Progress Reports

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Multi-Functional Distributed Fiber Sensors for Pipeline Monitoring and Methane Detections

Report Period
October 1st, 2016 to December 30, 2016

PI: Kevin P. Chen, email: pec9@pitt.edu, telephone: 412-624-9675, fax: 412-624-8003
Department of Electrical and Computer Engineering
University of Pittsburgh
1238 Benedum Hall, 3700 O'Hara Street
Pittsburgh, PA 15261

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This report is submitted by Principal Investigator: Kevin P. Chen

Signature of Submitting Official: _____

Name of Submitting Official: Kevin P. Chen

Objectives

As an abundant and cheap fossil energy source, natural gas has become a major energy supply to support the United States' economy. However, the large-scale extraction and utilization of natural gas also impose significant challenges on methane leakage. This problem is exacerbated by aging gas utility delivery systems including interstate high pressure pipelines, storage and transmission facilities.

The objectives of this project is to develop a cost-effective fiber optical sensing method that can perform multi-parameter real-time measurements of natural gas pipeline and other infrastructure systems cross long interrogation distance up to 100 km with 1-meter spatial resolution to evaluate overall pipeline efficiency and reduce methane emissions.

- This project will develop and optimize a new optical fiber for the specific application of natural gas infrastructure monitoring. Each part of optical fibers is designed and optimized for natural gas infrastructure monitoring.
- By developing new multi-core optical fibers and functional fiber polymer coating, for the first time to our best knowledges, both physical (temperature and strain) and chemical (methane concentration) parameters can be monitored with 1-m spatial resolution across the entire span of the fiber and attached pipeline up to 100 km.

This progress report documents actual project accomplishments with the project goals and objectives listed above for the reporting period.

Summary of the Accomplishment for the reporting period between October 1, 2016 and December 30, 2016

Since this is the first reporting period of the project. Researchers at the University of Pittsburgh is working on establishing experimental setup for functional polymer synthesis and fiber optical sensor design. We have explored two types of polymer for functional fiber coating including fluoride-based polymers and acrylate based polymers.

At the same time, we are also working on the design of multi-functional distributed fiber sensor platform for simultaneous temperature and strain measurements. This work is critically important, which will allow the multi-functional sensors applications including methane and temperature measurements.

During this period, we are in preparation of submitting a journal paper to Optics Express. It highlights our early success of developing multi-core fiber sensors for simultaneous distributed temperature and strain measurements with ×4 times of accuracy improvement from previous arts.

Detailed Technical Reports:

1. Establish Experimental Setup for Polymer Synthesis

One task finished in this period is to establish a whole vacuum manifold system for chemical synthesis. The polymer synthesis system has been constructed in Benedum Hall as shown in Figure 1, which will be used to for the synthesis of the functional coating polymer materials.

This experimental setup is a two-way manifold, consisting of an adjustable trap, an adjustable oil bubbler, and four gas inlet/outlet stopcocks, provides the basic equipment for Schlenk work. The vacuum system is supported by the vacuum pump and the flow of N2 gas through a bubbler is used to monitor the N2 flow through the manifold. The vacuum/nitrogen cycle is the heart of minimizing the amount of oxygen in a Schlenk vessel, which is employed for the oxygen sensitive synthetic procedures.

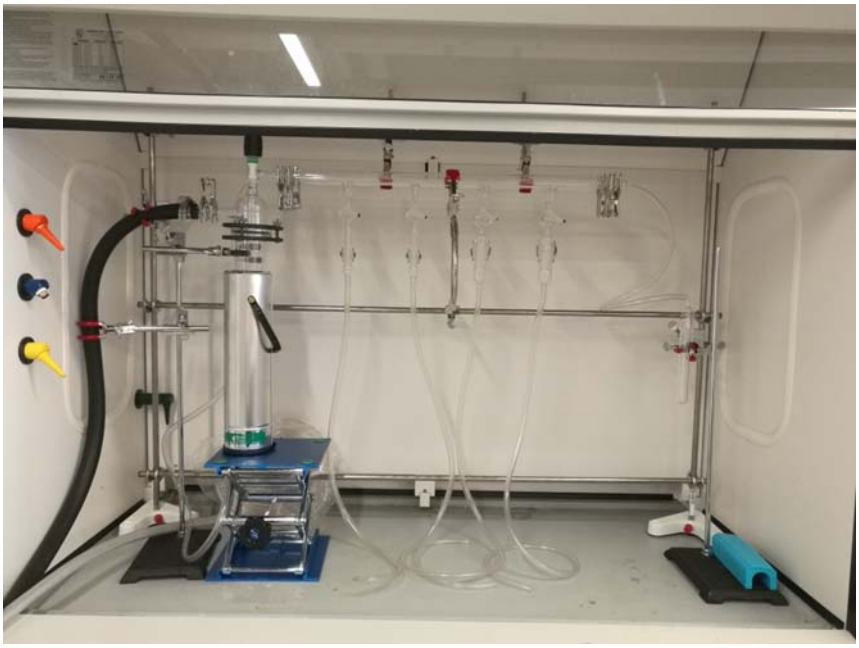


Figure 1: A photograph of the vacuum manifold experimental setup for the oxygen-sensitive synthesis of functional coating polymers.

Using the existing setup, we are developing two family of polymer groups with low refractive indices. Our goal is to develop the functional polymer coating for methane detection, which should have several key features to meet the requirement of the proposed applications:

1. The refractive index of the polymeric material should be less than 1.45 at wavelength 1550-nm to perform its function adequately for both evanescent absorption measurement and strain-based sensing.

2. The polymeric material naturally must be transparent with low optical loss.

3. The polymeric material should swell significantly in the presence of methane for strain-based measurement, and in addition should dilate as it swells.

4. The polymeric material should become absorbing materials in the presence of methane and the optical absorption change should be reversible.

5. The material should be amenable to UV light-induced or electron-based crosslinking to provide a resilient coating.

To obtain the ideal functional coating materials, we propose to synthesize two kinds of polymer or copolymer in the next step.

1.2. Synthesis of UV-curable fluorinated acrylate polymer

The presence of fluorine in a polymeric material can modify its main properties, such as repellency, lubricity, and chemical and thermal inertness. Fluorine atoms always distribute along the main carbon chain to tightly wrap the whole carbon chain owing to its low polarizability, strong electronegativity and high strength of C-F bond. This “shielding” effect makes light difficult to penetrate the polymer, resulting a low refractive index of fluorinated polymers, which make them ideal candidates as protective coatings for optical fibers. At the same time, UV-curing technique has found to be most useful application in optical fiber coating because this technology guarantees a fast cure, selectivity and flexibility in the use, energy saving, and no environmental pollution. Therefore, by introducing fluorinated monomer or polymers in the UV-curable systems, it would be possible to combine the properties of these molecules and the advantages of the UV curing technology, giving rise to cured products with out-standing properties. Base on this, we would like to synthesize a series of UV-curable fluorinated acrylate, as shown in Figure 2:

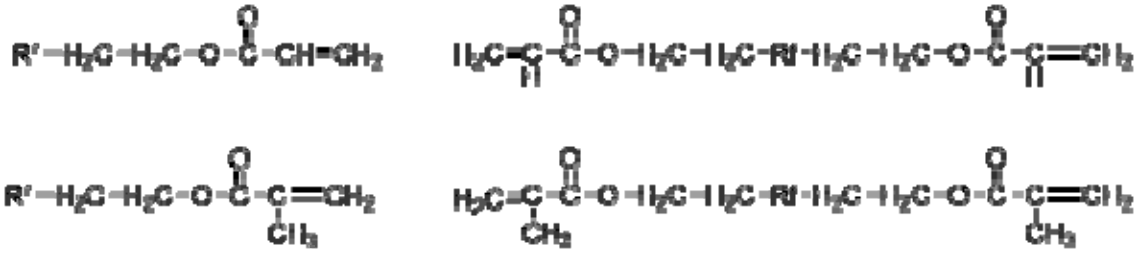


Figure 2. Structures of fluorinated monomers

Herein, Rf is a perfluorinated alkyl group which lower refractive index of coating polymers and (meth)acrylate moiety which give UV curable functionality to the oligomers. We decide to prepare acrylic networks through UV-curing technique using above series of fluorinated acrylates whose structure is tailored to understand the structure-property relationships of the cured systems.

2.2 Synthesis of UV-curable silicone acrylate polymer

Silicone (disubstituted siloxane) polymer or copolymer, whose indices of refraction is also lower than 1.45, at the same time, experimental work has shown that siloxane absorb significantly more methane than fluorinated analogs (possibly owing to the relatively unfavorable fluorocarbon-hydrocarbon interactions). Therefore, silicone polymer is another choice for us to prepare the functional coating materials. In this program, we propose to

synthesize the siloxane system with pendant groups (side groups), as shown in Figure 3, that (a) help to optimize the solubility parameter as much as possible to maximize methane swelling, and (b) contain functional groups that permit UV light-induced crosslinking. Groups within category (a) will include methyls and vinyls, as these have been shown to help reduce solubility parameter more than other functional groups and (b) will include (meth)acrylate, as these have been shown to help to give UV curable functionality to the oligomers.

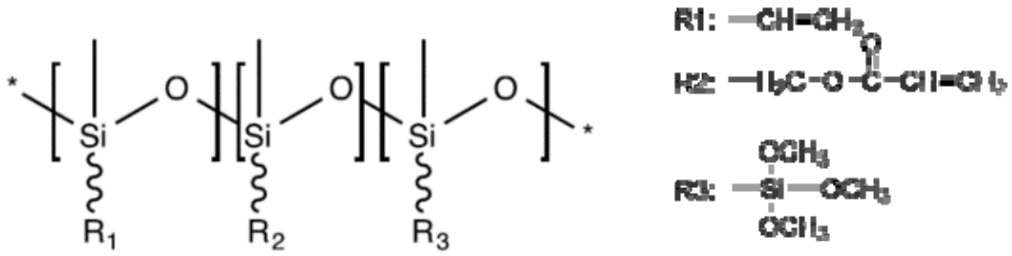


Figure 3. Structures of siloxane system

2. Polymer characterization

In order to achieve low refractive index coating on fiber, a variety of polymers such as UV Oligomer, Acrylate Monomer, Aliphatic PU Polyester Oligomer and FL Acrylate are studied in the experiment. By changing the composition of compound polymers, we are able to tune the polymer refractive index within different ranges. Two curing technologies (UV light, E-beam) is also confirmed to have significant impact on the polymer refractive index.

Equipment: The equipment used in the experiment is a prism coupler (Figure 4). The prism coupler is particularly suitable to characterize optical properties of the thin film with film thickness larger than 1-μm. In this period of performance, we established this capability of measuring refractive indices of polymer through refurbishing a Metricon 2010 systems.

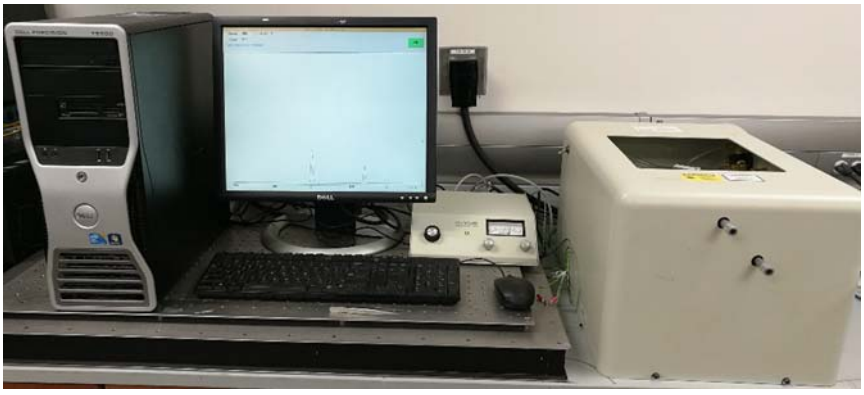


Figure 4: Metricon Prism Coupler 2010

The main body of the prism coupler is shown in Figure 5, while a polymer film is spun on a silicon wafer. Figure 5(a) is the sketch of each part in the main box. The prism coupler used in the experiment (Figure5(b)) equips with laser source A which is a 632.8nm Helium Neon laser. The output power of the laser is 0.9mW. Therefore, the refractive index of polymer samples are measured at 633 nm. The refractive indices of samples at 1550-nm are lower.

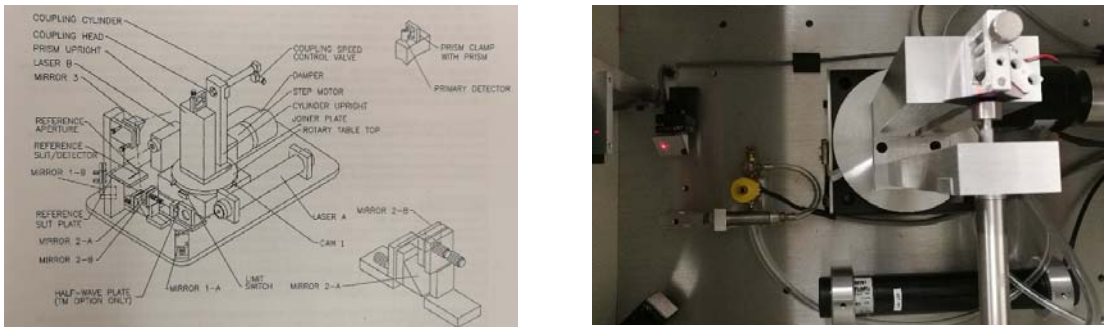
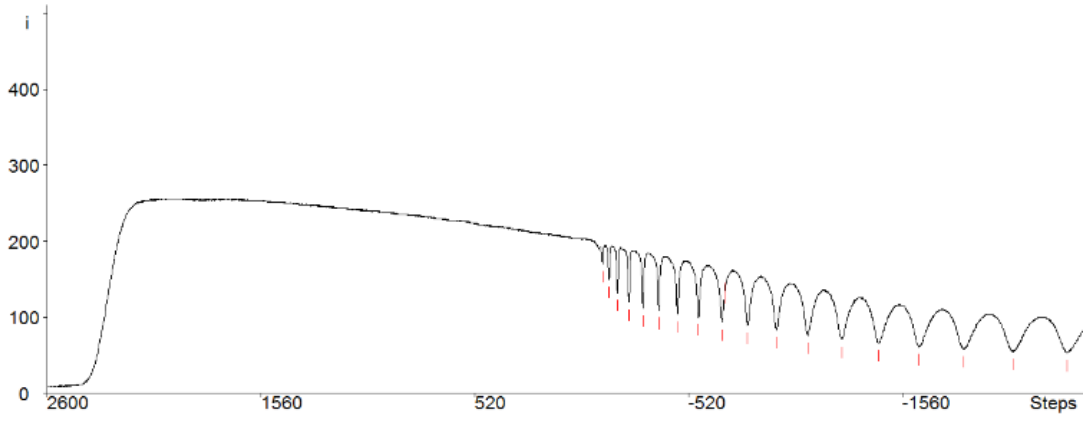


Figure 5: (a): sketch of the components in the mainbody, (b) image of the main body

A typical measurement results in this experiment in plotted in the Figure 6. There are total 18 guided mode coupled into the polymer film as shown as dips in Figure 6 when the coupling angles changes from 0^{o} and up. Using the coupling angles and known index of refraction of the prism, both refractive index and thickness of polymer films can be determined. The minimum standard deviation solution is the most self-consistent solution and will usually be the correction solution. So in order to get the reliable results, we limit the standard deviation to less than 1% in our experiment.



-102	(1.5027)	-134	(1.4973)	-175	(1.4903)	-230	(1.4809)
-298	(1.4691)	-376	(1.4555)	-467	(1.4395)	-569	(1.4213)
-683	(1.4007)	-808	(1.3779)	-949	(1.3519)	-1101	(1.3235)
-1266	(1.2924)	-1447	(1.2581)	-1643	(1.2207)	-1861	(1.1791)
-2100	(1.1337)	-2364	(1.0841)				

Off	n	SD	%SD	t	SD	%SD
0	1.5040	.0002	0.01	5.0454	0.3060	6.07
>> 1	1.5068	.0001	0.00	5.6017	0.0376	0.67
2	1.5105	.0005	0.03	6.0981	0.1867	3.06

Figure 6: Photodetector intensity vs rotational angle (in step)

Sample Preparation: To measure the coating material refractive index, we spin coat the synthesis polymer onto the Silicon substrate with 300um Silicon dioxide to form a film. The spin coating speed is 7000rpm and coating time is 60s. The coated film thickness is from 5-7 um according to the viscosity of different compound polymer compositions. After the film is being prepared, we cure them using two different methods: E-beam and UV light and compare the result (Figure 7).

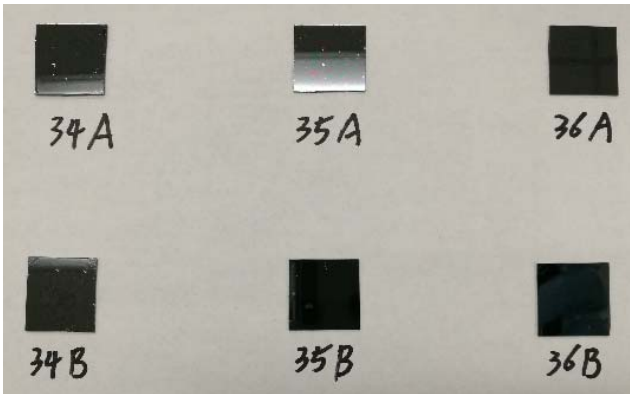


Figure 7: Some of the coated film

Five groups of samples with different polymer composition and curing method are listed in the following tables.

Table 1. Sample (UV Cure) without FL Acrylate A or B

Low RI UV coating for fiber optic cable (UV)						
	34A	**34B**	**35A**	**35B**	**36A**	**36B**
Flexible UV Oligomer	33.02	33.02	33.02	33.02	9.95	10.07
Aliphatic PU Polyester Oligomer	33.02	33.02	33.02	33.02	56.38	57.08
Acrylate Monomer	28.30	33.96	28.30	33.96	29.60	32.85
PI Surface and Deep Cure	5.66	0	5.66	0	2.87	0
PI Surface Cure	0	0	0	0	1.2	0

Table 2. Sample (E-beam Cure) with FL Acrylate A

Low RI UV coating for fiber optic cable FL Acrylate A additions (EB)						
	56A	**56B**	**56C**	**56D**	**56E**	**56F**
Flexible UV Oligomer	32.36	31.37	0	0	0	0
Allophanate Oligomer	0	0	32.36	31.37	9.87	9.57
Aliphatic PU Polyester Oligomer	32.36	31.37	32.36	31.37	55.94	54.23
Acrylate Monomer	32.28	32.26	32.28	32.26	32.19	31.20
FL Acrylate A	2.00	5.00	2.00	5.00	2.00	5.00

Table 3. Sample (E-beam Cure) with FL Acrylate B

Low RI UV coating for fiber optic cable FL Acrylate B additions (EB)						
	57A	**57B**	**57C**	**57D**	**57E**	**57F**
Flexible UV Oligomer	32.36	31.37	0	0	0	0
Allophanate Oligomer	0	0	32.36	31.37	9.87	9.57
Aliphatic PU Polyester Oligomer	32.36	31.37	32.36	31.37	55.94	54.23
Acrylate Monomer	32.28	32.26	32.28	32.26	32.19	31.20
FL Acrylate B	2.00	5.00	2.00	5.00	2.00	5.00

Table 4. Sample (UV Cure) with FL Acrylate A

Low RI UV coating for fiber optic cable FL Acrylate A additions (UV)						
	58A	**58B**	**58C**	**58D**	**58E**	**58F**
Flexible UV Oligomer	32.36	31.37	0	0	0	0
Allophanate Oligomer	0	0	32.36	31.37	9.87	9.57
Aliphatic PU Polyester Oligomer	32.36	31.37	32.36	31.37	55.94	54.23
Acrylate Monomer	27.73	26.88	27.73	26.88	29.01	28.12
PI Surface and Deep Cure	5.55	5.38	5.55	5.38	2.81	2.73
PI Surface Cure	0	0	0	0	1.18	1.14
FL Acrylate A	2.00	5.00	2.00	5.00	2.00	5.00

Table 5. Sample (UV Cure) with FL Acrylate B

Low RI UV coating for fiber optic cable FL Acrylate B additions (UV)						
	58A	**58B**	**58C**	**58D**	**58E**	**58F**
Flexible UV Oligomer	32.36	31.37	0	0	0	0
Allophanate Oligomer	0	0	32.36	31.37	9.87	9.57
Aliphatic PU Polyester Oligomer	32.36	31.37	32.36	31.37	55.94	54.23
Acrylate Monomer	27.73	26.88	27.73	26.88	29.01	28.12
PI Surface and Deep Cure	5.55	5.38	5.55	5.38	2.81	2.73
PI Surface Cure	0	0	0	0	1.18	1.14
FL Acrylate B	2.00	5.00	2.00	5.00	2.00	5.00

Experimental Results: After the measurement, the refractive index of the sample under 633nm laser is listed in Table 6

Table 6. Refractive measurement results

Sample	**34A**	**34B**	**35A**	**35B**	**36A**	**36B**
Refractive index	1.5123	1.5073	1.5108	1.5068	1.5123	1.5097
	56A	**56B**	**56C**	**56D**	**56E**	**56F**
	1.5065	1.5066	1.5060	1.5040	1.5079	1.5075
	57A	**57B**	**57C**	**57D**	**57E**	**57F**
	1.5060	1.5057	1.5049	1.5094	1.5075	1.5072
	58A	**58B**	**58C**	**58D**	**58E**	**58F**
	1.5085	1.5104	1.5095	1.5091	1.5097	1.5096
	59A	**59B**	**59C**	**59D**	**59E**	**59F**
	1.5120	1.5109	1.5103	1.5083	1.5118	1.5096

Observing from 34A to 36B, we find that by eliminating PI Surface and Deep Cure, a lower refractive index is achieved. Also, introducing the high ratio of FL Acrylate A and B (5%), a slightly decrease of film refractive index is observed. Meanwhile, compared with FL Acrylate B, samples with FL Acrylate A have lower refractive index. Finally, the table also indicates that curing sample with E-beam technology would also reduce the refractive index.

Summary of this period: During the first period of this project, all researchers are hired and under contract. We have successfully hired a postdoctoral fellow Dr. Hang-Jun Ding from Carnegie Mellon University. We have established all necessary experimental setup, polymer synthesis and characterization are well underway. We expect to perform methane test on fiber in the coming reporting period.