Progress Reports

DoE Award No: DE-FE00029063

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

Report Period
January 1st, 2017 to March 31, 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 1/1/17-3/31/17

During this performing period, we have achieve 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.

To make polymer sensitive to methane gas, we have made initial attempt to dissolve and integrate MOF (Metal Organic Frameworks) with an enforced cage structure with appropriate size for CH_4 molecule trapping into polymer matrices. MOF could be able to absorb methane with great quantity and specificity. MOF has been synthesized and have been incorporated into some polymer samples to form the emulsions.

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.

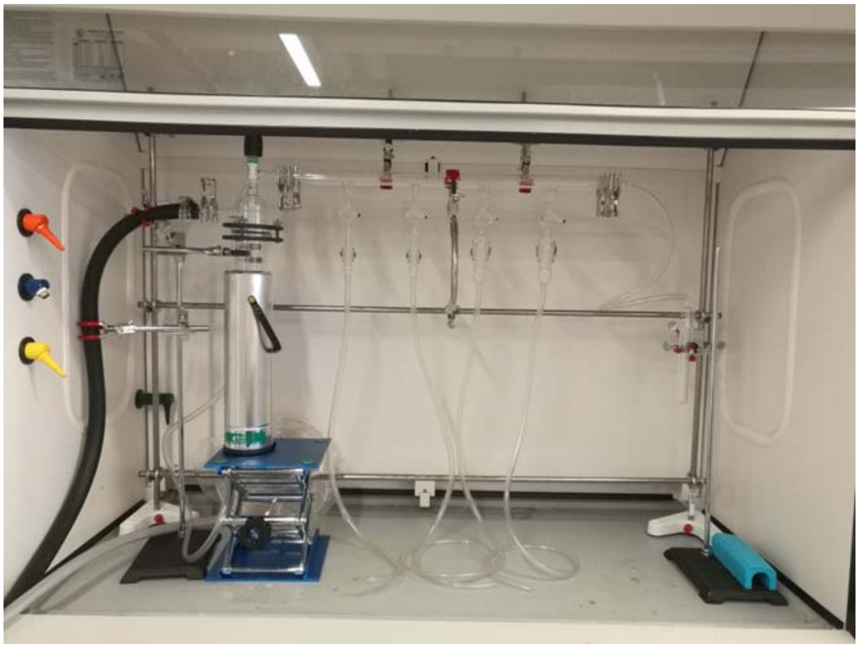


Figure 1: A photograph of the vacuum manifold experimental setup for the oxygen-sensitive synthesis of functional coating polymers.

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:

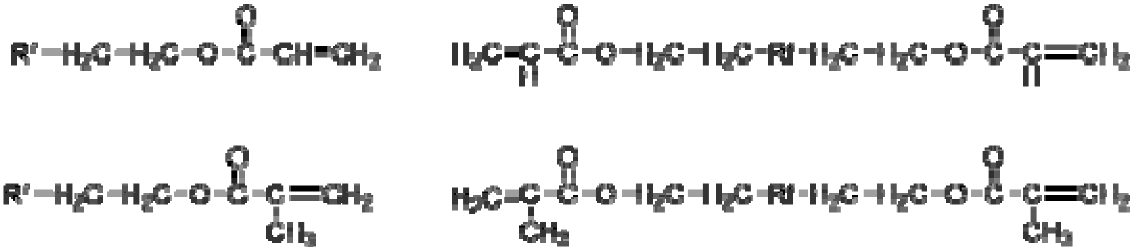


Figure 2. Structures of fluorinated monomers

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.

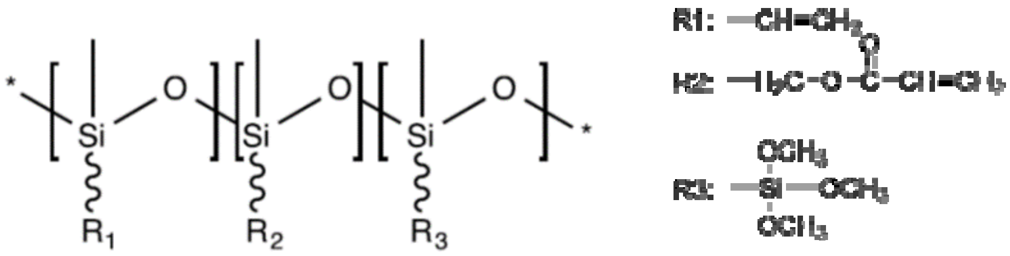


Figure 3. Structures of siloxane system

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.

<u>Equipment:</u> 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.

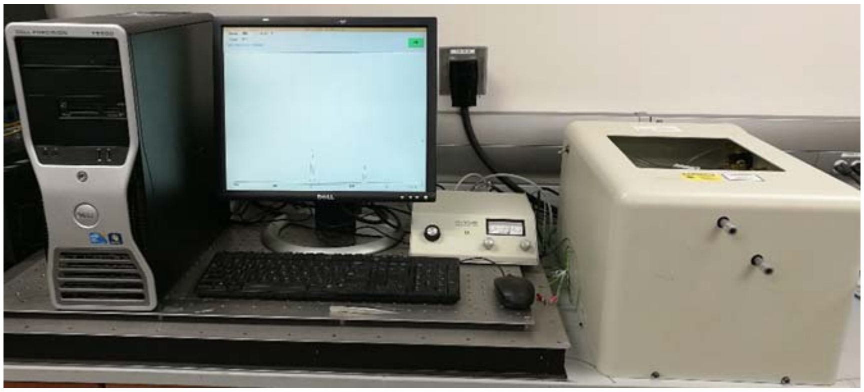


Figure 4: Metricon Prism Coupler 2010

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.

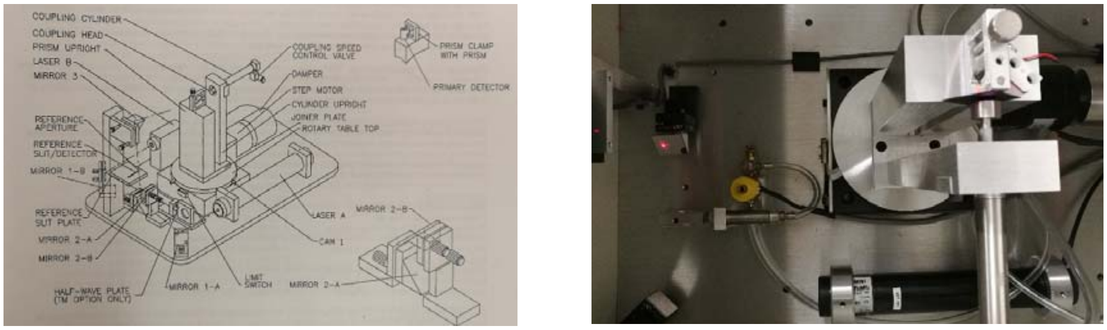
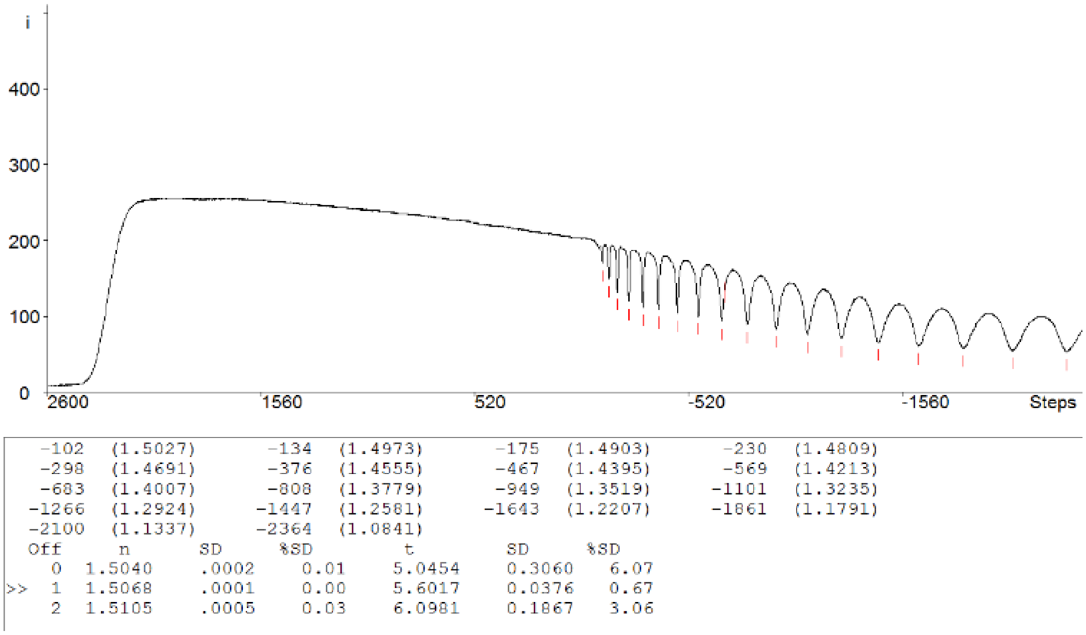


Figure 5: (a): sketch of the components in the mainbody, (b) image of the main body

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.



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  -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).

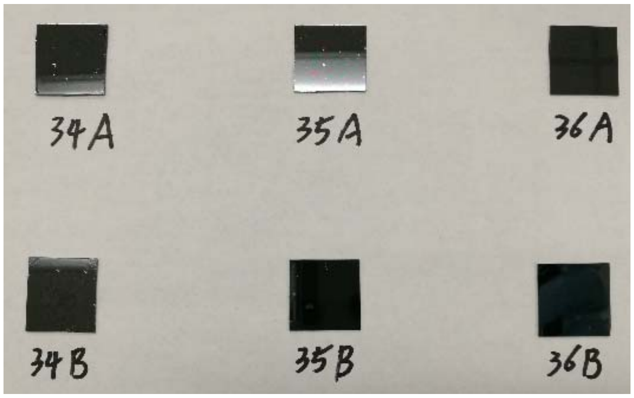


Figure 7: Some of the coated film

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.

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:

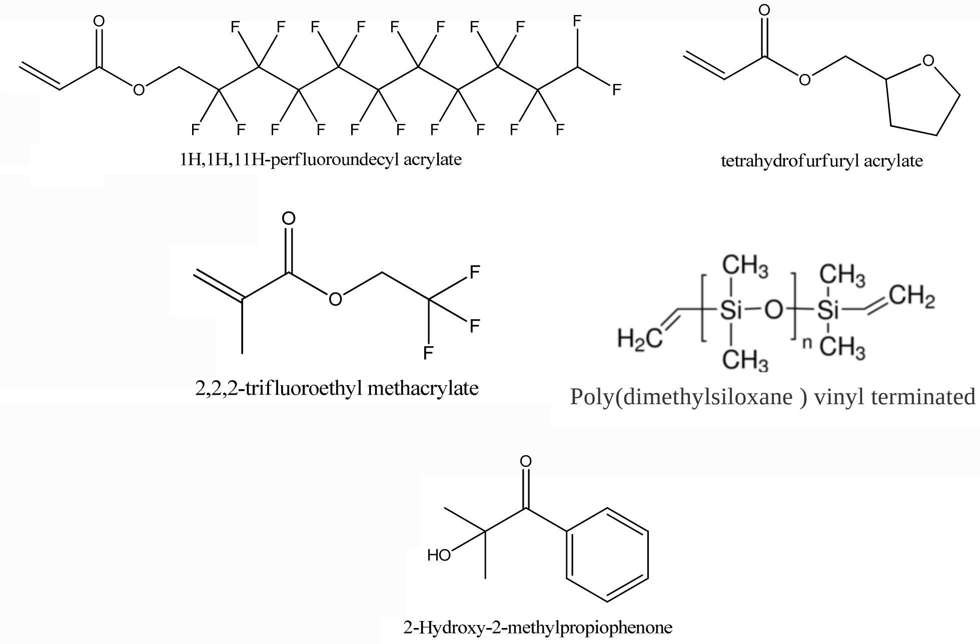
1. The refractive index of the polymeric material should be less than 1.45 to perform its function adequately for both evanescent absorption measurement and strain-based sensing.
2. The polymeric material naturally must be transparent with low optical loss for absorption base measurement.
3. Alternatively, 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.


1H,1H,11H-perfluoroundecyl acrylate

tetrahydrofurfuryl acrylate

2,2,2-trifluoroethyl methacrylate

Poly(dimethylsiloxane) vinyl terminated

2-Hydroxy-2-methylpropiophenone

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 tetrahydrofuturyl 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.

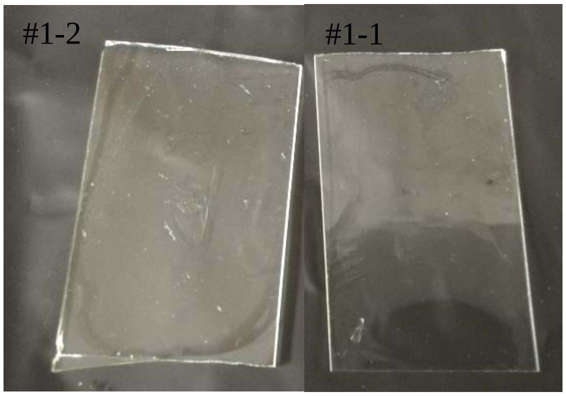


Figure R2-3. UV cured films of sample #1-1 and #1-2 on the glass slides

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.

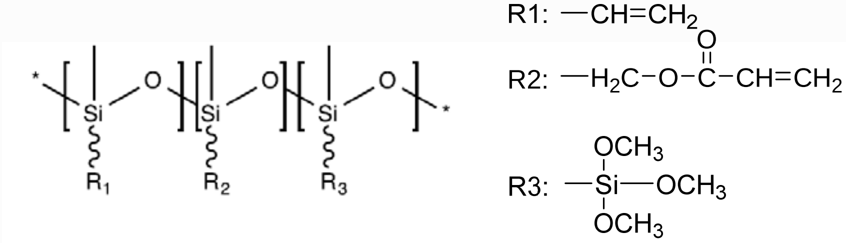
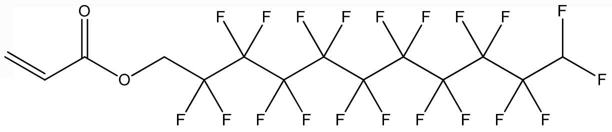


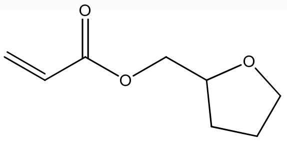
Figure R2-4. Proposed structures of siloxane systems

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

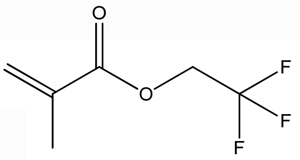
Vinyl terminated polymers are employed in addition of cure systems. The bond forming chemistry is the platinum catalyzed hydrosilylation reaction. Vinylmethylsiloxane copolymers and vinyl T-structure fluids are mostly employed in peroxide activated cure systems, which involve peroxide-induced free radical 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.



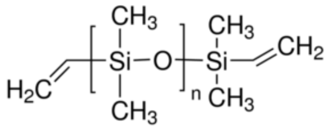
1H,1H,11H-perfluoroundecyl acrylate



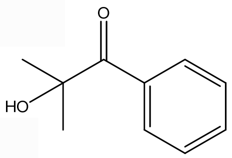
tetrahydrofurfuryl acrylate



2,2,2-trifluoroethyl methacrylate



Poly(dimethylsiloxane) vinyl terminated



2-Hydroxy-2-methylpropiophenone

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 tetrahydrofuturyl 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).

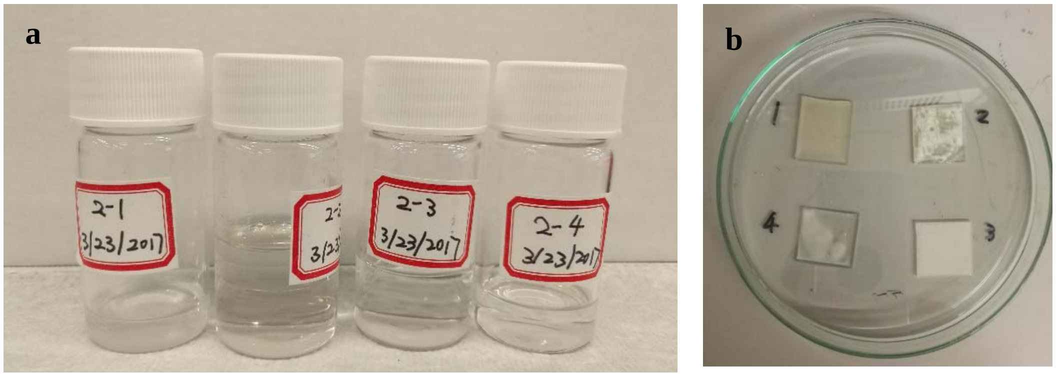
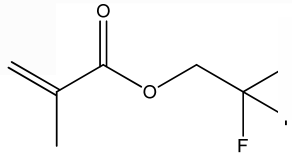


Figure R2-6. (a) Photo of the mixtures and (b) cured films of sample series #2

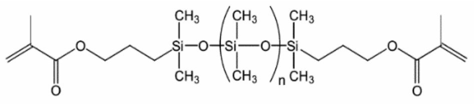
R2-3 UV-curable methacrylate terminated Poly(dimethylsiloxane)

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.

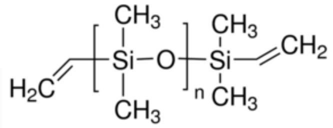
Therefore, we prepared the sample series #3 mainly comprised of methacrylate terminated Poly(dimethylsiloxane), which methacrylate moiety give UV curable functionality to the oligomers. Mono-methacrylate terminated Poly(dimethylsiloxane) was used for a comparative study and mercapto-functional siloxanes 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.



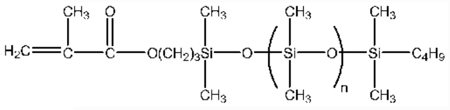
2,2,2-trifluoroethyl methacrylate



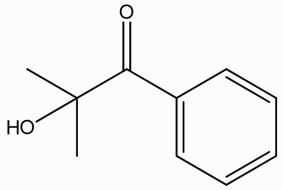
Methacryloxypropyl terminated polydimethylsiloxane



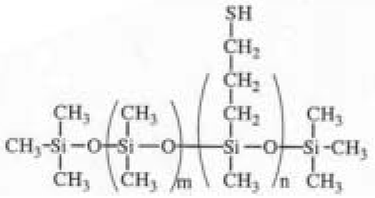
Poly(dimethylsiloxane) vinyl terminated



Monomethacryloxypropyl terminated polydimethylsiloxane



2-Hydroxy-2-methylpropiophenone



(mercaptoppopyl)methylsiloxane homopolymer

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
(mercaptoppopyl)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 from 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.

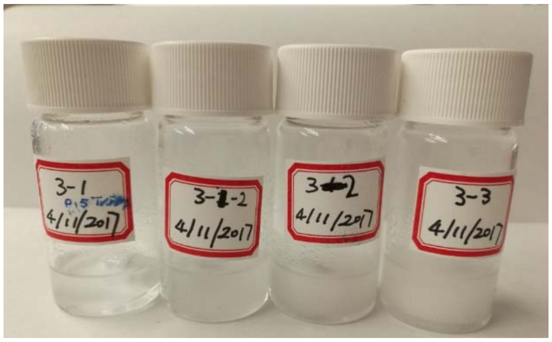


Figure R2-8. Photo of the mixtures of sample series #3

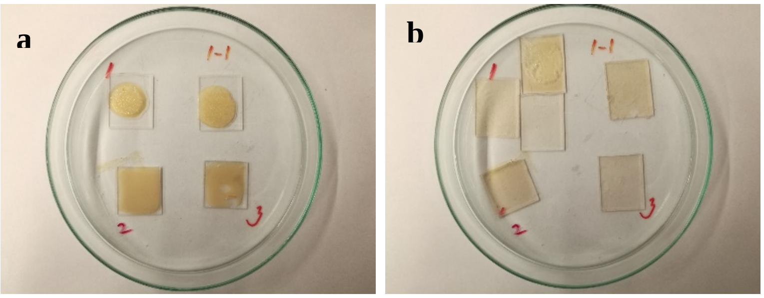


Figure R2-9. Films made from (a) drop-casting and (b) spinning-coating of sample series #3

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
(mercaptoppopyl)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.

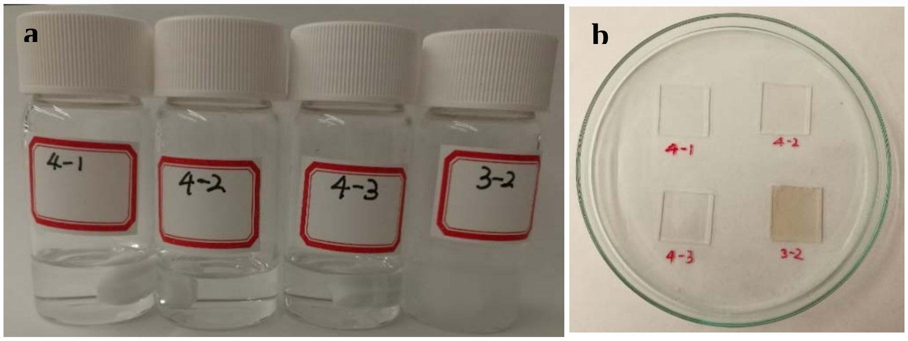


Figure 10. (a) Photo of the mixtures and (b) cured films of sample series #4

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.

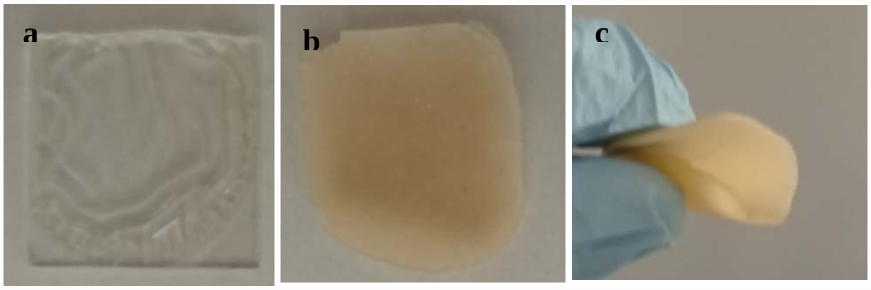


Figure R2-11. (a) Photo of the film of sample #4-2, (b and c) films of sample series #3-2 peeled away from the glass slide

Summary and Tasks for the next stage

As demonstrated in this report, we have achieve 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.

To further improve the quality of polymer and its ability to form polymer coating on fiber, we will continue to optimize mechanic qualities and its adhesion properties to glass substrates. We will perform structural analysis of our polymer materials in the coming quarter. The structures of the synthesized polymers will be characterized by Fourier transform infrared (FTIR) spectrometry. Copolymers will be characterized via ^{1}H and ^{29}Si NMR, the latter is particularly powerful for these materials as it will allow us to distinguish between the various Si species and hence understand the final composition (in terms of crosslinking versus other side chains) of the materials. The properties of the UV-cured films will also be tested through contact angle, water absorption, thermogravimetric analysis and mechanical properties analysis. The fractured-surface morphologies of the UV-cured coatings will be investigated by scanning electron microscopy (SEM).

To make polymer sensitive to methane gas, we will dissolve and integrate MOF (Metal Organic Frameworks) with an enforced cage structure with appropriate size for CH_4 molecule trapping into polymer matrices. MOF could be able to absorb methane with great quantity and specificity. MOF has been synthesized and have been incorporated into sample #1 to form the emulsions, as shown in Figure R2-12. In the next step, we will optimize the integration of MOF with elastic siloxane polymers and explore their methane sensitivity.

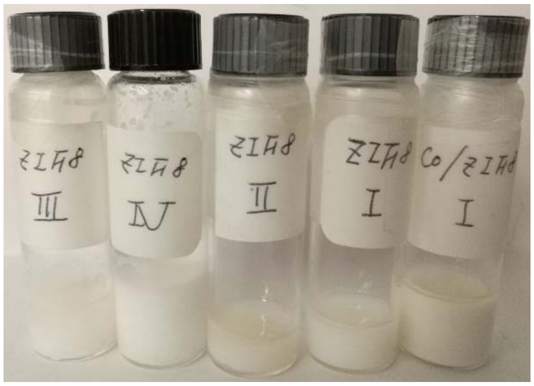


Figure R2-12. Photo of the mixtures of sample series #1 with