

4-15-2021

Microparticles and latexes prepared via suspension polymerization of a biobased vegetable oil and renewable carboxylic acid

Anthony Q. Mai
Louisiana State University

Jackie Davies
Louisiana State University

Dan Nguyen
Louisiana State University

Arturo Carranza
Louisiana State University

Michael Vincent
Louisiana State University

See next page for additional authors

Follow this and additional works at: https://digitalcommons.lsu.edu/chemistry_pubs

Recommended Citation

Mai, A., Davies, J., Nguyen, D., Carranza, A., Vincent, M., & Pojman, J. (2021). Microparticles and latexes prepared via suspension polymerization of a biobased vegetable oil and renewable carboxylic acid. *Journal of Applied Polymer Science*, 138 (15) <https://doi.org/10.1002/app.50180>

This Article is brought to you for free and open access by the Department of Chemistry at LSU Digital Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of LSU Digital Commons. For more information, please contact ir@lsu.edu.

Authors

Anthony Q. Mai, Jackie Davies, Dan Nguyen, Arturo Carranza, Michael Vincent, and John A. Pojman

Mai Anthony (Orcid ID: 0000-0002-4171-3272)
Pojman John A. (Orcid ID: 0000-0003-4788-8767)

Microparticles and Latexes Prepared via Suspension Polymerization of a Biobased Vegetable Oil and Renewable Carboxylic Acid

Anthony Q. Mai, Jackie Davies, Dan Nguyen, Arturo Carranza, Michael Vincent, and John A. Pojman*

Department of Chemistry, Louisiana State University and Agricultural and Mechanical College, Baton Rouge, Louisiana 70803, USA

Correspondence to: John A. Pojman (john@pojman.com)

Abstract

Novel bio-based microparticles and latexes are synthesized using green chemistry principles through the reaction of aconitic acid (a sugarcane byproduct) and epoxidized linseed oil (ELO). No volatile solvents have been used, and no initiators are present in this polymerization. Using different agitation techniques, we investigate the particles and latexes formed via suspension polymerization in contrast to bulk dispersion polymerization. With the addition of water and a small amount of surfactant to the ELO and aconitic system, a thermally stable material up to 250 °C is created that exhibits adhesive and hydrophobic properties. These microparticle latexes are anticipated for applications in hydrophobic coating and personal care products.

1. Introduction

Thermosets are ubiquitous in their everyday use from consumer glues to industrial coatings. Sustainable chemistry is a forever burgeoning field to source renewable feedstocks and to recycle finished products.¹⁻⁴ However, many of the thermoset resins are petroleum based. The polymer properties are then tailored to last per their usage lifetime. This in turn makes them more resilient and less degradable, further adding to the amount of unrecyclable material persisting in our world. It is estimated that 3 million tons of epoxy resins were produced in 2017 alone.⁵

Thus, many are endeavoring to create sustainable materials to supplement this large market. One example of a renewable material is from the epoxidation of common vegetable oils.⁶ Most notably are the soybean oil and linseed oil variants.⁷ They are currently in mass production and are primarily used as a biobased plasticizer for PVC. Many are studying the polymerization of these monomers with small molecules or traditional amines.⁸⁻¹⁶ Some use naturally occurring carboxylic acids to cure the epoxidized vegetable oils.¹⁷⁻²³ With the use of these water soluble acids, a dispersion is usually created of aqueous acid and epoxidized oil.²⁴ The curing then occurs at elevated temperature, which requires more energy and requires extra steps to attain usable polymer.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: [10.1002/app.50180](https://doi.org/10.1002/app.50180)

Since the passing of H.R. 1321: The Microbead-Free Waters Act of 2015, polymer manufacturing companies have been working on improving the biodegradability of microparticles. Some have used starch or lignin as a renewable and green substitute.²⁵ Finding a source of biodegradable microparticles may help fill the niche of plastics formerly occupied by the materials outlawed by this bill's passing.

With the previous work utilizing dispersion bulk polymerization, we thought the epoxidized vegetable oil cured with an aqueous acid system would be a suitable candidate for suspension polymerization. By inverting the phase from water-in-oil to oil-in-water, we reacted epoxidized linseed oil (ELO) with a trifunctional carboxylic acid, aconitic acid. One main source of aconitic acid is from sugarcane biomass. Every ton of sugarcane leaf matter yields an extracted 2-3 kilograms of aconitic acid.²⁶⁻²⁷

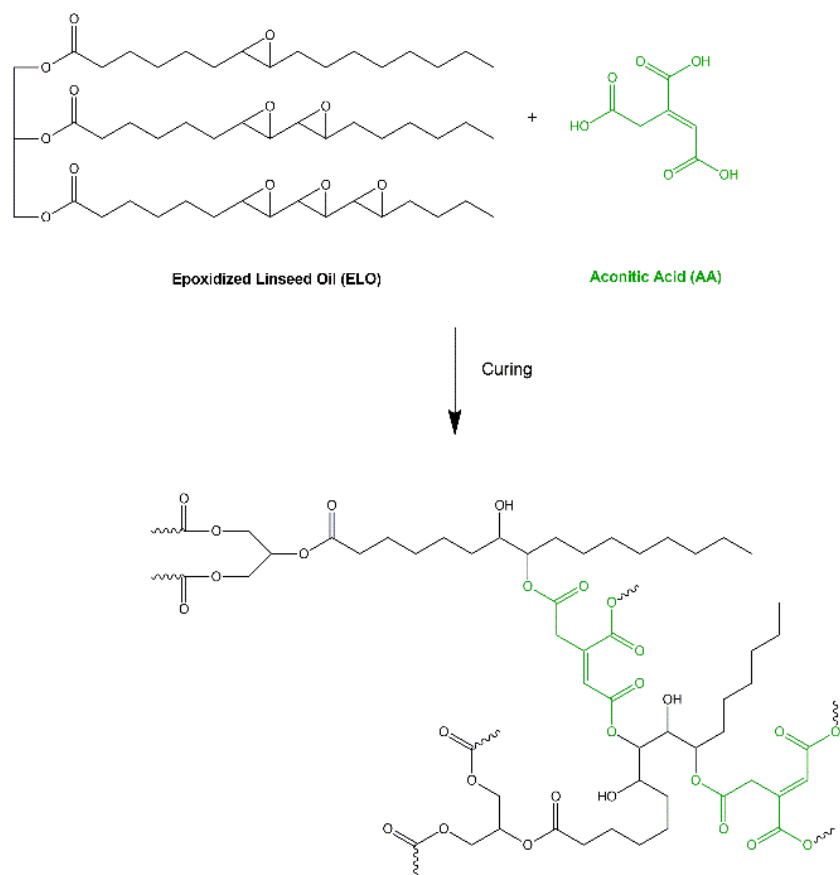


Figure 1. Structures and synthesis of crosslinked ELO

By performing the polymerization in suspension, a slurry of cured polymer is produced. This material can then be filtered and dried for use or can be kept in suspension as a latex or slurry, depending on particle size. This alleviates the end user from having to cure the resin with extended heating. We studied the suspension polymerization parameters, and the resulting

material has promising properties as a biobased microparticle and coating, oleophilic carrier, or as an adhesive.

2. Experimental Section

2.1. Materials

Epoxidized linseed oil (ELO) and epoxidized soybean oil (ESO) were acquired from Arkema (Vikoflex® 7190 and 7170 respectively). Trans-aconitic acid (AcA) and citric acid (CA) were purchased from Sigma Aldrich. Sodium lauryl sulfate (SLS) was purchased from VWR. Antifoam AF emulsion, food grade, was purchased from Spectrum. Hydroxypropyl methylcellulose, Methocel® K100LV, was obtained from Dow Chemicals, and polyvinyl alcohol (medium viscosity 88% hydrolyzed Selvol® 523S, PVA) was obtained from Sekisui. Caprylic capric triglyceride (CCT) was obtained from Univar and dimethicone (20 cst) was obtained from Ashland. Lavender oil was purchased from Aromatic Infusions. Sodium hydroxide and hexane were purchased from VWR. All chemicals were used as received.

2.2. Suspension Polymerization

The aqueous phase was made by adding 0.4 g of 30% SLS in deionized water to a total water amount of 171 g, then slowly dissolving 0.9 g of Methocel® or PVA (up to 2% of the phase). 5-7 drops of 10% antifoam in deionized water was metered in while agitating using an overhead stirrer with impeller blade. The addition of the stabilizers should be performed with suitable shearing and timing to prevent agglomeration or skin from forming on the powder. The aqueous can be prepared beforehand to further dissolution of the Methocel® or PVA. After a clear solution is seen, 3.9 g aconitic acid was added (a minimum of 2% of the total aqueous phase). The inner oil phase was made of 58.7 g of ELO. The formulation as mentioned has been optimized to minimize surfactant amount while maximizing the yield of polymer. Various agitation speeds were investigated to change the particle size. The oil-in-water suspension was then agitated for a minimum of 30 minutes to stabilize the oil droplet size distribution. Heat was then applied to polymerize the droplets, maintaining a minimum of 80 °C and overhead agitation for a minimum of 10 h.

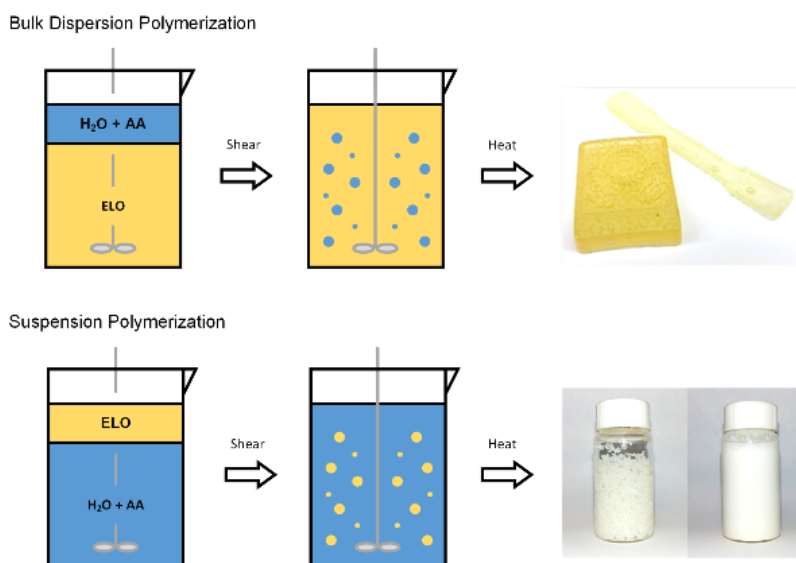


Figure 2. Graphic of the various phases for bulk dispersion and suspension polymerization.

2.3. Post Reaction Processing

After the heating cycle, the polymer slurry was cooled and either left in suspension or filtered to yield polymerized ELO particles. Washing of the particles or latex may be desired for removal of the surfactants, an aqueous rinse or dilution then centrifugation was performed on initial batches. Some particles were then dried in a drying oven at 105 °C.

2.4. Bulk Dispersion Polymerization

To create monoliths for a means of comparing the bulk polymerization to our particles, ELO was reacted with a small aqueous amount of aconitic acid. To 58.7 g of ELO, a solution of 3.9 g aconitic acid in 13.0 g deionized water was added. This resulting mixture was homogenized and poured into silicon molds and cured in a 90 °C oven for a minimum of 10 hours.

2.5. Oleophilic Ingredient Encapsulation in Particles

Prior to the addition of the ELO to the aqueous phase, CCT or dimethicone was added to the ELO and incorporated via magnetic stirring. Various amounts of the encapsulated ingredient have been tested, up to 75% of the oil phase, though as expected an increase in particle friability was observed. Several drops of lavender oil were added to some batches as an olfactory indicator of encapsulation.

2.6. Latex Preparation

Agitation with the impeller or dispersion blade generally yields particles from 100 microns to several millimeters. By using a rotor-stator homogenizer, VWR® 25D, we were able to shear the suspension up to 20,000 rpm to yield a latex that was polymerized in the conditions mentioned above.

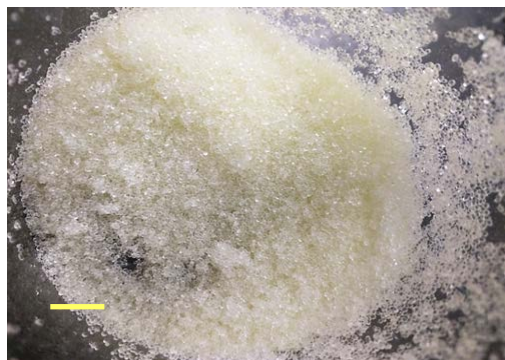


Figure 3. Particles of epoxidized linseed oil cured via suspension polymerization with aqueous aconitic acid (1 cm scale).

2.7. Characterization

Light Microscopy. Microscopy imaging was performed on a Nikon Eclipse 50i with a Nikon DS-Fi1 camera attachment.

Scanning Electron Microscopy (SEM). SEM imaging was performed with a JEOL JSM-6610LV. Samples were coated with a 5 nm layer of gold.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectroscopy was performed with a Bruker Tensor 27. 32 scans were performed from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1} .

Laser Diffraction Particle Size Analysis. Particle size analysis was performed in water with a Beckman Coulter LS200 equipped with a micro volume module.

Thermogravimetric Analysis (TGA). The thermal profile was analyzed with a TA Instruments TGA 2950 Thermogravimetric Analyzer. The sample was analyzed from room temperature to 600 °C with a heating rate of 10 °C/min under nitrogen.

Contact Angle. Contact angle was measured via imaging the droplet of water with a Nikon D3200 DSLR and performing an image analysis with ImageJ with the DropSnake plugin.

Lap Shear Wood Adhesive Testing. Lap shear testing was performed with an Instron 5582. Two pieces of southern pine were glued together according to ASTM 1037 – 12 and tested for glue-line shearing.

3. Results and Discussions

3.1. Bulk Polymer, Particles, and Latexes

The curing of epoxidized vegetable oils has been of great interest, especially with multifunctional carboxylic acids.^{2, 9-11, 13-15, 20-22} This curing behavior has been previously shown to ring open the epoxide groups reacting with an aqueous mixture of acid.²⁰⁻²¹ We used a similar approach to create the bulk polymerization; however, instead of a pre-heating step prior to oven curing we simply sheared the water-in-oil dispersion to create a stable mixture.

Suspension polymerization to create particles is analogous to the previous bulk dispersion; however, with the opposite addition of oil into an outer aqueous phase. Impeller blades (30 to 600 rpm) were used to agitate the mixture for creating particles ranging from 250 μm to 2 mm. To yield smaller sized droplets or particles, a dispersion or Cowles agitator (30 to 2000 rpm) is preferred when using an overhead stirrer. This is because the blades on the agitator are pitched to prevent fluid movement but have higher shearing capacity.

The particles exhibited a similar IR spectrum to its bulk polymerized counterpart. The characteristic broad -OH stretch at $\sim 3300\text{ cm}^{-1}$ is seen in both the bulk and suspended material. This is indicative of the ring opening of the epoxide groups from reaction with the carboxylic acids. The fingerprint regions also correspond to both polymerized materials with the C-O peak²⁸⁻²⁹ at $\sim 830\text{ cm}^{-1}$ slightly decreasing in the cured resin versus monomer.

These two methods yield different products, as bulk dispersion polymerization requires a final curing in the oven to create a monolith or thin coating of sorts, and suspension polymerization yields cured particles.



Figure 4. ELO microparticles and ELO latex in 20 mL vials.

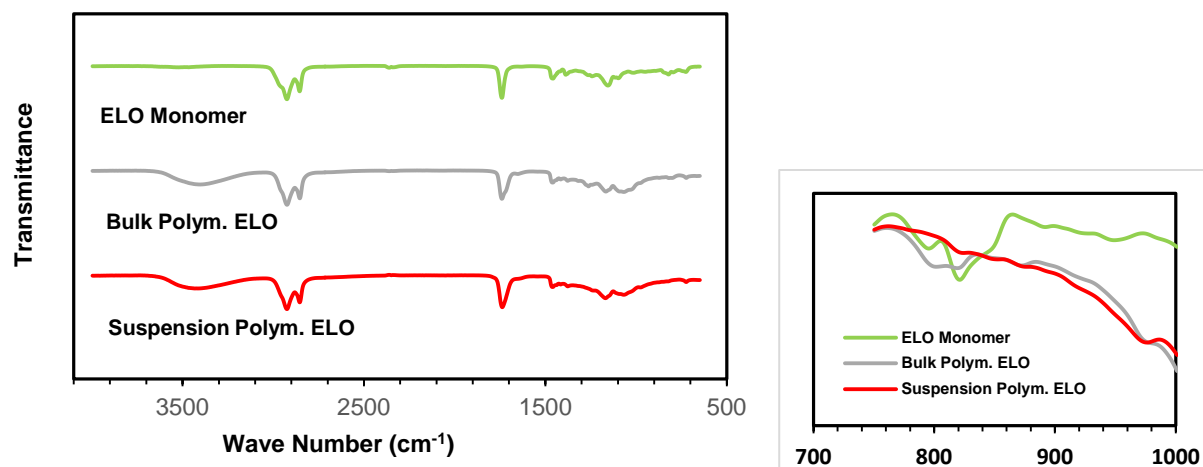


Figure 5. FTIR spectra of epoxidized linseed oil, bulk polymerized and suspension polymerized materials with zoomed in spectra in the 700 – 1000 cm^{-1} range.

Citric acid is a similar carboxylic acid to aconitic acid. When using aconitic acid as the curing agent for suspension polymerization, we back titrated with sodium hydroxide the residual acid amount in the outer aqueous phase. By maintaining the original water volume, we determined that 0.05 g of aconitic acid is consumed in the reaction with 1.0 g of ELO. When the same molar amount of citric acid is added to the aqueous phase, the reaction did not cure after 2 days at temperature. Additional citric acid, totaling 3 times the original amount, enabled the oil phase to cure. We think this may have some relation to the $-\text{OH}$ group in citric acid greatly increasing its solubility in water versus the double bond in aconitic acid. Again we took the remaining aqueous phase and titrated it to yield the same amount (0.055 g) of citric acid was consumed per 1.0 g of ELO.

Continuing with our shearing studies, a rotor-stator homogenizer was used to achieve high shear (1000 to 25k rpm) allowing for further size reduction of the particles. With the homogenizer set to 12k rpm, *Figure 6*, details the particle size distribution changing with increasing shearing time. Using the Fraunhofer model, the means were calculated for each distribution to be 16.5, 12.5, 9.0, and 6.9 μm respectively of 1, 5, 10, and 15 minutes. The distributions are seen to be multimodal, but as we increased shearing time, the larger diameter peaks decreased, and the smaller diameter peaks increased, as expected. Polymerizing the latex still showed multimodal peaks, but maintained a 6.88 μm mean.

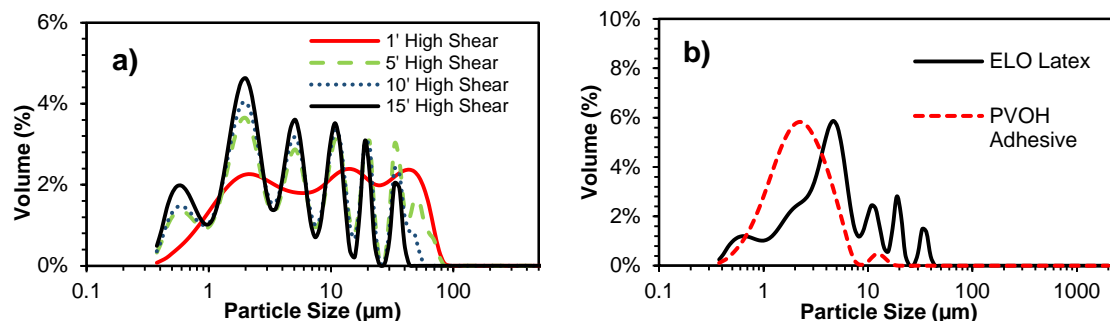


Figure 6. Particle size distributions of a) varying shear times b) polymerized ELO latex versus commercial PVOH glue.

The oil phase can also contain oleophilic components. In our studies we use caprylic capric triglyceride as an encapsulant with some lavender oil added in a few batches. With this diluent the particles become friable, and when some force is applied they release the emollient and fragrance. Thus, the ELO particles can be a carrier for lyophilic systems, with batches having been prepared with as much as 75% encapsulant and 25% ELO.

3.2. Physical Properties

The ELO particles, as compared to the bulk material, show little to no difference in their TGA temperature profiles. Both have onset temperatures above 350 °C and similar 1st derivative peaks around 395 °C. TGA was also performed on a 50% CCT encapsulated ELO batch, to determine encapsulation efficiency. The resulting CCT was the first peak coming off around 289 °C and showed 53% of the particle weight. We also tested the encapsulation's robustness by stirring the CCT encapsulated particles in hexane for 30 minutes then decanting and filtering, to determine if any e. TGA then exhibited a slight difference of 4% in that 289 °C region.

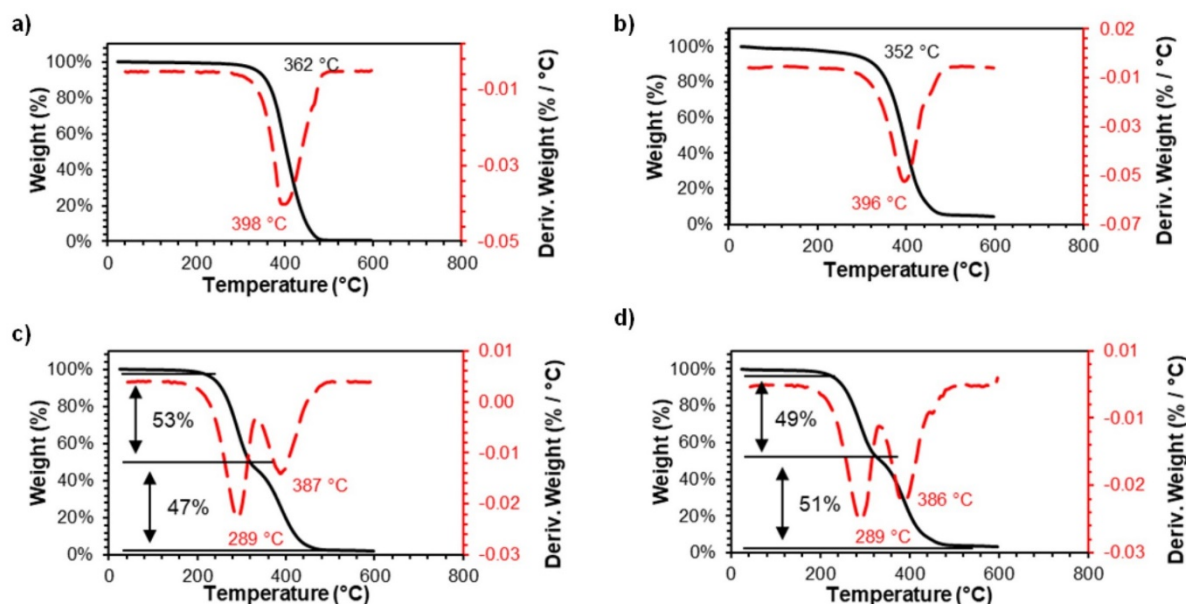


Figure 7. TGA and DTG temperature profiles for a) bulk polymerized ELO, b) suspension polymerized ELO, c) CCT encapsulated in ELO microparticles, d) hexane washed CCT encapsulated ELO microparticles

When the particles and latexes were dried, they adhered to various substrates from glass to aluminum to wood. The large particles themselves adhered to each other and could form a sponge-like monolith. The latexes too, when left in bulk quantities, could form into a single translucent mass. It was initially thought that perhaps residual stabilizer, either Methocel® or PVOH, was contributing to this adhesive property. This was ruled out as the particle or latex monoliths do not break apart when immersed in water. Further confirmation was made by subsequently washing the particles and latex with water to remove any residual stabilizer which could have potentially act as a binding agent. Adhesion was still seen in the particles and slurry.

A study was performed to test this adhesion using ASTM 1037-12 to test the lap shear of glue joints in wood. Table 1, presents the resulting data after the southern pine wood blocks were adhered together. The latexes tested showed significant loss in strength when the samples were placed in the oven overnight. Furthermore, a sample left for 60 days at RT also displayed a 350 kPa (30%) loss in strength, though not as considerable as the same sample placed in the oven for one night—about 750 kPa (66%) loss.

Table 1. Mechanical testing of ELO latex as an adhesive for lap-shear compressive joints.

Sample	Description	Drying	Max Load (kN)	Bond Strength (MPa)
1	Base Formula, 12000 rpm Shear	RT	2.39 ± 0.2	1.24
2	Sample 1 Formula	90 °C	1.84 ± 0.2	0.95
3	Base Formula, 0.75% SLS (30% aq) and 0.5% Methocel®	RT	2.21 ± 0.3	1.14
4	Sample 3 Formula	90 °C	0.75 ± 0.1	0.39
5	Sample 3 Formula	RT, 60 Days	1.54 ± 0.2	0.79
6	Base Formula, 1.5% PVOH, 1.5% Methocel®, and 1% SLS (30% aq)	90 °C	1.43 ± 0.2	0.74

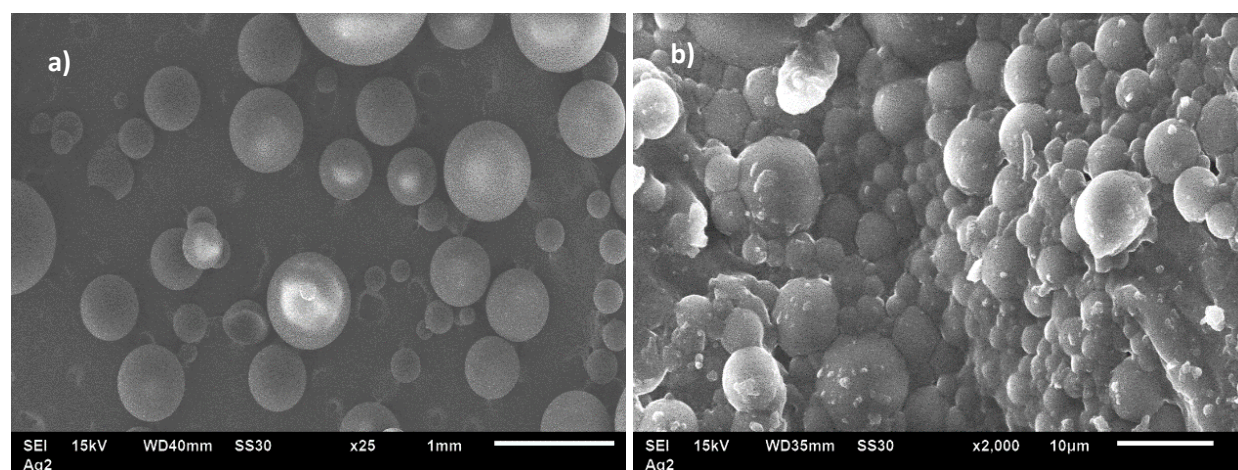


Figure 8. SEM micrographs of a) ELO microparticles and b) ELO latex

Morphology of the latex and particles were imaged via SEM, which indicated that the latex may have some smaller particles fusing the layers and larger particles together. The distribution of particles helps in making a tighter more fused packing and layering may have some hydrophobic coatings applications, as the latex can be applied with a brush to glass, metal, or wood.

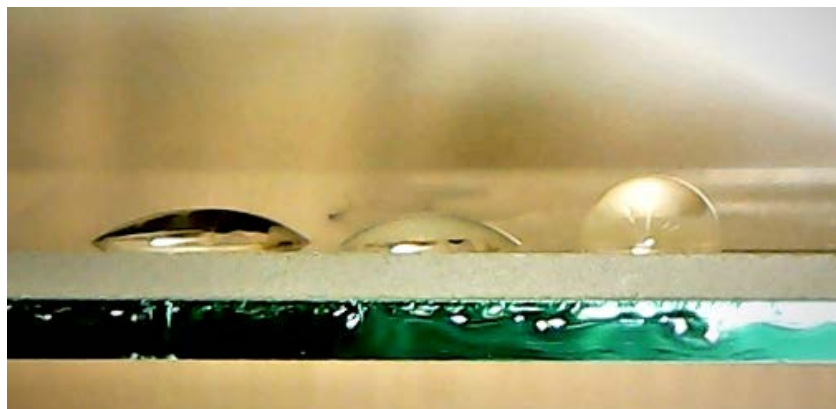


Figure 9. Water droplets on a glass slide, left two are placed on the uncoated slide and the right most is placed on a single brush coat of the aqueous latex.

Contact angle measurements of the bulk polymerized ELO and suspension polymerized latex revealed they were indeed hydrophobic as expected from a polymerized vegetable oil— $113^{\circ} \pm 7^{\circ}$ and $128^{\circ} \pm 8^{\circ}$ for the bulk material and suspension polymerized particles, respectively. The coating was applied with a single brush application and then let to air dry for a minimum of 1 hour.

Observations of the latex after 1 year show little to no settling of the particles. The adhesive properties were also retained as long as the mixture was not dehydrated. As these particles are crosslinked with aconitic acid, we anticipated they are resilient to acidic conditions.

4. Conclusions

Microparticles and a biobased synthetic latex have been synthesized using green chemistry. Through the use of aconitic acid, sourced from sugar cane, and epoxidized linseed oil a sustainable sourced polymer was created. Furthermore, the reaction uses mild conditions with no initiator or catalyst needed.

Bulk polymerization of epoxidized linseed oil with aconitic acid is an interesting material, but has limitations due to length of time required to cure the material and amount of heat required. By polymerizing the oil in a suspension, the end user would have access to a finished crosslinked polymer product. Furthermore, there is no difference in material properties between the two processes, just the morphology.

Agitation is key in suspension polymerization, from using low shear to create large particles or beads, to using high shear homogenization techniques to create a latex of epoxidized linseed oil. Encapsulation of oleophilic materials can be done up to 75% of the organic phase, and have been tested with scents and emollients. ELO microparticles exhibit high thermal stability up to 250°C with promising adhesive, coatings, and potential encapsulants for personal care applications.

Acknowledgments

The materials and work presented were supported by the Louisiana Board of Regents and LSU AgCenter under grant no. 2011-69005-30515 awarded by the United States Department of Agriculture, National Institute of Food and Agriculture, Agriculture and Food Research Initiative.

References

1. Babu, R. P.; O'Connor, K.; Seeram, R., Current Progress on Bio-Based Future Trends. *Progress in Biomaterials* **2013**, 2 (8).
2. Cheng, Q.-Y.; An, X.-P.; Li, Y.-D.; Huang, C.-L.; Zeng, J.-B., Sustainable and Biodegradable Superhydrophobic Coating from Epoxidized Soybean Oil and ZnO Nanoparticles on Cellulosic Substrates for Efficient Oil/Water Separation. *ACS Sustainable Chemistry & Engineering* **2017**, 5 (12), 11440-11450.
3. Lambert, S.; Wagner, M., Environmental performance of bio-based and biodegradable plastics: the road ahead. *Chem Soc Rev* **2017**, 46 (22), 6855-6871.
4. Garcia, J. M.; Jones, G. O.; Virwani, K.; McCloskey, B. D.; Boday, D. J.; ter Huurne, G. M.; Horn, H. W.; Coady, D. J.; Bintaleb, B. D.; Alabdulrahman, A. M. S.; Alsewaleem, F.; Almegren, H. A. A.; Hedrick, J. L., Recyclable, strong thermosets and organogels via paraformaldehyde condensation with diamines. *Science* **2014**, 344, 732-735.
5. Remi Auvergne, S. C., Ghislain David, Bernard Boutevin, Jean-Pierre Pascault, Biobased Thermosetting Epoxy: Present and Future. *Chem. Rev.* **2014**, 114 (2), 1082-1115.
6. Pan, X.; Sengupta, P.; Webster, D. C., Novel biobased epoxy compounds: epoxidized sucrose esters of fatty acids. *Green Chemistry* **2011**, 13 (4).
7. Sitz, E. D.; Bajwa, D. S.; Webster, D. C.; Monono, E. M.; Wiesenborn, D. P.; Bajwa, S. G., Epoxidized sucrose soyate—A novel green resin for crop straw based low density fiberboards. *Industrial Crops and Products* **2017**, 107, 400-408.
8. Rosch, J.; Mulhaupt, R., Polymers from renewable resources: polyester resins and blends based upon anhydride-cured epoxidized soybean oil. *Polymer Bulletin* **1993**, 31, 679-685.
9. Hernandez, S.; Viguera, E., Acrylated-Epoxidized Soybean Oil-Based Polymers and Their Use in the Generation of Electrically Conductive Polymer Composites. In *Soybean - Bio-Active Compounds*, 2013.
10. Liu, K. Novel plant oil-based thermosets and polymer composites. Iowa State University, 2014.
11. Gogoi, P.; Boruah, M.; Sharma, S.; Dolui, S. K., Blends of Epoxidized Alkyd Resins Based on Jatropha Oil and the Epoxidized Oil Cured with Aqueous Citric Acid Solution: A Green Technology Approach. *ACS Sustainable Chemistry & Engineering* **2015**, 3 (2), 261-268.
12. Wang, R. Manufacturing of vegetable oils-based epoxy and composites for structural applications. Missouri University of Science and Technology, 2014.
13. Jian, X.-Y.; An, X.-P.; Li, Y.-D.; Chen, J.-H.; Wang, M.; Zeng, J.-B., All Plant Oil Derived Epoxy Thermosets with Excellent Comprehensive Properties. *Macromolecules* **2017**, 50 (15), 5729-5738.

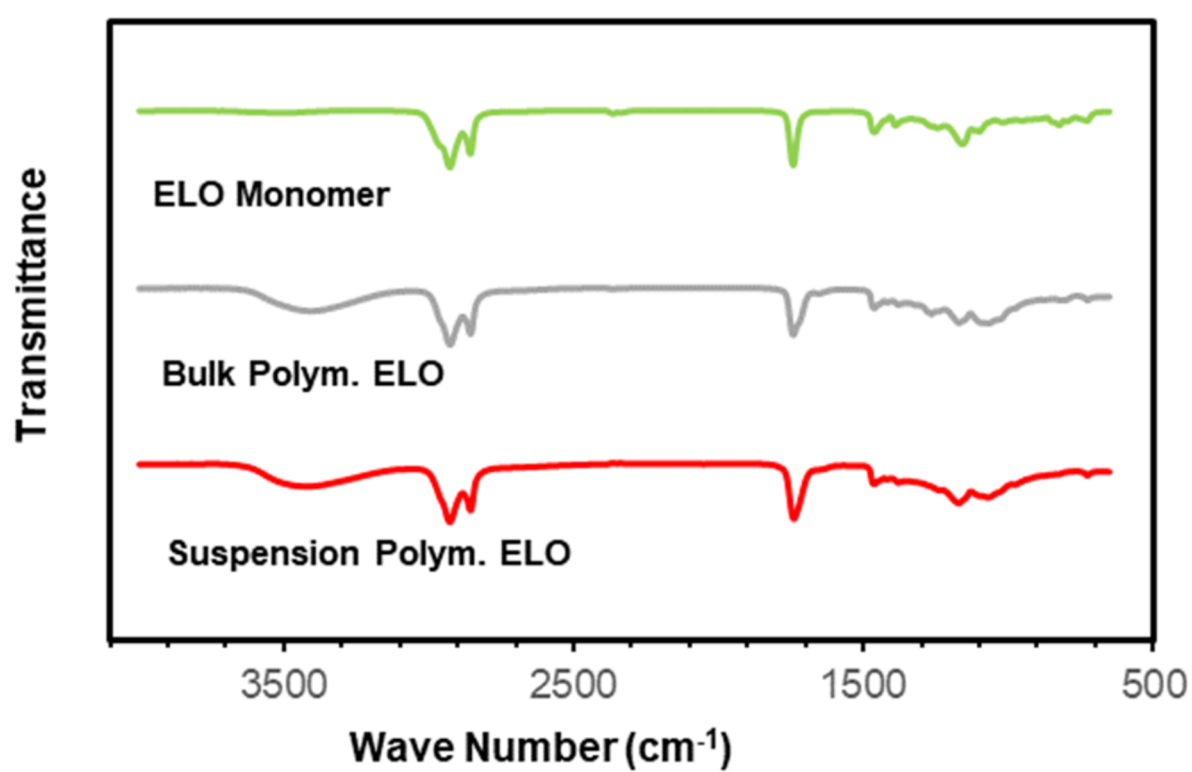
14. Jian, X.-Y.; He, Y.; Li, Y.-D.; Wang, M.; Zeng, J.-B., Curing of epoxidized soybean oil with crystalline oligomeric poly(butylene succinate) towards high performance and sustainable epoxy resins. *Chemical Engineering Journal* **2017**, *326*, 875-885.
15. Frias, C. F.; Serra, A. C.; Ramalho, A.; Coelho, J. F. J.; Fonseca, A. C., Preparation of fully biobased epoxy resins from soybean oil based amine hardeners. *Industrial Crops and Products* **2017**, *109*, 434-444.
16. Aouf, C.; Nouailhas, H.; Fache, M.; Caillol, S.; Boutevin, B.; Fulcrand, H., Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. *European Polymer Journal* **2013**, *49* (6), 1185-1195.
17. Ma, S.; Kovash, C. S.; Webster, D. C., Effect of solvents on the curing and properties of fully bio-based thermosets for coatings. *Journal of Coatings Technology and Research* **2016**, *14* (2), 367-375.
18. Ma, S.; Webster, D. C., Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules* **2015**, *48* (19), 7127-7137.
19. Ma, S.; Webster, D. C.; Jabeen, F., Hard and Flexible, Degradable Thermosets from Renewable Bioresources with the Assistance of Water and Ethanol. *Macromolecules* **2016**, *49* (10), 3780-3788.
20. Chen, Y.; Xi, Z.; Zhao, L., New bio-based polymeric thermosets synthesized by ring-opening polymerization of epoxidized soybean oil with a green curing agent. *European Polymer Journal* **2016**, *84*, 435-447.
21. Chen, Y.; Xi, Z.; Zhao, L., Curing kinetics of bio-based epoxy resin based on epoxidized soybean oil and green curing agent. *AIChE Journal* **2017**, *63* (1), 147-153.
22. Pradhan, S.; Pandey, P.; Mohanty, S.; Nayak, S. K., Synthesis and characterization of waterborne epoxy derived from epoxidized soybean oil and bioderived C-36 dicarboxylic acid. *Journal of Coatings Technology and Research* **2017**, *14* (4), 915-926.
23. Zeng, R.-T.; Wu, Y.; Li, Y.-D.; Wang, M.; Zeng, J.-B., Curing behavior of epoxidized soybean oil with biobased dicarboxylic acids. *Polymer Testing* **2017**, *57*, 281-287.
24. Zhang, C.; Garrison, T. F.; Madbouly, S. A.; Kessler, M. R., Recent advances in vegetable oil-based polymers and their composites. *Progress in Polymer Science* **2017**, *71*, 91-143.
25. Sameni, J.; Krigstin, S.; Jaffer, S. A.; Sain, M., Preparation and characterization of biobased microspheres from lignin sources. *Industrial Crops and Products* **2018**, *117*, 58-65.
26. Naniwadekar, M. Y.; Jadhav, A. S.; Ghosh, A.; Sahu, A., Cost Estimation & Optimum Route Selection for the Production of Aconitic Acid. *Journal of Basic and Applied Chemical Sciences* **2013**, *3* (4), 79-87.
27. Zapata, N. J. G. Aconitic Acid from Sugarcane: Production and Industrial Application. Louisiana State University and Agricultural and Mechanical College, Baton Rouge, 2007.
28. Henna, P. H.; Andjelkovic, D. D.; Kundu, P. P.; Larock, R. C., Biobased thermosets from the free-radical copolymerization of conjugated linseed oil. *Journal of Applied Polymer Science* **2007**, *104* (2), 979-985.
29. Vlček, T.; Petrović, Z. S., Optimization of the chemoenzymatic epoxidation of soybean oil. *Journal of the American Oil Chemists' Society* **2006**, *83* (3), 247-252.



APP_50180_contact angle.tif



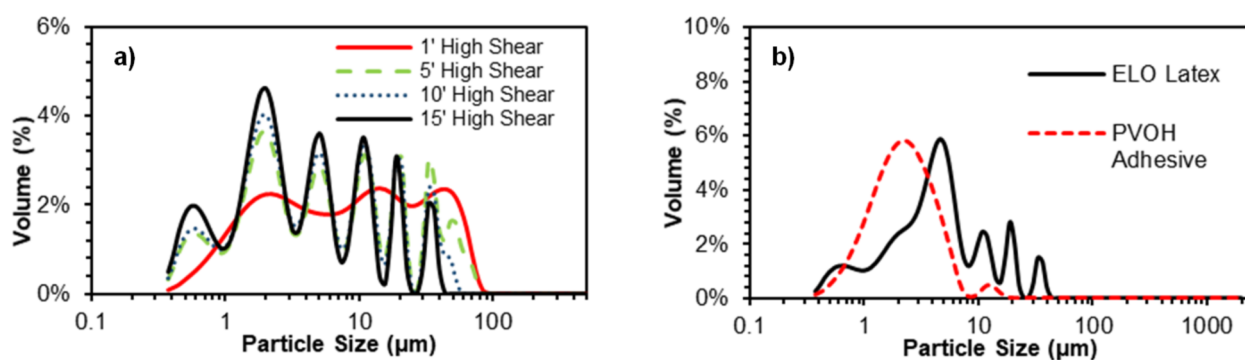
APP_50180_elo microparticles.tif



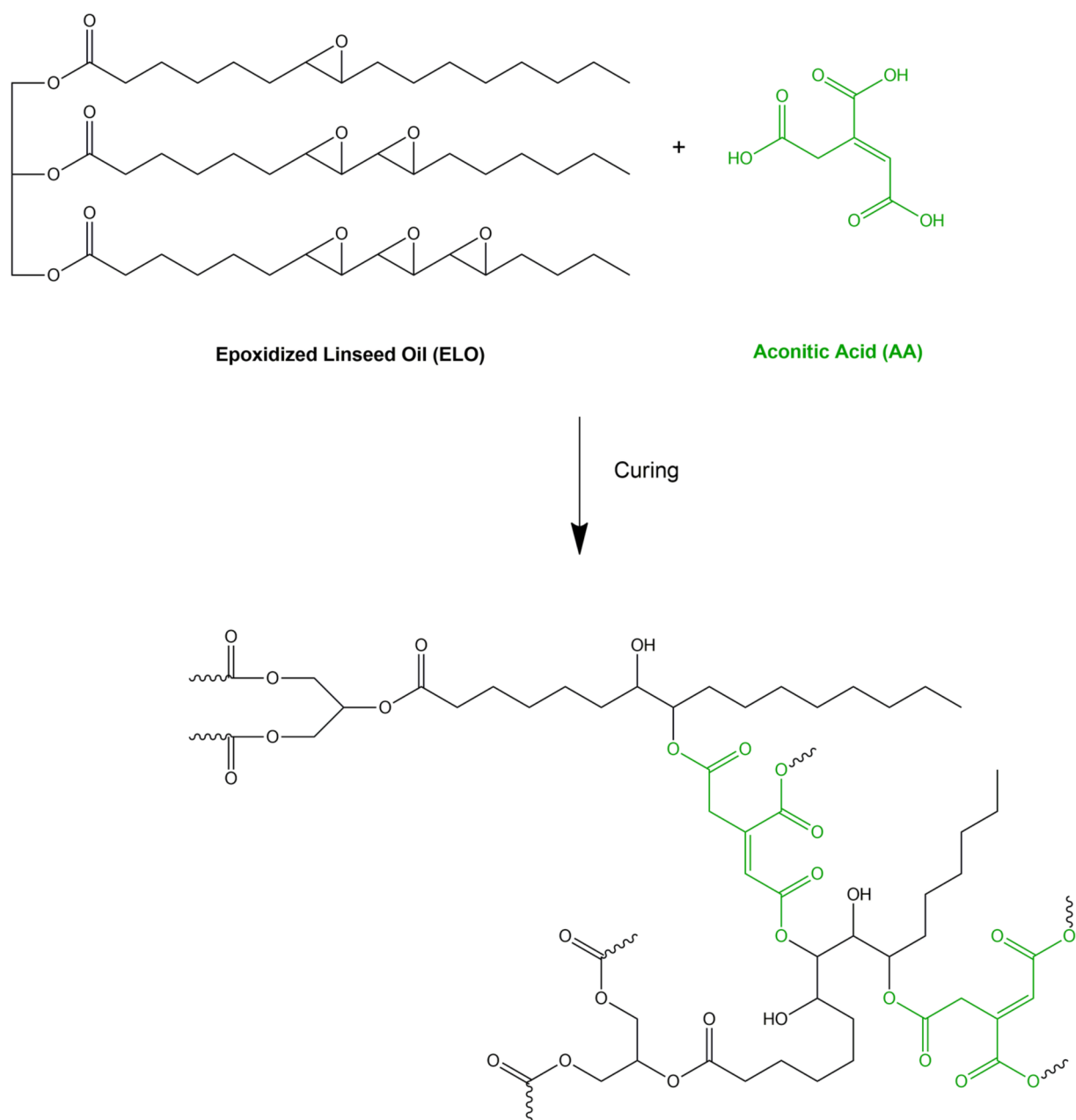
APP_50180_ftir.tif



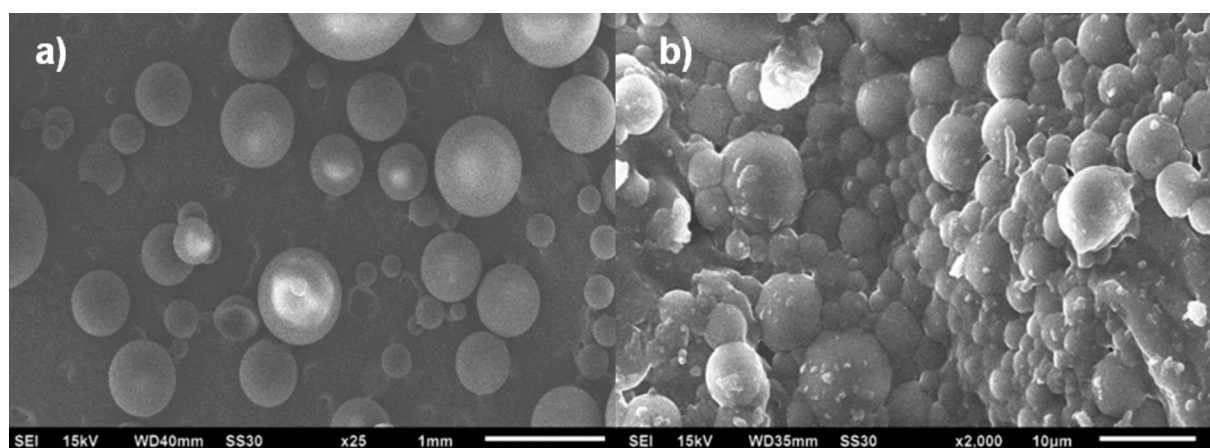
APP_50180_microparticles and latex.tif



APP_50180_psd plot.tif

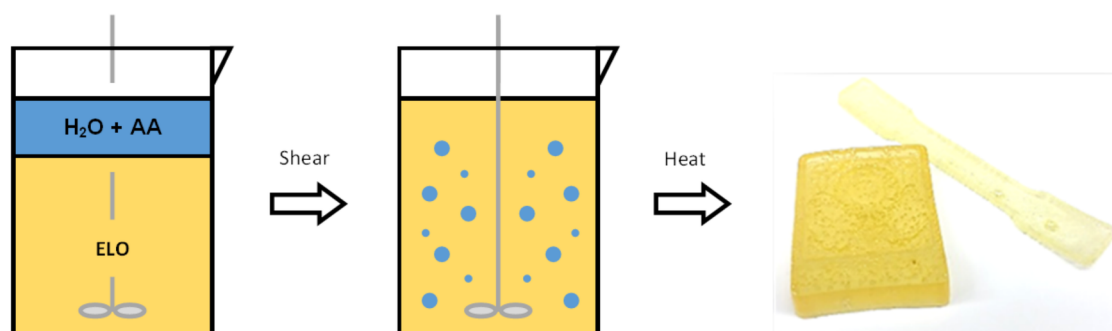


APP_50180_reaction scheme.tif

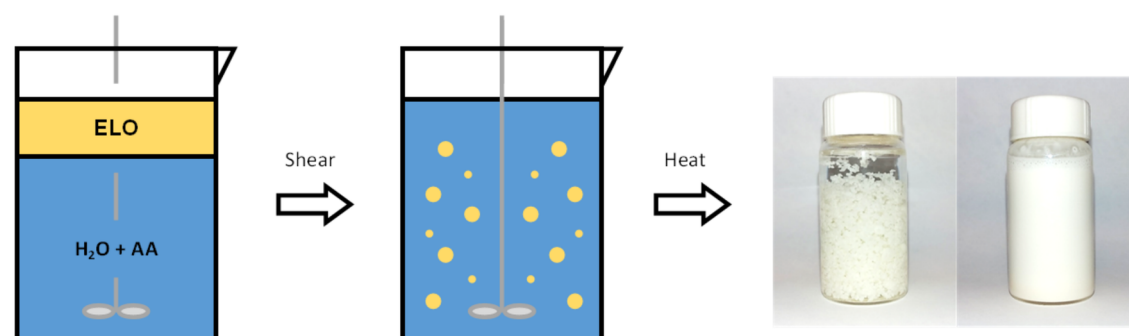


APP_50180_sem image.tif

Bulk Dispersion Polymerization

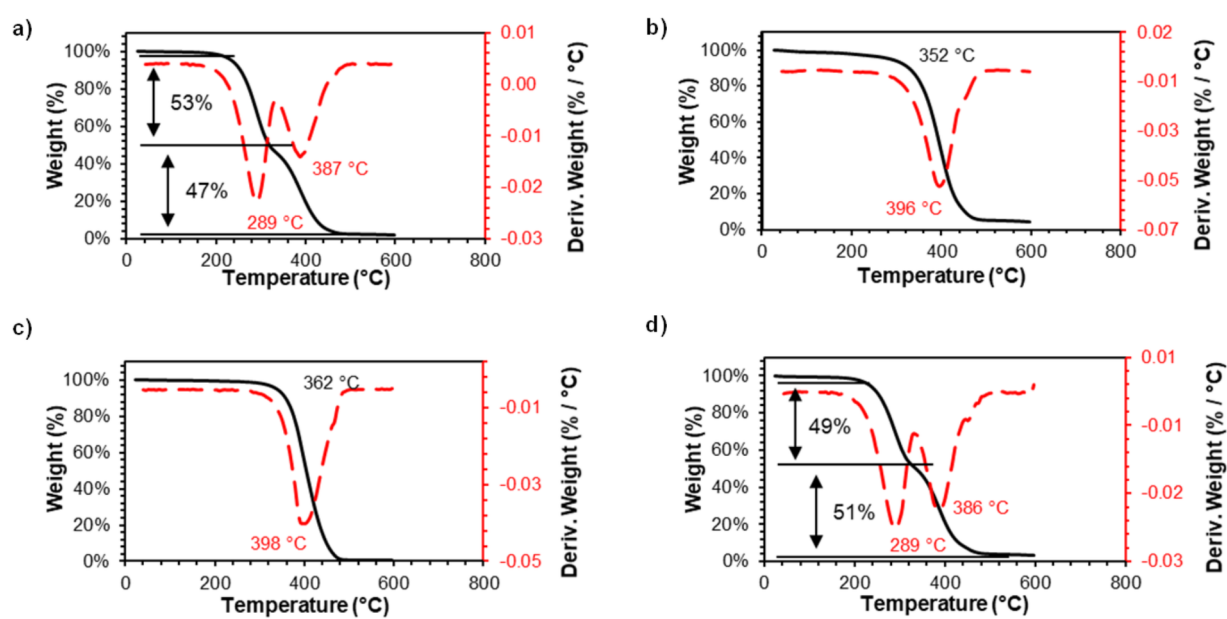


Suspension Polymerization



APP_50180_suspension diagram.tif

Sample	Description	Drying	Max Load (kN)	Bond Strength (MPa)
1	Base Formula, 12000 rpm Shear	RT	2.39 ± 0.2	1.24
2	Sample 1 Formula	90 °C	1.84 ± 0.2	0.95
3	Base Formula, 0.75% SLS (30% aq) and 0.5% Methocel®	RT	2.21 ± 0.3	1.14
4	Sample 3 Formula	90 °C	0.75 ± 0.1	0.39
5	Sample 3 Formula	RT, 60 Days	1.54 ± 0.2	0.79
6	Base Formula, 1.5% PVOH, 1.5% Methocel®, and 1% SLS (30% aq)	90 °C	1.43 ± 0.2	0.74



APP_50180_tga plot.tif