Effects of microwave and ultrasound exposure to microsphere particles made out of different classes of inorganic and organic materials

Chandima Weerakkody[+], Curtis Guild[+], Laura A. Achola, Joseph Palo, Steven L. Suib*

Department of Chemistry and Institute of Materials Science, University of Connecticut, 55 North Eagleville Road, U-3060, Storrs, CT 06269, United States

Abstract

In this study polymer, metal oxide and polymer-PZT composite microsphere materials were prepared by either hydrothermal or microwave assisted methods. Materials were subjected to microwave and ultrasound irradiation under specific conditions in order to understand their mechanical stability and morphological changes in dimensions. Scanning electron microscopy imaging was carried out before and after each irradiation and clear differences were observed depending on irradiation method and sample composition.

Key words: Microsphere, Ultrasound, Microwave, Irradiation

Introduction

The effect of energy adsorption by materials is highly dependent on several factors including composition, dielectric constant, morphology, and other attributes. Absorption of energy typically involves retaining of the energy to a point (*capacity*) upon which processes of dissipation may take place. These processes include radiative and non-radiative processes, the latter of which may be utilized to effect a chemical or/and morphological change in the material, thereby crate a change

in material dimensions. This strategy is heavily used in chromophoric sensing of temperature or radiation.

There are numerous classes of materials, which may adsorb energy and convert it to heat. During the past decade, significant progress has been made in the field of medical science for the advancement of medical therapies through the application of degradable polymers [1]. Carbonaceous polymers are composed of chains of carbon affixed with pendant groups either branching off the main backbone or incorporated within. Degradable materials are used for the treatment of cancer, development of vaccines and many other applications in medical sciences. However, suitability of polymer materials in these sophisticated applications has become a serious concern [2]. Therefore, understanding of the polymer degradation process is a key factor for the progression of these methodologies in various applications. Ceramic materials contain a wide range of typically crystalline compositions, and are widely used for their unique electronic and magnetic properties (Piezoelectric Properties of ferroelectric PZT-Polymer composites).

Composites made of ceramics combined with polymers have several advantages over pure ceramics [3]. Ferroelectric ceramics such as PZT have high values of piezoelectric strain coefficient (d) but their piezoelectric voltage coefficient (g) values are low because of their high dielectric constant values, which is disadvantageous in many transducer applications. Ceramics display a high stiffness constant and high density, which make them mechanically less stable [4]. Polymers are less dense and mechanically more obedient than the ceramics, but their d coefficient values are much lower. However, they have high g values due to their low dielectric constant values. To overcome these problems composites containing piezoelectric ceramics and polymers/copolymers have been proposed [5]. Here we discuss how ultrasound and microwave radiation can be used to effect morphological changes in PZT- polystyrene composite materials.

Two dimensional (2D) and three dimensional (3D) structures of metal oxides and hydroxides are continuing to be at the forefront of applications such as catalysis and energy storage due to their unique chemical and physical properties, which can be attributed to their dimensional anisotropy [6]. The improvement of their overall performance, mainly including the activity and stability, significantly depends on the advancement of new materials and their architectures. Understanding the dependence of physical and chemical properties under different irradiation methods can be used as a tool in the advancement of these materials for the above-mentioned applications [7,8].

These different classes of materials are of interest to this study due to their variable dielectric constants, compositions, and chemical attributes. They also vary widely in their thermal stabilities before decomposition to parent oxides.

The use of electromagnetic (EM) radiation to effect localized heating in materials is widely used by society, ranging from commercial to military applications. We refer to these methods as *Non-contact heat generation methods.*

Microwave transmission (300 MHz- 300 GHz) is a polarized radiation and is either horizontally or vertically oriented to the substrate when adsorbed. Microwaves can be transmitted through air and water over long ranges. Microwave irradiation creates efficient internal heat-transfer, resulting in uniform heating throughout the sample compared to wall heat-transfer via thermal heating. Therefore, the tendency for seed formation is reduced, and superheating is achievable even at atmospheric pressure [9].

Ultrasound is radiation typically in the near-acoustic spectrum and can be transmitted through air and water at short ranges. Acoustic waves of which frequencies are higher than the upper limit of the human hearing range, are called ultrasound [10]. In engineering applications, ultrasound is

favorably used to enhance systems efficiencies. Regulating chemical reactions, drying, welding, and cleaning are among the various potential applications of ultrasonic waves. Acoustic streaming could be used to modify heat transfer where such streaming can induce heating of the medium due to the dissipation of mechanical energy [11].

Overall our goal of this work focuses on understanding the behavior of microspheres made out of different chemical substances, in order to alter their dimensions by applying non-contact energy transfer methods. We demonstrate ultrasound / microwaves can be transmitted and directed a usable distance to change dimensions of microspheres made out of a variety of substances in order to create physical space inside the material.

Experimental Methods

Synthesis of Materials

The materials were sourced either from Sigma Aldrich (PVDF) or synthesized in house. The crystalline attributes of the samples were examined by X-ray powder diffraction *(Figure 2)*.

Nickel Nitrate (1.454g), Glycine (2g) and sodium sulfate (2g) was dissolved in 25 mL water. 5M $NaOH_{(aq)}$ was added dropwise to form a clear blue solution. The resulting solution was sealed in a Teflon autoclave and hydrothermally treated for 24 hr at 140˚C. The solid hydroxide was centrifuged from the mother liquor, washed in excess DI water. The solids were then treated at 600˚C for 2hours.

About 0.299 g of lead acetate was dissolved in 1 mL of glacial acetic acid. 0.102 g of zirconium acetate and 0.140 g of titanium isopropoxide were dissolved in 4 mL of ethanol and then added to

the lead acetate solution. The mixture was stirred on a string plate for 30 min. Next, 10 mg of azobisisobutyronitrile (AIBN), 0.1 g of polyvinyl pyridine (PVP) and 1.25 mL of styrene was added to the mixture and then stirred for another 30 min. Finally, the mixture was diluted to 10 mL with ethanol and heated under microwave irradiation at 150 °C for 30 min. The formed solid was collected by filtration and dried under vacuum for 24 h. PDVF was bought from Sigma.

Material Characterization

Powder X-Ray Diffraction was performed with a Rigaku Ultima IV diffractometer using Cu Kα radiation and a quartz sample holder. Thermogravimetric Analysis (TGA) was performed utilizing a TA Instruments Q500 Analyzer. The sample was heated at 10°C/min to 900°C under flowing air. Scanning electron microscopy (SEM) was performed using an FEI NovaSEM at 2.0 kV and 4 mm working distance. Samples were mounted on carbon tape on aluminum stubs. Fourier-Transformed Infrared Spectroscopy (FT-IR) was performed in the mid-IR range (400-4000 cm^{-1}) using a Thermo Nicolet 8700 FTIR with potassium bromide beam splitters.

Microwave Studies were performed with a CEM Mars 5 microwave digester system. Briefly, 5-10 mg of sample was spread on a Pyrex watch glass, which was suspended in the center of the microwave cavity. Power was delivered in 30 second pulses at 2.1 GHz with various power levels (300W, 600W, 1200W). Non-contact ultrasound was performed using an Ultran NGC30-D50 transducer powered by a Trek AC power supply operating at 3.0 kHz at 100 V. The signal was generated using an INSTRUMENT signal generator. The signal and high-voltage output was monitored by a Tektronix oscilloscope.

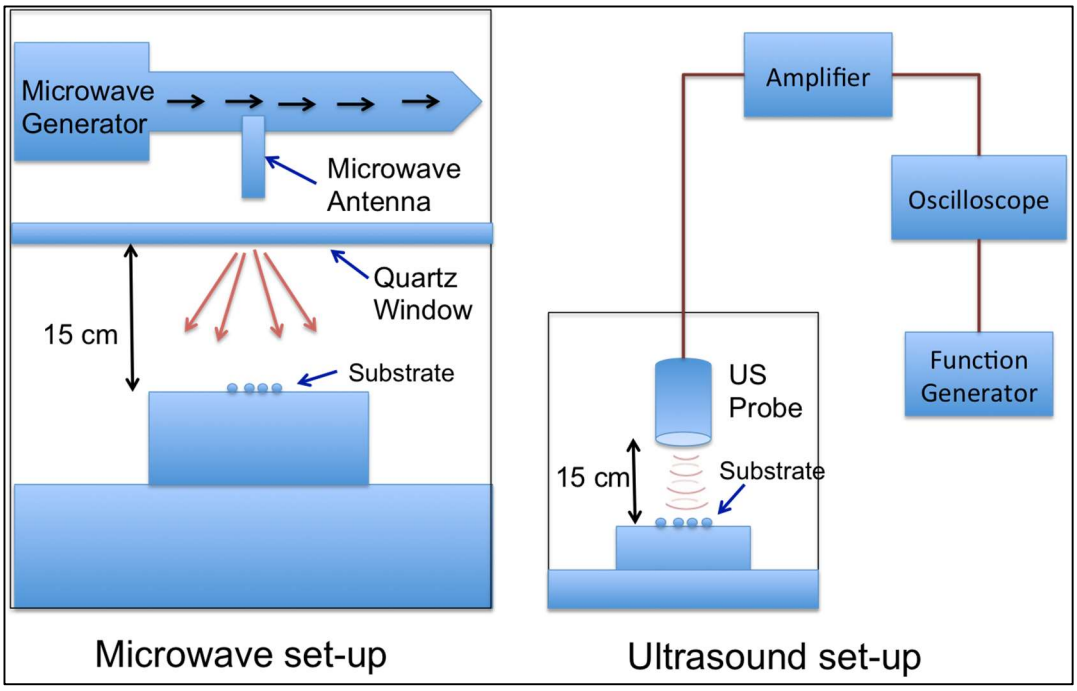

Figure 1. Experimental set-up and Methods of Energy Transfer

Results and Discussion

Pure phases of each material were identified by PXRD analyses. An amorphous structure was detected for polystyrene with two broad peaks around 10 and 20 two theta values. In PZT-PS composites, peaks for the $PbZr_{0.53}Ti_{0.47}O_3$ structure was identified along with a hump around 20 degrees due to the presence of PS. The PXRD pattern of PVDF matched with its reported pattern [12]. NiO microspheres gave cubic NiO phase via powder X-ray diffraction analysis[13].

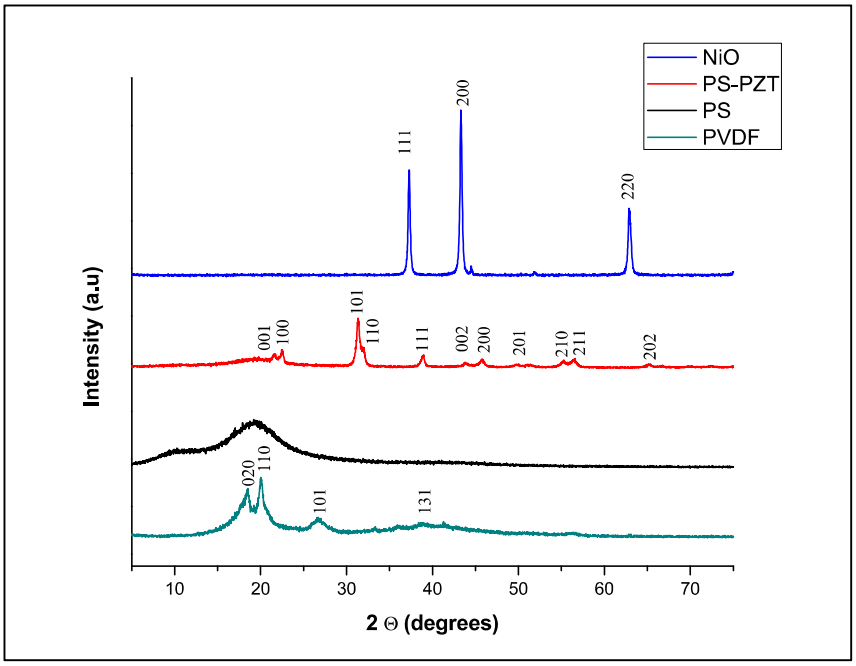

Figure 2. Powder X-ray diffraction patterns of the polymer, polymer composite, and hydroxide materials.

Effects of US and MW irradiation on the above-mentioned materials were detected by SEM imaging. Figure 3 shows the SEM images for NiO, PS and PZT-PS materials before and after US/MW treatment. Under ultrasound a morphological change was identified in NiO and polystyrene but PZT-PS remained intact. On the other hand, NiO and PZT-PS showed a noticeable change in appearance when subjected to microwave irradiation. PVDF showed a change in particle size in both US and MW treatments and the particle size distribution charts are given in Figure 4.

Both NiO and PS exhibited particle aggregation with US exposure and the deformation of the particles could be observed in both cases. Ultrasound triggered the change in particle size of PVDF while not any aggregation was detected. However, no significant effect was observed in PZT-PS under US irradiation suggesting that the material is quite stable under an ultrasound frequency of 3.0 kHz. Physical effects of ultrasound, which often also create chemical effects, include increased

mass transport, emulsification, and bulk thermal heating [14]. Inter-particle collisions created by ultrasound radiation are capable of inducing striking changes in surface morphology, composition, and reactivity of solid materials. Even though this type of behavior was previously reported for solid-liquid systems, the present study reveals the possibility of application of ultrasound on solid-air systems for structural modifications. In the recent past, search for new polymers with improved properties continued to attract great research interest and led to a large effort in modifying existing polymers. Physical and chemical changes induced by ultrasound in polymer systems include polymer degradation for drug delivery applications, the encapsulation of inorganic particles with polymers, modification of particle size in polymer powders, and the welding and cutting of thermoplastics [14]. PVDF used in this study showed changes in particle size due to shrinkage and swelling upon exposure to ultrasound (Figure 4) signifying that ultrasound transmitted through air can be used as a tool for the modification of particle size in polymer materials.

The temperature of each material was measured before and after subjecting to US and MW irradiation. A 4-6 °C temperature difference was clearly observed in all samples in MW testing. However a significant temperature difference was not seen under US. The heat absorbed under microwave heating was calculated for each material using $Q = mc\Delta t$, where m=mass of the substance, c=specific heat capacity, and Δt=temperature change. The thermal energy for polystyrene, PZT-PS, and NiO were calculated as 0.075, 0.014, and 0.035 J, respectively. The interaction of microwaves with solid particles takes place through the electric field vector and the magnetic field vector [15]. Therefore, microwave heating is dependent on the dielectric constant, electronic conductivity, and permeability of a particular compound. On the other hand, the effects of ultrasound are typically divided into chemical and mechanical effects. The high temperatures

are responsible for chemical effects such as radical formation, whereas the shear gradients produce mechanical effects. Since we use a low energy waveform of US (3 kHz), we might not see a temperature rise even though the mechanical effect is visible. Mechanical effects play an important role in ultrasound induced polymerizations as they may trigger scission of the polymers [16].

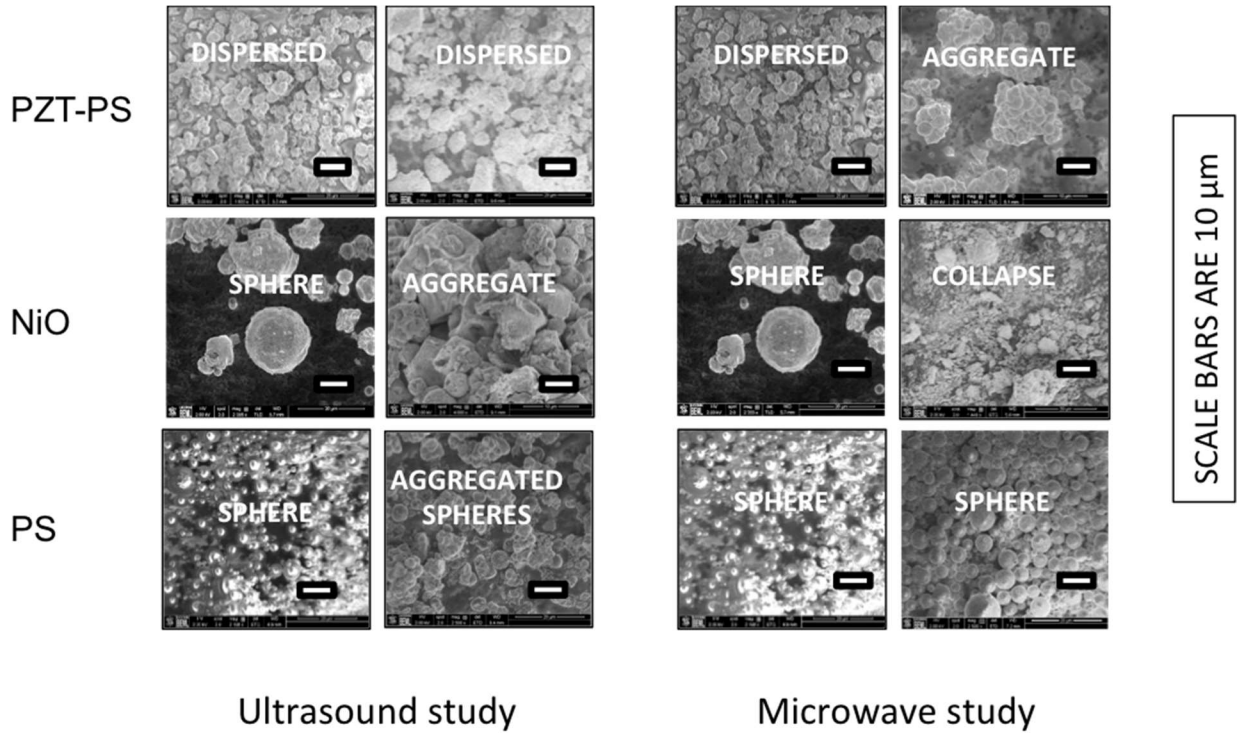

Figure 3. SEM images of polystyrene, NiO and PZT-polystyrene materials before and after ultrasound and microwave exposure

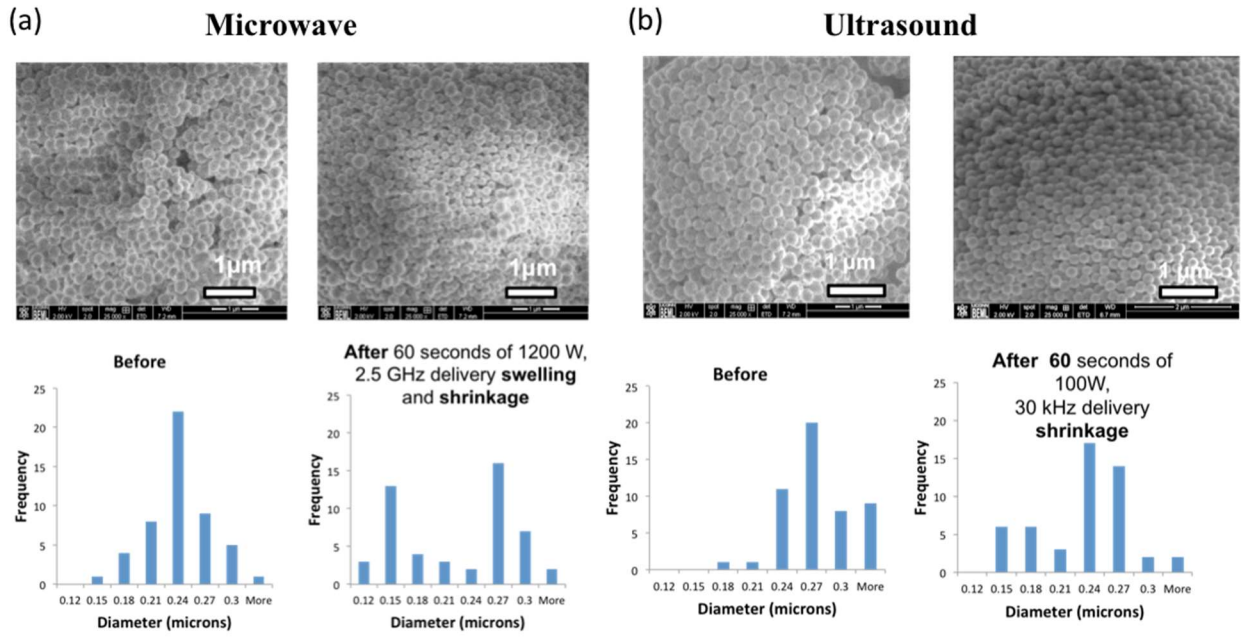

Figure 4. SEM images and particle size distribution charts for PVDF before and after (a) microwave exposure and (b) ultrasound exposure (50 particles counted, diameters taken only on fully visible spheres).

Thermal stability is a key factor when comes to energy related applications of theses materials. Thermal behavior of the materials was studied by thermo gravimetric analysis and the TGA-MS profile for as synthesized polystyrene microspheres is given in Figure 5. It indicates material is stable up to 300°C and slowly starts degrading at 300°C. However, material degraded completely around 425°C, giving off benzene and other hydrocarbon fragmentations.

Moreover, the use of ultrasound to accelerate chemical reactions and modification of materials in solid inorganic systems has become a widespread application. When the US waves pass over particles in close arrangement to one another, high velocity inter-particle collisions can take place. If the collision is at a direct angle, metal particles can be forced together at a sufficiently high

speed to start melting at the point of collision [17]. This melting can cause particle agglomeration as observed with PS and NiO in this work.

Microwave radiation caused aggregation of PZT-PS materials into larger solid masses and collapse of NiO spheres. The efficiency of microwave flash heating in reduced reaction times has been proven in several different fields of industrial chemistry [9]. Therefore, the time saved by using focused microwaves is given a greater importance in the field of high-speed combinatorial and medicinal chemistry. The heating rate is affected by the dielectric properties of the sample. The applied field interacts with the alignment of the molecular electric dipoles in the sample, and this interaction creates the microwave dielectric heating [9].

The composite systems of polymers and ferroelectric PZT ceramics exhibit piezoelectric properties if they have been subjected to a high electric field [3]. This process, called poling, causes the orientation of PZT in the composites and the composites show a mechanical response due to an electrical excitation. Agglomeration of PZT-PS composite particles upon microwave heating can be explained as a mechanical response due to the electrical field generated by electromagnetic radiation. Moreover, with the aid of microwave heating, sintering has been found to be advantageous in the reduction of particle sizes in ceramics [8]. However, microwave energy was only sufficient to deform the PVDF particles due to the non-contact heating, which resulted in a change in particle size distribution before and after treatment as shown in Figure 4.

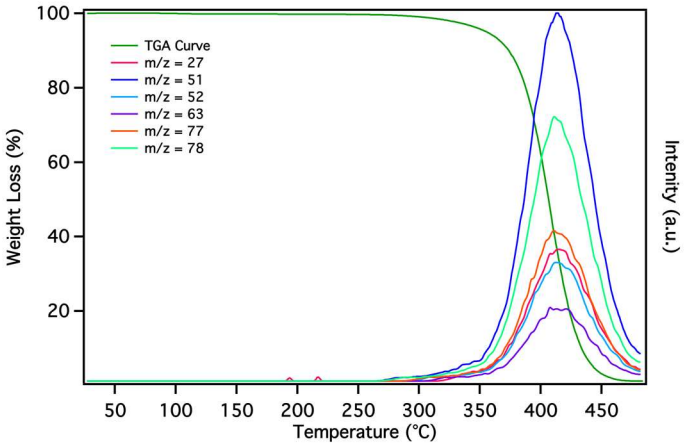

Figure 5. TGA-MS profile of the as synthesized polystyrene microspheres

Summary

In summary, we analyzed structural and morphological changes of selected set of materials, which have varying dielectric constants. Use of these materials in the manufacturing of high value capacitors is highly dependable on their stability under irradiation or heating. Polymers, metal oxides and ceramic materials were studied upon irradiation with ultrasound and microwave and the morphological changes were identified through SEM imaging. Polystyrene microspheres showed aggregation when irradiated with ultrasound, whereas no significant change was observed with microwave. Polyvinylidene fluoride microspheres exhibited swelling and shrinkage when exposed to ultrasound and microwaves, hence differences in particle size distribution were observed in SEM imaging. This change in particle size distribution probably leads to the creation of space in between particles with in the material. Collapse and aggregation of microspheres was observed in NiO, upon exposure of ultrasound and microwaves, respectively. PZT-PS ceramic materials showed particle aggregation only with ultrasound irradiation. Overall we observed a

significant change in dimensions of microspheres made with variety of materials, which could be induced via non-contact energy transferring techniques.

Author information

Corresponding Author

*Fax: (+1) (860)-486-2981. E-mail: steven.suib@uconn.edu

[+] These authors contributed equally.

Notes

The authors declare no competing financial interest.

Acknowledgements

We thank JD Pharma, LLC. for support of this work. This work was partly funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical, Biological and Geological Sciences under grant DE-FG02-86ER13622.A000.

References

[1] A. Gopferich, Mechanisms of polymer degradation and erosion, Biomaterials. 17 (1996) 103–114. doi:10.1016/0142-9612(96)85755-3.

[2] J. Kost, K. Leong, R. Langer, Ultrasound-enhanced polymer degradation and release of incorporated substances., Proc. Natl. Acad. Sci. U. S. A. 86 (1989) 7663–7666.

doi:10.1073/pnas.86.20.7663.

[3] T. Furukawa, K. Ishida, E. Fukada, Piezoelectric properties in the composite systems of polymers and PZT ceramics, J. Appl. Phys. 50 (1979) 4904–4912. doi:10.1063/1.325592.

[4] H. Search, C. Journals, A. Contact, M. Iopscience, I.P. Address, Piezoelectric properties of ferroelectric PZT – polymer composites, 487 (2001).

[5] Y. Daben, Composite piezoelectric film made from PVDF polymer and PCM-PZT ferroelectric ceramics, Ferroelectrics. 101 (1990) 291–296. doi:10.1080/00150199008016529.

[6] Q. Yang, Z. Lu, J. Liu, X. Lei, Z. Chang, L. Luo, X. Sun, Metal oxide and hydroxide nanoarrays: Hydrothermal synthesis and applications as supercapacitors and nanocatalysts, Prog. Nat. Sci. Mater. Int. 23 (2013) 351–366. doi:10.1016/j.pnsc.2013.06.015.

[7] D. V. Lysov, D. V. Kuznetsov, A.G. Yudin, D.S. Muratov, V. V. Levina, D.I. Ryzhonkov, Preparation of nickel oxide nanostructured powders under the action of ultrasound, Nanotechnologies Russ. 5 (2010) 493–497. doi:10.1134/S1995078010070098.

[8] L. Xu, Y.S. Ding, C.H. Chen, L. Zhao, C. Rimkus, R. Joesten, S.L. Suib, 3D flowerlike alpha-nickel hydroxide with enhanced electrochemical activity synthesized by microwave-assisted hydrothermal method, Chem. Mater. 20 (2008) 308–316. doi:10.1021/cm702207w.

[9] M. Larhed, A. Hallberg, Microwave-assisted high-speed chemistry: A new technique in drug discovery, Drug Discov. Today. 6 (2001) 406–416. doi:10.1016/S1359-

6446(01)01735-4.

[10] J.L. Luche, Synthetic Organic Sonochemistry, Springer US, 1998. https://books.google.com/books?id=jndfWoDUPygC.

[11] M. Legay, N. Gondrexon, S. Le Person, P. Boldo, A. Bontemps, Enhancement of heat transfer by ultrasound: Review and recent advances, Int. J. Chem. Eng. 2011 (2011). doi:10.1155/2011/670108.

[12] L. Priya, J.P. Jog, Poly(vinylidene fluoride)/clay nanocomposites prepared by melt intercalation: Crystallization and dynamic mechanical behavior studies, J. Polym. Sci. Part B Polym. Phys. 40 (2002) 1682–1689. doi:10.1002/polb.10223.

[13] E. Sathiyaraj, G. Gurumoorthy, S. Thirumaran, Nickel(II) dithiocarbamate complexes containing the pyrrole moiety for sensing anions and synthesis of nickel sulfide and nickel oxide nanoparticles, New J. Chem. 39 (2015) 5336–5349. doi:10.1039/C4NJ02250E.

[14] R.S. Davidson, A. Safdar, J.D. Spencer, B. Robinson, Applications of ultrasound to organic chemistry, Ultrasonics. 25 (1987) 35–39. doi:10.1016/0041-624X(87)90009-6.

[15] R.E. Newnham, S.J. Jang, M. Xu, F. Jones, This Paper Is a Component Part of the Following Compilation Report : Authored Sections of Proceeding , Annals , Symposia , Etc . However , the Component Should Be Considered Within The Context of the Overall Compilation Report and Fundamental Interaction, Ceram. Trans. Vol. 21. Proceedsing Symp. Microw. Theory Appl. Mater. Process. Annu. Meet. Am. Cermic Soc. 21 (1991).

[16] Jos M. J. Paulusse and Rint P. Sijbesma, Ultrasound in Polymer Chemistry: Revival of an Established Technique, J. Polym. Sci. Part A Polym. Chem. 44 (2006) 5445–5453.

doi:10.1002/pola.

[17] A.B. Clark, The Stomach Signals Satiety Author (s): J . A . Deutsch , W . G . Young and T . J . Kalogeris Published by : American Association for the Advancement of Science Stable URL : http://www.jstor.org/stable/1746704 JSTOR is a not-for-profit service that help, 201 (2017) 165–167.