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The long-term goal of this exploratory study was to understand the mechanisms of strain strengthening in poly-isoprene (PI) matrices loaded with polystyrene (PS)-coated gold nanorods. Our results show that PI thin films, manufactured via dip molding, exhibit a significant increase in Young’s modulus and hardness in the presence of a block PS-PI-PS copolymer additive when the content of styrene in the block is kept at 14%. In addition, tensile testing experiments have shown that the PI films prepared in the presence of the block copolymer retain their elastic

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Final Report: Use of gold nanorods for fine tunable strain strengthening of synthetic poly-isoprene

ABSTRACT

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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NA

Number of Presentations: 0.00

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

NA

Patents Awarded

NA

Awards

NA

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Riyanka Pai	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
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Names of Faculty Supported

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NAME

Total Number:

Names of personnel receiving PHDs

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Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

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Scientific Progress

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Technology Transfer

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FINAL REPORT

PROJECT TITLE: Use of Gold Nanorods for Fine-Tunable Strain Strengthening of Synthetic Poly-*iso*prene.

PI: Dr. Laura Fabris, Associate Professor, Department of Materials Science and Engineering, Rutgers University.

PROPOSAL NUMBER: 66991CHII

CONTRACT NUMBER: W911NF-15-1-0132

REPORT DATE: 08/31/2016

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STUDENTS SUPPORTED: Riyanka Pai, PhD candidate, Department of Materials Science and Engineering, Rutgers University (100% support).

PhDs AWARDED: Ms. Pai's dissertation defense is planned for January 2017.

ABSTRACT: The long-term goal of this exploratory study was to understand the mechanisms of strain strengthening in poly-*iso*prene (PI) matrices loaded with polystyrene (PS)-coated gold nanorods. It was anticipated that, by varying the aspect ratio and the nanorod alignment within the polymer matrix, and by fine-tuning the interfacial interactions between the PS chains grafted onto the nanorods and the PI molecules in the matrix, an effective strengthening of the polymer would occur without effective loss in overall elongation under tensile stress. Our results show that PI thin films, manufactured via dip molding protocols, exhibit a significant increase in both Young's modulus and hardness in the presence of a block PS-PI-PS copolymer additive at 5% and 10% w/w when the content of PS is kept at 14%. In addition, tensile testing experiments have shown that the PI films prepared in the presence of the block copolymer retain their elastic behavior and overall elongation, fracturing at or above 3000% strain. Comparative mechanical studies carried out with nanoindentation, show significantly higher values of modulus and hardness in the presence of the block copolymer compared to those determined via tensile tests, leading us to determine that this increase might be a surface effect due to the percolation depth of the block copolymer within the film, which depends to the polymer chain size and surface properties. We have manufactured PI films in the presence of PS-capped gold nanorods, PS-capped gold nanospheres (control) and citrate-capped gold nanospheres (control) and we are currently determining the mechanical properties of the composite films via tensile tests and nanoindentation studies. Overall, our results are promising as they demonstrate that the presence of the block copolymer does affect the local mechanical properties of the PI films in a significant way, and that this might become an alternative approach to finely tuning the mechanical properties of PI even in the absence of the traditionally used fillers such as carbon nanotubes.

LIST OF FIGURES AND TABLES

Figure 2: Stress-strain curves for PI films prepared with different temperature mandrels.

Figure 3: Effect of mandrel's roughness on PI film quality.

STATEMENT OF THE PROBLEM: Studies of polymer reinforcement and strengthening have primarily focused on ceramic and graphitic materials as nanofillers [1-24]. Although these materials are well suited to significantly increase elastic modulus, tensile strength, toughness, hardness, and wear resistance, their morphology and surface properties are not conducive to establish sufficiently strong interfacial interactions between filler and polymer matrix, and do not enable straightforward polymer grafting to increase their miscibility with the matrix. As a consequence, systematic studies on the mechanisms at the basis of nanofiller/polymer interactions are not possible, and finely tunable modifications of the mechanical properties of the polymer are difficult to achieve. **This project sought to overcome these limitations by systematically synthesizing and studying polymer-nanoparticle composites for which the mechanical properties can be finely tuned.**

SUMMARY OF MOST IMPORTANT RESULTS

Preparation of PI films: PI films for this project were manufactured employing *coagulant dip molding*. In this process, a former (also herein called mandrel; stainless steel or glass) is first dipped into a coacervant. In our process, which is dry-coagulant dip molding, calcium nitrate was used as the coacervant, which was dissolved in a solvent, in our case water. The coacervant also has calcium carbonate as a parting agent, which facilitates polymer film removal from the former. The water was then evaporated in an oven, leaving behind only calcium carbonate and calcium nitrate. The former was then dipped into the polymer. We selected PI from Kraton Polymers Inc., from their Cariflex products (IR0401), which is composed of 92 wt% cis-1,4 polymer and the remaining wt% is from trans-1-4 and 3,4 polymer. Its acceptable tensile properties are compared to those of natural rubber in **Table 1**, measured according to the ASTM D3577-01 standard. The polymer was stabilized anionically, polymerized using an alkyl-lithium initiator, and allowed to mature for 24 hours after the addition of stabilizer and vulcanizing reagents.

Table 1: Ideal mechanical properties of synthetic PI and natural rubber established by ASTM D3577-01.

	Before Aging			After Accelerated Aging	
Polymer type	Minimum Tensile Strength (MPa)	Minimum Elongation (%)	Max stress at 500% elongation (MPa)	Minimum Tensile Strength (MPa)	Minimum Elongation (%)
Synthetic PI	17	650	7	12	490
Natural rubber	240	750	5.5	18	560

To prepare a PI film, the former is vertically dipped into the latex (typically at a rate of 0.5-1 cm/sec), the polymer molecules in suspension are electrostatically destabilized due to the high concentration of salt on the mandrel, and adsorb to the mandrel for stabilization. The former is then left inside the polymer to increase the thickness of the polymer film, and the total time inside the polymer is defined *dwell time*. The former is withdrawn at the same rate as it was dipped, and then inverted to provide uniform thickness (as the last part of the former has been in the polymer the longest it is the thickest region) before inverting again. The polymer undergoes pre-vulcanization at an elevated temperature for one minute, followed by a leaching step in deionized water at room temperature for five minutes. Finally, the polymer is vulcanized at an elevated temperature for fifteen minutes. It is then cooled to room temperature and stripped off the mandrel. The benefit of using this technique is that it provides a thicker polymer film, without the need of multiple dipping steps.

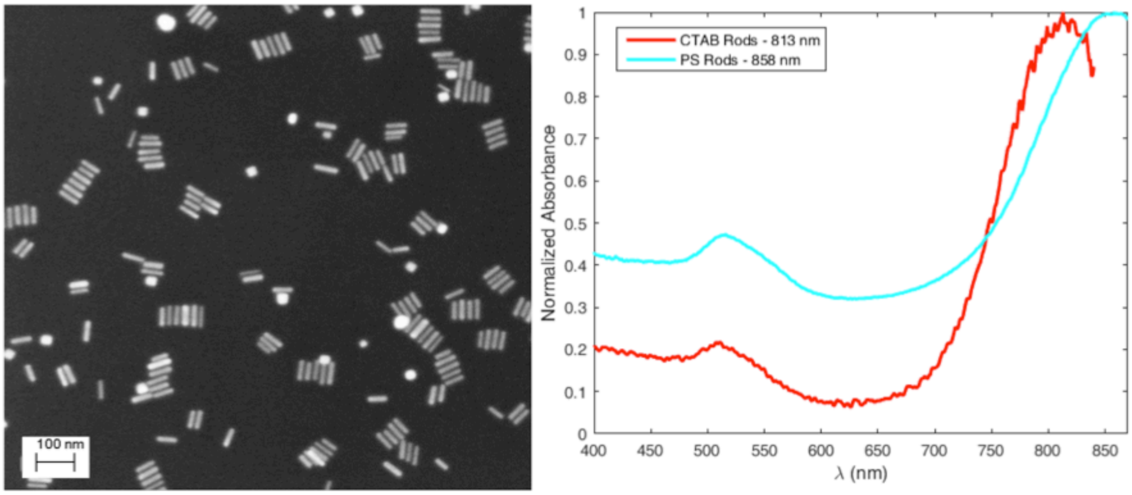

Figure 1: Scanning electron micrograph (left) and UV-Vis spectra (right) of gold NR fillers synthesized. CTAB-capped NRs (left) pair-up side-by-side in the SEM micrograph due to the interaction with the electron beam, but are separated and stable in suspension. On the right, it is possible to observe a red-shift in the longitudinal surface plasmon resonance of the NRs when capped with PS. This is due to the higher dielectric function of PS compared to CTAB and it is an indication of the successful re-capping of the rods.

Synthesis of gold nanorods: Gold nanorods (NR) fillers for addition to the PI films were synthesized following standard seed-mediated *bottom up* protocols. Briefly, 2-5 nm seeds were synthesized via addition of ice-cold $NaBH_4$ to a solution containing $HAuCl_4{\cdot}3H_2O$ and cetyltrimethylammonium bromide (CTAB) in water under vigorous stirring. The 2-minute aged seeds were then added to a growth solution containing $HAuCl_4{\cdot}3H_2O$, $AgNO_3$, ascorbic acid (AA), and CTAB in water at 30°C and left to react for 1 hour under mild stirring. The NRs were then left to mature for 24-48 hours, purified with centrifugation, and characterized with scanning electron microscopy and UV-Vis spectrophotometry (**Figure 1**). Ligand exchange protocols, modified to ensure NR stability during phase transfer from water to toluene, were then employed to recap the NRs and replace CTAB with thiolated PS. The PS-capped NRs were characterized via SEM and UV-Vis spectrophotometry (see spectra in Figure 1). PS at 5 and 10 kDa molecular weight were employed. PS-capped and citrate-capped

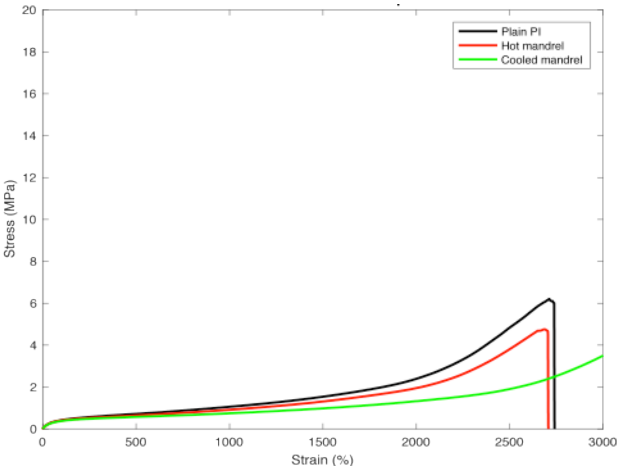

Figure 2: Cooled mandrels enable fabricating PI films with increased elongation at fracture. In this example (green curve) fracture cannot be achieved even at 3000% because maximum vise run was reached.

nanospheres were used as controls.

Block copolymer additive: To determine the importance of polymer-NR interfacial interactions, a PS-PI-PS block copolymer was added to modulate them depending on the amount of styrene. Block copolymers with 14% and 22% w/w styrene content were employed, and added at 5% and 10% w/w concentration levels. The block copolymer pellets were initially dissolved in several solvents such as THF, chloroform, toluene, acetone, and dichloromethane, but none of them led to sufficient miscibility with PI. We therefore decided the incorporate the block copolymer in PI after film formation. In this approach, the block copolymer was initially dissolved in THF (5 wt% in THF) and sonicated for an hour to ensure thorough dissolution. For experiments including nanoparticles, a small volume of THF was added to the PS-capped rods and spheres pellets, sonicated, and then transferred to the block copolymer/THF and mixed. Two different methods for incorporation were used: In one method the PI film was air dried and dipped into the block copolymer, followed by the same steps employed in PI-only films: cure for 1 minute, leach out salts, and cure for 15 minutes. In the second method, the PI film is initially formed, cured for 1 minute, leached out of salts, and then dipped into the block copolymer.

Mechanical Testing: The mechanical properties of the polymer films were determined via tensile testing (employing an Instron 5869 with Bluehill 2 software and 100 N load cell) and through nanoindentation, using a Hysitron TriboIndenter with a Berkovich Tip. Ideally, dogbone specimens for tensile testing would be required to comply with the ASTM D412-06a standard using die C, which, however, is intended for injection-molded polymers. We attempted to die cut our PI films following a dogbone shape, but incurred in several problems, that ended up impacting the accuracy of the results. Therefore we decided to cut the PI films in rectangular specimens and study the effect of the additives as *relative* improvements over those of PI alone. For nanoindentation studies, the PI films were dip-molded using thick glass formers instead of stainless steel formers to enable placement of the sample horizontally underneath the indenter tip. No significant differences in film properties were detected in going from stainless steel to glass, even though we have observed improved elongation in polymer films prepared with cooled mandrels, thus leading us to hypothesize that the heat capacity of the mandrel might have an impact on the overall polymer properties (**Figure 2**). Notably, the quality of the film significantly improved upon roughening of the mandrel's surface due to higher adhesion of PI to the mandrel during dip molding (**Figure 3**).

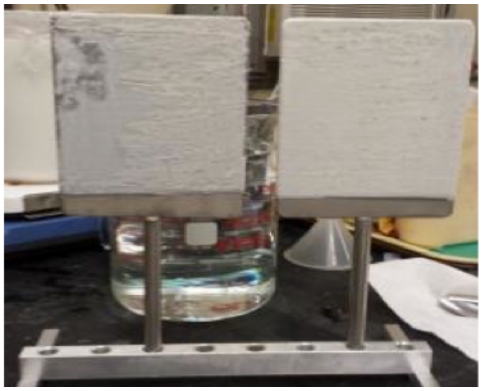

Figure 3: PI films dip molded using as received (left) and sand-blasted (right) stainless steel mandrels. It is possible to observe the increased uniformity of the film when using the roughened mandrel.

The mechanical properties of PI and PS-PI-PS/PI films measured with tensile tests are reported in **Table 2**. Young's modulus was measured at 10% strain to avoid the plastic deformation regime. With a close look to the results it is possible to observe how the modulus of PI added with 5 wt% of PS-PI-PS containing 14% styrene leads to a 8.4% increase in modulus compared to the films prepared with PI alone. The maximum increase obtained with 22%-styrene PS-PI-PS was instead reported to be 7.2%. Importantly, both polymers retain excellent elongation, with fracture well above 3000% strain.

Table 2: Values of Young's modulus for polymer films prepared under various conditions, as listed.

Styrene % in PS-PI-PS	Drying procedure	% Block copolymer	Modulus at 10% strain (KPa)
N/A	N/A	0	8.3
14	Cured	5 wt%	8.4
14	Air dried	5 wt%	9.0
14	Cured	10 wt%	8.6
14	Air dried	10 wt%	7.8
22	Cured	5 wt%	8.5
22	Air dried	5 wt%	1.5
22	Cured	10 wt%	8.0
22	Air dried	10 wt%	8.9

Nanoindentation was employed as well to study the mechanical properties of the polymer films. As nanoindentation is more sensitive to the surface properties of the manufactured films, and by virtue of the process employed to incorporate the block copolymer in the PI films, the results obtained with this technique are sensitive to the morphology of the block copolymer macromolecules, their surface charge and properties, and most importantly, to their effective percolation path within the PI film. Furthermore, because of the intrinsic properties of the technique, the results obtained provide an excellent insight into the local properties of the nanostructured composite. The mechanical properties obtained from nanoindentation are reported in **Table 3**. Importantly, PI films prepared with the addition of 5 wt% of 14% styrene-containing PS-PI-PS show a significant increase in both modulus and hardness, going from 4.87 MPa and 1.62 MPa respectively for the plain PI film, to 14.81 MPa and 4.04 MPa, with increase of 292% and 249%, respectively. It is important to remember that tensile tests and nanoindentation cannot be directly compared, but that similar trends in both are observed. These results are promising as they anticipate that the presence of nanostructured fillers will impact the mechanical properties of the PI film as a consequence of improved interfacial interactions, thus predicting that the presence of the PS-capped NRs will further increase the values of modulus and hardness.

Table 3: Values of Young's modulus and hardness for polymer films prepared under various conditions, as listed.

Styrene % in PS-PI-PS	Drying procedure	% Block copolymer	Modulus (MPa)	Hardness (MPa)
N/A	N/A	0	4.87	1.62
14	Cured	5 wt%	14.81	4.04
22	Cured	5 wt%	5.76	1.65
22	Air dried	5 wt%	5.29	1.51
22	Cured	10 wt%	5.22	1.57

Work under completion and future work: Currently, citrate-capped nanospheres, PS-capped nanospheres, and PS-capped NRs are being employed for the fabrication of composite PI films, with and without the presence of PS-PI-PS. Tensile tests and nanoindentation tests are being run to determine the effect of these fillers on the mechanical properties of PI. At the completion of the mechanical tests, surface enhanced Raman scattering (SERS) experiments will be run to determine variations in polymer conformation at the polymer-nanoparticle interface, whose vibrational signatures are amplified by the presence of the metallic nanostructures.

OTHER REPORTS: Results of this work are currently being compiled in Riyanka Pai's PhD dissertation. The entire document will be submitted as soon as completed.

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