

Progress Reports

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

Report Period
April 1st, 2017 to June 30, 2017

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



Signature of Submitting Official: _____

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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 4/1/17-6/30/17

During this performing period, we have achieve significant progress on functional polymer syntheses. Both optical and mechanic properties of polymer films have been significantly improved. While maintaining low refractive indices of the polymer films, we have improve the elastic performance of the polymer.

To make polymer sensitive to methane gas, we have successfully dissolve and integrate MOF (Metal Organic Frameworks) with an enforced cage structure with appropriate size for CH₄ molecule trapping into polymer matrices. MOF-dissolved polymer have been used to absorb methane with great quantity and specificity. MOF has been synthesized and have been incorporated into some polymer samples to form the emulsions. Initial optical measurements have been carried out with methane response.

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.

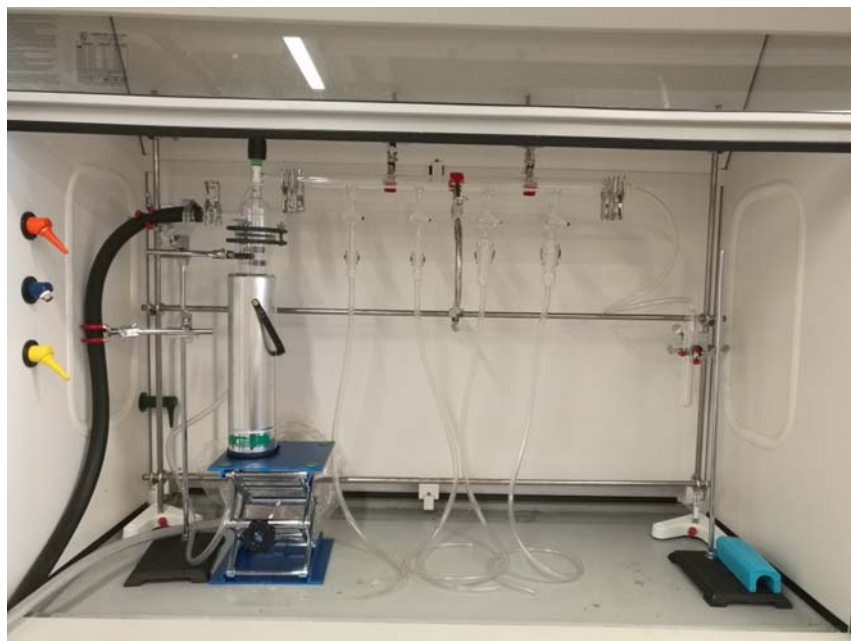


Figure 1: A photograph of the vacuum manifold experimental setup for the oxygen-sensitive synthesis of functional coating polymers.

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:

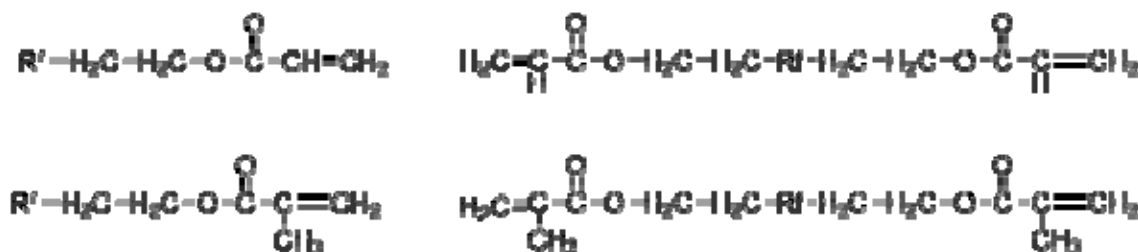


Figure 2. Structures of fluorinated monomers

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.

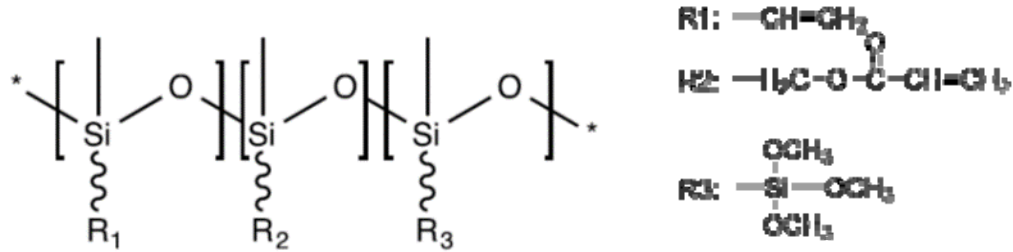


Figure 3. Structures of siloxane system

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 (Figure 5(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.

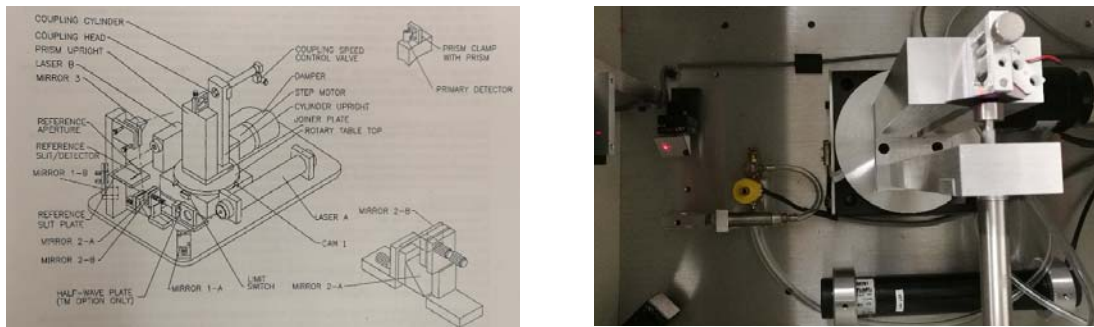


Figure 5: (a): sketch of the components in the mainbody, (b) image of the main body

A typical measurement results in this experiment is 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° 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.

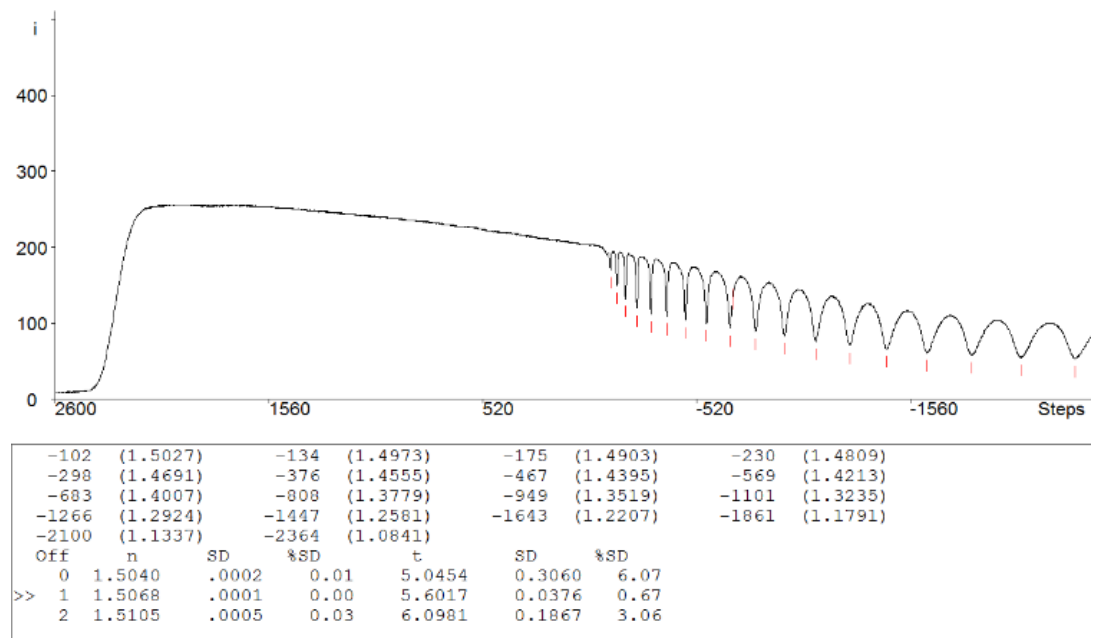


Figure 6: Photodetector intensity vs rotational angle (in step)

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).

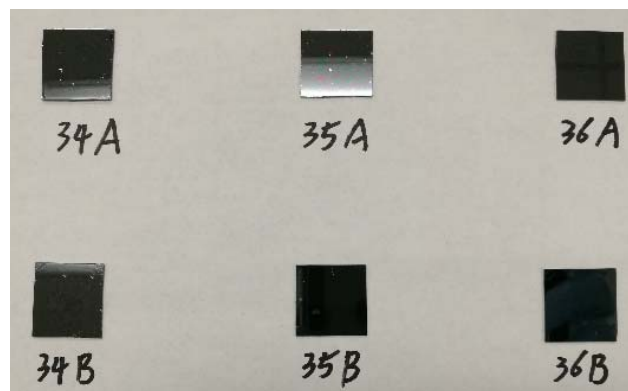


Figure 7: Some of the coated film

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)						
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	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.

Report Period 2:

Tasks Performed during January 1, 2017 to March 31, 2017

Preparation of UV-curable fluorinated and siloxane acrylate polymers and copolymers

In our project, a sensory film with appropriate refractive indices needs to be deposited on the surface of the fiber to enable gas sensing because silica materials are inert to methane and other fuel gases. 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 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 for absorption base measurement.
3. Alternatively, another class of polymeric materials 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 prepared two kinds of UV-curable fluorinated and siloxane acrylate polymers or copolymers in this period.

R2-1.1: 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 wrap tightly 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 outstanding properties.

In this period of the project, we prepared a major series of sample series (Designated as Group #1) mainly comprised of 1H,1H,11H-perfluoroundecyl acrylate, which perfluorinated alkyl group gives lower refractive index of coating polymers and acrylate moiety gives UV curable functionality to the oligomers. Tetrahydrofurfuryl acrylate was used as active solvent and 2,2,2-trifluoroethyl methacrylate helped to dissolve perfluoroundecyl acrylate monomers in the active solvent and copolymerize with monomers. Poly(dimethylsiloxane) vinyl

terminated was added into sample #1-2 to strengthen the film. Darocur 1173 was used as photoinitiator. The structures of components were shown in Figure 1 and formulation of the samples was listed in the Table R2-1.

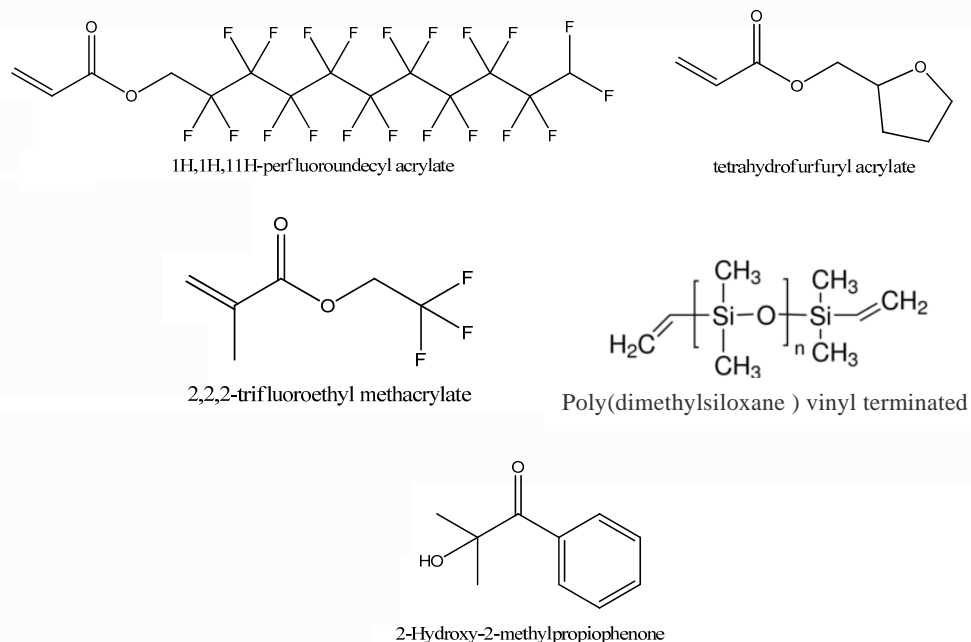


Figure R2-1. Structure of components in sample series #1

Components of the samples	#1-1 (% by weight)	#1-2 (% by weight)
1H,1H,11H-perfluoroundecyl acrylate	2	2
2,2,2-trifluoroethyl methacrylate	2.5	2.5
tetrahydrofurfuryl acrylate	1.25	1.25
poly(dimethylsiloxane) vinyl terminated(Mw=20,000)	0	1
2-Hydroxy-2-methyl-1-phenyl-1-propanone(PI)	3%	3%
Refractive index	1.4356	1.4365

Table R2-1. The formulation of the samples #1

These above components were mixed based on the formulation (Table R2-1) and stirred for 48h to form the homogeneous mixtures, as shown in Figure R2-2. The sample #1-1 is transparent, demonstrating that 2,2,2-trifluoroethyl methacrylate can help to dissolve monomers well in the active solvent. Poly(dimethylsiloxane) vinyl terminated made sample #1-2 a little turbid because of the poor miscibility of poly(dimethylsiloxane) vinyl terminated with tetrahydrofuryl acrylate. The mixtures were spread on a glass slide by drop-casting and the films were obtained by curing at high pressure mercury lamp UV, as shown in Figure R2-3.



Figure R2-2. Photo of the mixture of sample series #1

The refractive index of the film was measured by thin film thickness/refractive index measurement system (Metricon corporation). The refractive index of polymeric film is 1.4356 and 1.4365, both are less than 1.45 to perform its function adequately for both evanescent absorption measurement and strain-based sensing.



Figure R2-3. UV cured films of sample #1-1 and #1-2 on the glass slides

R2-2 UV-curable silicone acrylate polymer

Another group of polymer materials we are focusing on is elastic polymers, which will swell upon methane absorption. 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). Silicone polymer is another choice for us to prepare the functional coating materials. Therefore, we proposed to synthesize the siloxane system with pendant groups (side groups), as shown in Figure R2-4, 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.

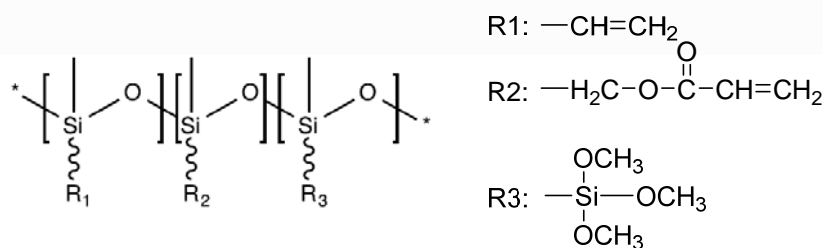


Figure R2-4. Proposed structures of siloxane systems

R2-3: UV-curable vinyl terminated Poly(dimethylsiloxane)

Vinyl terminated polymers are employed in addition of cure systems. The bond forming chemistry is the platinum catalyzed hydrosilylation reaction. Vinylmethylsiloxane copolymers and vinyl T-structure fluids are mostly employed in peroxide activated cure systems, which involve peroxide-induced free radical coupling between vinyl and methyl groups. Herein, we prepared the sample series #2 mainly comprised of vinyl terminated Poly(dimethylsiloxane), which vinyl moiety give UV curable functionality to the oligomers. Tetrahydrofurfuryl acrylate was also used as active solvent and 2,2,2-trifluoroethyl methacrylate gave lower refractive index of coating polymers. Darocur 1173 was used as photoinitiator. The structures of components were shown in Figure R2-5 and the formulation of the samples was listed in the Table R2-2.

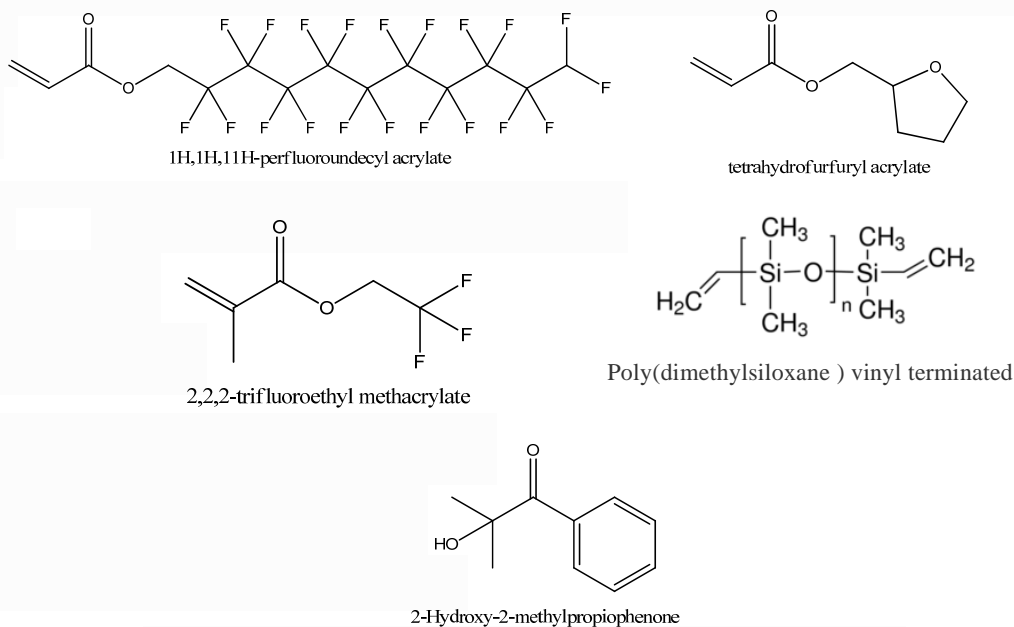
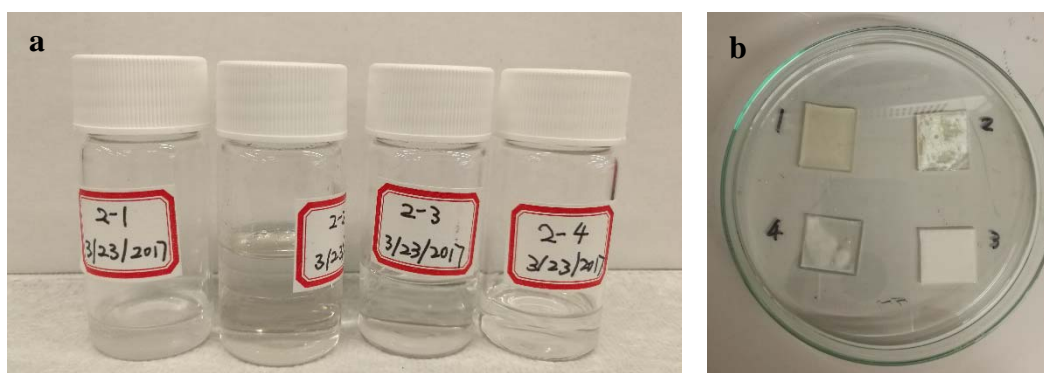


Figure R2-5. Structure of components in sample series #2

Table R2-2. The formulation of the samples series #2

components	Sample 2-1 Weight ratio	Sample 2-2 weight ratio	Sample 2-3 Weight ratio	Sample 2-4 weight ratio
1H,1H,11H-perfluoroundecyl acrylate	0	0	0.4	0.4
2,2,2-trifluoroethyl methacrylate	1	1	1	1
tetrahydrofurfuryl acrylate		1	0.25	0.25
poly(dimethylsiloxane) vinyl terminated(Mw=20,000)	83	83	2	1
2-Hydroxy-2-methyl-1-phenyl-1-propanone(PI)	3%	3%	3%	3%
Refractive index				

These above components were mixed based on the formulation (Table R2-2) and stirred for 48h to form the homogeneous mixtures. The mixtures were spread on a glass slide by drop-casting and the films were obtained by curing at high pressure mercury lamp UV. Except that the sample #2-1 without tetrahydrofurfuryl acrylate is transparent, sample series #2-2 to #2-4 are heterogeneous even after 48h careful stirring due to the poor miscibility of vinyl terminated poly(dimethylsiloxane) with tetrahydrofurfuryl acrylate (Figure R2-6a). Sample #2-1 cannot form the uncomplete solid film even after long time exposure to UV because that vinylsiloxanes are generally sluggish compared to their organic counterparts (Figure R2-6b).

**Figure R2-6.** (a) Photo of the mixtures and (b) cured films of sample series #2

R2-3 UV-curable methacrylate terminated Poly(dimethylsiloxane)

Unlike vinylsiloxanes which are sluggish compared to their organic counterparts, methacrylate and acrylate siloxanes have similar reactivity to their organic counterparts. Methacrylate and Acrylate functional siloxanes undergo the same reactions generally associated with methacrylates and acrylates, the most conspicuous being radical induced polymerization. The principal applications of methacrylate functional siloxanes are as modifiers to organic systems. Upon radical induced polymerization, methacryloxypropyl terminated siloxanes by themselves only increase in viscosity. Mercapto-functional siloxanes

strongly adsorb onto fibers and metal surfaces. High performance toner fluids for reprographic applications are formulated from mercapto-fluids. They also act as internal mold release agents for rubber and semi-permanent lubricants for automotive weather stripping.

Therefore, we prepared the sample series #3 mainly comprised of methacrylate terminated Poly(dimethylsiloxane), which methacrylate moiety give UV curable functionality to the oligomers. Mono-methacrylate terminated Poly(dimethylsiloxane) was used for a comparative study and mercapto-functional siloxanes was used as crosslinkers and adhesion agents. 2,2,2-trifluoroethyl methacrylate was used as active solvent and gave lower refractive index of coating polymers. Darocur 1173 was used as photoinitiator. The structures of components were shown in Figure R2-7 and the formulation of the samples was listed in the Table R2-3.

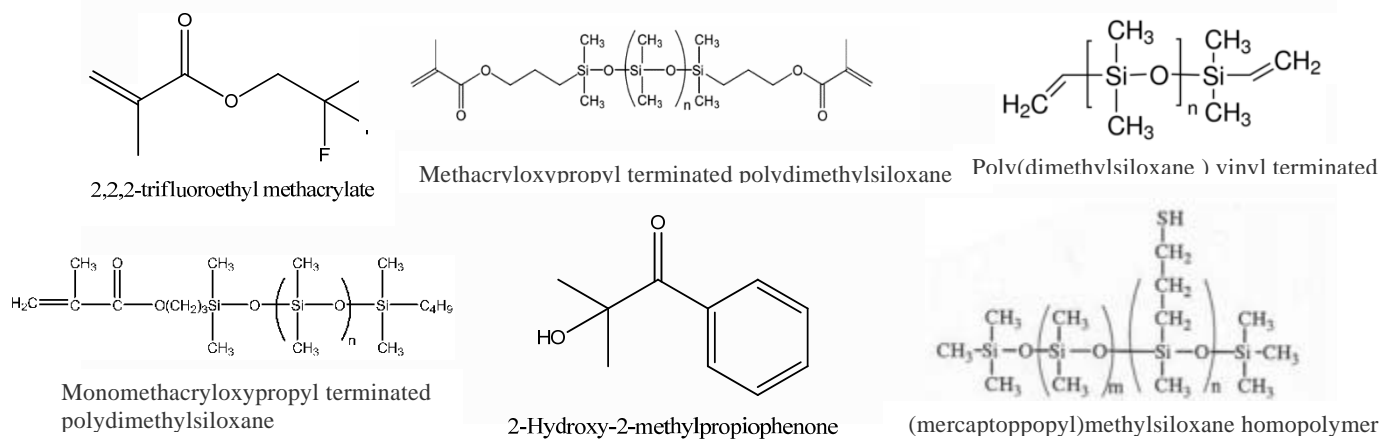


Figure R2-7. Structure of components in sample series #3

components	Sample 3-1 Weight ratio	Sample 3-1-2 weight ratio	Sample 3-2 Weight ratio	Sample 3-3 weight ratio
2,2,2-trifluoroethyl methacrylate	10	1	1	1
poly(dimethylsiloxane) vinyl terminated(Mw=20,000)	83	83	0	0
Methacryloxypropyl terminated polydimethylsiloxane			83	
Monomethacryloxypropyl terminated polydimethylsiloxane				83
(mercaptopyl)methylsiloxane homopolymer	14	14	14	14
2-Hydroxy-2-methyl-1-phenyl-1-propanone(PI)	3%	3%	3%	3%
Refractive index	1.4138	1.4107	1.4249	1.4179

Table R2-3. The formulation of the Sample series #3

Oxygen is an inhibitor for methacrylate polymerization in general. The high oxygen permeability of siloxanes usually makes it necessary to blanket these materials with nitrogen or argon in order to obtain reasonable cures. Therefore, these above components were added based on the formulation (Table R2-3) into a sealed flask under N_2 protection and stirred for 48h to form the homogeneous mixtures. All of the mixtures can form uniform emulsion, as shown in Figure R2-8. The mixtures were spread on a glass slide by drop-casting and spinning-coating. It can be seen from Figure R2-9 that the film formed by spinning-coating is much more uniform and thinner than those made by drop-casting. It will take longer time for sample #3-1 and #3-1-2 to be cured due to the sluggish activity of vinylsiloxanes compared to sample #3-2, resulted in a clear shrinkage of the film. For sample #3-3, it also cannot form the complete solid film because of the lower activity of the Mono-methacrylate terminated group.

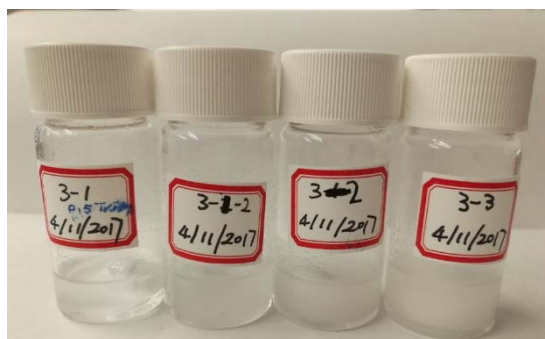


Figure R2-8. Photo of the mixtures of sample series #3

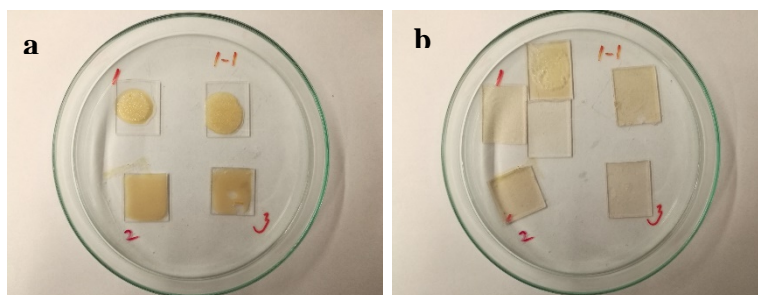


Figure R2-9. Films made from (a) drop-casting and (b) spinning-coating of sample series #3

The refractive index of the film series #3 was measured to be 1.4138, 1.4107, 1.4249 and 1.4179, respectively, all of them are less than 1.45 to perform its function adequately for both evanescent absorption measurement and strain-based sensing. Taking accounting to the film properties, sample #3-2 is the optimized product for the potential optical coating. The poor miscibility of mercapto-functional siloxanes with polydimethylsiloxane resulted in the formation of the emulsion. In order to get transparent solution, we prepared sample series #4 with only polydimethylsiloxane and active solvent 2,2,2-trifluoroethyl methacrylate at different ratios (Table R2-4).

components	Sample 4-1 Weight ratio	Sample 4-2 weight ratio	Sample 4-3 weight ratio	Sample 3-2 Weight ratio
2,2,2-trifluoroethyl methacrylate	20	10	5	1
Methacryloxypropyl terminated polydimethylsiloxane	80	90	95	83
(mercaptopyl)methylsiloxane homopolymer	0	0	0	14
2-Hydroxy-2-methyl-1-phenyl-1-propanone(PI)	3%	3%	3%	3%
Refractive index	1.4065	1.4064	1.4058	1.4263

Table R2-4. The formulation of the Sample series #4

All of the series #4 are transparent, demonstrating that 2,2,2-trifluoroethyl methacrylate is a good solvent for polydimethylsiloxane, as shown in Figure R2-10a. The transparent film were also obtained by photo-polymerization imitated by Darocur 1173 under UV lamp (Figure R2-10b). The refractive index of these films are around 1.4058 ~ 1.4065, indicating that the content of 2,2,2-trifluoroethyl methacrylate has no obvious effect on the refractive index of the films.

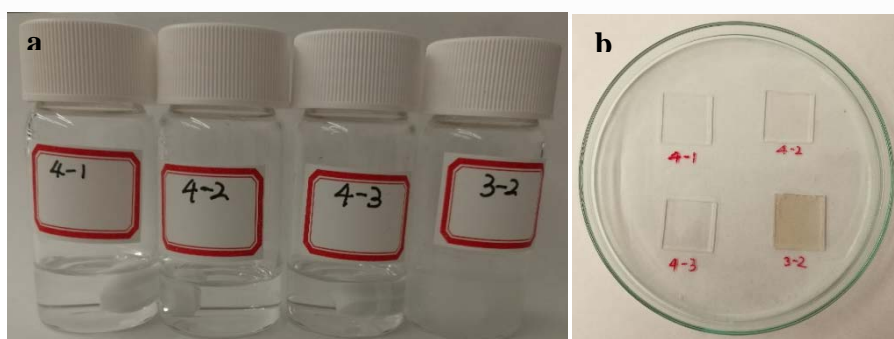


Figure 10. (a) Photo of the mixtures and (b) cured films of sample series #4

However, the film of series #4 are too soft to form the free-standing film. It is clear to see from Figure R2-

11a that polymerization of methacrylate groups brings obvious shrinkage on the glass slide. Comparatively, the addition of mercapto-functional siloxanes in sample #3-2 played a role of crosslinker to strengthen the film. This film can be peeled away from the glass slide to form the flexible, free-standing film, as shown in Figure R2-11b and c. Mercapto-functional siloxanes also increased the refractive index from 1.4058 ~ 1.4062 to 1.4263.

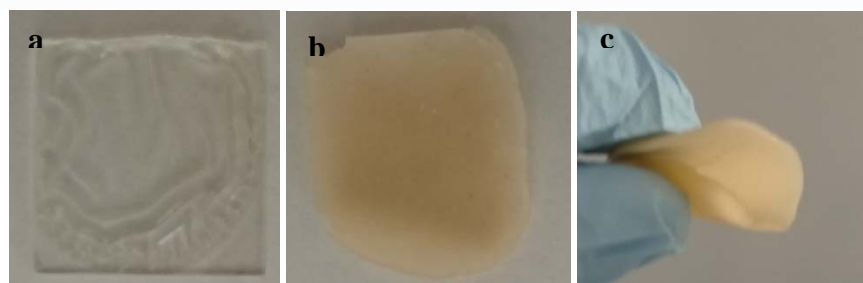


Figure R2-11. (a) Photo of the film of sample #4-2, (b and c) films of sample series #3-2 peeled away from the glass slide

Summary and Tasks for the next stage

As demonstrated in this report, we have achieved significant progress on functional polymer syntheses. Both optical polymer for absorption-based measurements and elastic polymer for strain-based measurements have been successfully fabricated. While further optimization of polymer materials are still needed to be carried out, the polymer chemistry and its synthesis routes have been validated. Controls of refractive indices of both classes of polymers are successfully. We were able to lower their refractive indices to be lower than 1.45 of fiber core, which make them useful for fiber coating.

Report Period 3:

Tasks Performed during April 1, 2017 to June 30, 2017

The final goal of this project is to develop an optical fiber sensor with appropriate coating film deposited on the surface of the fiber to enable gas sensing to methane. Based on the previous results, we continue to synthesize the functional polymer films and fabricate the experiment setup for fiber sensor in this period.

1. Optimize the parameter to synthesize the free-standing polymer films and try to coat on the surface of the optical fibers.
2. Choose suitable fiber and optimize the experiment parameter to fabricate the setup for strain-based sensing and power loss sensing.

R3-1-1 UV-curable silicone acrylate free-standing films

As we know, silicone polymer is a good choice as functional coating material with lower refractive index than 1.45. At the same time, as elastic polymers, silicone polymer absorb significantly more methane than fluorinated analogs (possibly owing to the relatively unfavorable fluorocarbon-hydrocarbon interactions). Therefore, we would like to choose silicone acrylate polymers as functional materials for coating films on fibers. In this period, we continue to optimize the parameter to synthesize the free-standing polymer films. There are mainly four compositions for the UV curable polymers, pre-polymer, assistant agents, active solvent and photo-initiator. Herein, we discussed one by one as follows.

1. Optimized pre-polymers

We have synthesized several kinds of silicone acrylate polymers, including vinyl terminated Poly(dimethylsiloxane), methacrylate terminated poly(dimethylsiloxane), mono-methacrylate terminated poly(dimethylsiloxane). It can be seen from the previous results that vinyl terminated poly(dimethylsiloxane) cannot completely form the solid film after long time exposure to UV due to the sluggish activity of vinylsiloxanes compared to the corresponding organic counterparts. Unlike vinylsiloxanes, methacrylate siloxanes have similar reactivity to their organic counterparts. Methacrylate functional siloxanes undergo the same reactions generally associated with methacrylates, the most conspicuous being radical induced polymerization. It is obvious that mono-methacrylate siloxanes with one side of curable terminated groups have the lower activities than methacrylate siloxanes resulted in the weaker film. Therefore, methacrylate terminated poly(dimethylsiloxane) are chosen as the optimized pre-polymers containing functional groups that permit UV light-induced crosslinking for preparation of the fiber coating films.

2. Optimized assistant agents

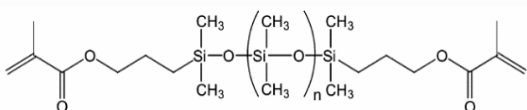
Mercapto-functional siloxanes with strong adsorption on the surface of the glass and metal, are always used as internal mold release agents for rubber and semi-permanent lubricants for automotive weather stripping. It has been proved that addition of mercapto-functional siloxanes into curable system strongly increased the strength of the film and reduced the shrinkage on the glass caused by the polymerization of methacrylate groups (see series #4). Therefore, mercapto-functional siloxanes are assistant as crosslinkers and adhesion agents for the curable system.

3. Optimized Photo initiator

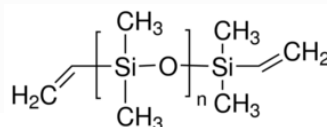
DAROCUR 1173 is a versatile highly efficient liquid photoinitiator which is used to initiate the photo-polymerization of chemically unsaturated pre-polymers - e.g. acrylates - in combination with mono- or multifunctional monomers. As a liquid UV curing agent with excellent compatibility, DAROCUR 1173 is especially easy to incorporate with other chemicals. It has also been demonstrated that it is highly suitable for our curable system (see previous report).

4. Optimized active solvent

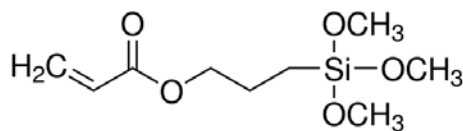
The active solvent is another important composition for the UV curable system. The active solvent is kind of functional agent which could help to disperse uniformly pre-polymers in system to get high efficient polymerization. At the same time, active solvent contains functional groups that permit UV light-induced copolymerization with pre-polymers. As we know, silicone polymer should swell significantly in the presence of methane. Taking accounting to maximize methane swelling, we would like to choose silicones with low molecule weight as active solvent.



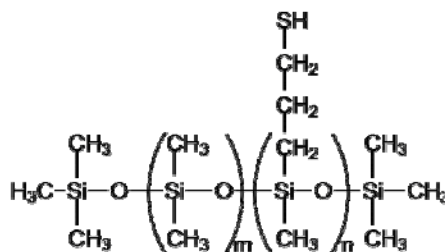
Methacryloxypropyl terminated polydimethylsiloxane



Poly(dimethylsiloxane) vinyl terminated



(3-acryloxypropyl)trimethoxysilane



(mercaptopyl)methylsiloxane homopolymer

Figure R3-1. Structure of components in sample series #7

In this period of the project, we prepared the sample series #7 mainly comprised of methacrylate terminated poly(dimethylsiloxane), which methacrylate moiety gives UV curable functionality to the oligomers. Mercapto-functional siloxane was used as assistant agents to strengthen adhesion on the surface of the fiber and Darocur 1173 was used as photoinitiator. (3-acryloxypropyl)trimethoxysilane and two kinds of vinyl terminated polydimethylsiloxane with low molecule weight was added into the curable system as active solvent, respectively. The structures of components were shown in Figure R3-1 and the formulation of the samples was listed in the Table R3-1.

Table R3-1. The formulation of the Sample series #7

Components	Sample 7-1 Weight %	Sample 7-2 weight %	Sample 7-3 Weight %
Methacryloxypropyl terminated polydimethylsiloxane ($M_w=25,000$)	83	83	83
(mercaptoppopyl)methylsiloxane homopolymer ($M_w = 4,000\sim 7,000$)	14	14	14
(3-acryloxypropyl)trimethoxy Silane ($M_w = 234.32$)	1	0	0
Vinyl terminated poly(dimethyl siloxane)-V ₂₁ ($M_w= 4,000$)	0	1	0
Vinyl terminated poly(dimethyl siloxane)-V ₂₂ ($M_w= 9,400$)	0	0	1
2-Hydroxy-2-methyl-1-phenyl-1-propanone (PI)	2~3	2~3	2~3

Oxygen is an inhibitor for methacrylate polymerization in general. In this reaction, the high oxygen permeability of siloxanes usually makes it necessary to blanket these materials with nitrogen or argon in order to obtain reasonable cures. Therefore, these above components were added based on the formulation (Table R3-1) into a sealed flask under N₂ protection and stirred for 48h to form the homogeneous mixtures.

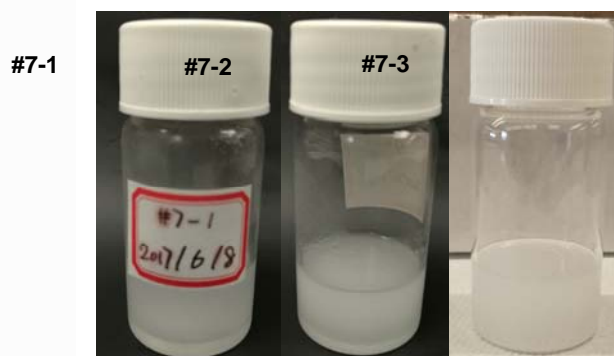


Figure R3-2. Photos of the mixtures of sample series #7

All of the mixtures can form uniform emulsion, as shown in Figure R3-2. The emulsions look a little turbid because of the poor miscibility of (mercaptopropyl)methylsiloxane homopolymer with methacryloxypropyl terminated polydimethylsiloxane. It can be seen that there is no obvious effect of the active solvent on the formation of the emulsion. The mixtures were spread on a glass slide by drop-casting and the films were obtained by curing at high pressure mercury lamp UV, as shown in Figure R3-3. It is obvious that the active solvents are resulted in the formation of the different films even with the similar produced emulsions.

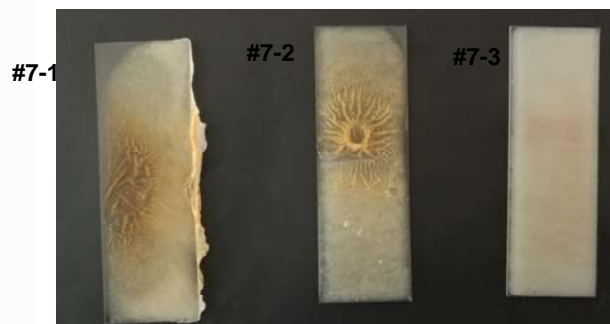


Figure R3-3. Photos of the films of sample series #7 on the glass substrates

(3-acryloxypropyl)trimethoxysilane has low molecule weight of 234.32 and low boiling point of only 68 °C. It is easily boiling when exposed to high temperature environment from high pressure mercury lamp UV. It can be seen that the film #7-1 is yellow and shrinkage from the glass substrate due to the formation of the bubble at high pressure mercury lamp UV. The film #7-2 is also nonuniform with partly yellow bubble probably caused by low molecule weight of vinyl terminated poly(dimethylsiloxane)-V₂₁ of 4,000. Vinyl terminated poly(dimethylsiloxane)-V₂₁ of 9,400 as active solvent formed the uniform and solid film as shown as sample #7-3 in Figure R3-3 and R3-4. This sample is strong enough to be peeled from the glass substrate to be the free-standing film and the film is very strong, elastic and flexible and can form the different shapes. The unique properties of the film #7-3 make it ideal matrix candidate for the coating materials for the optical fiber sensors.



Figure R3-4. Photos of the free-standing films of sample series #7-3

R3-1-2 Mixture of MOF in UV-curable silicone acrylate free-standing films

As we know, MOF (metal-organic frameworks) have recently been intensively studied as a new class of porous materials. They comprise metal ions or metal containing clusters linked by multitopic organic ligands to form 3D networks. A large number of possible organic linkers combined with a plenty of metal ions and metal ion clusters lead to a huge range of potential porous materials with unique surface properties and chemically tunable structures. However, the interaction energy between methane and the surface of MOFs is already large enough to give reasonable adsorption at room temperature. Therefore, to make polymer coatings more sensitive to methane, we proposed to integrate MOFs with an enforced cage structure for CH₄ molecule trapping into polymer matrices. MOFs could be able to absorb methane with great quantity and specificity. MOFs have been synthesized by NETL. The menthol solution containing MOFs were added into the sample #7-3 by weight ratio of 1:2 in a sealed flask under N₂ protection and stirred for 48h to form the homogeneous mixtures. The mixture is uniform and more milky emulsion compared with sample #7-3 due to the addition of MOFs (Figure R3-5).

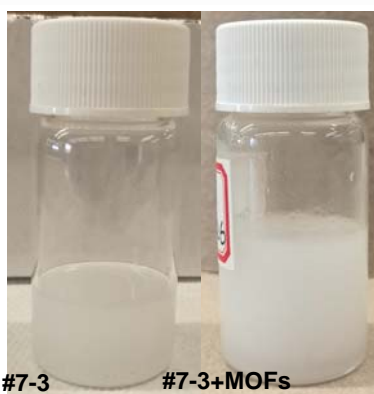


Figure R3-5. Photos of sample #7-3 and mixtures with MOFs

The mixtures were spread on a glass slide by drop-casting and the films were obtained by curing at high pressure mercury lamp UV. It is clear to see from Figure R3-6 that the mixture with sample #7-3 and MOFs can form uniform and more turbid film compared to that of sample #7-3.

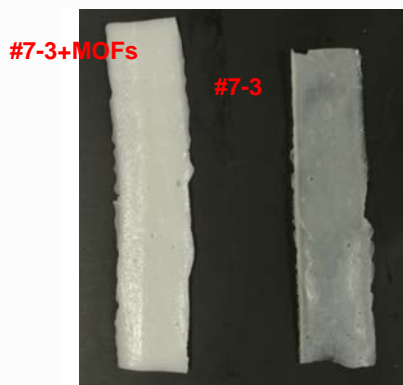


Figure R3-6. Photos of the films of sample #7-3 and mixtures with MOFs

The mixture of MOFs is strong enough to be peeled from the glass substrate to be the free-standing film and the film is very strong, elastic and flexible and can form the different shapes (Figure R3-7). And it is also interesting to find if the film exposed to UV lamp a little longer time it is easily to form the bubble resulted the formation of shrinkage from the substrates. It probably caused by the trapping of the air of MOFs because the huge porous structures of MOFs give reasonable adsorption of gas.

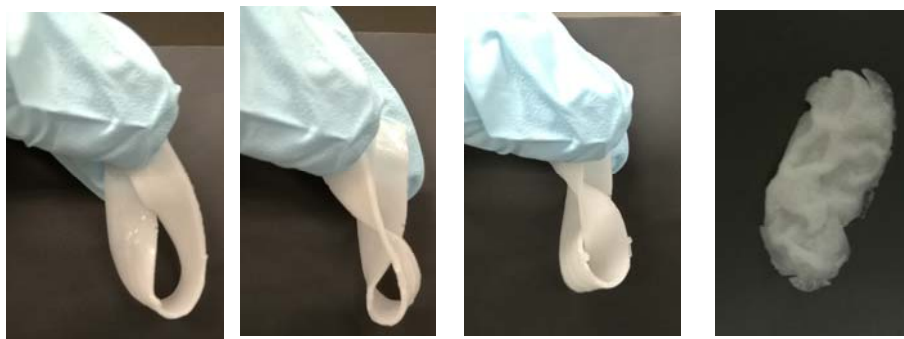


Figure R3-7. Photos of the films of mixture of sample #7-3 with MOFs

R3-1-3 Coating the silicone acrylate and mixture with MOFs on fiber surface

Above results demonstrate that the silicone acrylate sample #7-3 and the mixture with MOFs are ideal matrices for coating materials for the optical fiber sensors. Herein, we tried to apply two methods, dip-coating and embed-coating, to make the coating film of the polymers on the fiber surface.

1. Dip-coating

Because we would like to coat the middle area of the fiber in convenience of measure, typical dip-coating is difficult to get this goal. We modified the dip-coating method as follow: the fiber was mounted vertically and silicone acrylate polymer (sample #7-3) was dropped along the fiber by a needle. The drops traveled along the fiber as a result of gravity and then cured by exposure to UV lamp. Repeated this process for two times. The microscope image of coated fiber was shown in Figure R3-8. It can be seen that the diameter of the coating film is decent in the range of 141 μm ~ 147 μm . The thickness of the coating film is around 10 μm .

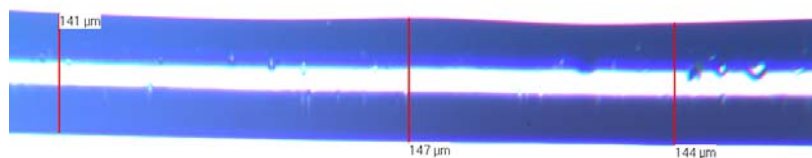


Figure R3-8. The microscope image of the fiber with 2-time dip-coating of sample #7-3

2. Embed-coating

In order to get more uniform and thicker coating films on the fiber, we tried to apply the embed-coating method. The fiber was mounted horizontally on the top of a hand-made trench substrate and silicone acrylate polymer (sample #7-3) and mixture with MOFs was poured into the trench, respectively and then cured together with the fiber under UV lamp. After peeled from the trench substrate, the fiber with polymer coating were successfully obtained, as shown in Figure R3-9. Both sample #7-3 and mixture with MOFs form the uniform film coated on the fibers, which is suitable for the next measurement.

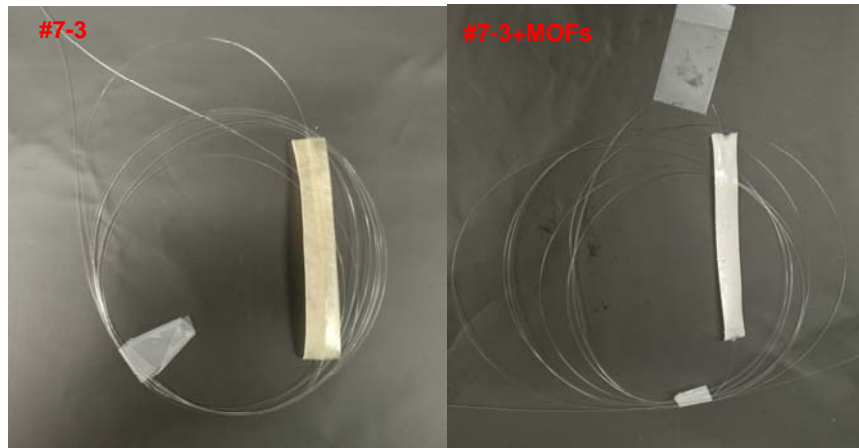


Figure R3-9. The photos of the fibers cured with film of sample #7-3 and mixture with MOFs

R3-2 Optical fiber sensor measurement

R3-2-1 Fiber strain sensing induced by gas absorption

Herein, single mode SMF28 fiber or D-shape fiber was used to detect the applied strain. The jacket of the fibers were firstly stripped in order to increase the accuracy of the sense to applied strain, then the silicone polymers and/or mixtures with MOFs were cured on the fiber surface. When methane gas is introduced into the chamber, silicone polymers and/or mixtures with MOFs begin to expand due to the trap of methane molecule, resulted in the rendering an in-axis strain across the fiber. The backscatter Rayleigh signals caused by strain change could be detected.

The experimental setup is shown as the following Figure R3-10. An optical backscatter Reflectometer (OBR) is used to measure the distributed strain along the fiber with a resolution as high as millimeter level. The wavelength of the laser in OBR is around 1550 nm. Two gas sources (air and methane) are used in the experiment and their flow is manipulated by the flow controller as well as their ratios. The cross-section view of D-shape fiber is shown in Figure R3-11.

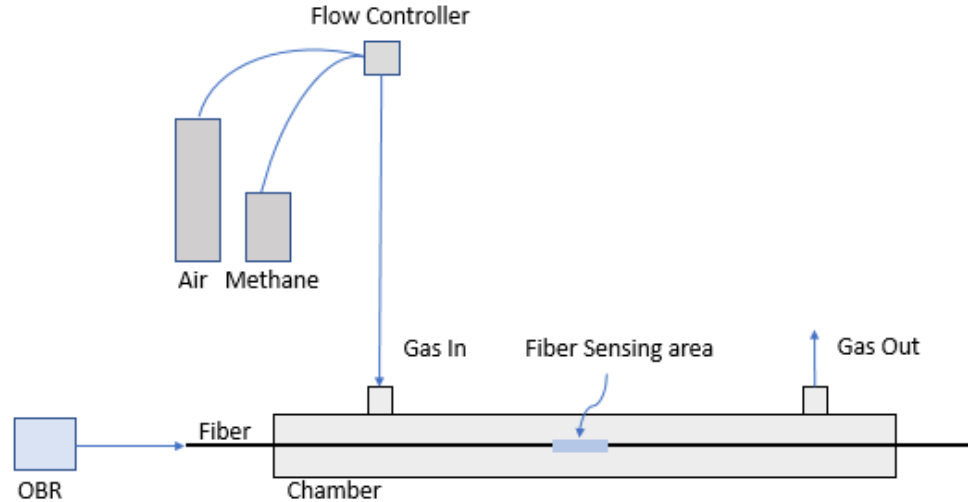


Figure R3-10. Experimental setup for fiber strain sensing

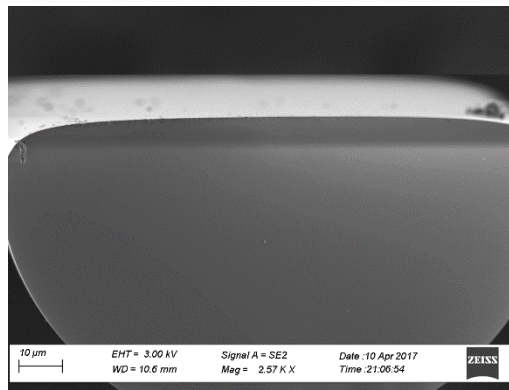


Figure R3-11. The SEM image of the cross-section view of D-shape fiber

The resulted distributed strain after methane influx is shown in Figure R3-12. The section of fiber in chamber is in the range of 3.3 ~ 4.1m and the sensing area is in the range of 3.6 ~ 3.75m. It is clear to notice that there is no any change in the aimed sensing part, indicating that there is no noticeable strain detected. The sharp drop on both side of sensing area was proved to the temperature effect. The influx of compress gas will cool down temperature around the fiber jacket, resulted in a shrinkage tightly connected jacket and then formation of a strain along the fiber. However, the fiber jacket was stripped in the sensing part, resulted in a loosen connection between the coated polymer and core compared to that coated by jacket. The generated strain will be released by the polymer itself and cannot be transferred to the fiber. At the same time, the diffusion rate of methane into polymer coating film is relatively low of $6.02 \times 10^{-11} / \text{cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, therefore, only very limited gas penetrating into the polymer generates a very minor strain that is far beyond the OBR test limit range. In conclusion, fiber strain measurement seems to be not sensitive enough for detecting the methane in the environment.

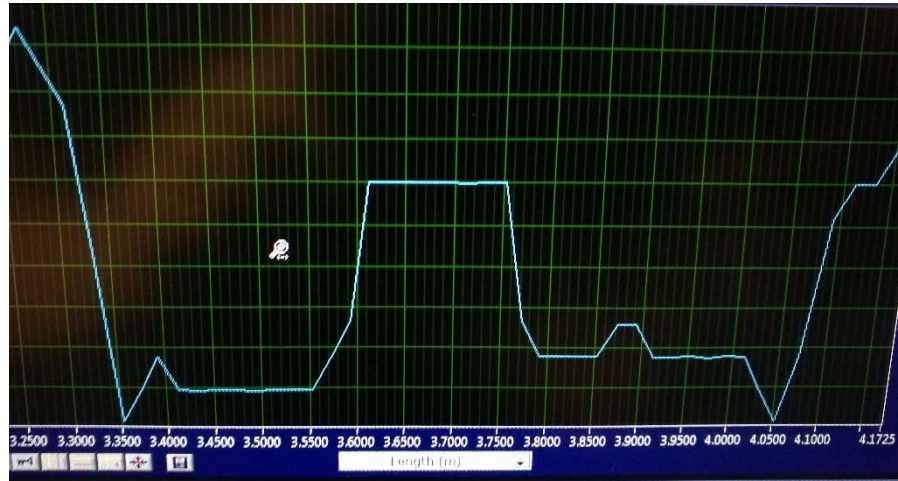


Figure R3-12. Distributed strain profile after 30 min methane flux

R3-2-2 Fiber power loss sensing induced by gas absorption

As we know, when the refractive index of the polymer coating is lower than the fiber core, most of the light will be quenched in the core. However, there are still evanescent wave traveling in the air. The refractive index of polymer coating would increase on absorption of the methane molecule to rend more light traveling across the cladding and air so that more light would be adsorbed in the polymer coating films accordingly.

The setup for fiber power loss sensing induced by gas absorption is shown in Figure R3-13. Compared with strain sensing, the laser source is changed with a broadband laser source of the wavelength in the range of 1520 ~1620 nm. Thorlabs PDA10CS is used as detector to monitor the output power and the power is plotted in the PC through software.

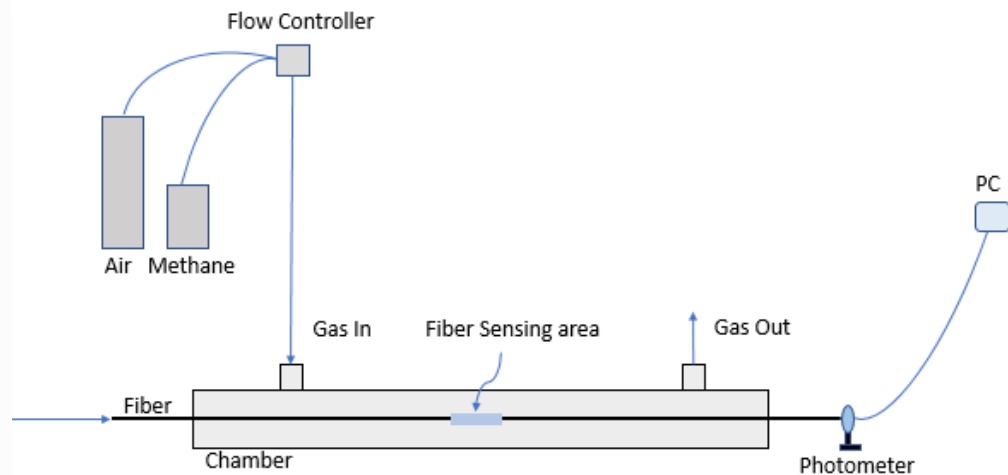


Figure R3-13. Experimental setup for fiber power loss sensing

D-shape fiber was used in the experiment. Etching technique was introduced to strip off the cladding of the fibers and the etching time was optimized to establish the correlation. The buffered oxide etchant containing 6 parts of 40% NH_4F and 1 part of 49% HF was used as etching solution and the etching rate is 70 nm/min at room temperature. 3 samples with 0, 30 min and 60 min etching time were prepared to study the effect of cladding thickness on fiber sensing. In the experiment, we set the methane flux around 30 sccm and flush the chamber for 5min before testing.

Figure R3-14 to R3-16 show the power distribution versus time plots of the samples prepared at different etching time. It can be seen from Figure R3-14 that the initial output power is around 0.6V and keeps almost constant during the methane flush, indicating no loss is introduced the whole time. This minor light absorption of the polymer coating films, probably resulted from the lack of evanescent wave in the polymer, could be neglected. However, for the fiber under 30 min etching, change of the output power becomes more obviously (Figure R3-15). This is clearly because that the decrease of thickness of the cladding could give more light exposure to the polymer films. With etching time increase to 60 min, the response of output power to the influx of methane becomes quicker and shaper in amplitude, as shown in Figure R3-16. Therefore, the fiber output power loss has proven to be an effective way to detect the methane in the environment.

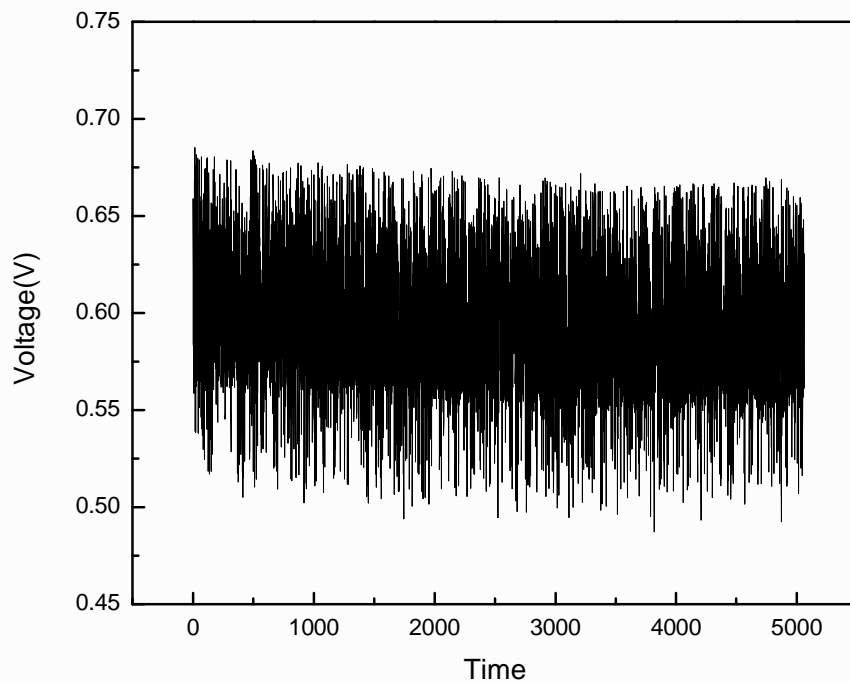


Figure R3-14. Distributed power loss profile of the fiber under 0-min etching

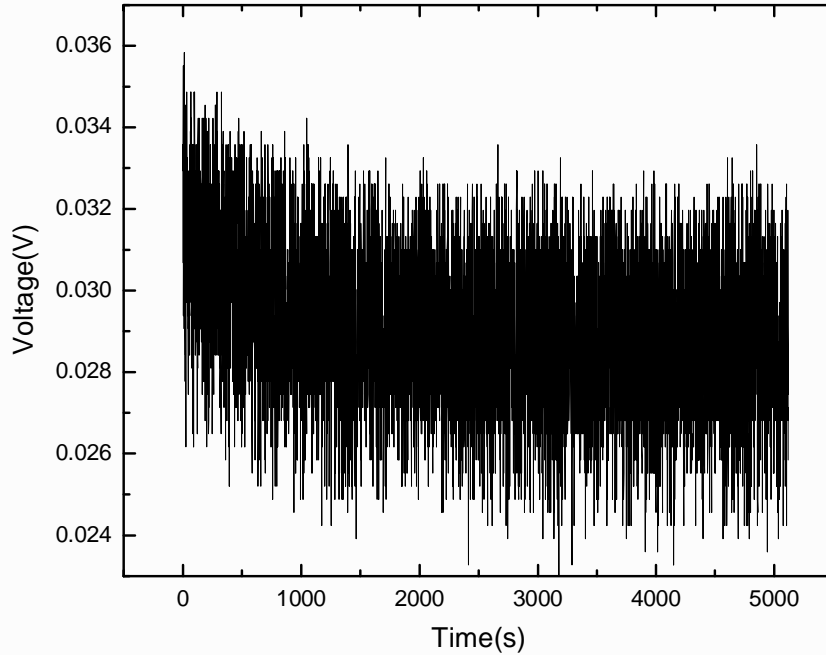


Figure R3-15. Distributed power loss profile of the fiber under 30-min etching

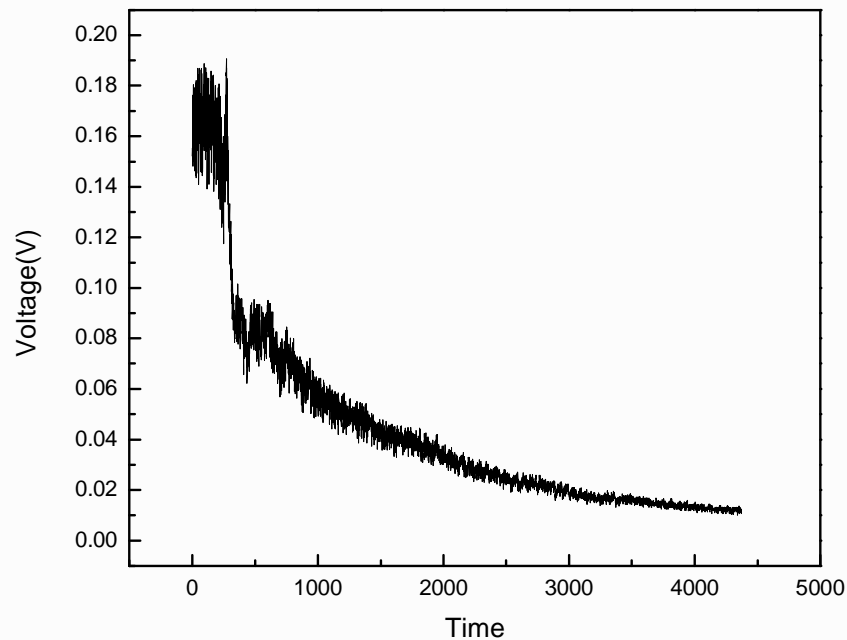


Figure R3-16. Distributed power loss profile of the fiber under 60-min etching

Summary and Tasks for the next stage

As demonstrated in this report, we have achieved significant progress on functional polymer coating film. Both elastic polymer for strain-based measurements and mixture with MOFs for power loss-based measurement have been successfully fabricated. We continued to further

optimize of polymer materials for curable silicone polymer and mix very well with MOFs. We successfully fabricate the film with elastic silicone polymer and mixture with MOFs. Both film are strong enough to be peeled from the glass substrate and are elastic and flexible. We also successfully coated these polymer films on the surface of fiber for the next measurement.

To further improve the quality of polymer and its ability to form polymer coating on fiber, we will continue to optimize mix parameter for MOFs in silicon polymers. We will perform structural analysis of our polymer materials in the coming quarter using by Fourier transform infrared (FTIR) spectrometry and ^1H and ^{29}Si NMR, contact angle, water absorption, thermogravimetric analysis and mechanical properties analysis.

In this period, we successfully fabricated the measure setups for fiber sensors. We tried fiber strain-based sensing induced by gas absorption and fiber power loss-based sensing induced by gas absorption. It has demonstrated that the fiber output power loss is an effective way to detect the methane in the environment. In the coming quarter, we will continue to optimize the parameter of the setup to increase the sensitivity of the fiber sensors.