

AFRL-ML-WP-TR-2006-4209

**COLLABORATIVE RESEARCH AND
DEVELOPMENT**

**Delivery Order 0024: Synthesis, Processing,
and Evaluation of Polymers for RF
Applications**

Christy R. Vestal, Ph.D.

**Universal Technology Corporation
1270 North Fairfield Road
Dayton, OH 45432-2600**



JANUARY 2006

Final Report for 01 June 2004 – 31 December 2005

Approved for public release; distribution is unlimited.

STINFO COPY

**MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750**

NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the Air Force Research Laboratory Wright Site (AFRL/WS) Public Affairs Office and is available to the general public, including foreign nationals. Copies may be obtained from the Defense Technical Information Center (DTIC) (<http://www.dtic.mil>).

AFRL-ML-WP-TR-2006-4209 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

*//Signature//

RITA SCHOLLES
Project Manager
Business Operations Branch
Integration and Operations Division

//Signature//

ROBERT ENGHAEUSER
Acting Chief
Business Operations Branch
Integration and Operations Division

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

*Disseminated copies will show “//signature//” stamped or typed above the signature blocks.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YY) January 2006		2. REPORT TYPE Final		3. DATES COVERED (From - To) 06/01/2004 – 12/31/2005	
4. TITLE AND SUBTITLE COLLABORATIVE RESEARCH AND DEVELOPMENT Delivery Order 0024: Synthesis, Processing, and Evaluation of Polymers for RF Applications				5a. CONTRACT NUMBER F33615-03-D-5801-0024	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 62102F	
6. AUTHOR(S) Christy R. Vestal, Ph.D.				5d. PROJECT NUMBER 4349	
				5e. TASK NUMBER L0	
				5f. WORK UNIT NUMBER VT	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Universal Technology Corporation 1270 North Fairfield Road Dayton, OH 45432-2600				8. PERFORMING ORGANIZATION REPORT NUMBER S-531-024	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Materials and Manufacturing Directorate Air Force Research Laboratory Air Force Materiel Command Wright-Patterson AFB, OH 45433-7750				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL-ML-WP	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-ML-WP-TR-2006-4209	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES PAO Case Number: AFRL/WS 06-2545, 26 Oct 2006.					
14. ABSTRACT (Maximum 200 words) This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at the Air Force Research Laboratory (AFRL) from 1 June 2004 through 31 December 2005. RF polymer nanocomposites containing ferrite nanoparticle and core/shell nanoparticles dispersed in polyurethane have been prepared. the permittivity in the X-band was found to increase with increasing nanoparticle volume inclusion and with increasing nanoparticle size. In the CoFeO ₄ /FeO ₄ core/shell nanoparticle nanocomposite, the addition of the Fe ₃ O ₄ shell lowered the permittivity compared to the native CoFeO ₄ particle and increasing the shell thickness further depressed the permittivity. In the FeO ₄ /CoFe ₂ O ₄ core/shell, the permittivity increase with the addition of the shell.					
15. SUBJECT TERMS RF polymer, nanoparticle nanocomposite					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON (Monitor) Rita Scholes 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

COLLABORATIVE RESEARCH AND DEVELOPMENT (CR&D) F33615-03-D-5801 DELIVERY ORDER 24 FINAL REPORT

Title: Synthesis, Processing and Evaluation of Polymers for RF Applications

Christy R. Vestal

Submission Date: 01/25/2006

Research Objectives: The goal of this task is to develop methods to produce materials with tailored electromagnetic properties over a broad frequency range. The research effort focuses on two primary objectives: (1) Create the fundamental understanding necessary to establish relationships for nanoparticle loading and nanoparticle size on the electromagnetic properties in polymer-based nanostructured materials and (2) develop novel materials with enhanced and improved performance properties to address unique military needs for RF/microwave systems.

Background:

RF polymer nanocomposites are unique materials that combine novel electric and magnetic attributes with the inherent structural and processing properties of commodity polymers such as polyurethanes and PTFE. The desired electromagnetic properties for RF applications such as microelectronics and microwave communication systems are high permeability (μ), high permittivity (ϵ) and low loss ($\tan \delta$), where $\mu = \epsilon \sim 3-5$ and $\tan \delta < 0.001$. By producing materials meeting these requirements, we enable the development of higher gain antennas or conversely the miniaturization of RF devices.

The understanding of the structure-property relationship of magnetic nanoparticles for RF applications is still in its infancy. Not only is there a need to develop materials with dielectric permeability and permittivity values that range from 3 to 5, with an essentially flat response over a broad frequency range, but another important objective is to develop an understanding of the properties of the fine particles inclusions and a correlation with their frequency response properties. Previous research findings published in the literature have focused on bulk materials or micron-sized particles (which behave similar to bulk materials) – very little information has been realized concerning structure-property relationship of magnetic nanoparticles for RF applications. This effort has focused upon developing an understanding of the effects of nanoparticle size, nanoparticle volume loading, and core/shell structure with the frequency dependent response from 10MHz-1GHz and 2–20 GHz.

Research and Findings:

The research efforts can be focused into three categories – magnetic nanoparticle fabrication, polymer composite processing, and composite characterization. Highlights from each of these areas include:

Nanoparticle Fabrication: development of synthesis protocols for preparation of $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ and $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ core/shell nanoparticles, Fe_3O_4 particles with prescribed size.

Composite Fabrication: utilization of surface chemistry to disperse nanoparticles into polymer matrix, molding of composites into geometries suitable for electromagnetic characterization

Characterization: characterize every particle produced by transmission electron microscopy (TEM) to determine particle size, size distribution, morphology, and crystal structure; characterize nanocomposites by TEM to determine dispersion quality; analyze the frequency dependent response of the permittivity and permeability of nanocomposites over 2-20GHz

Example efforts during DO24 with noteworthy findings include:

- 1) *Development of magnetic nanoparticle/polymer nanocomposites for RF/microwave evaluation* – 10 nanocomposites containing variable nanoparticles loadings from 0.5 – 80 wt%, 5 nanocomposites at 36.6 wt% containing variable sized nanoparticles from 2-12 nm, and 8 nanocomposites at 36.6 wt% containing different core/shell particles were produced.
- 2) *Established correlation between nanoparticle volume loading with microwave permittivity and permeability of polymer nanocomposites* – Permittivity and permeability increase with volume loading in agreement with Bruggeman model. Loss increased slightly with loading
- 3) *Established correlation between nanoparticle size with microwave permittivity and permeability of polymer nanocomposites* - Permittivity and permeability increase with nanoparticle size. Loss did not increase with size.
- 4) *Development of core/shell magnetic particles* – $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ core/shell particles and $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ core/shell particles with 0.9 – 1.5 nm shell thicknesses
- 5) *Evaluation of composites with core/shell inclusions demonstrating novel enhanced frequency dependent properties not achieved from their independent magnetic material components properties* - The permittivity increases for Fe_3O_4 particles upon addition of CoFe_2O_4 shell, but decreases for CoFe_2O_4 particles with a Fe_3O_4 shell. The values of permittivity are different from solid particulates of the same size. The permeability increased, then decreased at shell thicknesses >1.5 nm for both architectures.

During DO24, 1 conference proceedings paper, 1 invited journal review article (prepared), and 5 presentations (1 invited) were recorded. A detailed list of publications and presentations is included in Appendix A. The conference proceedings paper is included as Appendix B and provides detailed scientific descriptions of data, procedures, and results.

The impact of these successes is demonstrated in the initiation of evaluation with SNHA of the potential of core/shell nanoparticle/polymer nanocomposite for antenna fabrication and testing to determine the potential for improvement and miniaturization utilizing these new materials.

APPENDIX A: Publication and Presentations

Publications:

Vestal, C.R. “Fabrication and Frequency Dependent Properties of Polymer Nanocomposites Containing Magnetic Nanoparticles.” *Nanocomposites 2005 Proceedings*, 153.

Vestal, C.R. and Zhang, Z.J. “Superparamagnetic Properties of Magnetic Nanoparticles.” *Advanced Materials* in preparation.

Presentations: (Presenting Author in Bold)

Vestal, C.R. and Alexander, Jr., M.D. “Fabrication and Frequency Dependent Properties of Polyurethane Nanocomposites Containing Core/Shell Ferrite Nanoparticles” 50th Annual Conference on Magnetism and Magnetic Materials, San Jose, CA, 2005. (*poster presentation*)

Vestal, C.R. “Fabrication and Frequency Dependent Properties of Polymer Nanocomposites Containing Core/Shell Magnetic Nanoparticles” Nanocomposites 2005, San Francisco, CA, 2005 (*invited talk*)

Vestal, C.R. and Alexander, Jr., M.D. “Synthesis and Frequency Dependent Properties of Ferromagnetic Nanoparticle/Polyurethane Nanocomposites.” Spring Meeting Ohio Section of the American Physical Society, Dayton, OH, 2005 (*poster presentation*)

Vestal, C.R. and Alexander, Jr., M.D. “Synthesis and Frequency Dependent Response of Core/Shell Ferromagnetic Nanoparticle/Polyurethane Nanocomposites.” Materials Research Society Spring Meeting, San Francisco, CA, 2005. (*poster presentation*)

Vestal, C.R. and Alexander, Jr., M.D. “Ferromagnetic Nanoparticle/Polyurethane Nanocomposites for RF Applications.” Materials Research Society Fall Meeting, Boston, MA, 2004. (*poster presentation*)

APPENDIX B: Papers

Fabrication and Frequency Dependent Properties of Polymer Nanocomposites Containing Magnetic Nanoparticles

Christy R. Vestal

Universal Technology Corporation, 1270 N. Fairfield Rd. Dayton, OH 45432

Abstract

RF polymer nanocomposites containing ferrite nanoparticles and core/shell nanoparticles dispersed in polyurethane have been prepared. The permittivity in the X-band was found to increase with increasing nanoparticle volume inclusion and with increasing nanoparticle size. In the $\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ core/shell nanoparticle nanocomposite, the addition of the Fe_3O_4 shell lowered the permittivity compared to the native CoFe_2O_4 particle and increasing the shell thickness further depressed the permittivity. In the $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ core/shell system, the permittivity increased with the addition of the shell.

Introduction

RF polymer nanocomposites are unique materials that combine novel advanced electric and magnetic attributes with inherent structural and processing properties of commodity polymers. Desired electromagnetic properties for RF applications such as microelectronics and microwave communication systems are high permeability (μ), high permittivity (ϵ) and low loss ($\tan \delta$).^{1,2} By producing materials meeting these requirements, we enable the development of higher gain antennas or conversely the miniaturization of RF devices. The polymer matrix can be chosen such that it allows for integration into traditional plastic processing technologies to produce shapes of any size or geometry. The most difficult challenge in producing these

materials is increasing the permeability at high frequencies while maintaining low loss. The objective is to eventually produce materials where $\mu = \epsilon \sim 3-5$ and $\tan \delta < 0.001$.

Although ferromagnetic materials display the high permeabilities desired, they have limited applications in microwave applications due to their large conductivities that limit the ability of microwaves to penetrate into bulk materials and therefore the materials exhibit a very high loss factor. One approach commonly taken to overcome the limitations of bulk ferromagnetic materials is to disperse ferromagnetic inclusions in an insulating matrix (i.e. a dielectric material).³⁻⁷ Here we achieve this by incorporating ferrite based magnetic nanoparticles into a polyurethane matrix.

The microwave properties of nanoparticle/polymer nanocomposites depend on both the intrinsic characteristics of the particle and their volume concentration. Previous efforts have focused on bulk materials or micron-sized magnetic particles (which behave similar to bulk materials).³⁻⁷ However, understanding of the structure-property relationship of magnetic nanoparticles for RF applications is still in its infancy.² An important objective of this study is to develop an understanding of these relationships and correlate the frequency dependent response from 2-18 GHz. Here we report current efforts focused upon systematically characterizing the microwave properties of ferrite/polyurethane nanocomposites with the effect of nanoparticle size and volume concentration. Theoretical studies and preliminary experimental measurements of the permeability and permittivity of micron-sized core/shell-type materials show improved properties compared to the solid particulates.^{8,9} Here we seek to extend the prior work to nanometer scale core/shell materials. Preliminary results for the synthesis of core/shell nanoparticles with a tunable ferromagnetic core and shell and the frequency dependent

permittivity of the polymer nanocomposites containing these designed inclusions will be described.

Experimental

Fe_3O_4 and CoFe_2O_4 nanoparticles with size 4 nm were prepared following the thermal decomposition of metal acetylacetonates in organic solvents methods developed by Sun, et.al.¹⁰ Advantages of this method include the formation of high quality nanocrystals with a small size distribution and an oleic acid/oleylamine capped surface that allows for easy dispersion into a polymer matrix. Briefly, Fe_3O_4 nanoparticles were prepared by the heating of $\text{Fe}(\text{AcAc})_3$, 1,2-hexadecanediol, oleic acid and oleylamine were heated to 267°C in phenyl ether under a flow of N_2 . Larger size nanoparticles (4-12 nm) were prepared using the seed-mediated growth method, by varying the phenyl ether solvent concentration, or using benzyl ether as a solvent. CoFe_2O_4 nanoparticles were prepared similarly but using a 1:2 molar ratio of $\text{Co}(\text{AcAc})_2$: $\text{Fe}(\text{AcAc})_3$ metal salts. The nanoparticles were characterized using transmission electron microscopy (TEM) and the particle size was determined by manually counting 500+ particles. A typical TEM and size distribution for Fe_3O_4 nanoparticles is shown in Figure 1. The synthesis of Fe_3O_4 / CoFe_2O_4 and CoFe_2O_4 / Fe_3O_4 core/shell nanoparticles was achieved using seed-mediated growth procedures. The Fe_3O_4 or CoFe_2O_4 core nanoparticle was prepared as described above and these core particles were then used as seeds under the shell nanoparticle synthesis conditions.

Nanocomposites were prepared by dissolving known quantities of Morthane (Huntsman Morthane PS455-23, polyurethane) in THF and mechanically mixing in the magnetic nanoparticles produced using the procedure outlined above. The solution was cast into 1" x 3" Teflon trays and the THF was allowed to evaporate overnight, leaving a smooth thin film. The

films were compressed at 130°C under 10,000 lbs of pressure into a 20 mil thick mold using a Carver Model C hydraulic press.

Microwave properties of the nanocomposites were measured in the X-band (8.2 – 12.4 GHz) using an Agilent E8362B PNA Series Network Analyzer. The permeability and permittivity were determined using the Nicolson-Ross method using the Agilent 85071 program.

Results and Discussion

Figure 2 shows the real part of the permittivity (ϵ') in the X-band (8.2 – 12.4 GHz) for 4 nm Fe_3O_4 nanoparticles with varying loading concentrations. As can be seen, the permittivity increases with nanoparticle loading. This trend is more clearly seen in Figure 3, in which the value of the permittivity at 10GHz is plotted versus nanoparticle volume percent. The solid line in Figure 3 is the Bruggeman effective medium theory (EMT) prediction for the permittivity of the nanocomposite calculated from the measured permittivity for pure morphane and literature values for the permittivity of iron oxides,² and agrees reasonably well with the experimental data. Good agreement with the Bruggeman model has been found in other particle-insulating medium matrixes.^{7, 11, 12} The permeability (μ') (not shown) remained ~ 1 for all nanoparticle loadings over the frequency range investigated here, which was expected due to the reported resonance frequency of Fe_3O_4 at ~ 1.5 GHz. At lower frequencies (1MHz – 1GHz), the permeability also increased with nanoparticle volume loading, however a comparison with Bruggeman EMT has not yet been completed.

Figure 4 shows the permittivity in the X-band for nanocomposites as a function of diameter for Fe_3O_4 nanoparticles at a fixed 12.2 vol% loading. The diameters measured ranged from 4 to 12 nm and the permittivity decreased with decreasing nanoparticle diameter. Due to the fact no permittivity-size dependent studies of single domain nanoparticles have yet been

reported, one important result found here is this decrease in permittivity with decreasing nanoparticle size. This decrease in permittivity with size is consistent with observations found in diamond thin films in which the permittivity of the films decreased with decreasing grain size.¹³ This effect is suggested to result from changes in the crystal field at the particle surface due to the influence of the incomplete coordination sphere of metal atoms.

Figure 5 compares the permittivity for 6.4 nm CoFe_2O_4 nanoparticles with two differing Fe_3O_4 shell thicknesses, the native 6.4 nm CoFe_2O_4 nanoparticle core, a comparable size Fe_3O_4 nanoparticle core (6.0 nm), and a Fe_3O_4 nanoparticle with size (8.8 nm) comparable to the core/shell net diameter. The weight percentage was held constant at 36.5 wt% for all of the samples in Figure 5. The first feature to note is that the permittivity of CoFe_2O_4 nanoparticles is larger than that of the same size Fe_3O_4 nanoparticles. After the addition of a 1.5 Fe_3O_4 nm shell, the permittivity of CoFe_2O_4 nanoparticles was lowered and the permittivity for this core/shell sample ($\text{CoFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$) is much lower than a similarly sized solid Fe_3O_4 particle. Also observed in Figure 5 is that the permittivity continues to decrease when the Fe_3O_4 shell thickness is increased. The effect of reversing the components, i.e. a $\text{Fe}_3\text{O}_4/\text{CoFe}_2\text{O}_4$ core/shell nanoparticle upon the permittivity is shown in Figure 6. In contrast to the decrease in the permittivity with the addition of a shell seen in Figure 5, when CoFe_2O_4 is grown as a shell onto Fe_3O_4 nanoparticles, the permittivity *increases*. Figure 6 clearly shows that not only does the permittivity increase compared to the core Fe_3O_4 response, but that the permittivity for the core/shell sample is larger than a Fe_3O_4 particle with the same net size.

Core/shell systems offer the ability to select materials with known behavior and combine them such that the interplay of a number of factors including magnetocrystalline anisotropy, exchange anisotropy, and interparticle interactions may lead to enhanced or new physical

properties being demonstrated. The permittivity results for the core/shell nanoparticle systems highlight the significance of this approach. It is interesting that although the core/shell nanoparticle samples presented here are comprised of the same two components, Fe_3O_4 and CoFe_2O_4 , they show different frequency dependent responses depending upon the arrangement of the core and shell material. The reasons for the differing behavior are not yet understood and more samples are being prepared and measured to elucidate the origins of this behavior. However, it is clear that the core/shell structures give rise to frequency dependent properties not achieved from their independent magnetic material components.

Conclusions

A systematic study investigating the influence of ferrite nanoparticle loading and nanoparticle size upon the permittivity and permeability of polyurethane nanocomposites in the X-band frequency range has been conducted. The results suggest increasing the nanoparticle size and/or loading to increase the permittivity. Novel core/shell nanoparticles have also been prepared and the frequency dependence of their polyurethane nanocomposites measured. The samples show diverging behavior which is not yet fully understood. However, these nanocomposites are one of the first demonstrations of the ability to select materials with known behavior and combine them such that the interplay leads to new physical properties being demonstrated. The ability to independently chose and combine any number of materials to serve as the core or shell magnetic material offers a wealth of new materials that can be envisioned and the development of an extensive range of magnetic materials with unique improved properties.

References

1. Mosallaei, H.; Sarabandi, K., *IEEE Trans. Antennas Propagat.* **2004**, *52*, 1558.
2. Brosseau, C.; Talbot, P., *IEEE Trans. Dielectrics Elec. Insul.* **2004**, *11*, 819.
3. Ramprasad, R.; Zurcher, P.; Petras, M.; Miller, M.; Renaud, P., *J. Appl. Phys.* **2004**, *96*, 519.
4. Toneguzzo, P.; Viau, G.; Acher, O.; Fiévet-Vincent, F.; Fiévet, F., *Adv. Mater.* **1998**, *10*, 1032.
5. Viau, G.; Ravel, F.; Acher, O.; Fiévet-Vincent, F.; Fiévet, F., *J. Appl. Phys.* **1994**, *76*, 6570.
6. Viau, G.; Ravel, F.; Acher, O.; Fiévet-Vincent, F.; Fiévet, F., *J. Magn. Magn. Mater.* **1995**, *140-144*, 377.
7. Wu, M.; Zhang, H.; Yao, X.; Zhang, L., *J. Phys. D.: Appl. Phys.* **2001**, *34*, 889.
8. Abe, M.; Kuroda, J.; Matsumoto, M., *J. Appl. Phys.* **2002**, *91*, 7373.
9. Peng, C.-H.; Wang, H.-W.; Kan, S.-W.; Shen, M.-Z.; Wei, Y.-M.; Chen, S.-Y., *J. Magn. Magn. Mater.* **2004**, *284*, 113.
10. Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G., *J. Am. Chem. Soc.* **2004**, *126*, 273.
11. Wu, M.; Zhang, Y. D.; Hui, S.; Xiao, T. D.; Ge, S.; Hines, W. A.; Budnick, J. I.; Taylor, G. W., *Appl. Phys. Lett.* **2002**, *80*, 4404.
12. Paterson, J. H.; Devine, R.; Phelps, A. D. R., *J. Magn. Magn. Mater.* **1999**, *196-197*, 394.
13. Ye, H.; Sun, C. Q.; Hing, P., *J. Phys. D.: Appl. Phys.* **2000**, *33*, L148.

Figures

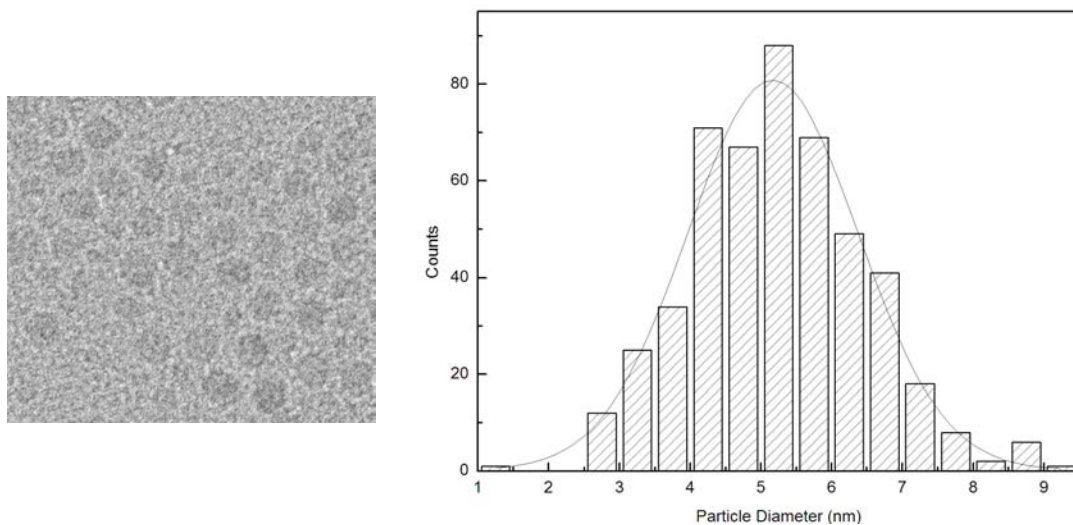


Figure 1. Typical size distribution and TEM image of Fe_3O_4 nanoparticles.

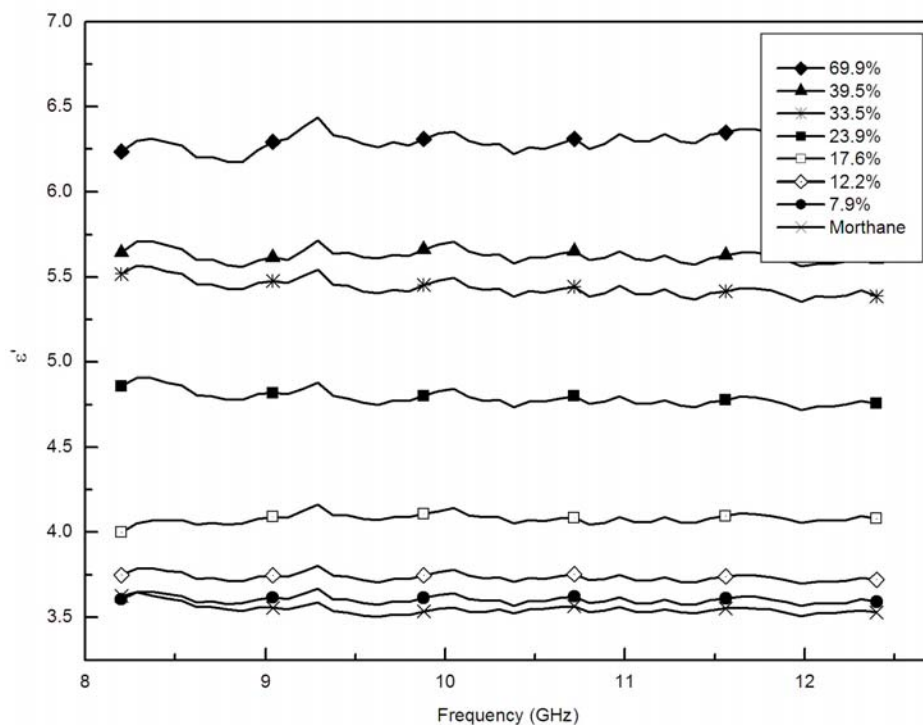


Figure 2. Frequency dependence of 4 nm Fe_3O_4 nanoparticles in morthane at varying loading concentrations.

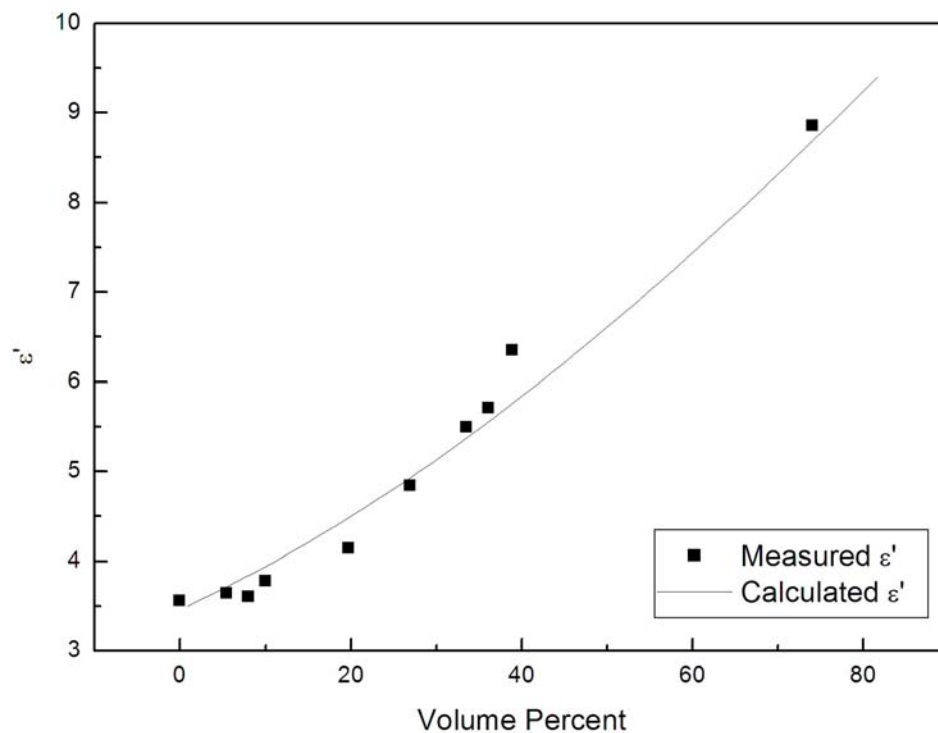


Figure 3. Value of permittivity at 10GHz of 4 nm Fe_3O_4 nanoparticles in morthane at varying loading concentrations compared to Bruggeman EMT.

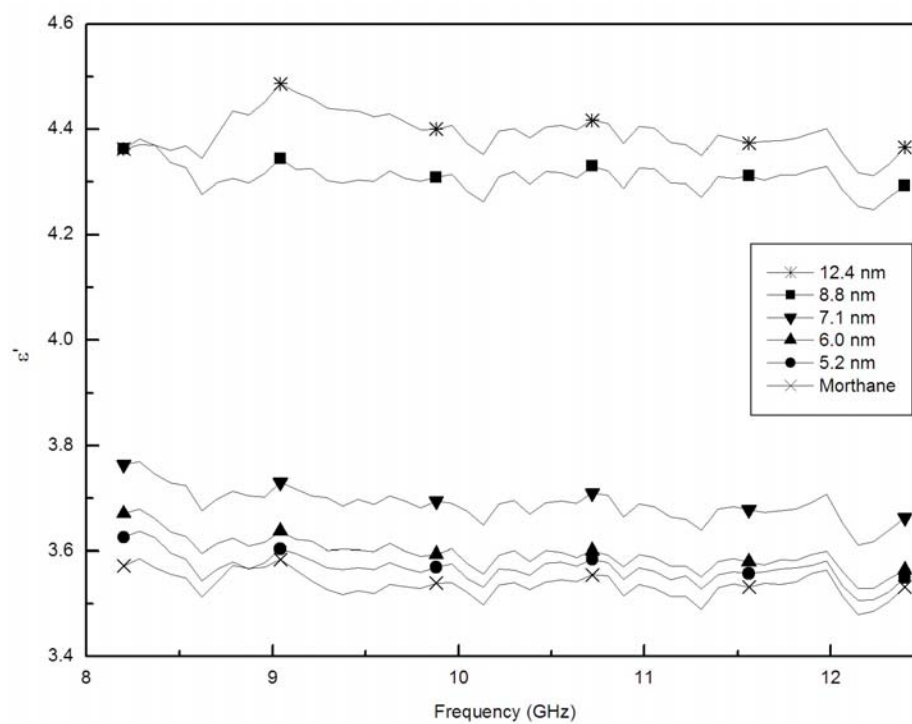


Figure 4. Frequency dependence 12.2 vol.% Fe_3O_4 nanoparticles of varying diameter in morthane.

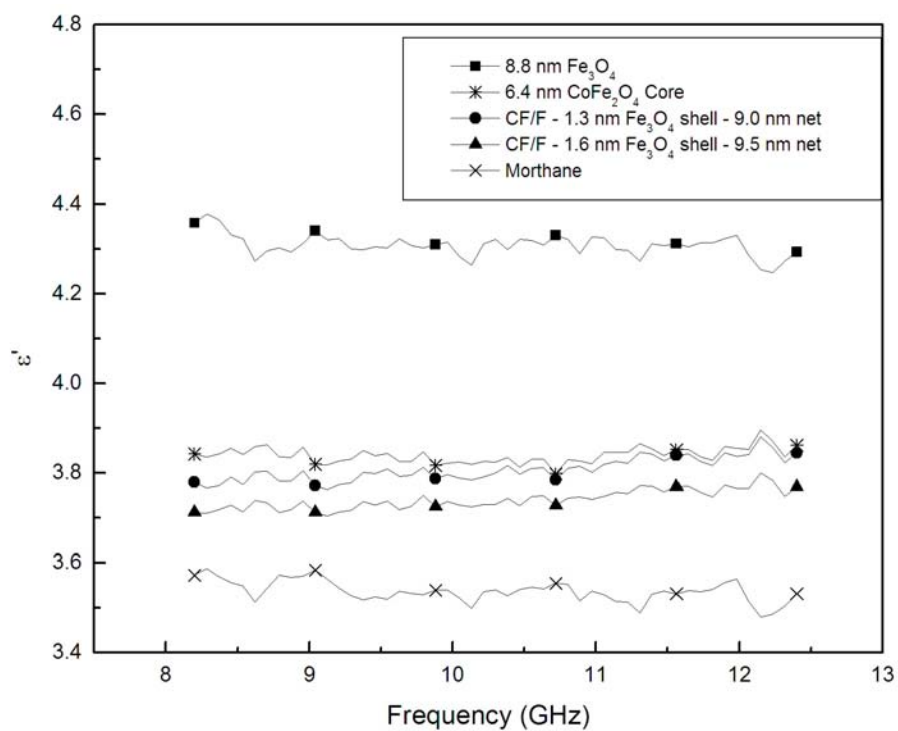


Figure 5. Frequency dependence 12.2 vol% CoFe₂O₄/Fe₃O₄ core/shell nanoparticles in morthane.

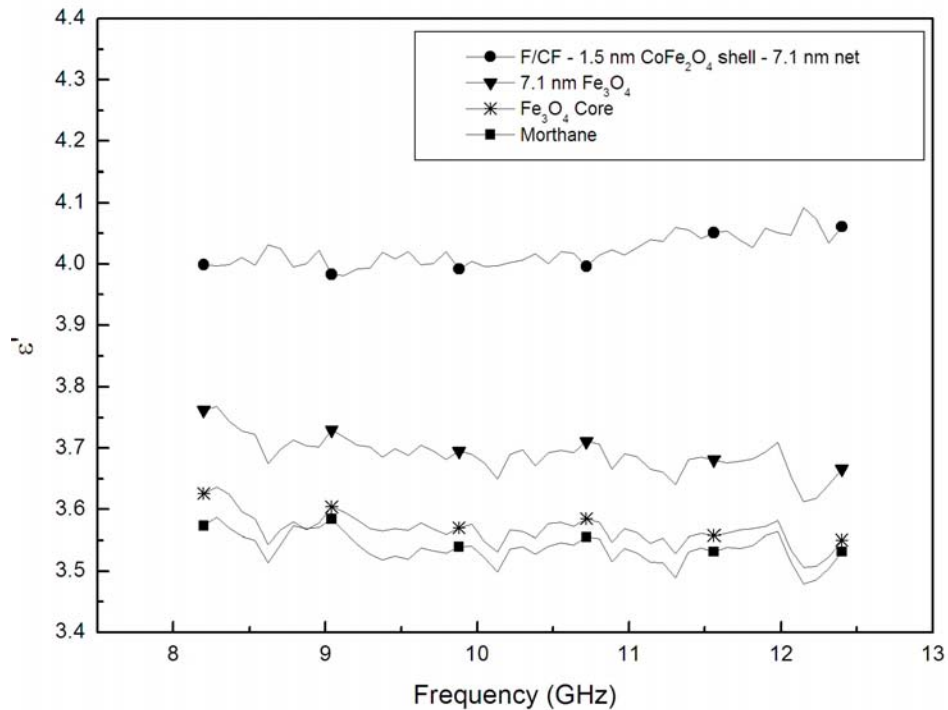
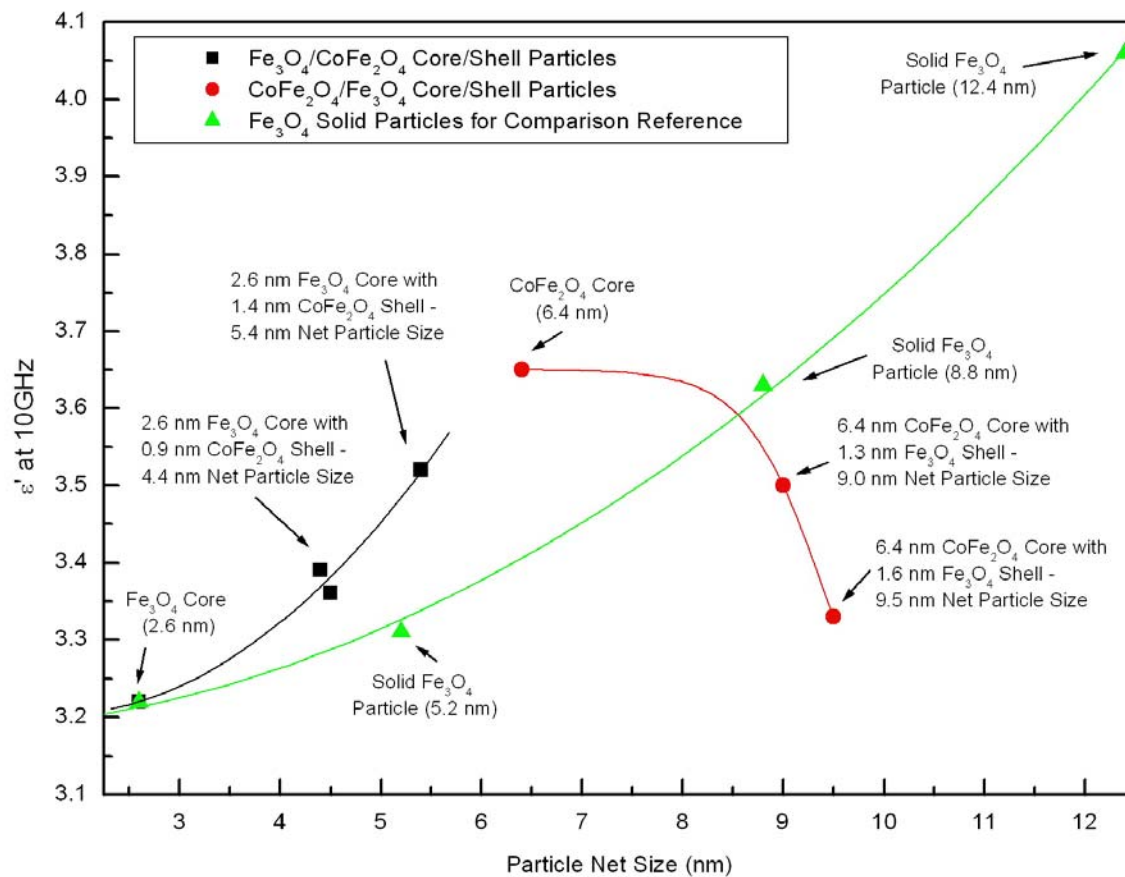


Figure 6. Frequency dependence 12.2 vol% Fe₃O₄/CoFe₂O₄ core/shell nanoparticles in morthane



Comparison of core/shell and solid particles. Addition of CoFe_2O_4 shell to 2.7 nm Fe_3O_4 core *increases* the permittivity (black curve). **The permittivity of a core/shell particle with this composition is larger than a solid Fe_3O_4 particle with comparable net size.** Addition of a Fe_3O_4 shell to a 6.4 nm CoFe_2O_4 particle *decreases* the permittivity (red curve). The permittivity of a core/shell particle with this composition is smaller than a solid Fe_3O_4 particle with comparable net size.