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Modulation of Zirconium Hydroxide Defect Chemistry via Functionalized Polymers

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14. ABSTRACT The reactivity of metal (hydr)oxides such as zirconium hydroxide (ZH) strongly depends on poorly-understood defect sites. The amorphous nature of ZH results in a highly defective crystal structure that has wide-ranging defect sites with differing stability and reactivity. Very little is known regarding how to control or modulate these defect sites, which has implications for a myriad of applications, including: catalysis, composite reactive materials, and energy storage. This work seeks to understand how variations in the electrical properties of acrylate-based polymers may modulate the surface defect speciation and reactivity (acidity/basicity) of ZH nanopowders within polymer matrixes. Simply combining the ZH nanopowder and polymer monomers enables the robust formation of polymer networks with minimal synthetic deviations. This platform facilitates the study of surface modified defect sites as a function of polymer moiety that can be extended to other systems such as metal organic frameworks, polyoxometallates, and other metal (hydr)oxides. These composite polymer matrixes are structurally and compositionally analyzed for surface defect speciation, modification of incorporated ZH surface acidity/basicity, and reactivity using existing in-house instrumentation.								
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EXECUTIVE SUMMARY

The Naval Research Laboratory (NRL) initiated an effort in September 2018 for modifying defects of polymer composites comprising embedded metal (hydr)oxide powders. Funding for this effort was provided internally through the Karle Research Fellowship program. This report details methods and results for preparing acrylate-based porous polymer composite monoliths containing embedded zirconium hydroxide (ZH) nanoparticles. Three potential monomers were investigated in this report: 2-hydroxyethyl acrylate (2-HEA), 2-dimethylaminoethyl acrylate (2-DMAA) and acrylic acid (AA).

Gas permeable and structurally robust monolithic polymer materials were prepared using high internal phase emulsions (HIPEs) comprising co-monomers, a surfactant, and an immiscible internal phase. For structural rigidity, poly(ethylene glycol diacrylate) (PEGDA) co-monomer was added to the monomer. Using hexanes as the internal phase yielded a durable and stable porous polymer monolith compared to toluene. Toluene was found to be unusable as an internal phase and yielded undesirable structural properties resulting from decomposition of the polymer.

Polymerization was initiated using ammonium persulfate (APS) and catalyzed using N,N,N',N' tetramethylethylenediamine (TMEDA). The porous polymer matrixes appeared fully cured within 12 h at room temperature. The trapped internal phase in the polymer matrix was removed post polymerization in vacuo at 60 °C overnight, resulting in sponge-like monoliths with high porosity. Such monoliths demonstrate wicking of both polar and non-polar liquids and swell by over 2x their original size when submerged in water. These polymer materials accommodate high wt % loadings of metal (hydr)oxide powders into the stabilized emulsion before curing, which provides gas-permeable porous polymer composites.

Electronic interaction and modification to the defect sites of ZH were investigated using probe molecules (CO and CO₂), coupled with diffuse reflectance infrared Fourier transform spectroscopy to quantitatively measure the electronic impact of the various polymer side-chains on the ZH defect sites incorporated within the polymer matrix. Recommendations and future work are also presented.

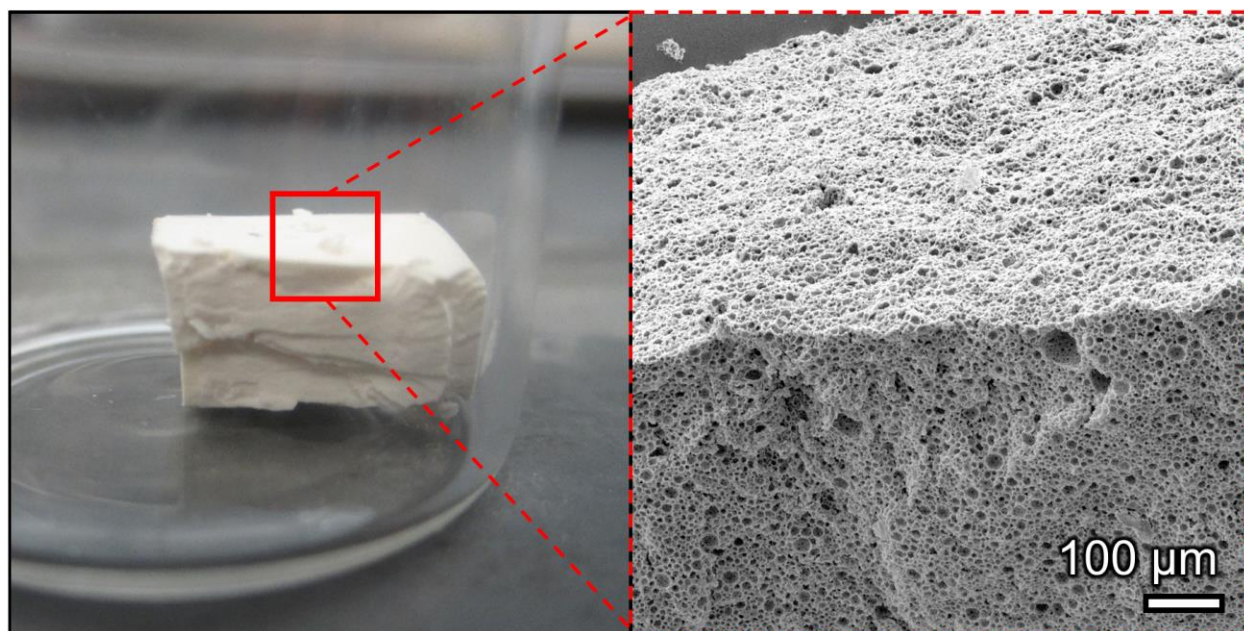


Fig. 1 — Vacuum dried 2-HEA porous polymer monolith.

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MODULATION OF ZIRCONIUM HYDROXIDE DEFECT CHEMISTRY VIA FUNCTIONALIZED POLYMERS

1. INTRODUCTION

The reactivity of metal (hydr)oxide nanopowders, such as zirconium hydroxide (ZH), strongly depends on poorly-understood defect sites. The amorphous nature of ZH results in a highly defective crystal structure having wide-ranging defect sites with differing stability and reactivity.[1-3] Under-coordinated $Zr^{3+/4+}$ and mono-, bi-, and tri-bridged hydroxyls provide both Lewis acidic and basic sites of varying reactivity.[4, 5] Such diverse defect sites lends itself to wide-ranging applications including catalysis, composite reactive materials, and energy storage. Other military applications include sequestration and decontamination of toxic chemicals and chemical warfare agents.[6, 7]

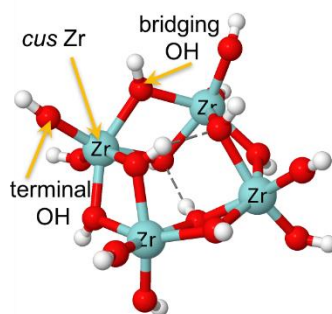


Fig. 1 Density functional theory calculation of a zirconium hydroxide cluster showing native defect sites. Image courtesy of Igor Schweigert, Code 61.

Modification of defect sites and defect density is achieved in similar systems such as metal organic frameworks (MOFs) via post-synthetic modification of the MOF, adjustment of the composition and organic linkers during synthesis, and/or by partial decomposition of the MOF by heat treatment.[8, 9] Unfortunately, these strategies are not as adaptable to metal (hydr)oxide powders such as zirconium hydroxide (ZH) due to relatively low thermal stability (~ 250 °C).[10] Above 250 °C, condensation of the reactive hydroxyls to form water has been observed. A general mechanism is shown in Fig 2 below. As such, new methods of modulating the activity of defect sites are needed.

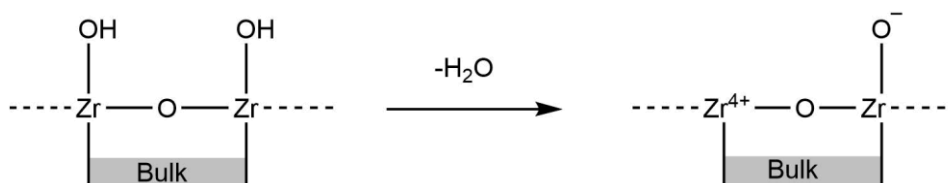


Fig 2. General mechanism of surface hydroxyl condensation at elevated temperature for zirconium hydroxide nanopowder.

One way to quantify active sites in metal (hydr)oxide systems is by dosing a reactive gas over the surface and monitoring for changes to the local bonding environment of the adsorbate. Much work has been demonstrated previously using a variety of “probe” molecules to identify acid/base sites, and coordinatively unsaturated (cus) metal sites on defective metal (hydr)oxides.[6, 7] Hill, et. al., show that identification and qualitative ranking of surface acid, base, and cus sites can be accomplished by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) while dosing probe molecules over the surface of a metal oxide.[11] Surface acidity was identified using carbon monoxide[12-14] and pyridine,[15, 16] basicity can be assessed via formation of carbonates and bicarbonates with CO₂,[17-19]

and bifunctional acid-base sites were observed using acetylene and glycine.[11] Several other probe molecules have been suggested such as ammonia, SO₂, alcohols, and chloroform to more finely differentiate similar defect sites.[20]

Preventing unintended chemical reactions or species desorption while monitoring the surface reactivity is of great importance. As such, interrogation of the surface during in situ probe molecule dosing is performed using IR spectroscopic techniques. IR radiation used in IR spectroscopy techniques such as DRIFTS is too low in energy to break or drive new chemistry on the surface, unlike other spectroscopic methods such as X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS). As such, interrogating metal (hydr)oxide materials for defects is often accomplished using either DRIFTS or attenuated total reflectance spectroscopy (ATR), depending on the form factor and desired application (Fig. 3A and 3B, respectively). Currently, NRL is equipped with operando ATR and DRIFTS instrumentation that is coupled to a gas dosing manifold, enabling ambient, real-time, and temperature controlled gas dosing experiments.

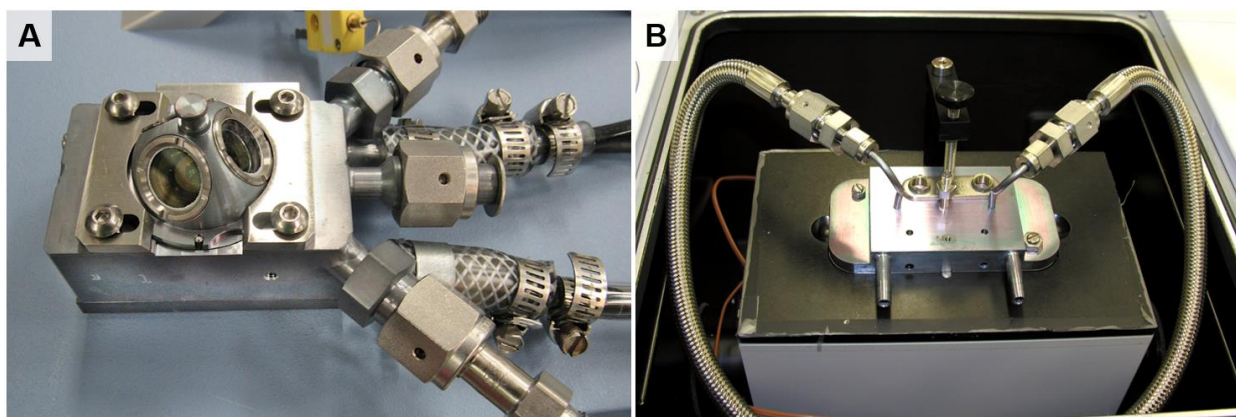


Fig. 3. Photograph of NRL's (A) operando diffuse reflectance infrared Fourier transform spectroscopy reaction chamber and (B) attenuated total reflectance gas dosing cell.

Unpublished previous work performed at NRL has shown the stability of coordinatively unsaturated (cus) oxygen sites, as well as cus Zr^{3+/4+} on ZH nanopowder upon dehydrating the surface using dry N₂ (Fig. 4). After removing loosely bound surface water, the defect sites were identified using carbon monoxide as a probe molecule. The surface bound CO molecules redshifts once adsorbed to the ZH surface, suggesting back-donation from the surface.[12] This has been previously interpreted as “ketene-like” species from adsorption of CO to O²⁻ cus sites.[21] Blue shifted complexes could also be due to low-coordinate Zr^{3+/4+} or possibly Zr⁴⁺-O²⁻ acid-base pair sites.[21]

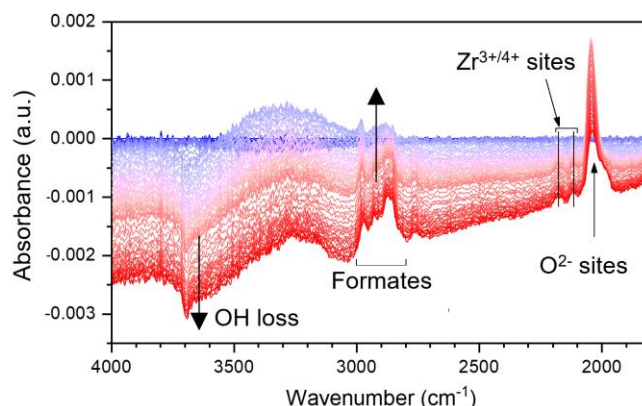


Fig. 4. Time-resolved attenuated total reflectance spectra of CO (1%, balance N_2) dosed on N_2 -purged $Zr(OH)_4$ thin film over 10 min showing CO adsorbing to $Zr^{3+/4+}$ and O^{2-} defect sites. Additionally, CO reacted with free hydroxyl species forming bound formates.

Using similar methodology, one should be able to quantify the amount of electronic interaction between a probe molecule and a reactive surface by measuring a change to adsorbed probe molecule vibrational frequency. More specifically, the electronic interaction (if any) between side-chain functional groups of polymers and metal (hydr)oxides should, in theory, be measurable. For example, shifting due to electronic withdrawal or donation should manifest as vibrational shifts of the adsorbed CO molecule to the surface and hence act as a useful metric to directly quantify changes to the local bonding environment of metal (hydr)oxide polymer composites.

Access directly to defect sites of metal (hydr)oxides embedded in a polymer matrix has already been demonstrated at NRL by using a porous polymer system comprising poly(dicyclopentadiene) (pDCPD) and ZH (Fig. 5 below). A hydrolysis reaction product resulting from interaction of the ZH with the reagent Demeton-S is observed, indicating intimate access between the ZH embedded within the porous polymer and Demeton-S. This demonstrates that ZH polymer composites can retain reactivity when incorporated into a polymer matrix. One question left unanswered by this work is a systematic study of the impact of the sidechain functional groups of the polymer matrix on the reactivity of the incorporated composite metal (hydr)oxide.

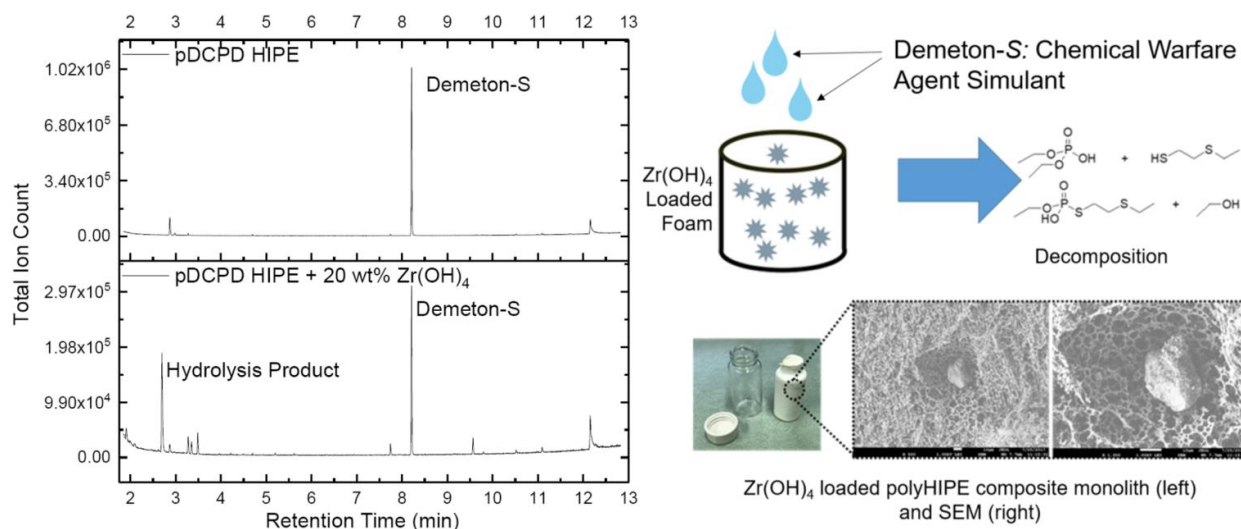


Fig. 5. Gas chromatography mass-spectrometry chromatograms of Demeton-S degradation with zirconium hydroxide (ZH) porous polymer composites showing significant formation of hydrolysis decomposition product with ZH loaded polymers (left). Schematic of experimental dosing procedure (right, top), photograph of composite monolith (bottom, left) and scanning electron microscopy (SEM) micrographs (bottom, right).

ZH defect sites within the polymer matrix can be envisioned to potentially communicate electronically through electron donating/withdrawing polymer moieties. To systematically explore this concept more, several polymers of varying functional groups were chosen and synthesized. Acrylate-based polymers were chosen due to being a well-studied system with many low-cost and commercially available monomers.[22-26] In this work, three monomers have been initially chosen to form ZH polymer composites: 2-dimethylaminoethyl acrylate, 2-hydroxyethyl acrylate, and acrylic acid (Fig. 6). Electronic interaction between the polymer sidechain and ZH defect sites was investigated.

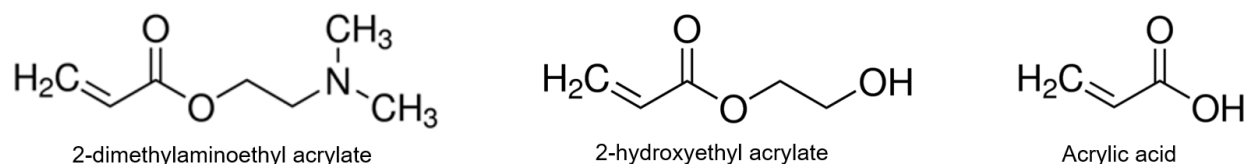


Fig 6. Structure of acrylate-based monomers used in this work.

To improve the rate and probability of probe molecules reaching the ZH active sites within the polymer, high surface area, porous, polymer monoliths were synthesized. A simple and scalable way to achieve porosity within the polymer matrix is by forming high internal phase emulsions (HIPEs) before initiating polymerization. This powerful technique produces open-cellular porous polymer monolithic foams with interconnecting channels.[27]

PolyHIPE materials are synthesized by dispersing a non-miscible “internal” phase consisting of a minimum of 74% total volume, with a continuous phase (comprising monomer of interest and possibly other additives).[27, 28] After initiating polymerization of this stabilized emulsion, the polymer monolith is dried to remove the internal phase, typically by heating under vacuum, and is often washed to remove any residual unreacted monomer. The resulting polyHIPE foams often exhibit robust and flexible mechanical properties, which can be tuned depending on application.[27, 29-31] Additionally, the porosity can also be adjusted to accommodate smaller or larger pores and varying degree of interconnected channels depending on structural, compositional, and application requirements.[32, 33]

Mechanical stirring is commonly used to produce stabilized emulsions for polyHIPE synthesis. However, such methods are time-consuming, requires several steps, can introduce bubbles, and produces significant waste. Therefore, a more practical approach is to use a centrifugal mixer. These differ from common planetary mixers (kitchen mixers) by utilizing 2-axis of rotation (rotated in a traditional circular path and along the z-axis of the mixing cup) producing two levels of centrifugal forces. The combination of centrifugal forces enables rapid and rigorous mixing of the polyHIPE precursors. Such systems provide much shorter mixing times, deaeration and air-bubble removal, minimal cleanup and waste (no blades, glassware, etc.), high scalability, and compatibility with powders, pastes, putties, and liquids. Utilizing these synthesis techniques to form stabilized emulsions will reduce the total synthesis time from several hours to less than one hour.

Very little is known about how to control or modulate defect sites for metal (hydr)oxide materials compounds, which enables exciting opportunities in a myriad of applications including: catalysis, composite reactive materials, and energy storage. The scope of this research seeks to understand the fundamental interaction and potential perturbation of the electronics and defect speciation/reactivity (acidity/basicity) of surface defect sites of ZH nanopowders within acrylate-based polymer matrixes. Simply combining the ZH nanopowder and polymer monomers into a single cup and mixing provides a robust synthetic framework to form porous polymer networks with minimal synthetic deviations. This platform facilitates the study of surface modified defect sites as a function of polymer moiety that can potentially be extended to other systems such as metal organic frameworks, polyoxometalates, and other metal (hydr)oxides. These composite polymer matrixes are analyzed for surface defect speciation,

modification of incorporated ZH surface acidity/basicity, and reactivity using existing in-house instrumentation.

2. METHODS

2.1 Synthesis of polyHIPEs

2.1.1 Synthesis overview

Porous polymer monoliths were synthesized via high internal phase emulsion polymerization in air. Emulsions were rapidly prepared using a FlackTek DAC 150.1 FVZ SpeedMixer, which provides a scalable mixing platform for future work. Prepared emulsions are stable for several hours and are easily polymerizable by introduction of the initiator to the emulsion. To improve structural rigidity, poly(ethylene glycol) diacrylate (PEGDA, $M_n=700$) was added as a co-monomer for crosslinking. To stabilize the emulsion, a bio-compatible surfactant, Pluronic F-127 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)) was also added. A polymerization catalyst N,N,N',N' tetramethylethylenediamine (TMEDA) was also added followed by the ammonium persulfate initiator. See Fig. 7 for a general schematic on preparing stabilized emulsions for polymerization.

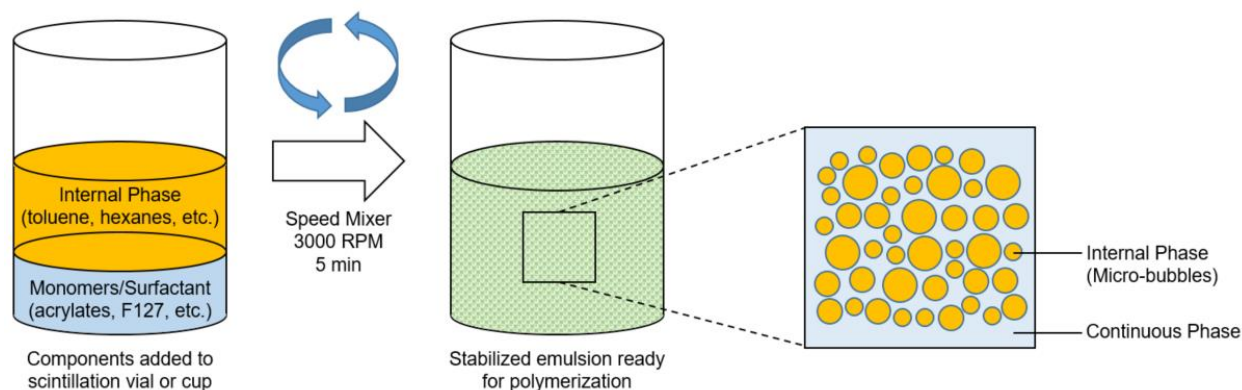


Fig 7. Schematic for preparation of stabilized emulsions for porous polymer synthesis.

2.1.2 2-Hydroxyethyl acrylate (2-HEA) polyHIPE synthesis

All reagents used as received and in air, unless otherwise specified. A stock solution of Pluronic F-127 (Sigma Aldrich) containing 0.55 g of F-127 in 100 mL of deionized water was prepared the night before by speed mixing the solution at 3500 RPM for 5 min. Solution left to completely dissolve overnight.

Pluronic F-127 (10 mL) and 3.62 mL of 2-HEA monomer (96%, Sigma Aldrich) were added to FlackTek mixing cup. This solution was mixed at 3500 RPM for 30 s. Then 2 mL of crosslinking additive poly(ethylene glycol) diacrylate (PEGDA, $M_n=700$, Sigma Aldrich) was added to the cup and mixed. The internal phase, hexanes (99.9%, Fisher Chemical, 15 mL), was then added to the mixing cup and mixed at 3500 RPM for 5 min. An additional 15 mL of hexanes was added to cup and mixed again at 3500 RPM for 5 min. Finally, 10 mL of hexanes was added to cup and mixed at 3500 RPM for 5 min. A stable, cloudy emulsion is formed following this step. Adding all internal phase at once produced irreproducible results due to less stable emulsions. Incorporation of the hexanes as 3 steps proved to be reproducible every time.

The polymerization catalyst N,N,N',N' Tetramethylethylenediamine (99%, TMEDA, 186 μL , Acros Organics) was then added to mixing cup and mixed at 3500 RPM for 30 s. Finally, the ammonium persulfate ($\geq 98\%$, APS, initiator, Sigma Aldrich) was added to begin polymerization. The cup was mixed one final time at 3500 RPM for 30 s to distribute the APS and then was rapidly poured into 20 mL scintillation vials for curing overnight.

The following day, the polymerized samples are cut into strips and placed in a vacuum oven (>30 in Hg vac) set to 60 $^{\circ}\text{C}$ for 6 h to remove the internal phase (hexanes) and other volatile impurities or unreacted precursors.

2.1.3 Acrylic acid polyHIPE synthesis

Synthesis of acrylic acid polyHIPEs followed the same procedure above for 2-HEA polyHIPE synthesis, but used 2.37 mL of acrylic acid monomer (99%, Sigma Aldrich) instead of 2-HEA monomer.

2.1.4 2-dimethylaminoethyl acrylate polyHIPE synthesis

Synthesis of 2-dimethylaminoethyl acrylate polyHIPEs followed the same procedure above for 2-HEA polyHIPE synthesis, but used 5.24 mL of 2-dimethylaminoethyl acrylate monomer (98%, Sigma Aldrich) instead of 2-HEA monomer.

2.1.5 Zirconium hydroxide polyHIPE composite synthesis

2-HEA/ZH composites polymers are prepared following the same procedure for 2-HEA polyHIPE, but the desired wt % of ZH is added to the reactants and mixed for 30 s at 3500 RPM before adding in the APS initiator. This ensures homogeneous mixing of the ZH before polymerization begins.

Optimal loading and particle stabilization within the HIPE was investigated by preparing 0, 5, 10, 25, and 50 wt % ZH to monomer. Additionally, ZH was incorporated into the polymer synthesis at different segments for ideal composite synthesis. ZH was also premixed with the F-127 and DI water in an attempt to “cap” the ZH nanoparticles and improve colloidal stabilization. Addition of ZH to the reactant before and after initiator was added was also explored. Regardless, some colloidal instability and subsequent settling of ZH was observed in all loadings and can be seen in photographs (Fig 12).

Additionally, a separate colloidal stability study was performed with ZH in DI and also in DI and F-127 surfactant. The suspensions were vortexed for 30 min and sonicated for 2 h then left to rest for 2 h.

2.2 Characterization

ATR spectra were collected using a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer with a deuterated triglycine sulfate detector and XT KBr beam splitter. Interferogram phase correction was performed using the Mertz algorithm with a phase correction factor of 32. Apodization was performed using the Norton-Beer strong function. Background and sample spectra consist of 128 scans averaged together with 4 cm^{-1} resolution at a scanner velocity of 10 kHz. Samples were placed directly onto a diamond internal reflection element and compressed with a screw anvil.

Scanning electron micrographs and energy dispersive X-ray spectroscopy (EDS) was performed on a JEOL-7600F field emission scanning electron microscope. Thinly cut samples of polyHIPE were mounted on adhesive copper tape and sputter coated with ~ 3 nm of gold using a Cressington Sputter Coater 108auto with a Cressington Thickness Controller MTM-20 under an argon plasma to reduce

charging. The sputter chamber was evacuated and refilled with argon three times before sputtering. EDS and SEM images were collected at 20 kV accelerating voltage, a working distance of 10 mm, and 150X, 1000X, and 5000X magnification.

All photographs were taken using a Canon PowerShot SD1400 IS digital camera.

DRIFTS spectroscopy was collected using a Bruker Vertex 70V FTIR spectrometer equipped with a Harrick Scientific Praying Mantis DRA optical accessory and a Harrick Scientific high temperature reaction chamber HVC-DRP-5, MCT detector, and KBr beam-splitter. Interferogram phase correction was performed using the Mertz algorithm. Apodization was performed using the Norton-Beer strong function. Background and sample spectra consist of 128 scans averaged together with 4 cm^{-1} resolution at a scanner velocity of 20 kHz.

3. RESULTS

3.1 2-HEA polyHIPE characterization

The 2-dimethylaminoethyl acrylate and acrylic acid polyHIPE polymers were found to be susceptible to degradation and oxidation as indicated by the yellowing and loss of structure following the vacuum drying procedure.

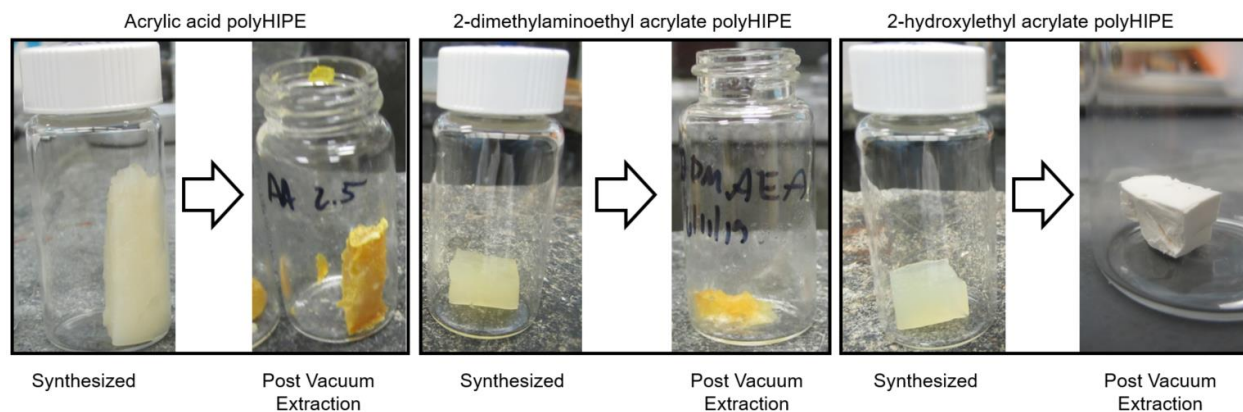


Fig 8. Degradation of synthesized AA and 2-DMAEA polyHIPE materials post vacuum extraction (left, middle, respectively). No degradation observed for 2-HEA polymer post vacuum extraction (right).

As such, the 2-HEA polyHIPE system was chosen as the sole system that was characterized and formulated with ZH to produce polymer composites. 2-HEA polyHIPEs synthesis and vacuum drying are highly reproducible and consistent (Fig. 8).

To determine the amount of unreacted monomer within the 2-HEA polyHIPEs, attenuated total reflectance spectra were collected. ATR spectra of 2-HEA monomer and polymerized film show clear evidence of polymerization to polyHIPE. Retention of the hydroxyl group ($\sim 3400\text{ cm}^{-1}$) and $-\text{CH}_2$ and $-\text{CH}$ groups ($\sim 2940, 2890\text{ cm}^{-1}$) is observed. Additionally, the carbonyl backbone ($\sim 1720\text{ cm}^{-1}$) supports no detectable degradation to the acrylate backbone in the polyHIPEs. Loss of the two vibrational modes near 1637 and 1618 cm^{-1} are attributed to $-\text{C}=\text{CH}_2$ bonds from the monomer, which indicates very little unreacted monomer remaining after polymerization (Fig. 9).

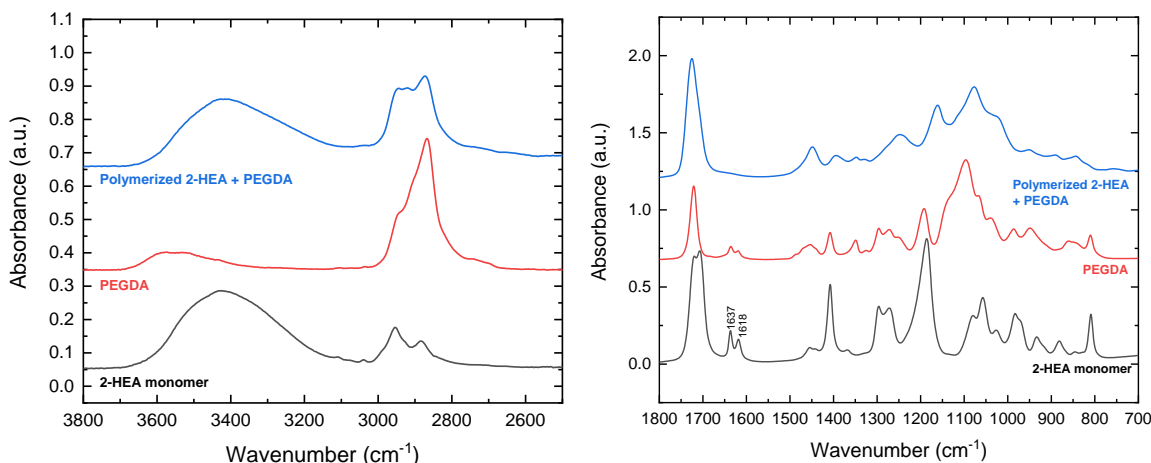


Fig. 9. ATR spectra of 2-HEA monomer, PEGDA crosslinking agent, and the polymerized foam in two wavelength regions. The spectra are offset vertically for clarity. Incorporation of the diacrylate crosslinking co-monomer with 2-HEA is observed with minimal unreacted monomer present.

Structurally, the 2-HEA polyHIPE foams are brittle before vacuum drying. This is likely due to the significant swelling of the 2-HEA polymer with the retained internal phase incorporated throughout the matrix. Such polymer swelling can be reduced by modifying the degree of crosslinking during synthesis if necessary.

However, after vacuum drying for 6 h, the foams are highly flexible, tear resistant, and have shape memory properties. Fig. 10 below shows several photographs of a piece of synthesized 2-HEA monolith after vacuum drying. The foam can be completely depressed (B) and regain its initial shape and size (C) upon release. In this form factor, the 2-HEA polyHIPE materials are quite durable and extremely lightweight – offering great promise for operationally robust materials and composites for fieldable technologies.

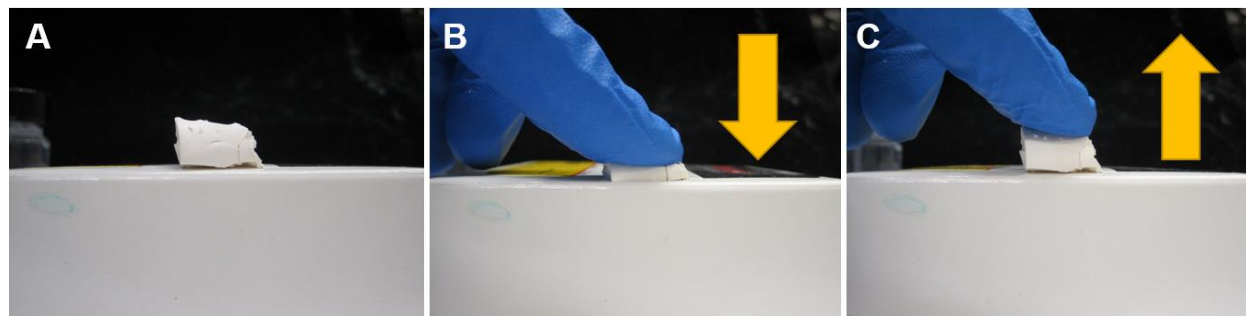


Fig. 10. Photographs of vacuum dried 2-HEA polyHIPE monolith (A) as synthesized, (B) pressed flat, and (C) released after pressing. These polyHIPE materials can be depressed many times without leading to failure. Additionally, they offer some shape memory properties and return to their originally casted shape after depression.

Scanning electron microscopy (SEM) micrographs of the vacuum dried 2-HEA polyHIPE monoliths (Fig. 11) were collected. The morphology shows large spherical voids that range from about 5 – 15 μm in diameter. Smaller interconnected channels (approximately 1 μm in diameter) are observed between the voids and throughout the matrix (Fig. 11, right). The size of the voids and interconnected channels can be tuned depending on application by modifying the synthesis parameters.

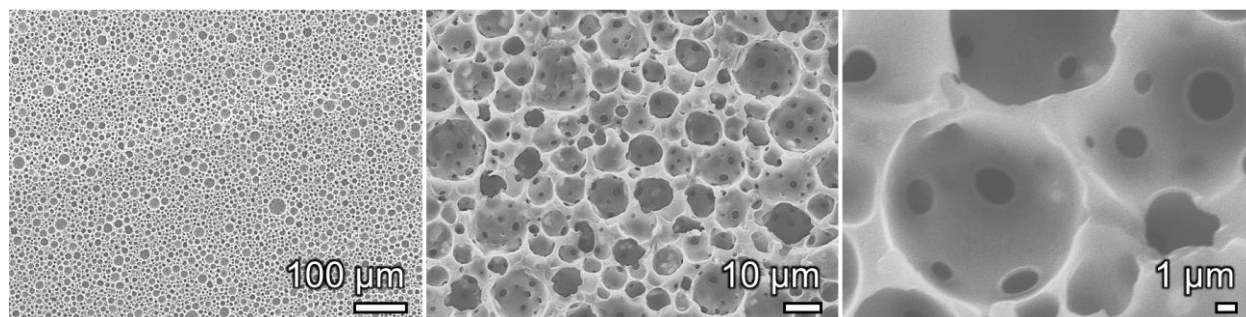


Fig 11. Scanning electron microscopy micrograph of vacuum dried 2-HEA polyHIPE foam at three different length scales.

3.2 PolyHIPE and zirconium hydroxide composites

ZH polymer composites qualitatively showed minimal changes to mechanical strength with up to 50 wt % ZH. This might be due to the highly porous morphology (at least 74% void space) of polyHIPE composites. Similar to the pristine 2-HEA polyHIPE, the ZH-loaded compositions also were easily compressible and would return to original shape within seconds. The monolithic pieces did not visibly crumble or degrade within 5 cycles of compressing and releasing.

The monoliths did show evidence of ZH colloidal instability resulting in a “settling” of ZH from the polymerizing solution (Fig. 12A). This settling occurs at all ZH loadings from 5 – 50 wt %. Several strategies to stabilize the ZH were attempted. ZH was added to the F-127 surfactant solution and vortexed for 30 s in both just DI and DI with surfactant in an attempt to cap the ZH nanopowder and improve the colloidal stability (Fig. 12B). Similarly, this process was repeated but with a 2 h sonication step to try to disaggregate the ZH nanopowder and improve stabilization (Fig. 12C). However, after 2 h of resting, no significant improvement was observed in the stability ZH. The sonicated suspensions visibly appear to be more colloidal stable, but a significant amount of ZH still settles on the bottom of all vials. This instability will likely lead to gradients throughout the polymer monoliths, but no composite gradients have been quantified or observed.

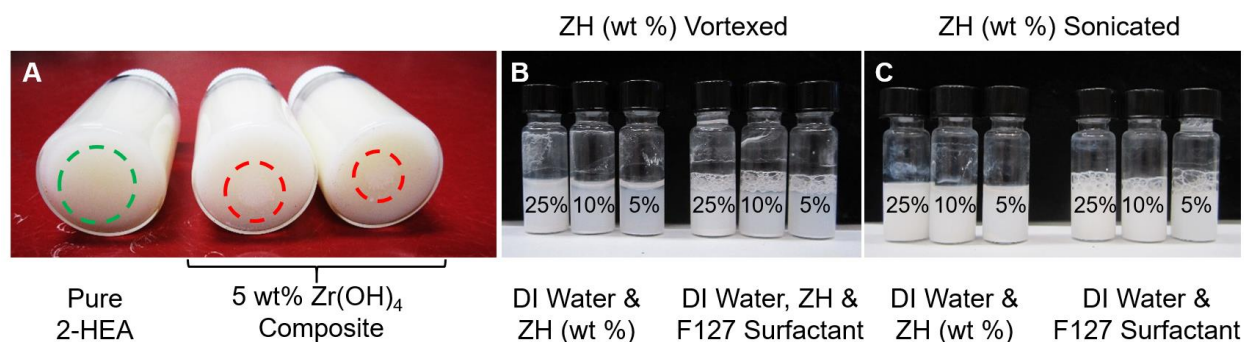


Fig. 12. Zirconium hydroxide added by the designated wt % to vials containing both DI water and F-127 surfactant dissolved in DI water. (A) Pure 2-HEA polyHIPE (green circle) and 5 wt % ZH polyHIPEs were prepared and show some settling of ZH during polymerization (red circles). The ZH was mixed with the solutions by (B) vortexing for 30 s and (C) by sonication for 2 h. The photographs show the colloidal stability of the ZH suspensions after 2 h of resting.

Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX) elemental mapping was performed on a cross section of 5 wt % loaded ZH polyHIPE (Fig. 13). From the figure, a 10 μm cluster of ZH is observed and appears to be well integrated into the matrix of the polyHIPE and likely isn't easily removed. This is an important feature for applications requiring robust integration of metal (hydr)oxides into porous polymers. An elemental map of zirconium (Fig. 13B), carbon (Fig. 13C), and

the superimposed images (Fig. 13D) identify the differences in the observed morphological features with their respective elements. The carbon signal can be primarily attributed to the polymer matrix, while the Zr is clearly from ZH. Additionally, small clusters of Zr signal are scattered throughout the image, suggesting that ZH is well distributed throughout the polymer matrix.

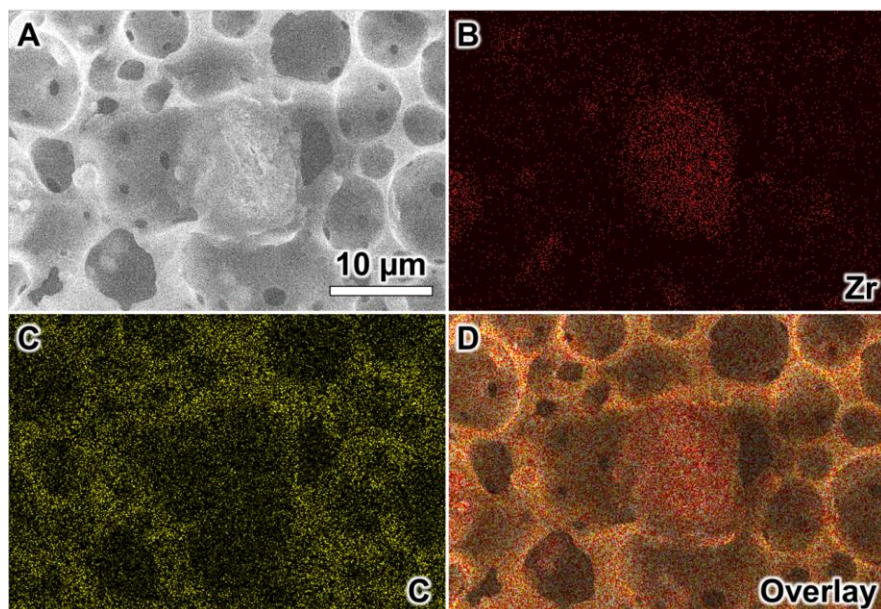


Fig. 13. Scanning electron microscopy energy dispersive X-ray spectroscopy maps of 2-HEA polyHIPE composites with zirconium hydroxide (ZH). These images show incorporation of ZH within the polymer matrix. Scale bar is 10 μm . (A) shows the secondary electron image of the surface of the composite foam, elemental maps of Zr (B) and carbon (C), and image of the elemental maps superimposed over the secondary electron image (D).

3.3 Probing defect sites

From the obtained SEM images and SEM-EDX spectra, it is likely that the polymer composites are gas permeable and ZH sites should be accessible and quantifiable when dosed with probe molecules. A pristine 2-HEA polyHIPE monolith did not show any interaction with CO or CO₂ gas dosed over the pristine polyHIPE monolith. This was expected and demonstrates that the polymer is unreactive and stable under this environment. Unfortunately, DRIFTS spectroscopy collected for CO and CO₂ dosing of a 5 wt % ZH 2-HEA polyHIPE composite also did not form any adsorbates. This indicates that the probe molecules were unable to find a sufficient quantity to ZH active sites to produce a signal above the instrumental noise. Previous research conducted with similar polyHIPE materials and ZH did show accessibility of a liquid reagent to the embedded ZH, which yielded quantifiable reaction products.

Collectively, previously unpublished experiments at NRL and the findings shown herein suggest that more ZH is likely needed to produce a quantifiable infrared signature that can be used to quantify if, and to what extent, the various polymer moieties modulate the defects sites of embedded ZH powders. Based on SEM-EDS data and visual inspection of the prepared samples, one possible solution is to increase the ZH loading of the polymer monolith to enhance the DRIFTS signal during CO dosing.

4. CONCLUSIONS

The work performed during Karle fellowship has produced several notable conclusions:

1. Highly porous polymer monoliths with spherical voids and highly interconnected channels has been successfully synthesized using three monomers: 2-dimethylaminoethyl acrylate, 2-hydroxyethyl acrylate, and acrylic acid.

2. Degradation of 2-dimethylaminoethyl acrylate- and acrylic acid-based polyHIPEs is observed during vacuum drying and yields unusable materials. Such degradation is likely to be remedied via modification of the polyHIPE synthesis precursors or by addition of a stabilizing or cross-linking co-monomer.
3. Porous polyHIPE 2-HEA materials are mechanically robust, tear resistant, and “sponge-like”. They offer some degree of shape memory and can be easily synthesized with metal (hydr)oxide additives to produce polymer composite materials. However, in the case of ZH, some settling occurs during polymerization.
4. SEM-EDX suggests ZH is well dispersed throughout the polymer and is strongly bound to the polymer matrix.
5. 2-HEA polyHIPEs were unreactive towards both CO₂ and CO probe molecules, suggesting stability under such an environment.
6. Zr loaded (5 wt %) 2-HEA polyHIPE produced no quantifiable DRIFTS signal during CO and CO₂ dosing. Higher Zr loadings will likely solve this problem and enable a method to probe for modulation to ZH defects site electronics.

5. FUTURE WORK

The foundation of research described herein can be continued in a number of directions. Completion of such work will help transition this fundamental study into more applied areas of research.

5.1.1 Particle settling

During composite formation, it is observed that the ZH nanoparticles do not remain colloidally stable and some degree of particle settling is observed on the bottom of the cured monoliths. While the majority of the monolith does in fact contain ZH as observed by SEM-EDX, there likely exists gradients throughout. One way to measure a nanoparticle concentration gradient throughout the polymer matrix would be to perform thermal gravimetric analysis of different slices of the monolith.

Stabilizing nanopowder within the polymer matrix may be difficult, but several potential solutions exist. One could change to a more colloidally stable solvent/polymerization system, cap the ZH nanoparticles with surfactants that provide stronger interaction with the solvent, and/or functionalize both the polymer and/or nanoparticles to have affinity for each other (e.g. click chemistry). It may also be possible to accelerate the rate of polymerization to prevent the ZH nanopowders from settling.

5.1.2 Synthesis of more stable acrylate polyHIPEs

Significant challenges occurred during the synthesis of several other acrylate based polyHIPE materials – particularly during the vacuum drying steps. More work is needed to finding a less detrimental internal phase that doesn't degrade the polymer matrix. Additionally, various washing/purifying steps may be necessary to prevent degradation of the polymer. Some possible solutions are soxhlet extraction and solvent exchange. Additionally, the vacuum drying step is quite aggressive to the highly porous polymer materials and may collapse channels and pores throughout the monolith. Softer methods like super critical CO₂ may be a safer route to maintaining the porosity throughout the polyHIPEs.

5.1.3 Defect site probing

Unfortunately, CO and CO₂ dosing yielded no interaction with 2-HEA polymer composite with 5 wt % loading of ZH. It is likely that a larger amount of ZH is necessary to observe defect site interaction with probe molecules. More work with larger loading of ZH would bring valuable insight to the interaction of the polymer constituents and embedded metal (hydr)oxides.

Additional probe molecules may also be interesting to explore such as pyridine, chloroform, acetonitrile, glycine, etc. This will provide insight into the relative acidity/basicity of the defect sites and important information about the accessibility of such sites.

5.1.4 Additive manufacturing

Many of the polymers used in this study have also been reported to be photo-initiated. Additionally, the polymers used in this work were polymerized without removing the monomer inhibitors. This provides a way to maintain the stability of the monomer under more “extreme environments” and provides a unique opportunity to incorporate additive manufacturing. A photo-initiator can be added to the polymer recipe, which then enables polymerization via UV illumination. Incorporation of the photo-initiator is relatively straightforward as the synthesis was designed to be top-down, providing simple modification to polymer recipes and ease of formulation using the FlackTek SpeedMixer. This combination provides a simple way to prepare stabilized emulsions that have the potential to be 3D printed via solid freeform fabrication (SFF). SFF of polymer matrixes offers a tunable and highly reproducible synthesis method with on-demand control over multiple synthesis parameters (size, monomer, and composition) and morphologies. Additionally, SFF allows simple integration of ZH nanopowders into these polymer matrixes for diverse interfacial chemistry and reactivity. The surface functionality of the polymer matrixes, the polymer interfacial chemistry with ZH, and the overall stability of the polymer matrixes is of great interest.

REFERENCES

- [1] Bandosz, T. J.; Laskoski, M.; Mahle, J.; Mogilevsky, G.; Peterson, G. W.; Rossin, J. A.; Wagner, G. W., Reactions of VX, GD, and HD with $Zr(OH)_4$: Near Instantaneous Decontamination of VX. *Journal of Physical Chemistry C* **2012**, 116, (21), 11606-11614.
- [2] Clearfield, A., Structural Aspects of Zirconium Chemistry. *Reviews of Pure and Applied Chemistry* **1964**, 14, (Sep), 91-108.
- [3] Southon, P. D.; Bartlett, J. R.; Woolfrey, J. L.; Ben-Nissan, B., Formation and Characterization of an Aqueous Zirconium Hydroxide Colloid. *Chemistry of Materials* **2002**, 14, (10), 4313-4319.
- [4] Peterson, G. W.; Karwacki, C. J.; Feaver, W. B.; Rossin, J. A., Zirconium Hydroxide as a Reactive Substrate for the Removal of Sulfur Dioxide. *Industrial & Engineering Chemistry Research* **2009**, 48, (4), 1694-1698.
- [5] Mogilevsky, G.; Karwacki, C. J.; Peterson, G. W.; Wagner, G. W., Surface Hydroxyl Concentration on $Zr(OH)_4$ Quantified by 1H MAS NMR. *Chemical Physics Letters* **2011**, 511, (4-6), 384-388.
- [6] Balow, R. B.; Lundin, J. G.; Daniels, G. C.; Gordon, W. O.; McEntee, M.; Peterson, G. W.; Wynne, J. H.; Pehrsson, P. E., Environmental Effects on Zirconium Hydroxide Nanoparticles and Chemical Warfare Agent Decomposition: Implications of Atmospheric Water and Carbon Dioxide. *ACS Applied Materials & Interfaces* **2017**, 9, (45), 39747-39757.
- [7] McEntee, M.; Peterson, G. W.; Balboa, A.; Jordanov, I.; Balow, R. B.; Pehrsson, P. E., Surface Chemistry of Sulfur Dioxide on $Zr(OH)_4$ Powder: The Role of Water. *The Journal of Physical Chemistry C* **2019**, 123, (28), 17205-17213.
- [8] Bobbitt, N. S.; Mendonca, M. L.; Howarth, A. J.; Islamoglu, T.; Hupp, J. T.; Farha, O. K.; Snurr, R. Q., Metal-organic frameworks for the removal of toxic industrial chemicals and chemical warfare agents. *Chemical Society Reviews* **2017**, 46, (11), 3357-3385.
- [9] Peterson, G. W.; Destefano, M. R.; Garibay, S. J.; Ploskonka, A.; McEntee, M.; Hall, M.; Karwacki, C. J.; Hupp, J. T.; Farha, O. K., Optimizing Toxic Chemical Removal through Defect-Induced UiO-66-NH₂ Metal-Organic Framework. *Chemistry – A European Journal* **2017**, 23, (63), 15913-15916.
- [10] King, G.; Soliz, J. R.; Gordon, W. O., Local Structure of $Zr(OH)_4$ and the Effect of Calcination Temperature from X-ray Pair Distribution Function Analysis. *Inorganic Chemistry* **2018**, 57, (5), 2797-2803.
- [11] Hill, I. M.; Hanspal, S.; Young, Z. D.; Davis, R. J., DRIFTS of Probe Molecules Adsorbed on Magnesia, Zirconia, and Hydroxyapatite Catalysts. *Journal of Physical Chemistry C* **2015**, 119, (17), 9186-9197.
- [12] Deiana, C.; Fois, E.; Martra, G.; Narbey, S.; Pellegrino, F.; Tabacchi, G., On the Simple Complexity of Carbon Monoxide on Oxide Surfaces: Facet-Specific Donation and Backdonation Effects Revealed on TiO₂ Anatase Nanoparticles. *ChemPhysChem* **2016**, 17, (13), 1956-1960.

- [13] Malyshev, M. E.; Paukshtis, E. A.; Malysheva, L. V.; Toktarev, A. V.; Vostrikova, L. A., N₂ and CO As Probe Molecules for Determining the Properties of Acid Sites on the Surface of Zeolites. *Kinetics and Catalysis* **2005**, 46, (1), 100-106.
- [14] Lustemberg, P. G.; Scherlis, D. A., Monoxide carbon frequency shift as a tool for the characterization of TiO₂ surfaces: Insights from first principles spectroscopy. *The Journal of Chemical Physics* **2013**, 138, (12), 124702.
- [15] Lefrancois, M., The Nature of the Acidic Sites on Mordenite Characterization of Adsorbed Pyridine and Water by Infrared Study. *Journal of Catalysis* **1971**, 20, (3), 350-358.
- [16] Hattori, H., The Nature of the Acid Sites on Cationized Zeolites Characterization by Infrared Study of Adsorbed Pyridine and Water. *Journal of Catalysis* **1968**, 12, (2), 111-120.
- [17] Aramendia, M. A.; Borau, V.; Jimenez, C.; Marinas, J. M.; Porras, A.; Urbano, F. J., Synthesis and Characterization of ZrO₂ as an Acid-Base Catalyst - Dehydration-Dehydrogenation of Propan-2-ol. *Journal of the Chemical Society, Faraday Transactions* **1997**, 93, (7), 1431-1438.
- [18] Ouyang, F.; Nakayama, A.; Tabada, K.; Suzuki, E., Infrared Study of a Novel Acid-Base Site on ZrO₂ by Adsorbed Probe Molecules. I. Pyridine, Carbon Dioxide, and Formic Acid Adsorption. *Journal of Physical Chemistry B* **2000**, 104, (9), 2012-2018.
- [19] Daniel, D. W., Infrared studies of carbon monoxide and carbon dioxide adsorption on platinum/ceria: the characterization of active sites. *The Journal of Physical Chemistry* **1988**, 92, (13), 3891-3899.
- [20] Lavalley, J. C., Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules. *Catalysis Today* **1996**, 27, (3-4), 377-401.
- [21] Martra, G.; Cacciatori, T.; Marchese, L.; Hargreaves, J. S. J.; Mellor, I. M.; Joyner, R. W.; Coluccia, S., Surface morphology and reactivity of microcrystalline MgO: Single and multiple acid-base pairs in low coordination revealed by FTIR spectroscopy of adsorbed CO, CD₃CN and D₂. *Catalysis Today* **2001**, 70, (1), 121-130.
- [22] Hayward, A. S.; Sano, N.; Przyborski, S. A.; Cameron, N. R., Acrylic-Acid-Functionalized PolyHIPE Scaffolds for Use in 3D Cell Culture. *Macromolecular Rapid Communications* **2013**, 34, (23-24), 1844-1849.
- [23] Yang, Y. S.; Qi, G. R.; Qian, J. W.; Yang, S. L., Acryloyl chloride polymer. *Journal of Applied Polymer Science* **1998**, 68, (4), 665-670.
- [24] Ahmad, N. M.; Charleux, B.; Farcet, C.; Ferguson, C. J.; Gaynor, S. G.; Hawket, B. S.; Heatley, F.; Klumperman, B.; Konkolewicz, D.; Lovell, P. A.; Matyjaszewski, K.; Venkatesh, R., Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate. *Macromolecular Rapid Communications* **2009**, 30, (23), 2002-2021.
- [25] Azhar, U.; Yaqub, R.; Li, H.; Abbas, G.; Wang, Y.; Chen, J.; Zong, C.; Xu, A.; Yabin, Z.; Zhang, S.; Geng, B., Di-block copolymer stabilized methyl methacrylate based polyHIPEs: Influence of hydrophilic and hydrophobic co-monomers on morphology, wettability and thermal properties. *Arabian Journal of Chemistry* **2019**.
- [26] Kircher, L.; Theato, P.; Cameron, N. R., Reactive thiol-ene emulsion-templated porous polymers incorporating pentafluorophenyl acrylate. *Polymer* **2013**, 54, (7), 1755-1761.
- [27] McGann, C. L.; Daniels, G. C.; Giles, S. L.; Balow, R. B.; Miranda-Zayas, J. L.; Lundin, J. G.; Wynne, J. H., Air Activated Self-Decontaminating Polydicyclopentadiene PolyHIPE Foams for Rapid Decontamination of Chemical Warfare Agents. *Macromolecular Rapid Communications* **2018**, e1800194.
- [28] Balow, R. B.; Giles, S. L.; McGann, C. L.; Daniels, G. C.; Lundin, J. G.; Pehrsson, P. E.; Wynne, J. H., Rapid Decontamination of Chemical Warfare Agent Simulant with Thermally Activated Porous Polymer Foams. *Industrial & Engineering Chemistry Research* **2018**, 57, (25), 8630-8634.
- [29] Le Gac, P. Y.; Choqueuse, D.; Paris, M.; Recher, G.; Zimmer, C.; Melot, D., Durability of polydicyclopentadiene under high temperature, high pressure and seawater (offshore oil production conditions). *Polymer Degradation and Stability* **2013**, 98, (3), 809-817.
- [30] Vallons, K. A. M.; Drozdak, R.; Charret, M.; Lomov, S. V.; Verpoest, I., Assessment of the mechanical behaviour of glass fibre composites with a tough polydicyclopentadiene (PDCPD) matrix. *Composites Part A: Applied Science and Manufacturing* **2015**, 78, 191-200.
- [31] Kovacic, S.; Krajnc, P.; Slugovc, C., Inherently reactive polyHIPE material from dicyclopentadiene. *Chemical Communications* **2010**, 46, (40), 7504-6.
- [32] Owen, R.; Sherborne, C.; Paterson, T.; Green, N. H.; Reilly, G. C.; Claeysens, F., Emulsion templated scaffolds with tunable mechanical properties for bone tissue engineering. *Journal of the Mechanical Behavior of Biomedical Materials* **2016**, 54, 159-172.
- [33] Kimmins, S. D.; Cameron, N. R., Functional Porous Polymers by Emulsion Templating: Recent Advances. *Advanced Functional Materials* **2011**, 21, (2), 211-225.