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30-12-2022	Final Report	12-Feb-2019 - 11-Feb-2022

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U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 74818-SM.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

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14. ABSTRACT

15. SUBJECT TERMS

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UU	UU	UU	UU		19b. TELEPHONE NUMBER 979-845-7506

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RPPR Final Report
as of 12-May-2023

Agency Code: 21XD

Proposal Number: 74818SM

Agreement Number: W911NF-19-2-0080

INVESTIGATOR(S):

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EIN: 741974733

Report Date: 11-May-2022

Date Received: 30-Dec-2022

Final Report for Period Beginning 12-Feb-2019 and Ending 11-Feb-2022

Title: Cooperative Interactions between Functionalized Particles and Binders in Polymer Composites and their Effect on Chemical Transport

Begin Performance Period: 12-Feb-2019

End Performance Period: 11-Feb-2022

Report Term: 0-Other

Submitted By: Yossef Elabd

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1

STEM Participants:

Major Goals: The overall objective of this collaboration is to investigate chemical transport in polymer composites with varying particle-binder interactions to develop a deep understanding of impact of these interactions on chemical transport. The recent development of a new technique by the TAMU PI, in situ pressure-contact Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy, and its demonstration of measuring diffusion of a small molecule liquid in a free-standing crosslinked polymer coating enables this investigation. In collaboration with ECBC, TAMU PI proposes to (1) select, (2) synthesize, and (3) measure and model chemical transport in a variety of polymer composite systems (i.e., polymer-particle systems).

Accomplishments: Please see attached PDF document

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Collaboration with CCDC CBC. Delivery of grafted nanoparticles and nano composite films to CCDC CBC.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Rui Sun
Person Months Worked: 3.00

Funding Support:

Project Contribution:
National Academy Member: N

Participant Type: PD/PI

RPPR Final Report
as of 12-May-2023

Participant: Yossef Elabd
Person Months Worked: 1.00
Funding Support:
Project Contribution:
National Academy Member: N

Partners

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I certify that the information in the report is complete and accurate:
Signature: Yossef Elabd
Signature Date: 12/30/22 5:25PM

Annual Report
Period of Performance (Reporting Period for this report)
Start: Feb, 12 2019 **End:** Jul, 31 2019

Award Information
Title: Cooperative Interactions between Functionalized Particles and Binders in Polymer Composites and their Effect on Chemical Transport
Contract Number: W911NF1920080

Accomplishments

1. A polymer composite model system was selected for transport investigation: a glassy polymer, poly(methyl methacrylate) (PMMA), with silica nanoparticles.

2. Measured and modeled chemical transport with in situ Fourier infrared attenuated total reflectance (FTIR-ATR) spectroscopy in this polymer composite model system as a function of particle loading to understand the impact of particle loading on small molecule transport and polymer relaxation.

Brief summary of several of the results below.

Summary: PMMA/silica nanocomposite films were solution cast onto ATR crystals (Figure 1) for the measurement of small molecule (water) transport in the films as a function of silica loading. Water transport in PMMA films at silica nanoparticle loadings of 0 wt%, 1 wt%, 3 wt% are shown in Figures 2, 3, 4, respectively. Figures 2, 3, and 4 highlight diffusion and relaxation of PMMA, where polymer relaxation or strain (CH_3 stretching absorbance vs. time) and water diffusion (OH stretching absorbance vs. time) are highlighted. Specifically, the time-resolved polymer relaxation and diffusion were modeled with a non-Fickian diffusion-relaxation model developed in our laboratory.[1]

Key Result: At 3 wt% silica nanoparticle loading, no polymer relaxation was observed yet water diffusion was non-Fickian. As nanoparticle loading increases, this impacts polymer relaxation and the diffusion of water. More results during the next reporting period will elucidate this unexpected result.

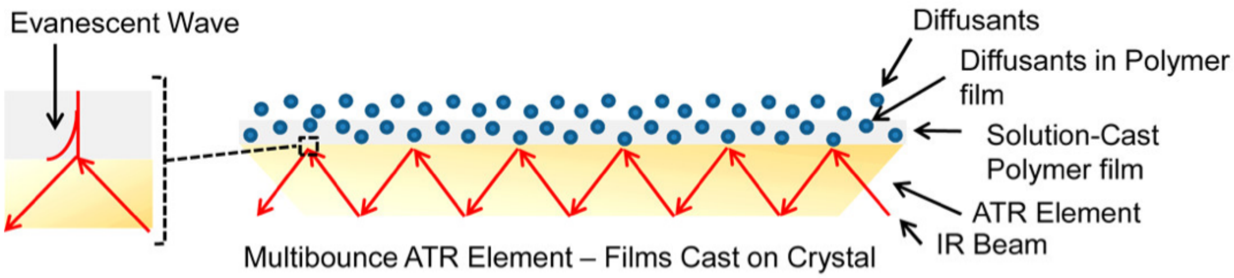
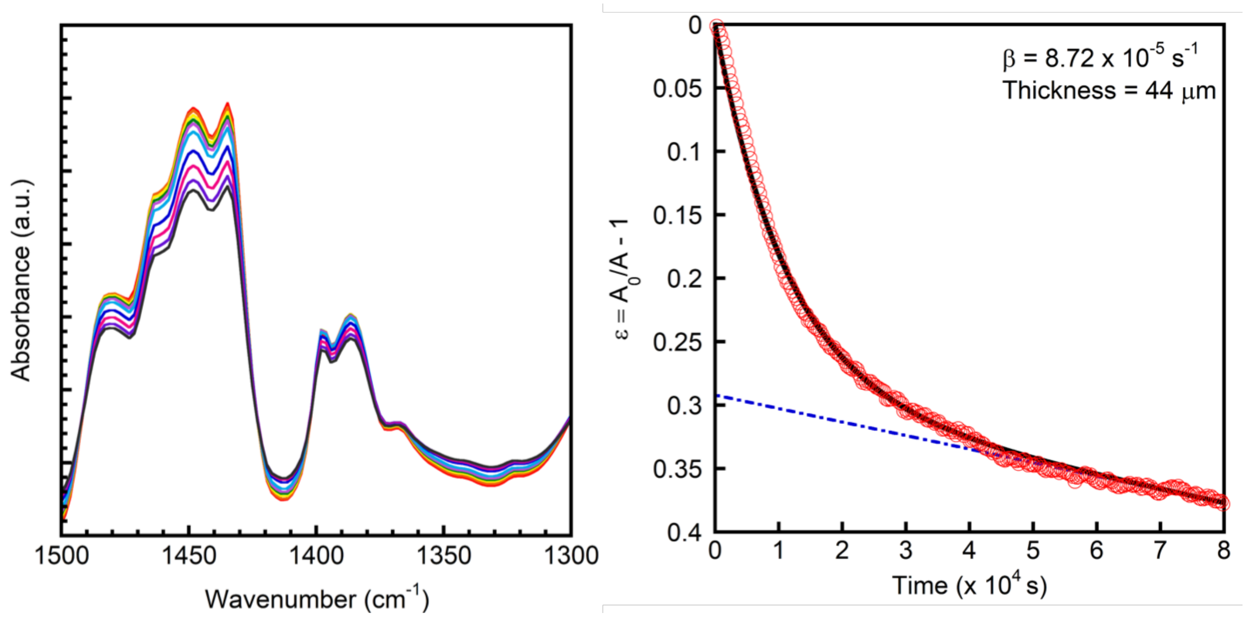


Figure 1. Schematic of multibounce FTIR-ATR apparatus with solution-cast polymer film for the measurement of chemical transport in polymer films. Evanescent wave highlighted in the magnified region.



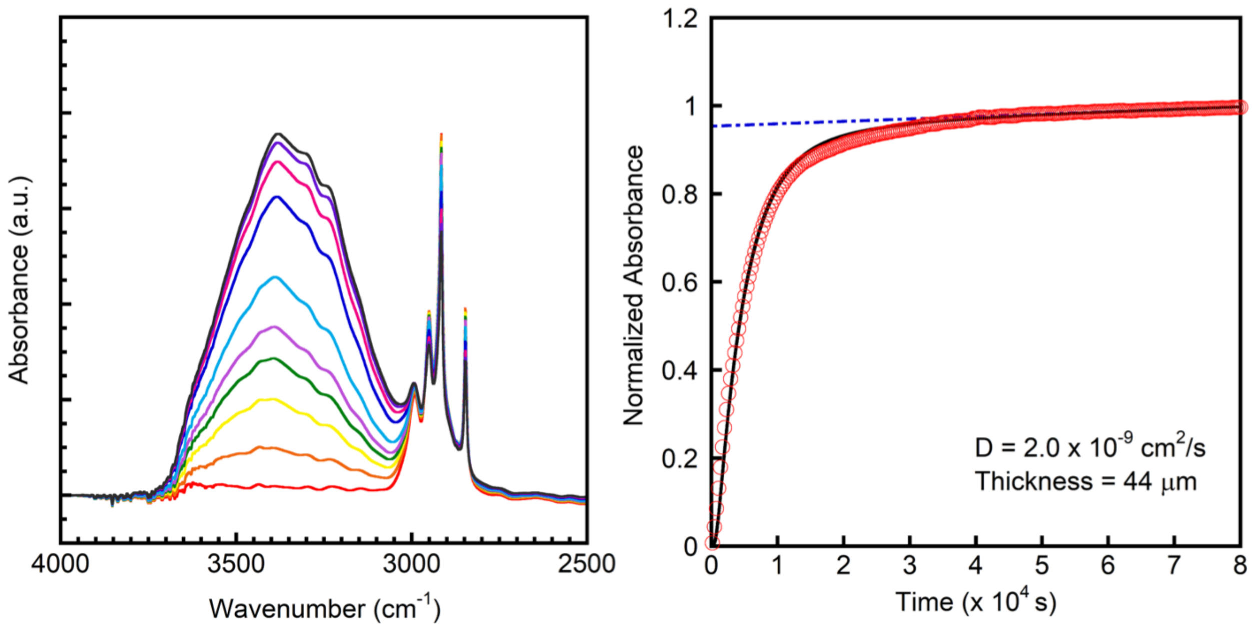
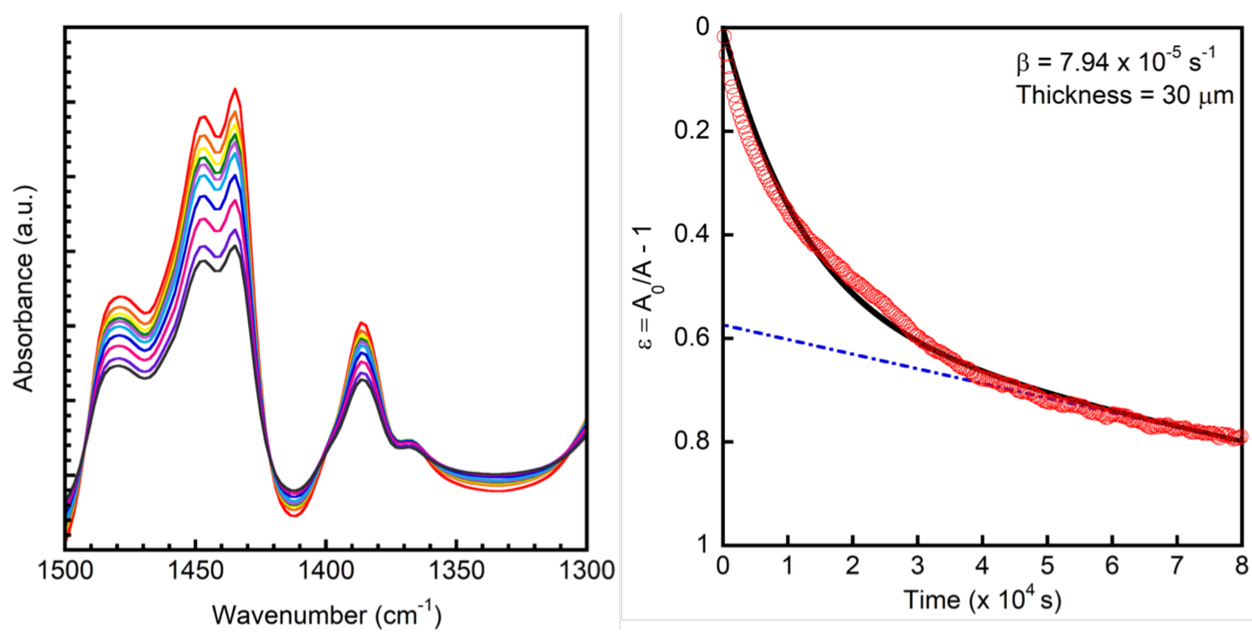


Figure 2. PMMA + **0 wt%** silica nanoparticles: (upper left) infrared spectra of polymer relaxation (CH_3 stretching absorbance) at selected times; (upper right) normalized integrated absorbance of CH_3 stretching absorbance regressed to polymer relaxation model; (lower left) infrared spectra of water diffusion (OH stretching absorbance) at selected times; (lower right) normalized integrated absorbance of OH stretching absorbance regressed to diffusion-relaxation model.



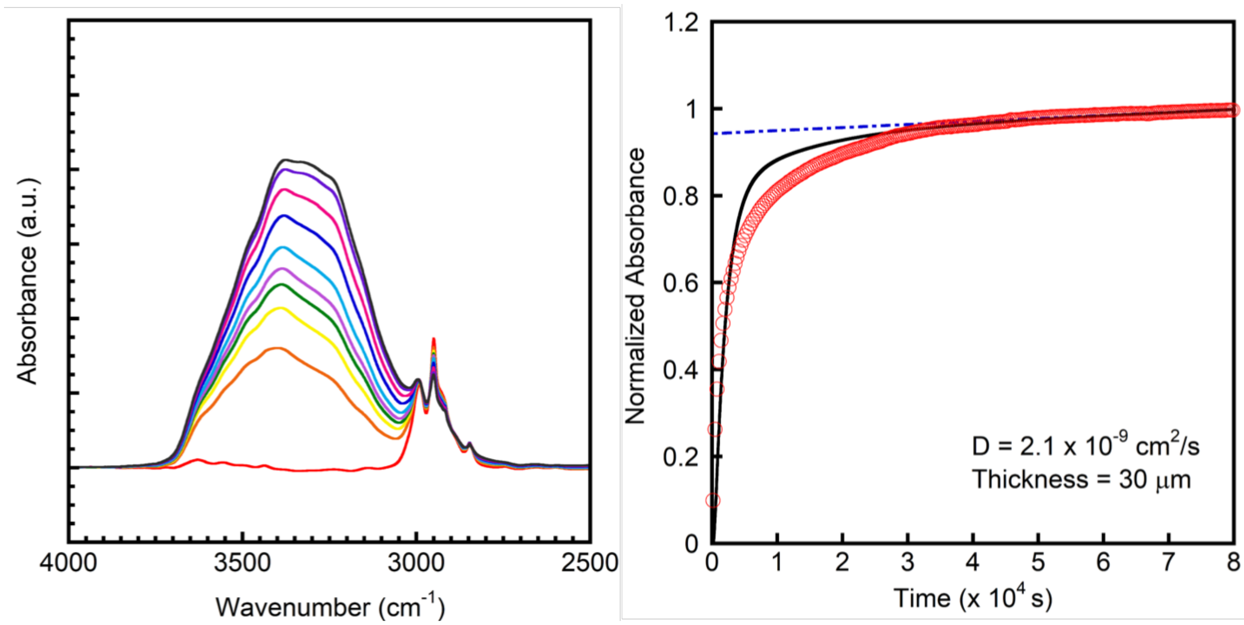
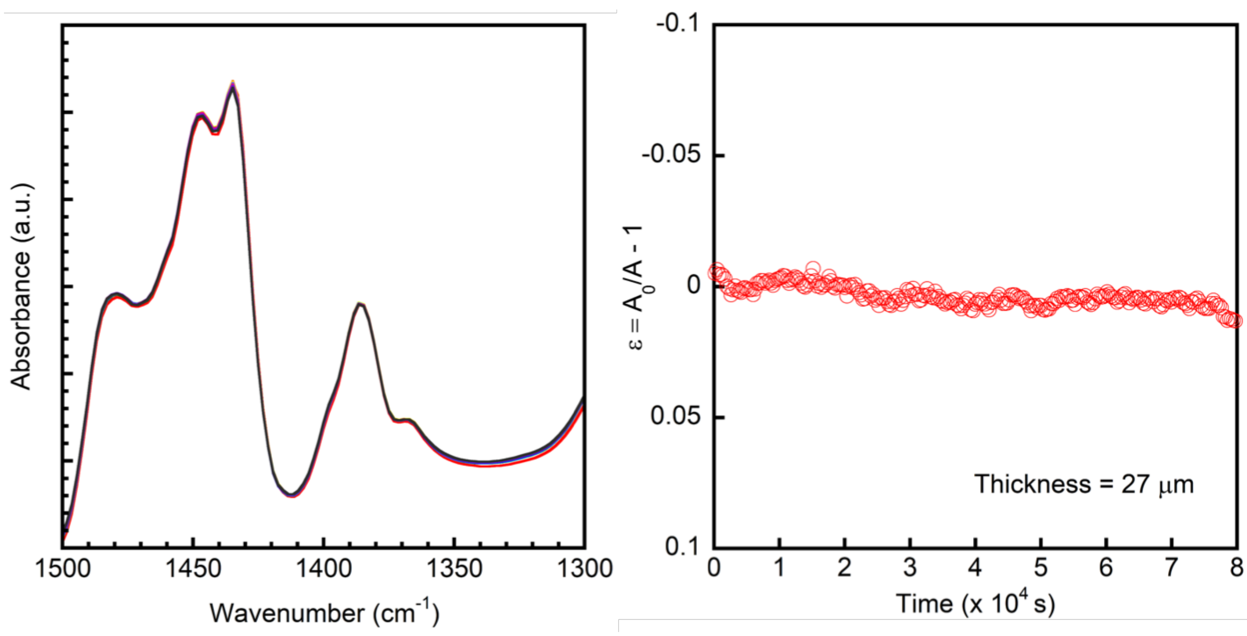


Figure 3. PMMA + **1 wt%** silica nanoparticles: (upper left) infrared spectra of polymer relaxation (CH_3 stretching absorbance) at selected times; (upper right) normalized integrated absorbance of CH_3 stretching absorbance regressed to polymer relaxation model; (lower left) infrared spectra of water diffusion (OH stretching absorbance) at selected times; (lower right) normalized integrated absorbance of OH stretching absorbance regressed to diffusion-relaxation model.



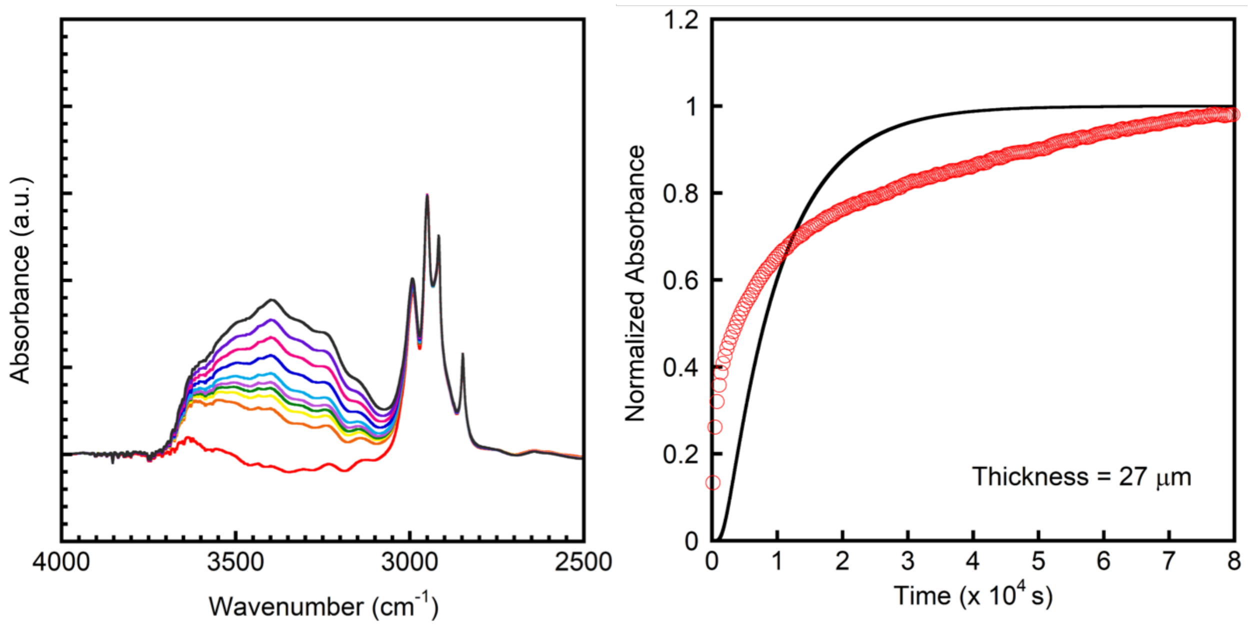


Figure 4. PMMA + **3 wt%** silica nanoparticles: (upper left) infrared spectra of polymer relaxation (CH_3 stretching absorbance) at selected times; (upper right) normalized integrated absorbance of CH_3 stretching absorbance regressed to polymer relaxation model; (lower left) infrared spectra of water diffusion (OH stretching absorbance) at selected times; (lower right) normalized integrated absorbance of OH stretching absorbance regressed to Fickian model (poor regression shows non-Fickian behavior of water diffusion).

References

1. Santos, M. C.; Bendiksen, B.; Elabd, Y. A., Diffusion of Liquid Water in Free-Standing Polymer Films Using Pressure-Contact Time-Resolved Fourier Transform Infrared Attenuated Total Reflectance Spectroscopy. *Ind Eng Chem Res* **2017,** *56* (12), 3464-3476.

Annual Report
Period of Performance (Reporting Period for this report)
Start: Aug, 1 2019 **End:** Jul, 31 2020

Award Information
Title: Cooperative Interactions between Functionalized Particles and Binders in Polymer Composites and their Effect on Chemical Transport
Contract Number: W911NF1920080

Accomplishments

Synthesis of poly(styrene) (PS) grafted silica nanoparticles via reverse addition fragmentation chain transfer (RAFT) polymerization

Summary/Key Result: Silica nanoparticles were grafted with PS via RAFT polymerization (Figure 1) to produce polymer chains with uniform chain lengths. **Progress beyond this was**

deterred due to COVID-19 and the closure of research laboratories at Texas A&M. Next funding period will include (1) chemical and physical characterization of grafted nanoparticles, (2) transfer of grafted nanoparticles to collaborators at CCDC CBC for single particle analysis, and (3) fabrication of nanocomposite films with grafted nanoparticles with subsequent characterization and transfer of nanocomposite films to collaborators at CCDC CBC for transport analysis.

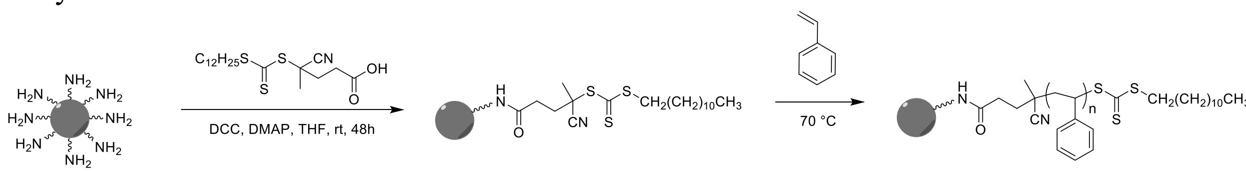


Figure 1. Scheme of silica grafted nanoparticles: amine-functionalized nanoparticles (500 nm) dispersed in THF reacted with chain transfer agent (CTA: 4-cyano-4 [(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid) at room temperature for 48 h followed by RAFT polymerization with styrene monomer at 70 °C.

Annual Report
Period of Performance (Reporting Period for this report)
Start: Aug, 1 2020 **End:** Jul, 31 2021

Award Information
Title: Cooperative Interactions between Functionalized Particles and Binders in Polymer Composites and their Effect on Chemical Transport
Contract Number: W911NF1920080

Accomplishments

Synthesis and characterization of poly(styrene) (PS) grafted silica nanoparticles via reverse addition fragmentation chain transfer (RAFT) polymerization

Enhanced grafting techniques developed including synthesis of amine-functionalized silica particles with higher degree of surface functionalization and activation of RAFT-CTA (chain transfer agent) to increase reaction selectivity for desired product.

Summary/Key Result: Silica nanoparticles were grafted with PS via RAFT polymerization to produce polymer chains with uniform chain lengths. Furthermore, this grafting technique was enhanced with the (1) synthesis of amine-functionalized silica particles (Figure 1) and (2) activation of RAFT-CTA (Figure 2) to increase reaction selectivity for desired product.

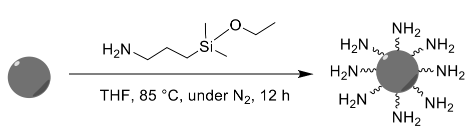


Figure 1. Scheme of amine-functionalized silica particles.

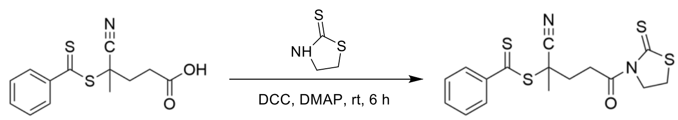


Figure 2. Scheme of activation of RAFT-CTA.