conscious decision to go into science. I had always enjoyed the sciences and yet I also enjoyed reading and drawing. I decided on engineering when I took a drafting class in the tenth grade and chemistry followed the next year. I haven't regretted it thus far. Regardless, I have to admit that I still haven't given the *building set back to my dad.*

Alicia is studying Chemical and Biomolecular Engineering at Georgia Institute of Technology. After she graduates in 2009, she plans to get a graduate degree in materials science and engineering before doing industry research.

Directed Printing of Self-Healing Capsules through Dielectrophoretic Force

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Abstract

Dielectrophoretic force applied by a non-uniform electric field over the sample manipulates self-healing capsules into a distinct monolayer. Suspended in distilled water with controlled pH levels, long chains form. The chains form on the lowest level, spanning the shortest distance between the two electrodes. Capsule concentration by weight of less than 2wt% has been shown to produce chains spanning the electrodes under an alternating field of 75V/cm with a frequency of 5kHz. Averaging 2.1μm, the chains cure in proportion to the diameter of the various capsules in the chain. When suspended in polymer, dispersion is difficult due to the increased viscosity. The nanocapsules form large aggregates instead of dispersing as individual capsules. The capsules chain within the aggregates as a result.

Introduction and Background

Self-healing with dicyclopentadiene (hereafter DCPD) occurs via ring-opening metathesis, a chemical reaction that allows mass polymerization in the presences of a catalyst. DCPD, encapsulated with poly (urea-formaldehyde) by in situ oil-in-water-emulsion reactions, is an organic monomer with two different conformational isomers. *Exo*-DCPD is the more reactive of the two isomers, but *endo*-DCPD is alternatively more stable. Likewise, while the *exo* isomer makes non-uniform shell walls, the *endo* isomer generates more uniform shell wall thickness. Because of the instability of the *exo*-DCPD, the resulting capsule shells form irregular spheres. As seen in Figure 1, the shell wall is non-uniform in shape and often has irregularities in thickness, causing leakage. While the *exo* isomer is more reactive, it exists in significantly smaller quantities than *endo*-DCPD. As a result, use of the *endo* isomer is more prevalent. The encapsulated microcapsules of DCPD are suspended in an epoxy matrix with the catalyst. The catalyst used for the reaction is Grubb's catalyst. In the case that the epoxy matrix is cracked, the crack may breach the shell of a capsule. As the crack propagates through the epoxy, the dicyclopentadiene leaks from the cracked shell and reacts upon contact with the Grubb's catalyst. This reaction fills the crack generated in the epoxy matrix and promotes self-healing.[1]

When the capsules are suspended in the epoxy matrix, they are rarely suspended uniformly. This non-uniform dispersion leads to unequal healing in the event that cracks appear under stress. Capsules often appear as aggregates in the epoxy. When studied under an electric field, silica particles with a diameter of 1μm have been found to form a uniform monolayer.[2] This monolayer is formed through dielectrophoresis (DEP), more specifically dielectrophoretic force. DEP force is a force exerted specifically on a dielectric particle when it is subjected to a non-uniform electric field. DEP force does not require the particle to be charged. In the case of the encapsulated DCPD, the microcapsules carry a net neutral charge. Under the non-uniform field, however, the capsules undergo a net dipole moment. The dipole moment causes one side of the capsule to gain a positive charge facing the

negative electrode. The other side of the capsule carries a net negative charge equal in magnitude but opposite in charge to the positive side. Because the two sides of the capsule have opposing charges, the microcapsule still has a net neutral charge once the field is gone. The capsule, once charged, attracts the oppositely charged side of the next closest capsule, thus lining up according to electric field lines.[3-5] The size of the dipole moment, sign and magnitude, can be determined through the Clausius-Mossotti function.[6,7]

$$K(\omega) = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \text{ where}$$

$$\varepsilon^* = \varepsilon - \frac{j\sigma}{\omega}$$

Where ω is the angular frequency of the applied field, σ is the conductivity, ε_p and ε_m are the dielectric constants of the particles and the media respectively.

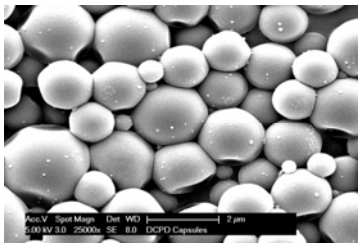

Figure 1: ESEM photograph of *exo*-DCPD nanocapsules averaging 2.1µm in diameter. The deformed poly(urea-formaldehyde) shell walls demonstrate the non-uniformity present with the *exo* isomer.

The average size of capsules is 2.1 µm in diameter with a standard deviation of 1.15µm. The mode produced is a diameter size of 1.5 µm. The overall range of microcapsule size runs from approximately 300nm to 10 µm. This is a result of the oil-in water emulsion used to create the DCPD microcapsules. Because of the irregularity in sizing, the dielectrophoretic assembly of the capsules into lines is increasingly difficult, more so than uniformly sized silica capsules. The emulsification process used to make the microcapsules does not exhibit great control over the resulting sizes of capsule produced. The range of capsule sizes produced can be seen in Figure 2.

The smaller the average size of the capsules in the electric field, the more sensitive the capsules are to field strength and distribution. Larger microcapsules react more slowly to lower field strengths than smaller capsules will. Because the capsules are smaller, a reduced amount of force will move the capsule the same manner as the larger capsule. Likewise, the amount of DEP force required also depends upon materials used in synthesis as well as the medium. More polarizable shell material will undergo dielectrophoresis more easily than nonpolar shell materials. Likewise, the medium the capsules are suspended in is also subject to field strengths and variations. When suspended in distilled water, if the electric field strength becomes too high water undergoes electrolysis, creating an air pocket inside the suspension.

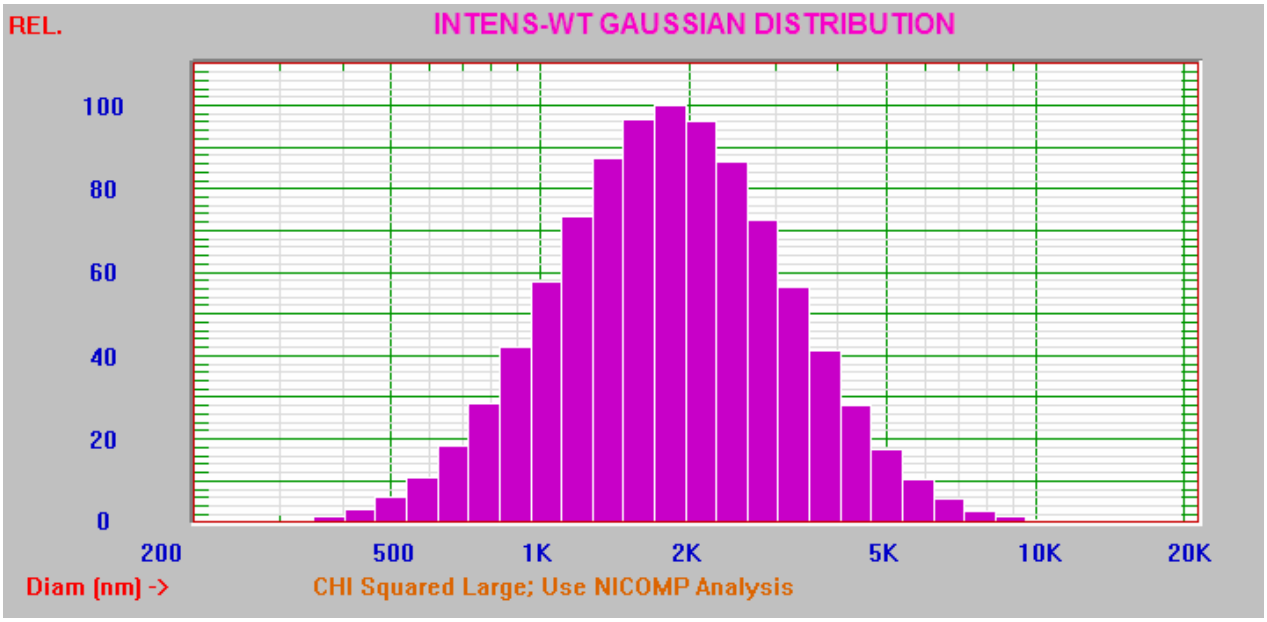

Figure 2: NiComp 388 distribution of capsule size. Microcapsules were measured as vesicles rather than solid particles. The mean distribution shown above is 2118.4nm, or 2.1184μm. The standard deviation for size analysis is 1152.4nm. The vertical axis describes the relative quantity of each size range while the horizontal axis describes the approximate diameter of the capsule. Most microcapsules range from approximately 1.5μm to 2.1μm. The coefficient of variation for this sample is 0.544.

Approach

Materials

DCPD microcapsules were suspended in distilled, deionized water and then placed upon a gap in between two planar vapor-deposited gold electrodes. The alternating, non-uniform field came from a function generator hooked in parallel to an amplifier. A voltmeter is likewise added in parallel in order to monitor field strength across the suspension sample. The various concentrations of separate samples are recorded by Thermogravimetric Analysis (TGA). Heat is ramped from 25 °C at a rate of 10 °C/min until 600 °C. The boiling point of water is 100 °C and DCPD microcapsules boil off at approximately 250 °C. The approximate concentration of microcapsules can be recorded by the plateau between 100 °C and 200 °C. See Figure 6.

Preparation

DCPD microcapsules were created by encapsulating DCPD monomer (15.5% w/v) in an *in situ* emulsification process with polymerization of urea and formaldehyde.[8] The surfactant solution consists of equal volumes deionized water and ethylene-maleic anhydride copolymer (Zemac™-400 EMA, ammonium chloride, resorcinol, and urea. The DCPD is added slowly to begin the emulsification before being allowed to equilibrate. The entire process takes place under stirring conditions of approximately 800 RPM. Sonication by a 750-Watt ultrasonic homogenizer (Cole-Parmer®) takes place after solution has reached static conditions for approximately 1.5 min. The sonication horn tip, 1/8″ across, is placed in the beaker next to the mixer blade without touching the beaker or the blade. The sonicator is turned on for the duration at 40%. Formalin (37% formaldehyde) is added in a ratio described by Brown et al.[1] Once the formalin is added to the emulsification, it is left to react for four hours under constant mixing conditions. The capsules are then left to sit overnight while the shells set once emulsification has finished.

The microcapsules are cleaned through centrifuging in a mixture of methanol and undistilled DCPD. The solution is approximately equal volume methanol and DCPD. The IEC Multi® Centrifuge (Thermo Electron Corporation) is run for an hour at 2000 RPM. Once the centrifuge stops, the excess surfactant and methanol are siphoned off with pipettes. The centrifuge tube is refilled with the methanol and DCPD mixture to weight. The centrifuge is subsequently run two more

times before the capsules separate out in a clear band from the surfactant. The capsules are then suspended in the medium, either polymer or distilled water.

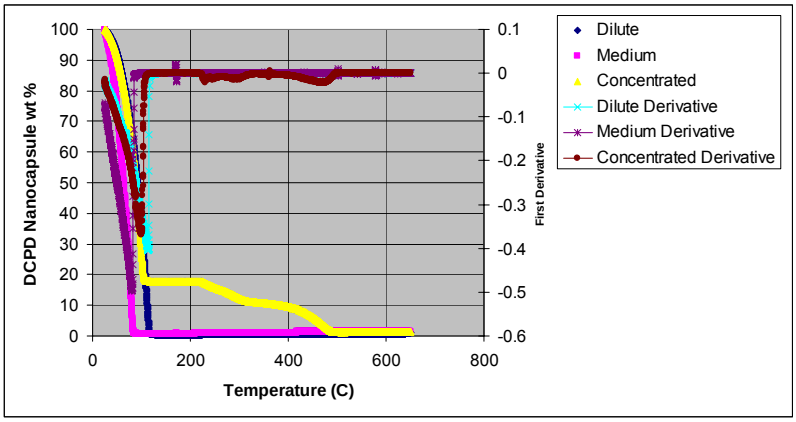

Figure 3: TGA data taken from three different concentrations of *endo* DCPD nanocapsules. The first major drop from 100wt% is the evaporation of water as the medium at 100 °C; the second drop, occurring at approximately 250 °C. This second drop happens at the boiling point of DCPD. All derivatives are first derivative functions from TGA data. The dilute solution concentration is 0.4817wt% nanocapsules. The medium concentration is 0.7584wt% and the concentrated solution contains capsules by 17.78wt%.

Experimental Cell and Setup

A diagram of electrode setup can be seen in Figure 4. The electrode is made by vapor deposition of 10nm chromium and then two planar depositions of 100nm gold. The deposition is made on a glass microscope slide, 25mm by 75mm. The depositions were made 2mm apart. Microcapsule suspension was placed in between the two electrodes over the 2mm gap. The suspension was enclosed by a hydrophobic barrier consisting of polytetrafluoroethylene (PTFE) thread sealant tape coated by a PAP hydrophobic barrier pen (abcam). The suspension was then covered by No. 1 cover glass slide (25mm x 25mm, Corning Labware and Equipment).

DEP Assembly

The alternating electric field was produced by a Powertron AC Power Source (Industrial Test Company, NY) in conjunction with an amplifier (wide range oscillator, Hewlett Packard). The amplitude was set at 100 with field intensities ranging 10-40 V (typically 15-20 V 0 and frequencies of 1000-15000 Hz (typically 5000 Hz). Once hooked to the electrode, the capsules were observed through the Leica Optical Microscope by transmission. The sample was colored through the microscope and the images were recorded by the QImaging Micropublisher camera.

Polymer Suspension

Endo DCPD nanocapsules were spray-dried using the Büchi 190 Mini Spray Dryer after diluting the nanocapsules with distilled water. The capsules were diluted to approximately twenty-times the original volume. The spray-dried capsules were sonicated for a half hour in the sonication bath to minimize clumping from collection after drying. The DCPD capsules were added to UV-curable polymer Norland Optical Adhesive 75 (NOA 75) according to mass percentage along the approximation of 2wt%. The polymer suspension is then put into the sonication bath for two hours in order to reach acceptable dispersion.

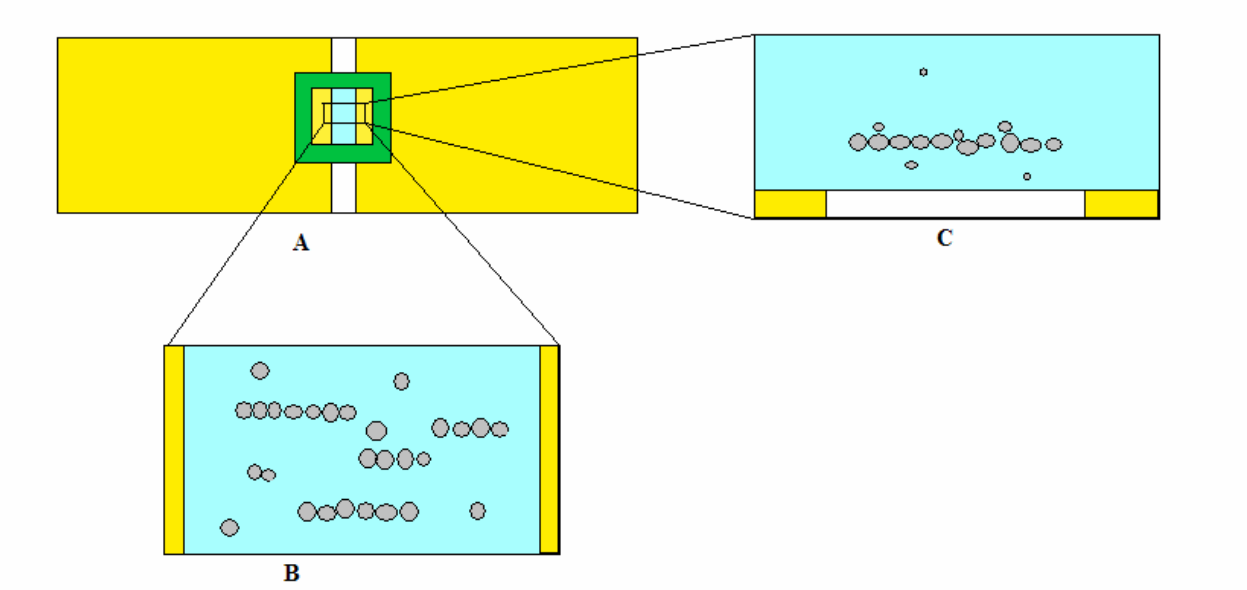

Figure 4: Electrode schematic and setup. **A** shows the general setup of the electrode. The two chromium and gold electrodes are shown in yellow with the 2mm electrode gap in between. The thin film barrier is shown in green with the capsules suspended in distilled water in blue. **B** shows capsules suspended in distilled water lined up according to electric field lines by DEP force. The concentration of capsules in the diagram is low enough that a complete monolayer does not form. **C** is the profile of the suspended capsules under dielectrophoresis.

Results and Discussion

The two-dimensional assembly of microcapsules under the influence of the non-uniform field is accomplished quickly. The microcapsules naturally disperse themselves in solution, with the exception of a couple of aggregates appearing. The aggregates usually contain between two and five capsules. In the event of large agglomeration, the solution can be sonicated to separate the capsules. In the first frame in Figure 5, small aggregates can be seen in the suspension. Once the electric field is applied, the capsules move quickly to assemble into chains. Short chains appear within seconds of the electric field application. Longer chains appear in two to four minutes. The chains begin to collect together at approximately five minutes before chaining together and forming a double chain. In the last frame, double chains can be seen in the middle of the longer chains. The double-capsule sections appear toward the middle of various chains.

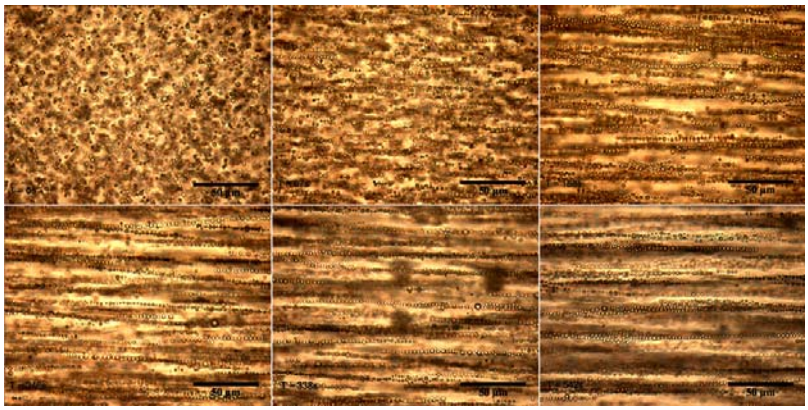

Figure 5: Progression from free capsules to capsules under a non-uniform electric field. The top left frame is at t = 0s and ends at t = 542s. The second frame is t = 67s, t = 188s, t = 246s, and the fifth frame is t = 338s. Concentration in this sample is too high and the chains became coarse after two minutes.

Higher electric field strengths result in quick chains and then chain distortions when the field starts to move the suspension liquid as well. The movement of the medium disrupts the formed chains and moves the capsules from stable positions in the chain. As a result, the chains are entirely destroyed if the field strength is too large. While the large magnitude field breaks the chains, the capsules clump after solution movement is in established equilibrium.

Alternatively, if the field is too weak, the capsules are affected very little by the presence of the field. Where the strong field takes under a minute to form long chains, a weak field takes several minutes to do the same thing. A weaker field polarizes the microcapsules less than a strong field does. A weaker field gradient has the effect of forming shorter, more stable chains over a longer period of time. Because the dipole moment is smaller for a weaker field, the chains have a shorter average length and are generally more dispersed in the suspension than the longer chains. The smaller dipole moment is a result of the lessened attractive DEP force between the various chains. Figure 6 shows the disparities between the two field magnitudes.

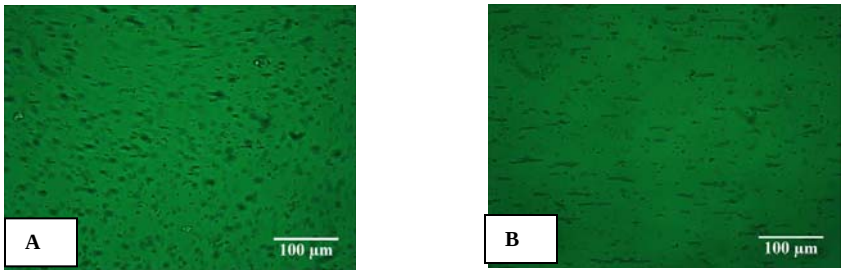

Figure 6: **A** shows the result of a field with a strong field gradient. The image was taken after 470s and shows chains averaging 5-10 capsules in length as well as small aggregates. The electric field is 251 V/cm and the frequency generated by the amplifier if 5 kHz. The movement of capsules according to field strength can be seen in curve formed by the capsules. **B** shows the effect of a weaker electric field magnitude. The image was recorded after 2824s with field strength of 125 V/cm and a frequency of 5 kHz. Unlike **A,** the voltage was ramped so that the medium did not move with the field.

Another contributing factor toward the rate of chaining is the pH value for the medium. For DEP to occur, the particle has to have a net neutral charge. If the capsule carries a charge going into the electric field, the effect of DEP force changes. For a low pH, in the range of pH 3-4, microcapsules carry a charge before the electric field is applied. Once the field is applied, the average net charge for a capsule will be net negative rather than net neutral. The net negative charge changes the way that microcapsules align themselves according to the field. As a result, the microcapsules aggregate and clump together rather than form chains. The same conclusion follows for higher pH values in the range of 7-8. The charge then carried on the capsule is net positive instead of net neutral. Likewise, a net positive charge also results in aggregation. Suspensions in a pH range of 5 to 6 form more chains than aggregations.

When the concentration of the suspension is high, the sample is likely to aggregate under applied field. Higher concentrations clump under an electric field due to crowding. In most cases, too many microcapsules form many layers. For the 17.78wt % suspensions, in between seven to ten layers of chains were formed. The chains also appeared as two separate chains directly on top each other. The field gradient present in the alternating field makes chaining along-side another chain difficult. Overall, higher concentration does not contribute to a monolayer. Instead, multilayer targeted printing is possible. Low concentrations of microcapsules have similar problems in chaining, but with a different way. If the concentration is low, the problem is that when the electric field is applied to the suspension, the capsules do not charge enough to attract other capsules. DEP force polarizes the microcapsule to a set charge dependent upon the electric field. The attraction between dipole moments is dependent upon the distance between the separate dipoles. The distance between the dipoles is too great for the capsules to move toward other capsules and then to chain. Such is the case for suspensions with a concentration 1wt % or under. The 0.4818wt % solution managed chains up to ten capsules in length in the most concentrated areas, but averaged at 5 microcapsule-length chains.

Norland Optical Adhesive 75 holds an approximate concentration of 2wt% nanocapsules easily. Dispersion in NOA 75 is significantly more difficult than dispersion in water due to the increased viscosity. In addition to increased viscosity, water is immiscible in polymer. The capsules were dried with the spray dryer in order to facilitate dispersion. Once suspended in NOA 75, the capsules appeared as aggregates with approximately thirty to fifty capsules per aggregate on average. Sonication in a bath aided dispersion in polymer to break down the sizeable clumps of capsules from spray drying. Dielectrophoretic force should have separated the individual capsules upon polarization, but the large agglomerates seemed to maintain shape. The concentration of nanocapsules by weight percentage was 8.18wt% ± 0.5wt% because the UV-curable polymer only disperses uniformly a concentration of 2wt%, 8.18wt% capsule concentration is too highly concentrated to completely break up the large aggregates. Because the concentration is too high, the capsules cannot spread out enough to for individual, separate chains. Short individual chains form with average length of three to five capsules. The chains usually appear side by side, or double-chained. Otherwise, most chains appear within the clumps. The aggregates are initially disorganized. After being under the alternating field for approximately ten minutes, the capsules inside the aggregate begin to organize into rows. The rows are not uniform in depth, but usually form as straight lines.

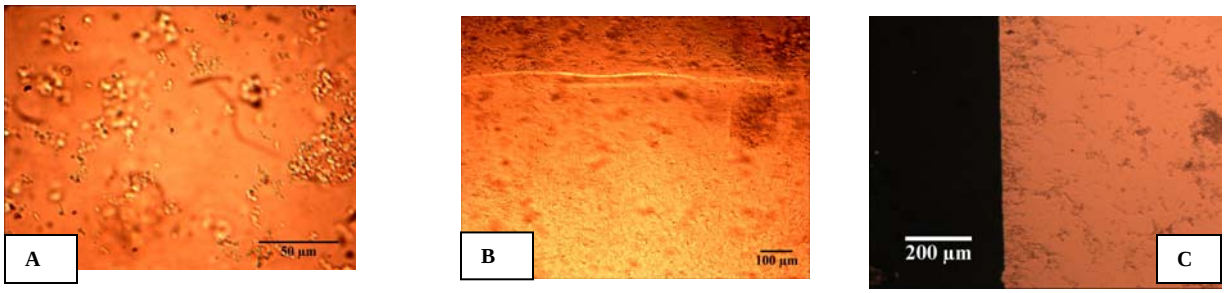

Figure 7: **A** Shows the suspension of nanocapsules in NOA 75 after 34 min under electric field strength of 137 V/cm and a frequency of 20 kHz. The polymer was placed in the sonication bath for two hours before being placed under the electric field. A large aggregate is shown on the left of the image and there is a small chain towards the top. **B** Displays the cure edge of the polymer. The line across the image is the edge of the cured NOA 75 area, with the cured polymer underneath. Above the cured edge, nanocapsules are still visible. Below, the wrinkles occurring from shrinkage can be seen. The polymer was slowly cured over three minutes to minimize shrinkage. **C** Shows chains appearing on the edge of an electrode, evidence of positive dielectrophoresis under electric field strength of 774.0 V/cm and a frequency of 50 kHz. .

Conclusion

Dielectrophoretic assembly is the use of DEP force to align nanoparticles in a specific manner. Chains appear most regularly at low function generator and amplifier settings of approximately 15 V and 5000 Hz. Long chains are produced in the pH range of 6 to 6.5. The approximate monolayer is formed by all microcapsules appearing on a similar plane with a few outlier microcapsules. The chains rarely emerge straight as size variation ranges from 300 nm to 10 µm. The variation in size causes the chains to curve to match the different diameters. In the polymer suspension, the chains form within the clumps rather than as individual chains. Because the 8.18wt% concentration is too high for NOA 75, the nanocapsules never fully dispersed in the polymer. The high concentration caused the capsules to chain within the aggregate. Once the concentration is sufficiently lowered, the chains should form independently of aggregates.

Acknowledgements

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