Stretchable Phase Change Composites

By

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Abstract

Currently phase change materials (PCMs) are widely used to store thermal energy and control the temperature by dissipating heat. Without simply embed PCMs into construction, more researchers are focus on utilizing PCMs into clothing and electronics, since the heat dissipation is always a problem of human body and electronic devices. However, different from utilizing PCMs in construction, the applications of clothing and electronics are requiring PCMs should be stretchable so that they can fit the motion of human body and the complex shapes of electronics. But PCMs are not capable to be stretchable, thus, some stretchable matrix materials should be used to form composites with PCMs. The purpose of this essay is to fabricate stretchable phase change composites with PCMs, with the highly-stretchable material PDMS used as the matrix of composites. And the paraffin is used as PCMs in composites since paraffin is safe, cheap, have high latent of heat and proper phase change temperature range which is close to human body. Three different kinds of composites are fabricated in this essay, a) simple PDMS-based phase change composites, b) reinforced phase change composites and c) modified phase change composites. From a) to b), carbon nanotubes are added into composites

to reinforce the tensile strength and thermal conductivity. Also, trying have high heat capacity for reinforce composites, the content of microcapsules is fixed at 35 wt.%. From b) to c), surface modification is applied to improve both tensile strength and thermal stability of composites. The results of thermal and mechanical characterizations of composites demonstrates that both thermal and mechanical properties are improved by reinforcement and modification. Based on the stress-strain curves, the strains of all composites are higher than 0.7 (mm/mm), which means the sample will elongate 70% of its original length and demonstrates the composites have high stretchability. With the reinforcement and modification, composites have high heat capacity, stretchability and tensile strength. This makes composites potentially useful in applications requiring materials with complex shapes and high strength such as cooling of human body and electronics.

Primary reader: Sung Hoon Kang

Seconder reader: Ryan Hurley

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Dedication

This essay is dedicated to my parents,

Mr. Jianli Wu and Mrs. Xiaojuan Zhu,

for their love, supports and encouragements on me, without them I cannot be the man I am today.

I always love you.

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Chapter 1 Introduction

1.1 Phase Change Materials

1.1.1 Introduction to Phase Change Materials

Phase change materials (PCMs) are the materials with a high latent of heat and absorb and release heat during the melting and solidifying processes. The melting and solidifying processes are called "phase change", during these processes, the temperature will not change is called phase change temperature. Usually due to the utilization of PCMs is to absorb or dissipate heat, the phase change indicates the melting processes and phase change temperature indicates the melting temperature.

PCMs can absorb a large amount of heat with small volume change with a short period of time. By absorbing heat, PCMs can control the temperature of the objects, in which they are contact. To understand how PCMs can store thermal energy and control temperature, we need to know the working principle of PCMs.
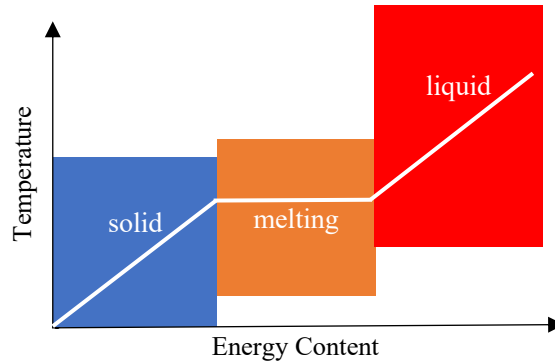
Figure 1 Principle of Phase Change Materials

Figure 1 shows the working principle of PCMs. The phase change of PCMs usually means the phase change from solid to liquid or the reverse. Since the volume change from solid to liquid is less than liquid to gas, and the temperature of phase change is lower, so that the phase changing state could be easily reached. When the temperature reaches to phase change (melting) temperature, the solid will start to melt to liquid, but the temperature will remain constant. During this temperature-constant period, heat is absorbed to melt the solid. And, when all the solid parts are changed to liquid, the temperature will rise again, and the phase change process is complete.

Usually PCMs can be divided into two groups, organic and inorganic (*Figure 2*). The organic PCMs are further described as paraffin and non-paraffin, such as fatty acids, alcohol and glycol [1]. And, the advantages of organic PCMs are they have little or no supercooling and usually are non-toxic. But, the phase change temperature of organic PCMs is lower than that of inorganic materials. Inorganic PCMs are further classified as salt hydrate and metallics, such as a typical crystalline solid of general formula AB·nH2O [1]. Usually the inorganic PCMs have higher melting temperature and supercooling. But, most of phase change salts are toxic.
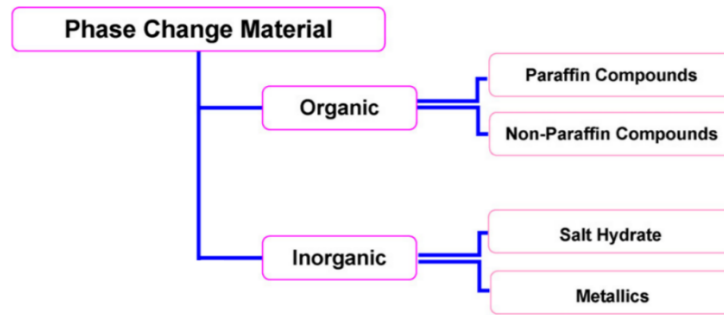
Figure 2 Classification of PCMs [1]. Reprinted from Renewable and Sustainable Energy Reviews, Vol 13 issue 2, Atul Sharma, V.V. Tyagi, C.R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications, 318-345, Copyright (2019), with permission from Elsevier

Considering the advantages and disadvantages of PCMs, paraffin is selected as the materials for this project, because it is safe, low-cost, has high latent heat capacity, and has a small volume change in phase changing. The most important factor is that the melting temperature of paraffin varies from nearly 0℃ to almost 80℃, covering the human body's temperature, temperature of electronic devices and cooling for construction.

However, PCMs alone are hard to utilize into those fields, since PCMs will leak after melting and the leakage may cause some severe results. Therefore, microencapsulation technology is used to provide a shell for PCMs to avoid the leakage in PCMs applications.

Usually the size of each microcapsule is on the order of micrometers, so that the microcapsuled PCMs are a powder-form material, which could be embedded into construction.

1.1.2 Current Researches about Phase Change Materials

Nowadays, PCMs are widely used to store thermal energy and control temperature, especially in the fields of clothing, construction and electronics. This is because the use of a latent heat storage system using phase change materials (PCMs) is an effective way of storing thermal energy and has the advantages of high energy storage density and the isothermal nature

of the storage process [1].

Current PCMs are used in many applications. For instance, PCMs can be used as a chip cooling solution using polydimethylsiloxane (PDMS) based microfluidic devices filled with *n*-Octadecane [2] *(Figure 3 a and b)*. The fabrication process for the microfluidic device includes the master mold fabrication and bonded with PDMS substrate to form microchannels. Then they injected paraffin into microchannels in PDMS base. During melting, this microfluidic device can absorb 216.6 J/g and melting temperature is 27.9°C. The IR results *(Figure 3c)* shows the cooling channel with PCMs can keep the temperature of chip around 27.4°C. Although phase change microchannel demonstrates the temperature of chips could be kept at phase change temperature, the microchannel cannot be used in fitting electronics with complex shapes. Because the microchannels may be broken under stretch to fit the complex shape, and the PCM will leak to electronics, which may damage the electronics. Thus, there is a need for protection of PCMs to avoid the leakage and hampering the heat transfer.

a

b

c
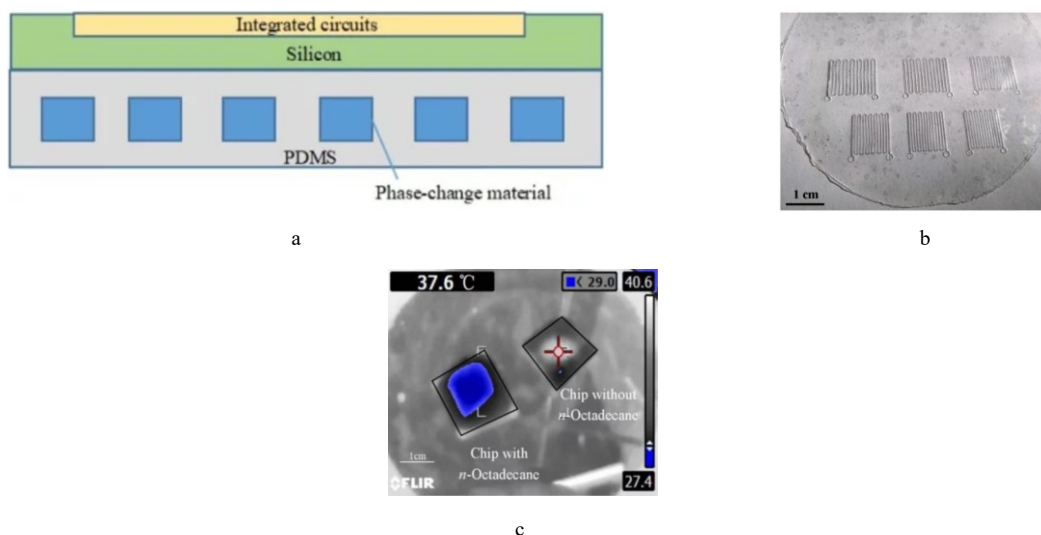
Figure 3 a), b) Phase change cooling channel and c) IR results [2]. Reprinted from "PDMS-PDMS Micro Channels Filled with Phase Change Material for Chip Cooling", which is an open access article distributed under the Creative Commons Attribution License.

PCMs can be used in concrete pavement as a method to store energy which can be used as a heat source during cooling events to melt ice/snow [3] *(Figure 4)*. The phase change material was embedded into the concrete with designed configuration. The phase change material would store the thermal energy and be used as a heating source to melt the ice/snow during cold events. However, once PCMs have been embedded into concrete, the whole composites could not be stretch to fit the different shape. So, there is a need for improving the stretchability and flexibility of the composites.
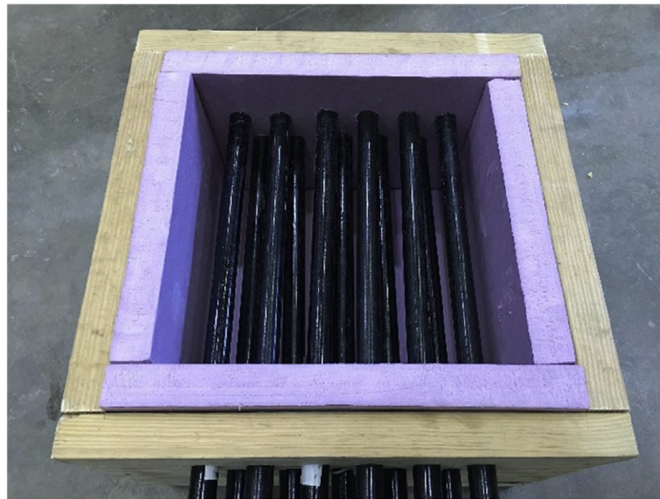
Figure 4 Phase change materials embedded into concrete [3]. Reprinted from Cement and Concrete Composites, Vol 84, Yaghoob Farnam,Hadi S. Esmaeeli,Pablo D. Zavattieri,John Haddock,Jason Weiss, Incorporating phase change materials in concrete pavement to melt snow and ice, 134-145, Copyright (2019), with permission from Elsevier

PCMs can be used in solar absorption cooling systems [4] *(Figure 5)*. The water was used as phase change material in this application, since water is safe, cheap and has high thermal capacity. This device was used to reduce summer cooling peak to have a substantial impact on reducing CO_2 emissions from the electrical generation sector [4]. But, the device is extremely large so that it is hard to utilize in daily life. Thus, there is a need for lower the size and keep

the high thermal capacity.
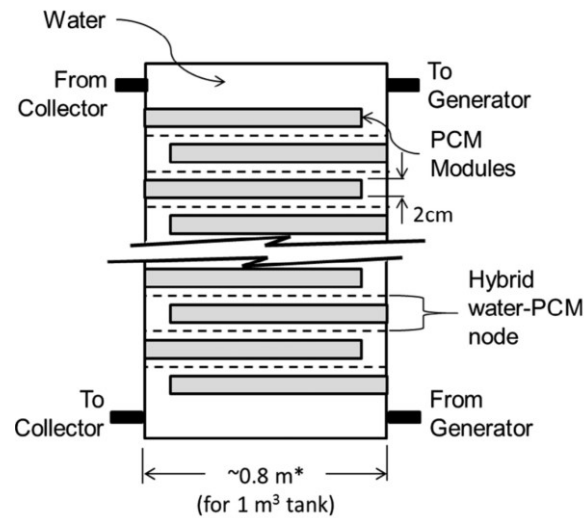
Figure 5 Water-PCMs cooling model [4]. Reprinted from Applied Energy, Vol 223, R. Hirmiz,M.F. Lightstone,J.S.

Cotton, Performance enhancement of solar absorption cooling systems using thermal energy storage with phase

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Summarized the current researches, all these phase change devices have great thermal capacity and performance. But, each of them has disadvantages, and all these disadvantages motivated us to make improvements, to avoid leakage of PCMs and to improve the stretchability and tensile strength. Therefore, we investigated to fabricate composites with high stretchability, high tensile strength, and high thermal capacity.

1.2 Characterization Tools for Thermal and Mechanical Properties of Composites

1.2.1 Thermal Properties Characterization Tools

To study the energy storage properties of phase change composites, the differential scanning

calorimetry (DSC, *Figure 6,* TA instrument Q20, Prof. Thao Nguyen's lab) is used to test the

materials. DSC is a machine used to do thermal analysis, its principle is keeping the same

temperature of sample and reference. When the phase change, glass transition or chemical

reaction occurs, the machine will increase or decrease the heat flow to balance the temperature.

If the materials have phase change property, their DSC curves will have absorbing and releasing

peaks, and the areas under the peaks are the amount of heat absorption/releasing.

Figure 6 DSC machine

And the Thermogravimetric analysis (TGA, *Figure 7*) located in Maryland Hall is used to

characterize the degradation temperature of paraffin. TGA is a machine to measure the mass

change of samples over time as temperature changes. Usually the TGA is used to analyze the

degradation process of materials. A typical TGA curve will have three regions, two horizontal

regions, which indicate no or less weight change, and one dropping region. The dropping region

indicates the degradation of materials.
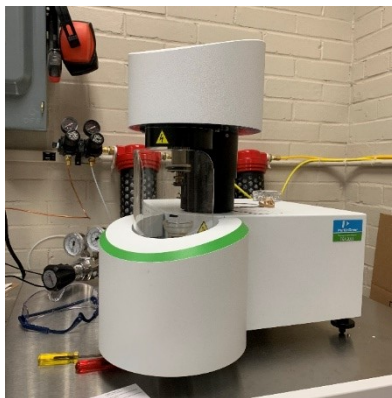
Figure 7 TGA machine

1.2.2 Mechanical Properties Characterization Tool

The mechanical properties (tensile strength and strain) were tested by using MTS machine (*Figure 8*). Before conducting the test, the specimen should be gripped by grips on two crossheads. The testing method of this machine is strain rate control, which means the machine pulls the two crossheads away with certain strain rate.
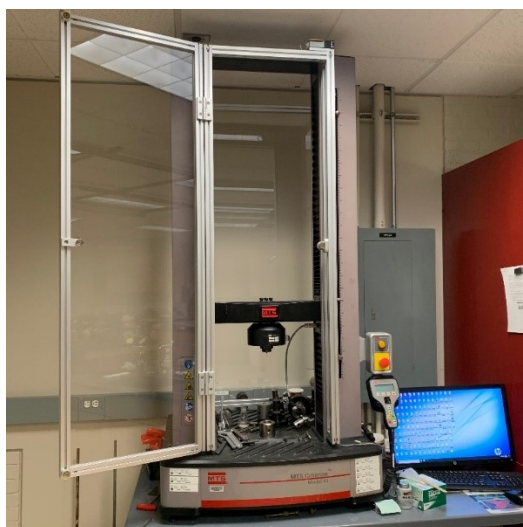
Figure 8 The MTS machine

1.3 Microcapsuled Phase Change Materials

To solve the leakage problem of PCMs, they can be microcapsuled by shell materials. By microencapsulating and isolating, the phase change material is separated from its surroundings and the carrier matrix. Since the shell is thin and only occupy small amount of weight for microcapsules *(Figure 9)*, it is less likely to hamper the heat transfer process [9]. With the protection of shell, the hazard of liquid PCMs could be minimized. As microcapsule shell materials for PCMs isolation, polystyrene (PS) [10], melamine-formaldehyde (MF) [11], urea-formaldehyde (UF) [12], polyurethane (PU) [13], high density polyethylene (HDPE) [14], styreneebutadieneestyrene (SBS) [15], polymethyl methacrylate (PMMA) [16-18], Styrene ethylene/butylene styrene (SEBS) [19] and silicon dioxide [20] are usually selected.
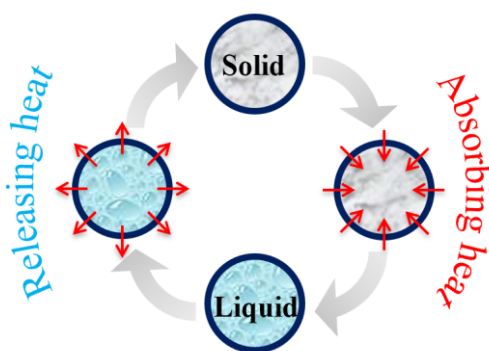
Figure 9 Microcapsuled Phase Change Materials

The microcapsules used in this project are MPCM 28D which are purchased from Microtek Laboratories, the information of the microcapsules is in the Table A1 of Appendix. *Figure 10* shows the DSC result of microcapsules and a non-PCMs (PDMS). The data was collected from 10 continuous cycles, with the protection of shell materials, the materials loss during phase change could be minimized, which indicates the repeatability of microcapsules. There are one absorbing (melting) and releasing (cooling) peak of microcapsules respectively. During the

phase changing period, PCMs can keep the temperature, which is 28°C for microcapsules, this temperature is good for human body and electronic devices. And there exists a small offset between two peaks, which is supercooling, but the supercooling of microcapsules is not significant, and is around 14°C. By integrating the absorbing region, the microcapsules absorb 187J/g during the phase changing period. Comparing to other phase change materials such as fatty acid, the estimated latent of heat is 193 J/g. But, the phase change temperature of fatty acid is usually over 45°C, which is a high temperature for human body and electronic devices. And for other phase change materials, like Phenol, it can only absorb 120 J/g. Considering the working temperature and the thermal compacity, the microcapsuled paraffin demonstrates great thermal ability. Compared to microcapsules, the DSC curve of non-PCM (PDMS, *Figure 10*) only has two vertical regions and two horizontal regions. The vertical regions indicate the heat flow keeps increasing to setting value, and the horizontal regions indicate the non-PCM cannot absorb any heat during the heating cycle.
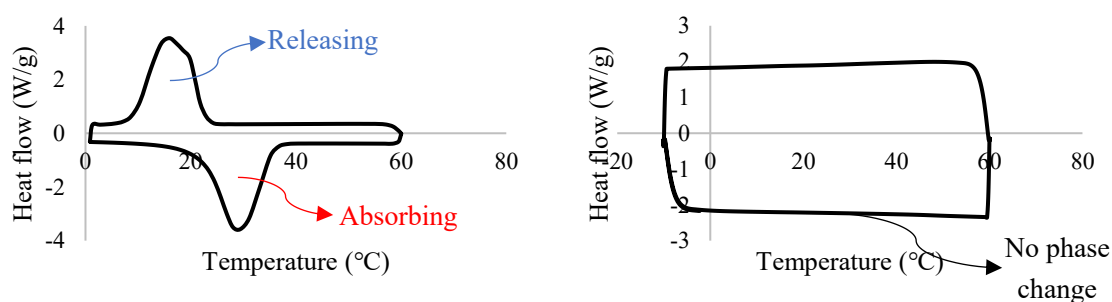
Figure 10 DSC loop of microcapsules and PDMS (non-PCMs)

Compared to paraffin, with the shell outside the PCMs, the degradation temperature of microcapsules has a great improvement (*Figure 11*). The difference of degradation temperature between two materials is almost 170°C. The microencapsulation technology therefore greatly increases the thermal stability of PCMs and increases the ultimate working temperature of

PCMs.
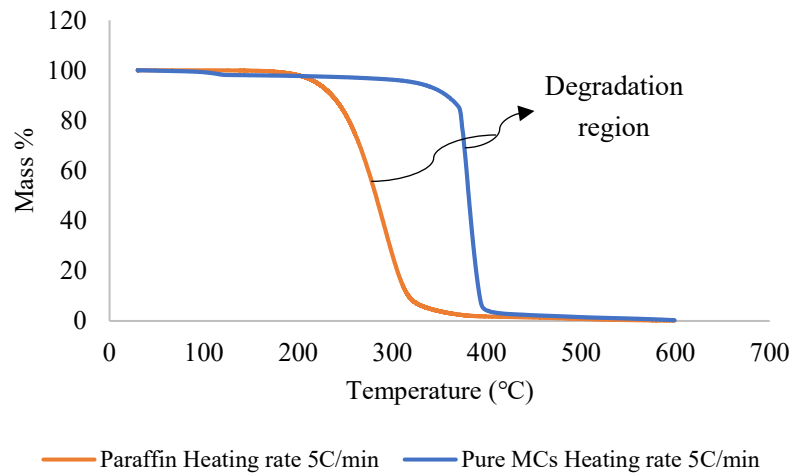
Figure 11 TGA of paraffin and microcapsules

1.4 Phase Change Composites

However, the powder form PCMs still cannot work for clothing and electronics. A stretchable and flexible matrix should be used as a carrier for powder microcapsules. PDMS, as a well-studied material, can be perfectly integrated with flexible shapes because of its flexibility [2]. Thus, the composites made by PDMS and PCMs should have both good heat absorption and stretchability. The *Figure 12* shows the tensile test result of pure PDMS, the stresses keep increasing until fracture, and the maximum stress that pure PDMS can bear is around 5.36 MPa. Due to the low Young's modules of PMDS, the specimen can elongate around 70% with respect to original gauge length.
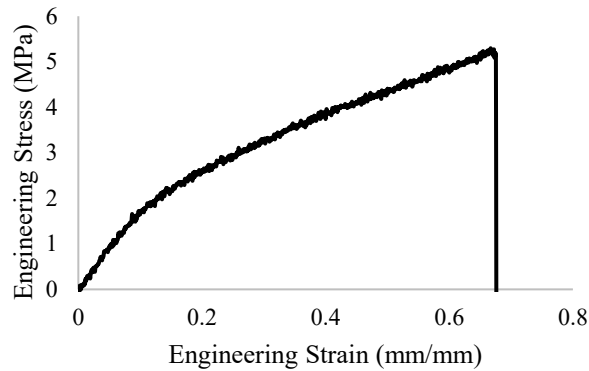
Figure 12 Stress-strain curve of PDMS

Due to the high stretchability of the composites, it could be utilized in multiple applications, such as clothing and cooling for electronics. Although PDMS is a perfect stretchable matrix material, the insulation property of PDMS could resist heat transfer. Thus, thermal conductivity of PDMS should be improved, some new materials with superior thermal conductivity, such as carbon nanotubes (CNTs), have recently been used to enhance the heat conduction [17-19]. CNTs could be added into composites to increase the thermal conductivity so that the heat can transfer into PCMs faster. Based on the stress-strain curve of PDMS, we could define when stress is over 2.5 MPa and strain is over 50% as good stretchability and strong tensile strength for composites.

In this essay, we investigated to make the composites with high stretchability, tensile strength and thermal properties so that the composites take complex shapes and bear large tension with high-level thermal absorption.

1.5 Structure of Essay

In this essay, three different kinds of phase change composites are discussed. Those three

composites stand for three different types of phase change composites, which are "simple" PDMS-based phase change composites, reinforced phase change composites and modified phase change composites. Those three types show the improvement in thermal and mechanical properties of phase change composites.

In Chapter 2, there will a story about the "simple" PDMS-based phase change composites, which simply mix the PDMS and microcapsules. This kind of composites is made by simply mixing PDMS with microcapsules. DSC and uniaxial tension test are applied to characterize the properties of composites.

In Chapter 3, there will be a story about reinforced phase change composites which showed improvement on tensile strength by reinforcing with CNTs. The CNTs are added into matrix to increase the thermal conductivity and tensile strength. The content of microcapsules is fixed at 35 wt.%, thus, the heat absorption keeps the same, only tensile strength is tested in this chapter.

In Chapter 4, there will be a story about the modified phase change composites. Polydopamine is used to modify the surface function of microcapsules and CNTs to increase the thermal stability and tensile strength.

Chapter 5 will give conclusion of this study and perspectives. The conclusion of all three stages and perspectives will be summarized in this chapter.

Chapter 2 The "Simple" PDMS-Based Phase Change Composites

2.1 Preparation of "Simple" PDMS-Based Phase Change composites

To prepare PDMS-based phase change composites, the following procedures were used. First, microcapsules were mixed with 99.5% ethanol under ultra-sonic (*Figure 13a, SHARPER TEK®*) for 30 minutes. In this step ethanol acted as a carrier, since ethanol could help microcapsules well-dispersed in PDMS. And the ultra-sonic makes microcapsules dispersed uniformly in ethanol. The PDMS we used is SYLGARD™ 184 Silicone Elastomer Kit (*Dow Corning*). Then certain weight of uncured PDMS base (*Table 1*) was measured and stored in plastic cups. Trying to eliminate the extra ethanol, after microcapsules-ethanol solution was poured into uncured PDMS solution without mixing, the solutions were stored in Quincy Oven (*Figure 13c, Quincy Lab, Inc*) to evaporate extra ethanol at 60°C for 1 hours. The solution was then fully mixed twice by using Mazerustar planetary mixer (*Figure 13b*) and stored in Thermal

Scientific Oven (*Figure 13d*) to evaporate the ethanol completely under 80°C and vacuum condition for 8 hours. The container was then place onto balance to make sure the ethanol was fully evaporated by observing if solution has significant weight drop. The curing agent was added into solution with the 1:10 curing agent vs. uncured PDMS base ratio and the solution was mixed in planetary mixer. Then the mixture was placed into mold and degassed under vacuum condition for 2 hours, followed by curing for 8 hours under 80°C. By using this method, the composites with different microcapsules weight ratio were made (0, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%), the recipe is shown in *Table 1*. By adding microcapsules into PDMS base, the solution became increasingly viscous. It is hard to fabricate composites with more than 40 wt.% microcapsule-composites by using simple mixing. In order to maintain the good thermal and mechanical properties, the content of PCMs should be controlled within 40 wt.%.

a

b

c   d

Figure 13 The equipment of preparation a) ultra-sonic cleaner, b) planetary mixer, c) Quincy oven and d)

Scientific oven

Table 1 Recipe of PDMS-PCMs composites

Sample	PDMS(g)	Curing agent (g)	Curing agent Ratio	Content of MCs (wt.%)	MCs(g)	Total Weight(g)
1	55	5.5	1:10	0	0	60.5
2	33	3.3	1:10	10%	4.03	40.33
3	31	3.1	1:10	15%	6.02	40.12
4	29	2.9	1:10	20%	7.98	39.88
5	27	2.7	1:10	25%	9.91	39.61
6	25	2.5	1:10	30%	11.79	39.29
7	23	2.3	1:10	35%	13.62	38.92
8	21	2.1	1:10	40%	15.41	38.51

2.2 Thermal properties of composites

Investigation of the thermal properties of phase change composites is important because the main function of PCMs is to utilize their phase change properties to absorb and release heat during the transition process. Thus, the study of thermal properties is important to understand the thermal capability of PCM composites. To characterize the thermal properties of phase change composites, DSC and TGA are used.

2.2.1 DSC Loop Test

The DSC was performed to measure the heat flow through the composites. The amount of heat absorption could be calculated by integrating the heat flow. Due to the function of PCMs, the composites are capable of absorbing heat. However, since most portion of composites were occupied by PDMS, which could not absorb any heat, the total amount of heat absorption is less than pure microcapsules. The heat absorption of pure microcapsules is around 187 J/g. *Figure 14* shows partial DSC curves of "simple" PDMS-based phase change composites, the amount of heat for each sample is summarized in *Table 2*
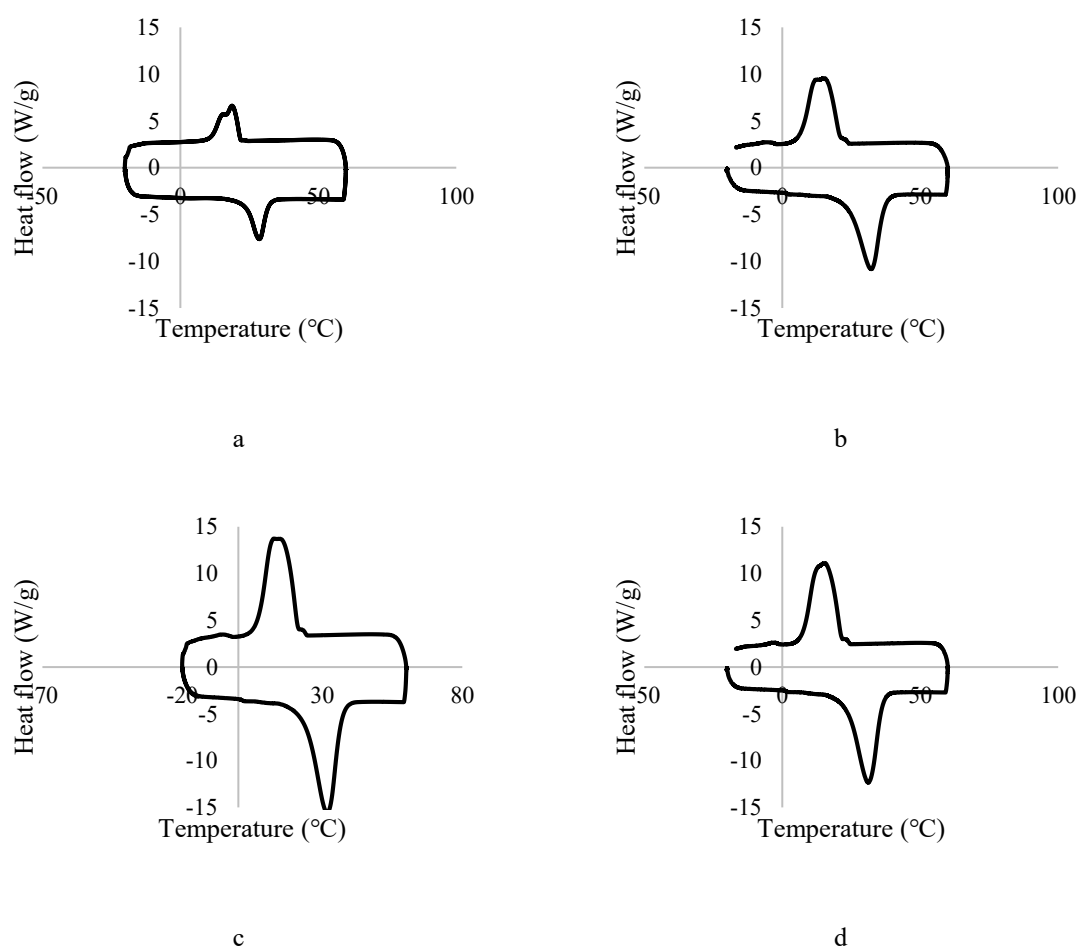
Figure 14 DSC curves of composites with different PCM contents (wt.%) a) 10 %, b) 30, c) 35 and d) 40

Table 2 Heat absorption of "Simple" PDMS-Based Composites

Sample	5 wt.%	10 wt.%	15 wt.%	20 wt.%	25 wt.%	30 wt.%	35 wt.%	40 wt.%	Microcapsules
Latent of Heat (J/g)	9.3	18.1	27.9	37.2	46.6	54.4	65.7	74.4	187

During the heat absorption process, the dominant heat absorbing peak occurs at 28°C due to the phase change temperature of the materials is 28°C. Since paraffin consists of a mixture of hydrocarbon, the composites would not start to absorb heat at exact 28°C but a little bit earlier around 20°C. When the composites cooled down, the process is not a perfect symmetry with heating process and the releasing, the releasing peak will have a slight shift compare with absorbing peak, the solidifying temperature is lower than 28°C even less than 20°C. This is because the paraffin has crystal habit, and then crystal start to solidify there exists a super-cooling phenomenon, which states that when a crystal starts to solidify without a nucleus the actual temperature will be lower than theoretical value.

2.2.2 Heat Latent of Composites with Different Content

Theoretically, the PDMS base will not contribute any heat absorption or heat release in the test, therefore the relationship between heat absorption and amount of PCM in the matrix should be linear. The results of DSC also confirm the linear relationships, the heat absorption of composites have linear relationships with PCM content which is x wt.% composites can absorb x% heat compare to pure microcapsules (*Figure 15)*. This relationship could help to estimate the total amount of heat of different content of composites.
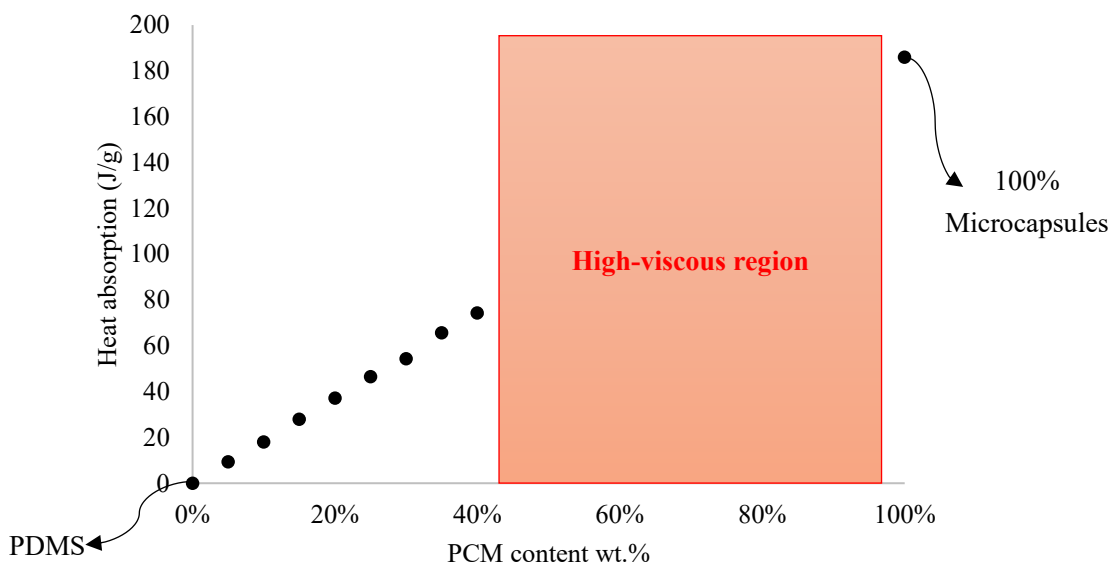
Figure 15 Heat absorption vs. PCM content

2.3 Mechanical Properties of Composites

Mechanical strength is an important property of PCM composites as well. Due to the composites will be used under stretch, it is required to have relatively good mechanical performance to avoid fracture under stresses. With the PDMS as the matrix of the composites, the composites have the corresponding PDMS habits. The composites have large elongation under tension, but due to the low Young's modules, the tensile strength is low. Thus, the composites could not bear much stress before tensile failure.

2.3.1 Standard of Tensile Test

In order to apply the tension test for composites, the ASTM standard D-412 (Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension) [20] has applied.

According to ASTM standard, the dog-bone test samples or dumbbell specimens were made

by cutting with dies based on the following dimensions (*Figure 16 and Table 3*). Due to the dimension of grips, the sample cut by Die C cutter *(Figure 17)* fit the best *(Table 3)*, the length of specimen is 115mm, grip length is 65mm, gauge length is 25mm and gauge width is 6mm.
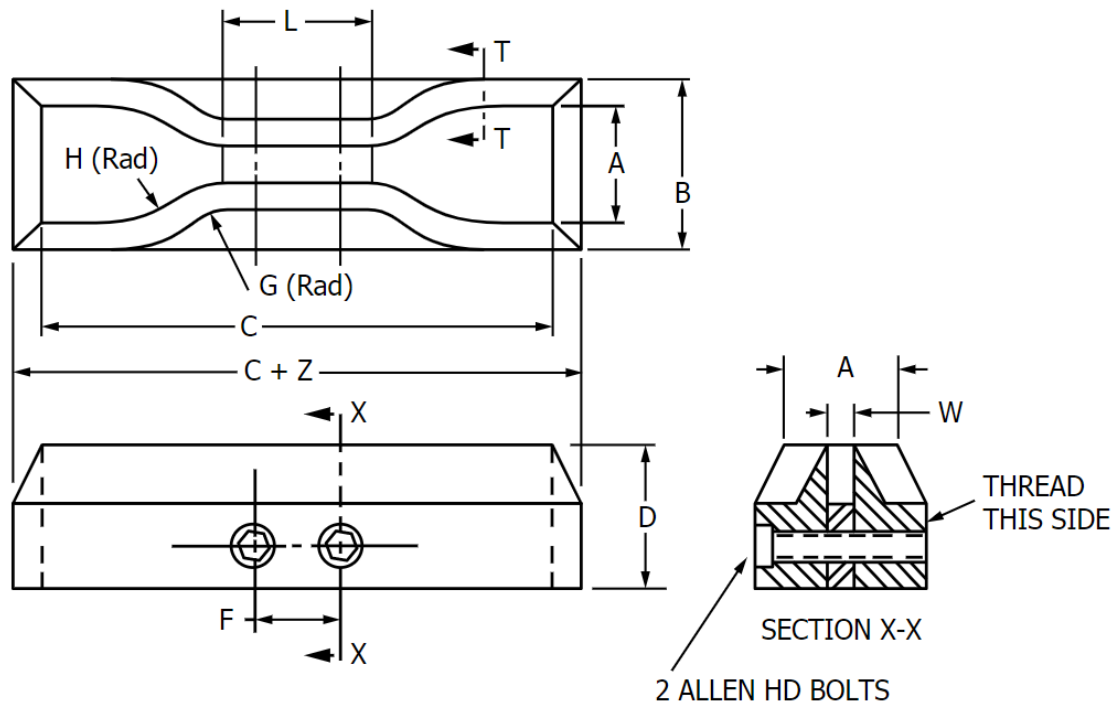
Figure 16 Three views of cutting die

Figure 17 Cutting dies

Table 3 Dimension of standard dumbbell dies [20]

Dimension	Units	Tolerance	Die A	Die B	Die C	Die D	Die E	Die F
A	mm	±1	25	25	25	16	16	16
B	mm	max	40	40	40	30	30	30
C	mm	min	140	140	115	100	125	125
Dimension	mm	±6	32	32	32	32	32	32
D-E	mm	±1	13	13	13	13	13	13
F	mm	±2	38	38	19	19	38	38
G	mm	±1	14	14	14	14	14	14
H	mm	±2	25	25	25	16	16	16
L	mm	±2	59	59	33	33	59	59
W	mm	0.05─0.00	12	6	6	3	3	6
Z	mm	±1	13	13	13	13	13	13

2.3.2 Equipment for Tensile Test

Due to the large elongation of the materials, the tensile tests are conducted by using MTS. Since the specimen is softer than metal, normal grips could not be applied onto test. During elongation elongating, the thickness of specimens will shrink, so that if using the normal grips, the specimen will slip, which will induce great error into the result. But, for the roller grips (*Figure 18, MTS, Prof. Thao Nguyen's lab*), it has springs on both sides which could self-tighten the specimen to avoid slipping during the test.

Figure 18 Roller grips

Figure 19 Dog bone samples for 25 wt.% composites

After the final dog-bone specimens (*Figure 19*) were made, they were marked with the content number to distinguish the different specimen. Their cross-section areas are measured multiple times from different positions of samples and the average values were taken.

2.3.3 Setting of Tensile Test

The testing method of MTS machine used in this test is strain rate control, which means the machine pulls the two crossheads away with certain strain rate. The entire test was conducted under a quasi-static condition (strain rate is 0.002 s^{-1}) to eliminate the effect caused by high strain rate. Based on the ASTM standard D412, the gauge length of specimens was 25mm, and the data was collected 100 points per second.

2.3.4 Tensile Test Results of Composites

Composites with different contents of microcapsules (0, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%, *Figure 20* shows a) the stress-strain curve of 10 wt.% phase change composites and b) the PDMS as the reference) were tested under the same condition to find the strain and

relationship between the content of microcapsules and tensile strength. The strain of simple PDMS-based phase change composites was around 1.15, which is 60% better than PDMS samples. The increasing of strain demonstrated the stretchability of composites is better than PDMS.

a   b
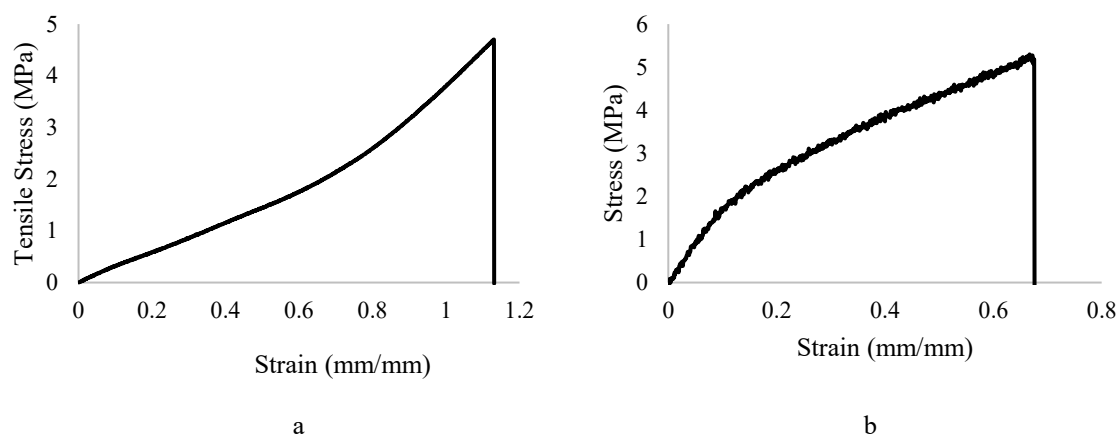
Figure 20 a) Stress-strain curve of 10 wt.% composites, b) stress-strain curve of PDMS

However, different from strains, when the microcapsules were added into PDMS to form composites, the maximum stress began to drop. With the increase of the content of microcapsule, the more maximum tensile stress drops (*Figure 21)*. The relationship between the content of microcapsules and the tensile stress is almost linear. The fitting function is $y = -9.8x + 5.4$ and $R^2 = 0.97$, which indicates the curve is close to but not exactly linear. So, the tensile strength of different composites could be easily predicted. When the content of microcapsules was over 40%, not only the viscosity of solution increased a lot, but also the tensile strength decreased. When the content reaches 40 wt.%, the tensile strength is already lower than 2 MPa. Thus, the whole composites cannot bear much loading when the tension is applied.
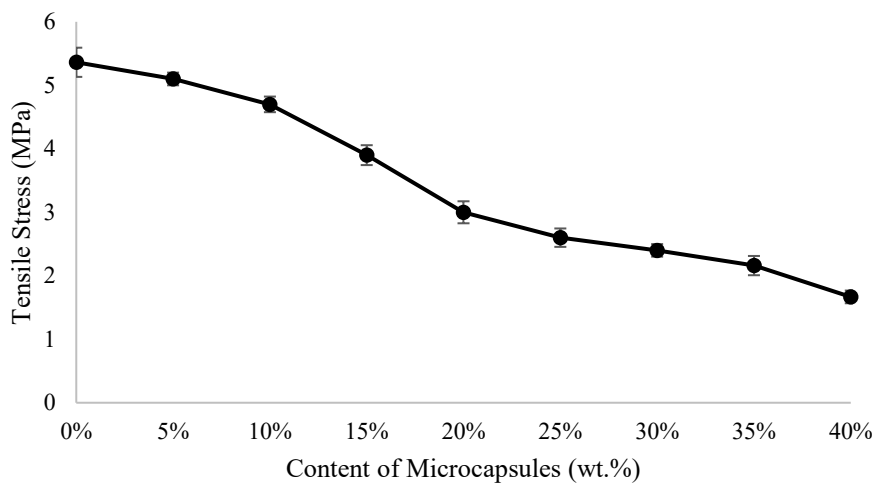
Figure 21 The relationship between the tensile strength and content of MCs

In order to find the reason of the tensile strength drop, SEM images were taken to observe

the fracture surface of different specimens *(Figure 22)*
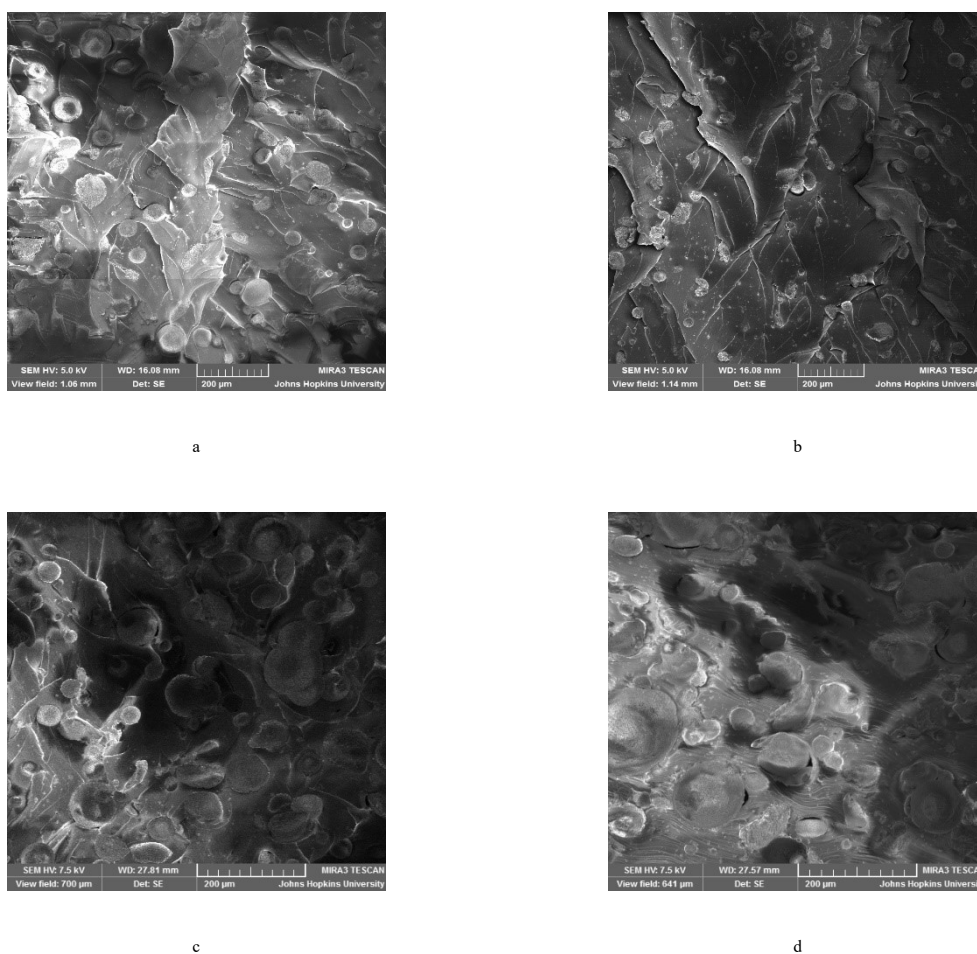
Figure 22 SEM images of composites with a) 5 wt.% b) 10 wt.% c) 15 wt.% d) 20 wt.%

It could be easily observed by SEM that when the content of microcapsules increased, there were more gaps between the capsules and matrix material. This may be caused by the poor bonding between the shell material of capsules and the matrix. When the gaps were created, the stress concentrated at the edge of gaps, so that the composites will fail easily. Moreover, when the number of particles increased, the particles could agglomerate together. Thus, this may also cause some pore defect.

2.4 Conclusion

The simple PDMS-based phase change composites (only PDMS and microcapsules) have good thermal performance and have good stretchability (60% higher than PDMS). Also, they have good tensile strength with less microcapsules inside the matrix. However, when the content of microcapsules increased, the tensile strength dropped approximately linear, and once the weight content of microcapsules exceeded 40 wt.% the tensile strength was lower than 2 Mpa, which is around 60% drop compare to pure PDMS sample. This is caused by many voids inside the composites, which could be created by poor bonding and caused by pores. When tension is applied on the specimen, the stress will concentrate on the edge of gaps such that will cause the composites fail.

To maintain the good thermal performance of composites, the content of microcapsules should be kept high so that the composites could absorb more heat. However, from the tensile strength analysis, when the content of microcapsules increased, the tensile strength dropped approximately linear, which indicates the composites with good thermal performance does not have high tensile strength. So that the simple PDMS-based phase change composites are

suitable to utilize in the areas which require high stretchability rather than high tensile strength. However, to explore more directions of application, especially for some fields require high tensile strength, the tensile strength should be improved. Thus, in next chapter the reinforcement was added into composites.

Chapter 3. Reinforced Phase Change Composites

3.1 Reinforcement of Composites with CNTs

To have both good thermal and mechanical performance, reinforcement should be applied to the composites. To improve the poor mechanical strength, some stronger materials could be added into the matrix to enhance the strength. But, the added material should have less weight relative to the matrix, so strong materials are considered. CNTs were selected due to their outstanding mechanical and thermal properties. Thus, by placing CNTs into matrices, it is postulated that the resulting composites will have enhanced thermal and mechanical properties [21]. Moreover, as mentioned in Chapter 1, CNTs have been also used to enhance the heat conduction [17-19]. Therefore, the thermal conductivity of reinforced phase change composites was expected to be improved as well. Ideally the tensile strength should be reinforced significantly with small amount of CNTs.

There are two main kinds of CNTs, one is single CNTs, and the other is multi-wall CNTs. The CNTs used in reinforcement of matrix in this project is multi-wall CNTs by considering

the cost and feasibility of the CNTs.
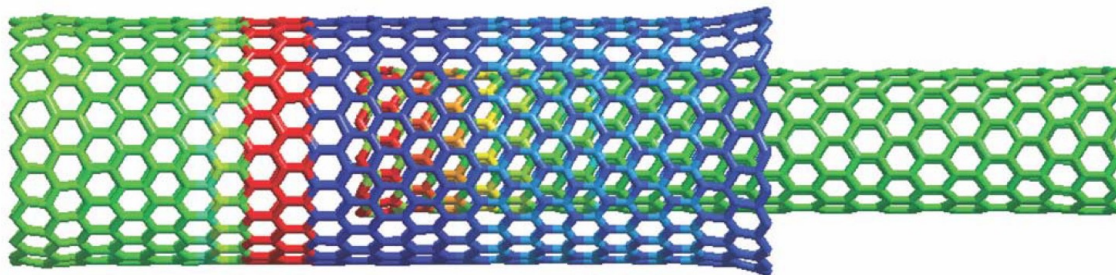
Figure 23 Triple-wall CNTs [22] Reprinted figure with permission from Xia, Z., and W. A. Curtin. "Pullout

Forces and Friction in Multiwall Carbon Nanotubes." *Physical Review B*, vol. 69, no. 23, 2004,

doi:10.1103/physrevb.69.233408. Copyright (2019) by the American Physical Society

Figure 23 shows the multi-wall CNTs, the CNTs of this project are purchased from *US*

Research Nanomaterials, Inc, and the table of properties for CNTs is in Table A2 of Appendix.

To maintain both good mechanical and thermal properties, besides improvement of the

mechanical performance, the thermal performance should also be considered. When the content

of microcapsules exceeds 40 wt.%, the tensile strength drops dramatically, and the fabrication

also become difficult due to the high viscosity. Thus, the content of microcapsules was set at

35 wt.% which is relatively large and close to 40 wt.%. And 35 wt.% can have relatively high

thermal absorption and is easy to fabricate.

3.2 Preparation of Reinforced Phase Change Composites

The fabrication method of reinforced phase change composites is almost the same with that

of simple PDMS-based phase change composites. However, due to the addition of CNTs, the

matrix solution become more viscous with more CNTs. Because of the high viscosity, the

curing process of the PDMS become difficult. The high viscosity could block the uniform

distribution of the particles inside the matrix. If the particles could not distribute uniformly

inside the matrix, the agglomerations occurred in the most parts of the matrix. Thus, based on

the original mixing method, the improvement was applied for the new composites.

Due to the small size of CNTs, few grams of CNTs could have a large volume. And only few

weight percent CNTs could have great reinforcement. So that the total weight of CNTs should

be controlled within a small wt.% region. Based on 35 wt.% content of microcapsules, *Table 4*

shows the recipe of reinforced phase change composites.

Table 4 Recipe of reinforced phase change composites with CNTs

Sample	PDMS(g)	Curing agent (g)	CA ratio	PCM Capsules(g)	CNT(g)	Total weight(g)	Content of CNTs (wt.%)
1	23	2.3	1:10	13.7	0.039	39.039	0.1%
2	23	2.3	1:10	13.7	0.078	39.078	0.2%
3	23	2.3	1:10	13.7	0.117	39.117	0.3%
4	23	2.3	1:10	13.7	0.156	39.156	0.4%
5	23	2.3	1:10	13.7	0.195	39.195	0.5%
6	23	2.3	1:10	13.7	0.234	39.234	0.6%
7	23	2.3	1:10	13.7	0.275	39.275	0.7%
8	23	2.3	1:10	13.7	0.314	39.314	0.8%
9	23	2.3	1:10	13.7	0.353	39.353	0.9%
10	23	2.3	1:10	13.7	0.392	39.392	1.0%

First, microcapsules were mixed with ethanol under ultra-sonic condition for 30 minutes. In

this step ethanol also acted as a carrier, to carry the particles dispersed well in uncured PDMS

base, and the ultra-sonic condition could help the microcapsules mixed well with ethanol. Then

the CNTs were also mixed with ethanol with the same condition. But, because the size of CNTs

particles are smaller than that of microcapsules, the mixing time should be longer than

microcapsules. To make sure the CNT particles are well dispersed in the ethanol, the mixing

time was set up to 3 hours. Then, the solution of microcapsules and CNTs were mixed together.

To make sure two different solutions were mixing well, another 30 minutes ultra-sonic was applied. But in this extra 30 minutes of mixing, it is important to avoid temperature rise above the melting temperature. Otherwise, the core material will change to liquid phase and the resulting increase of total volume may damage the shell, due to this reason the total 30 minutes mixing should be split into two 15-minute mixings and between these two mixings, the water in ultra-sonic should be changed. The required volume of ethanol to mix CNTs and microcapsules is larger than that of simple PDMS-based phase change composites because extra ethanol was used to mix CNTs, so that the duration of evaporation for ethanol should be longer. The solution was stored in oven at 60°C for 2 hours to evaporate extra ethanol. The solution was then fully mixed twice by using same planetary mixer and stored in oven at 80°C under vacuum for 8 hours to evaporate the ethanol completely. Then, to make sure the ethanol was fully evaporated, the container was placed onto balance to measure if solution has significant weight drop. After evaporating of ethanol, curing agent was added into solution with the 1:10 curing agent vs. base material ratio (fixed at 2.3g curing agent) and they were mixed in a planetary mixer. Due to the high viscosity, the mixture was placed into mold, it was degassed for 2 hours at 60°C with vacuum, followed by curing for 15 hours at 80°C. Since the weight ratio of microcapsules was fixed at 35 wt.%, the only variable in composites is the content of CNTs. By using this method, the composites with different CNTs weight ratio were made (0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9% and 1.0%).

3.3 Thermal Properties of Reinforced Phase Change Composites

The only difference between the CNT reinforced phase change composites and the simple

PDMS-based phase change composites is adding the CNTs. The total amount of heat absorption should keep the same with the composites without the CNTs, as the added CNTs will not contribute to the heat absorption of the composites because CNTs will not melt. The total heat absorption was 65.7J/g. *(Figure 24)*
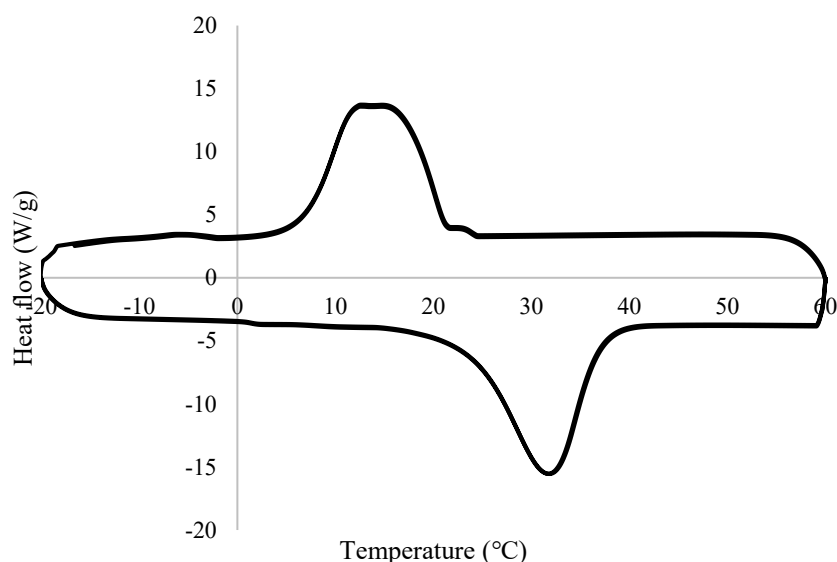
Figure 24 The DSC heat loop of 35 wt.% composites

3.4 Mechanical Properties of Reinforced Phase Change Composites

The purpose of adding CNTs is to enhance the tensile strength of the composites. So, the tensile was expected to increase compare to simple PDMS-based phase change composites.

3.4.1 Standard of Tensile Test

The standard of cutting die and the dog-bone specimen of the tensile test applied to the CNTs reinforced phase change composites was still based on the ASTM standard D-412. The cutting

die and the dog-bone specimens were the same as the die and specimens used in simple PDMS-based phase change composites in Chapter 2, the actual dog-done specimen made by this cutting die is shown in *Figure 25*:
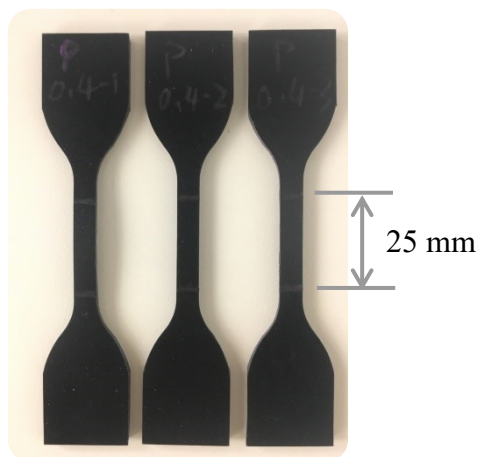
Figure 25 Dog-bone sample of CNTs reinforced phase change composites

3.4.2 Equipment of Tensile Test

The equipment used in this tensile test was same as the equipment mentioned in Chapter 2, which include the MTS machine and the roller grips. When the final dog-bone specimens were made, the mark with its content number will help to distinguish the different specimen. The cross-section areas are measured multiple times from different positions of samples and averages were taken.

3.4.3 Setting of Tensile Test

To control all the variables, the setting of tensile test should be the same with the simple PDMS-based phase change composites. The entire tensile tests were conducted under the quasi-static condition (strain rate $0.002s^{-1}$).

3.4.4 Tensile Test Results of Reinforced Phase Change Composites

The content of microcapsules is fixed at 35 wt.% for all specimens, so that the only difference between each sample is the content of CNTs. Analyzing the relationship between content of CNTs and tensile strength could help to find the optimal value of CNTs' content. The tensile strength of 35% sample is shown in *Figure 26*
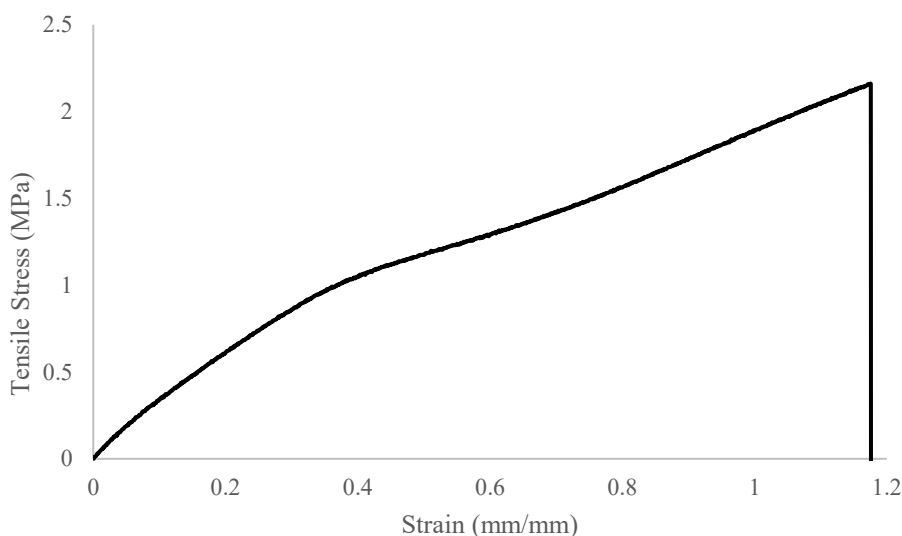
Figure 26 Stress-strain curve of 35 wt.% composites

The 35 wt.% composites have similar tensile trend with other simple PDMS-based phase change composites, but the maximum strength becomes lower due to high concentration of microcapsules. The maximum tensile stress is around 2.16 Mpa, and the failure strain is around 1.17.

The *Figure 27* shows the stress strain curve of reinforced phase change composites with different content, the total trend of all curves is similar. All tensile stresses keep increasing to reach the maximum tensile stresses and fractures occurred afterwards. And all the failure strains are over 0.7, which shows all the samples still have good stretchability.
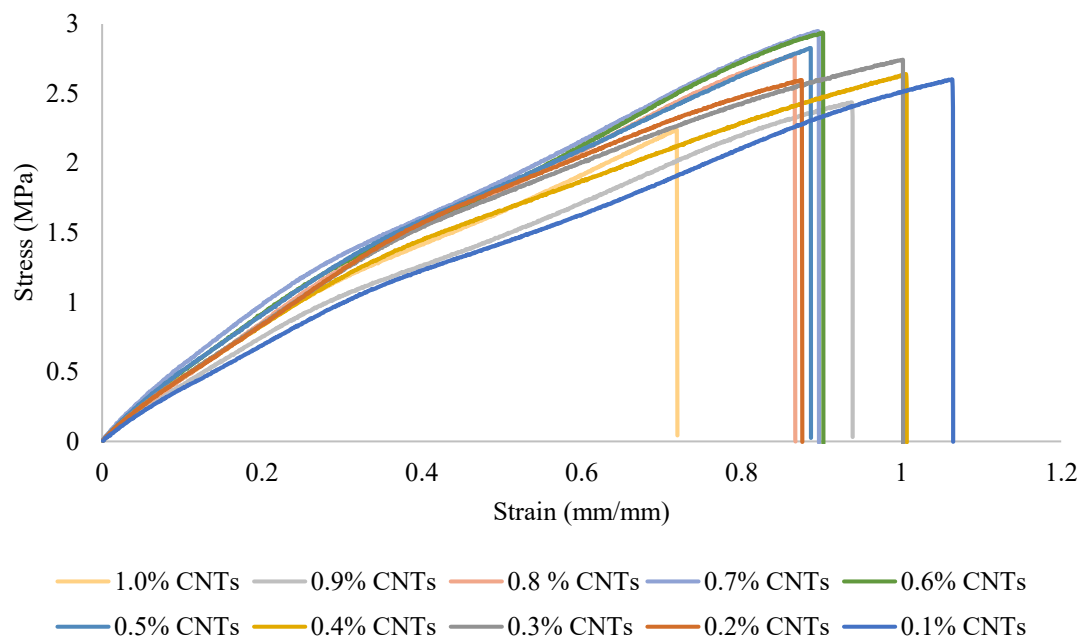
Figure 27 Stress-strain curve of composites with 0.1-1.0wt.% CNTs

When adding the CNTs into the matrix, the strains of all sample were decreased compare to simple PDMS-based phase change composites, but the values were still at a high level (over 70%, nearly same as PDMS), and the tensile strength will increase, but with the different content of CNTs the improvement is different as shown in *Figure 28*. The tensile stress is almost the same in 0.1-0.4wt.% region, the stresses fluctuating around 2.6 MPa, but from the content of CNTs increased to 0.5wt.%, the tensile strength kept to increasing up to 0.7wt.%. The maximum stress was located between 0.6wt.% to 0.7wt.%, and the value was around 2.94 MPa. After 0.7wt.%, the maximum tensile kept decreases, and when the content of CNTs reach to 1wt.% the tensile strength was almost the same as no CNTs added.
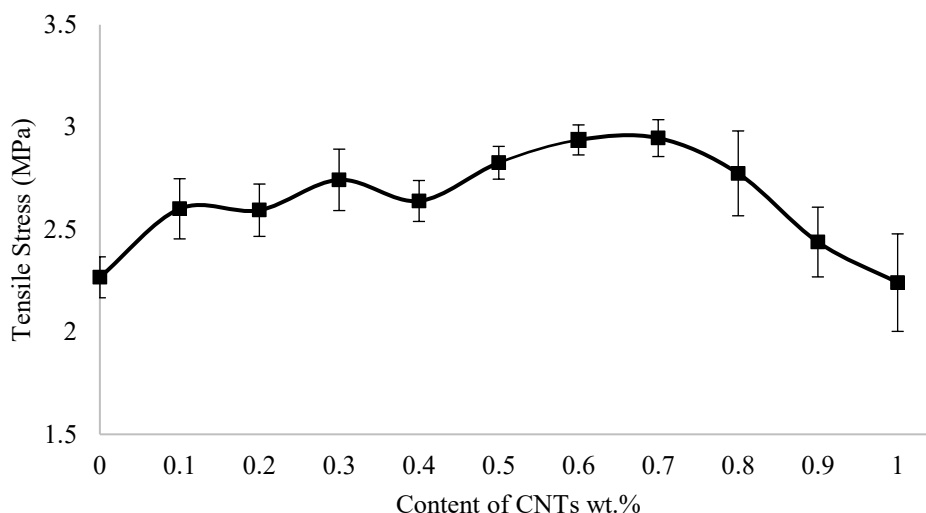
Figure 28 The tensile strength of different CNTs content

We expected the tensile strength will increase when the CNTs were added into the matrix.

However, according to the data of tensile tests, the tensile strength only increased in 0.1-0.7

wt.% region. Once the content of CNTs exceeded 0.7 wt.%, the tensile strength of samples

starts to drop. In order to find the cause of the drop of tensile strength, the SEM was applied to

observe the fracture surface of each sample. *Figure 29* shows the different fracture surface of

different specimens.
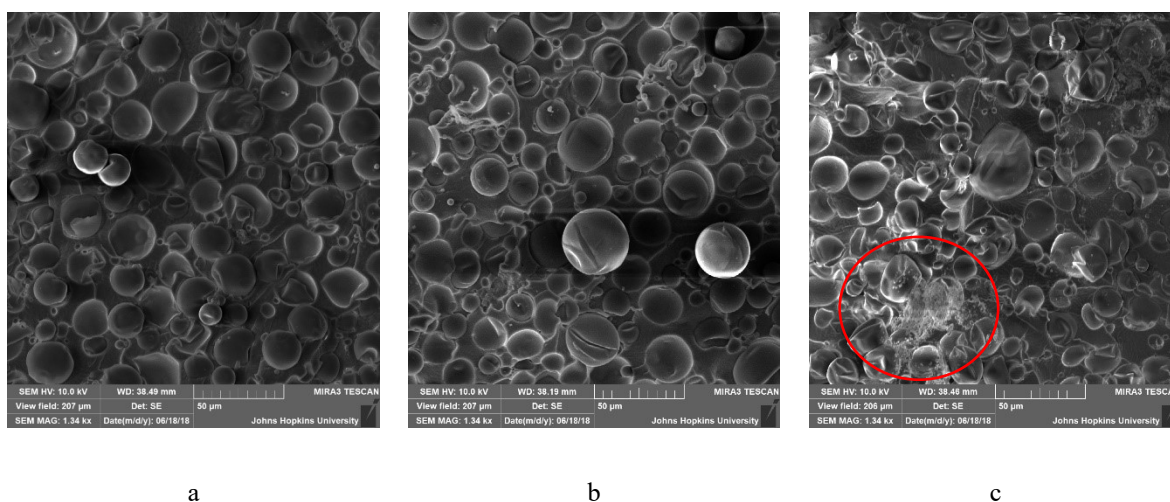
Figure 29 The fracture surface of a) 0.4 wt.%, b) 0.7 wt.% and c) 1.0 wt.%

In *Figure 29 a*, the particles are uniformly distributed with less gaps between the matrix and

capsules. Thus, the entire specimen has a relatively high enhancement compared to simple PDMS-based phase change composites. In *Figure 29 b*, the particles are still uniformly distributed, and less gap between the matrix and shell of microcapsules, so that with the higher content of CNTs, the 0.7 wt.% composites have the higher tensile strength. However, in *Figure 29 c*, when the content of CNTs is 1.0 wt.%, it could be observed that there exist many broken capsules inside the matrix. This is caused by when the content of CNTs increases, the high density CNTs will damage the microcapsules during the mixing process. Once the capsules are broken, the paraffin will leak into the matrix so that it will create a weak point in the composites. Therefore, the tensile strength will decrease when the content of CNTs is high. The 0.7 wt.% could be regarded as a critical value, at this value the CNTs also damage the microcapsules, but the effect of broken microcapsules is less than the effect of reinforcement. Moreover, due to the high viscosity of solution, the microcapsules maybe not distributed uniformly for high content samples. Also, when the CNTs is added into the matrix, the thermal conductivity increases. Thus, the curing time is shortened, the degassing time is not enough, it may cause some air bubbles remining in the matrix.

3.5 Conclusion

The reinforced phase change composites have better tensile strength than the simple PDMS-based phase change composites but have less strain while maintaining good thermal performance. When fixed the content of microcapsules and adding CNTs into the matrix, the total tensile strength will fluctuate in the 0.1-0.4 wt.% region, and will keep increasing in 0.5-0.7 wt.% region, but eventually in the 0.8-1.0 wt.% region the tensile strength will decrease

due to broken capsules, poor mixing and less time of degassing. Thus, the 0.7 wt.% CNTs should be the optimal value of the reinforced phase change composites.
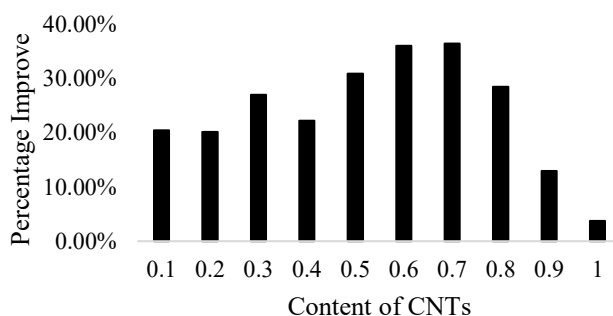
Figure 30 The percentage improvement compares to 35 wt.% simple PDMS-based phase change composites

Figure 30 shows almost all the samples were reinforced, which means the CNTs could improve the tensile strength of composites. These composites with high tensile strength could be utilize in the field which focus on tensile strength more than stretchability. However, the CNTs only enhance the matrix, from the SEM images, there were still many gaps between capsules and matrix, this is because the bonding between capsules and matrix is still weak. Thus, the composites will achieve the best tensile strength if the bonding between capsules and matrix could also be reinforced. The surface modification method in next chapter would help to enhance the bonding.

Chapter 4. Modified Phase Change Composites

Adding CNTs could increase the overall tensile strength for the composites, but there still exist some issues in bonding between microcapsules and matrix. *Figure 31* shows the model of two different kinds of composites, *Figure 31 a* is the simple PDMS-based phase change composites, the microcapsules particles just simply mixed with PDMS, and there was no reinforcement of matrix or bonding. *Figure 31 b* is the reinforced phase change composites. The CNTs were added into the matrix to enhance the total tensile stress, but the CNTs only enhance the matrix not the bonding. Therefore, if the bonding between microcapsules and the matrix could be reinforced as well, the overall tensile strength of composites will increase.
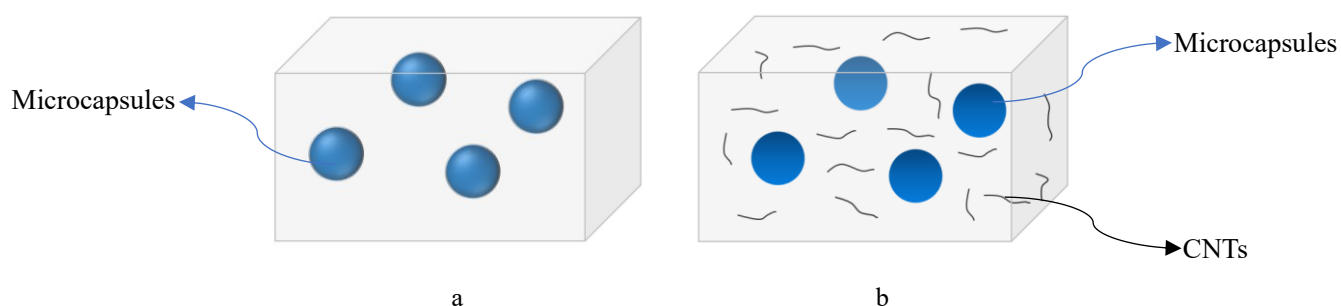
Figure 31 Different models of composites, a) simple PDMS-based phase change composites and b) reinforced phase change composites

However, the bonding between PDMS and other polymers was challenging because of the

hydrophobic nature and low surface energy of PDMS [23]. So, the simply mixing of microcapsules and matrix will not help to create a strong bond. Indeed, there were many methods that could improve the bonding between PDMS and other polymers, such as Oxygen plasma treatment [24] on PDMS surface to change it from hydrophobic to hydrophilic. But, the plasma treatment usually was used to treat the surface. It's hard to treat the entire uncured PDMS base. The same issue also applies to microcapsules. It's nearly impossible to treat microcapsules by plasma due to its size. Besides the surface treatment, some "glues" can be used to help microcapsules stick to PDMS. And, the CNTs could be used as a "glue" if poly-dopamine is applied to stick CNTs onto the surface of microcapsules [25]. Moreover, poly-dopamine could be also used to modify the CNTs to make CNTs well-dispersed in water and ethanol [26-28] and could help CNTs dispersed in PDMS.

Recently, it has been shown that poly-dopamine (PDA) has an excellent environmental stability, good biocompatibility, and an especially excellent dispersibility in water. Owing to the advantages of PDA, modifying CNTs with PDA can make it dispersible and in good combination with analytes. Compared with the oxidized CNTs, the coating of CNTs with PDA will keep the inherent properties of the pristine CNTs without the destruction of its structure [27]. Then, the combination of the modified CNTs and microcapsules will make the CNTs stick to the surface of microcapsules [25], the CNTs will perform as tentacles to insert into PDMS matrix, the *Figure 32* shows the model of modified phase change composites.
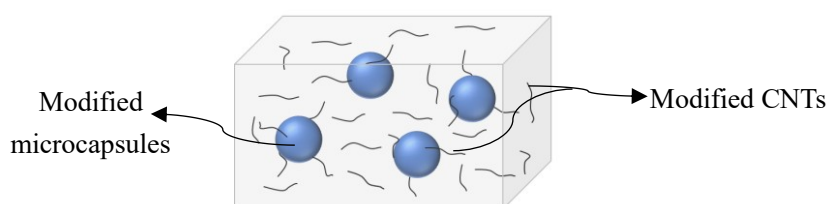
Figure 32 The model of modified phase change composites

4.1 Preparation of Modified Phase Change Composites

The procedures to mix particles (microcapsules and modified CNTs) with PDMS was the same as process of making reinforced phase change composites. But, for the modified phase change composites, the microcapsules and CNTs should be modified before mixing.
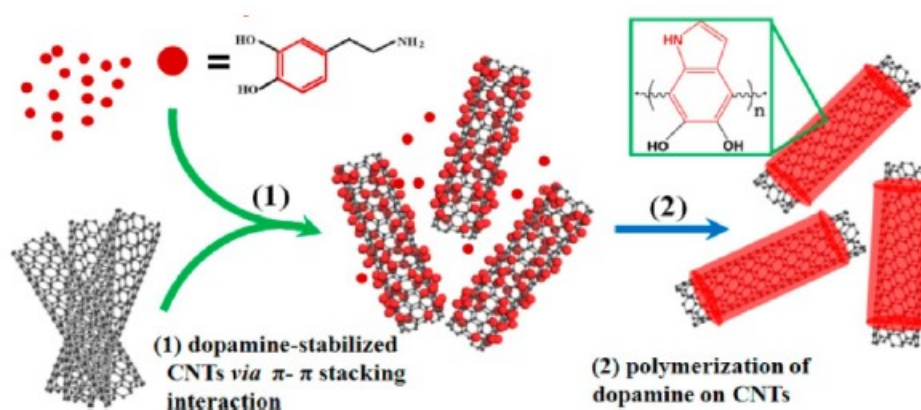
Figure 33 The fabrication of modified CNTs [29] Reprinted with permission from (Shi, Chenyi, et al. "Synthesis of Highly Water-Dispersible Polydopamine-Modified Multiwalled Carbon Nanotubes for Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry Analysis." *ACS Applied Materials & Interfaces*, vol. 5, no. 16, 2013, pp. 7770–7776., doi:10.1021/am4024143.). Copyright (2019) American Chemical Society.

Figure 33 shows the method to modify the CNTs. The CNTs were mixed with polydopamine (Purchased from Sigma-Aldrich, H8502-25g) with ratio 1:2 in the Tris buffer solution (Purchased from ThermalFisher Tris-HCL, pH~8.5) condition for 24 hours under 300-350 rpm at room temperature (*Figure 34*). The concentration of Tris buffer is 1 mole/ L, and for each unit of solution, 300mL buffer solution was mixed with 400mg polydopamine and 200mg CNTs.

Figure 34 Mixing CNTs with polydopamine in Tris buffer

After 24 hours mixing, the solution was collected by using Falcon tubes, then the modified CNTs were separated by using centrifuge machine with 3500 rpm for 5 min. To neutralize the pH value, the purified centrifugation was operated after the separation with Tris. This purified centrifugation is the same but was repeated 3 times with DI-water. Finally, the water-CNTs solutions were stored in an oven under 60°C to dry to the powder form.

<div align="center">a   b   c</div>
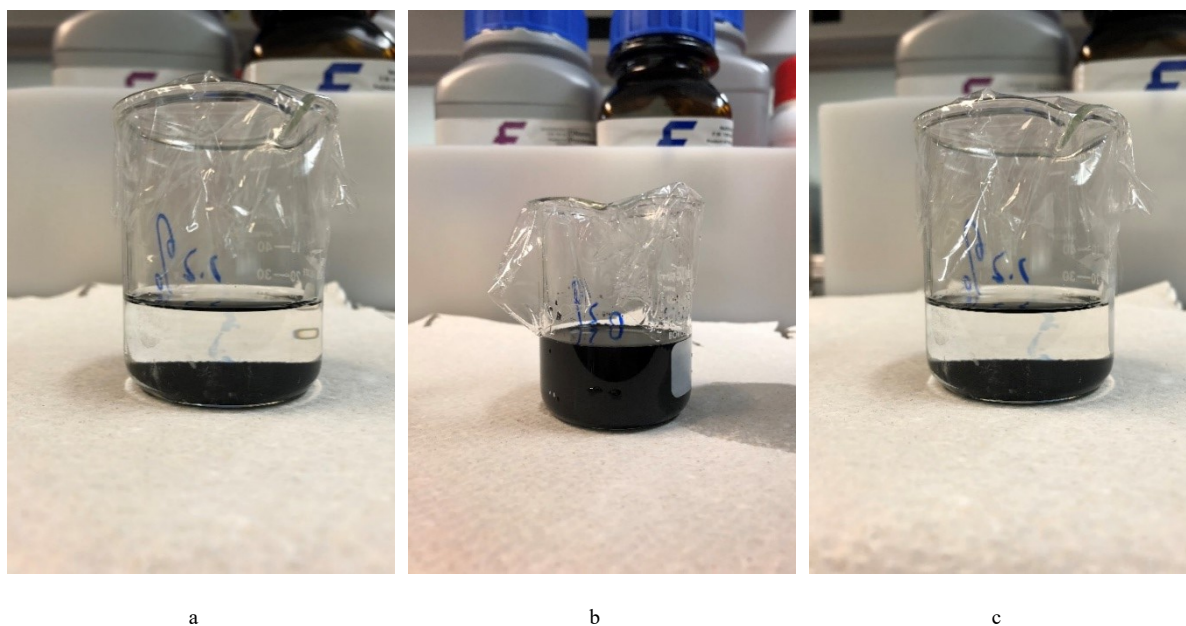
Figure 35 Unmodified CNTs, a) before mixing, b) mixing by ultra-sonic and c) solution after 1 hour standing

<div align="center">a   b   c</div>
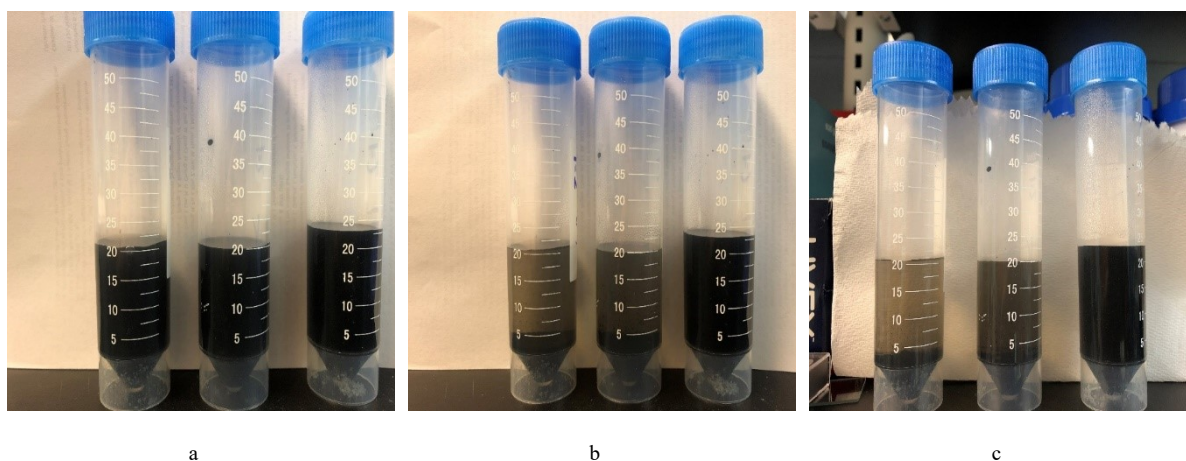
Figure 36 Modified CNTs, a) 1st day after mixing with water, b) 3 days after mixing with water and c) a month after mixing with water.

Figure 35 shows the unmodified CNTs mixing with DI-water, a) is the solution before mixing, b) is mixing under ultra-sonic condition for 3 hours, and c) is the solution after 1-hour standing. Obviously, the CNTs cannot disperse well in the water, and the CNTs will separate with water phase within a short time. Now, the *Figure 36* shows the modified CNTs mixing with water, a) is the first day of mixing, b) is 3 days after mixing and c) is a month after mixing.

In each subfigure, the left one is unmodified CNTs as a reference, the middle one is the failed modified CNTs and the right one is the modified CNTs. The modified CNTs demonstrated a strong ability to disperse in water and stay uniformly distributed in water without separation.
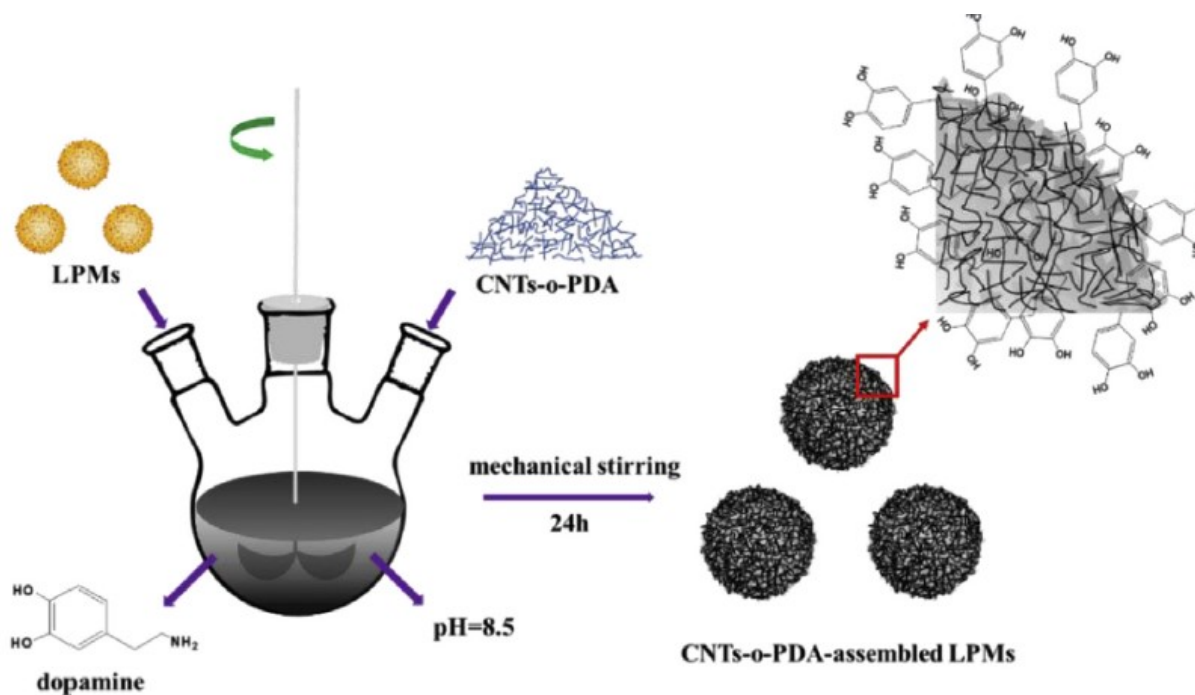
Figure 37 The fabrication of modified microcapsules [25]. Reprinted from Composites Science and Technology, Vol 164, Haiyan Li,Yingjie Ma,Zhike Li,Yexiang Cui,Huaiyuan Wang, Synthesis of novel multilayer composite microcapsules and their application in self-lubricating polymer composites, 120-128., Copyright (2019), with permission from Elsevier

After the modification of CNTs, the microcapsules were modified, so that we could use both modified materials to prepare composites. *Figure 37* shows the procedure of fabrication of modified microcapsules. When the modified CNTs were made, CNTs were used to mix with microcapsules in a ratio 1:10 (200mg:2g) in the same 200ml Tris buffer solution. To make the CNTs stick onto the surface of microcapsules the 400mg polydopamine is added into solution. The total solution is mixed by using magnetic stirrer for 24 hours at 300-350 rpm. Due to the lower density of microcapsules, the modified microcapsules cannot be separated by

centrifugation. Therefore, the suction filtration was applied to separate the water phase with microcapsules. Then the microcapsules were dried in an oven for 60 minutes at 60°C.

To examine the modification of microcapsules, SEM images were used to characterize the surface condition of microcapsules. *Figure 38 a* shows the modified microcapsules. The surface is almost covered by the CNTs, but as the reference, the surface of unmodified microcapsules (*Figure 38 b*) is clear and smooth. The difference of two different kinds of microcapsules indicates the success of surface modification.

a   b
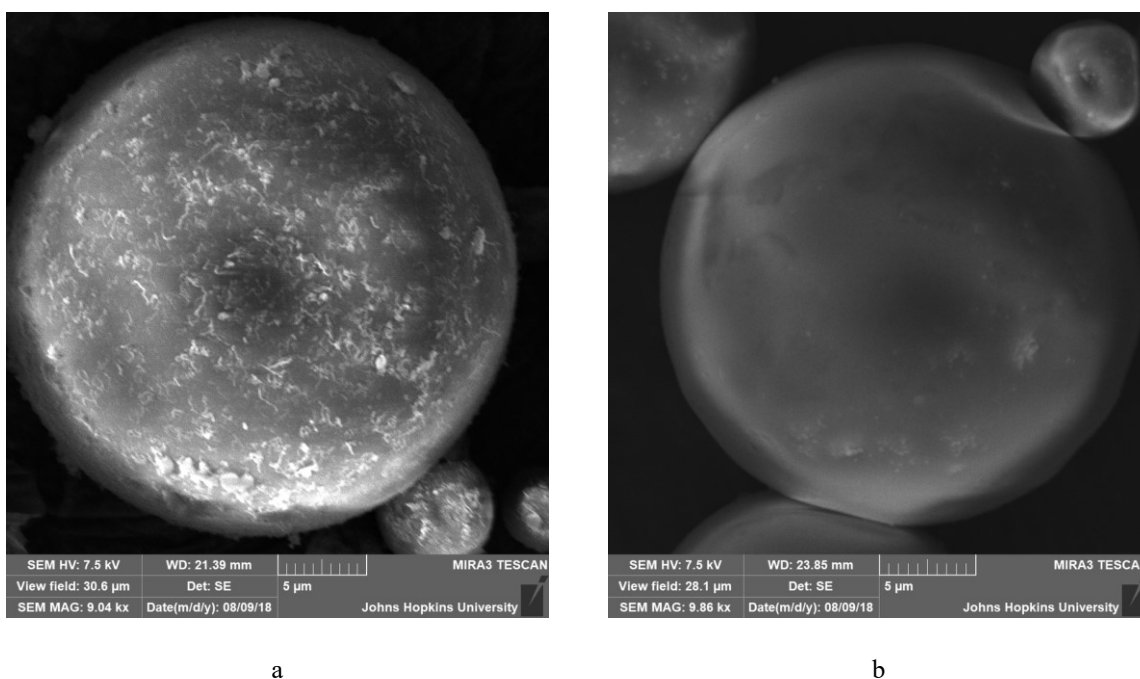
Figure 38 SEM images of a) Modified microcapsules with polydopamine and CNTs, b) unmodified

microcapsules

4.2 Thermal Properties of Modified Phase Change Composites

4.2.1 DSC Test of Modified Phase Change Composites

To study the thermal properties of the modified composites, DSC was performed to measure

the heat flow through the composites, then the amount of heat absorption was calculated by integrate the heat flow. Because some portion of total weight of the microcapsules are occupied by modified CNTs, the total heat absorption should lower than 35 wt.% composites. Since the ratio of CNTs to microcapsules is 1:10, the total heat absorption drop will be around 9.1%. The *Figure 39* shows the result of DSC test of modified phase change composites. The entire trend of the result is the same with other composites, but the overall heat absorption is 9% lower than 35wt.% simple PDMS-based phase change composites, which is 59.74 J/g. However, even if the amount of heat absorption of modified phase change composites decreases, the modified phase change composites still have the high capability to absorb large amount of heat.
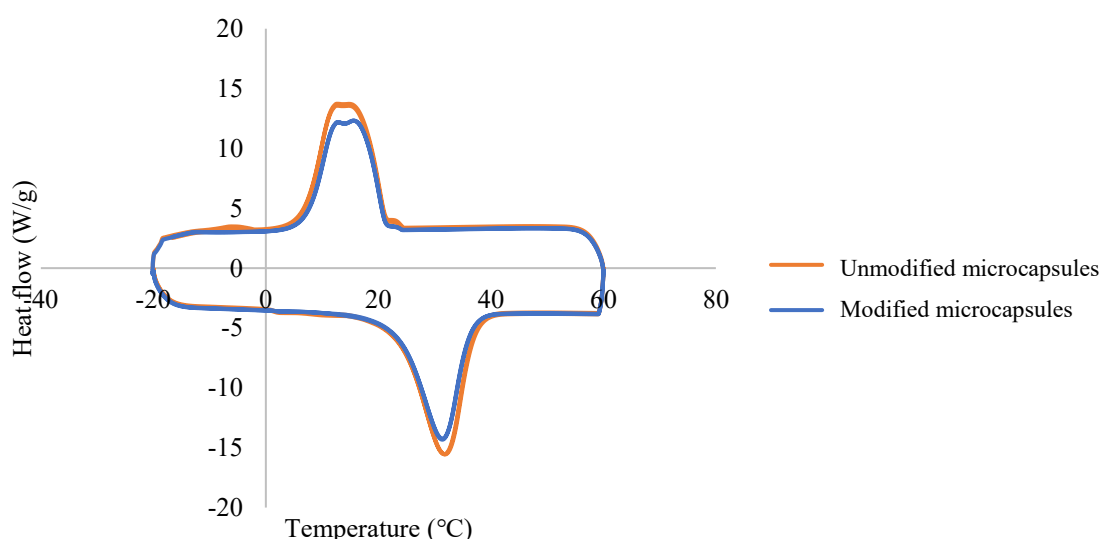
Figure 39 DSC test of modified and unmodified phase change composites

4.2.2 TGA Test of Modified Phase Change Composites

In chapter 1, the TGA shows the degradation temperature of microcapsule. Now, the surface of microcapsules was modified by polydopamine and CNTs, which is equivalent to coating a film onto the surface. So, the TGA test was applied again to examine the change of degradation

temperature of microcapsules.

The *Figure 40* shows the result of TGA tests. The degradation temperature of modified microcapsules is about 350℃, however as the reference the degradation temperature of unmodified microcapsules is around 300℃. The 50℃ difference indicates that the modified microcapsules have higher working temperature, which also means the modification of microcapsules can make the microcapsules have higher thermal stability. The temperature range of TGA tests was from 30℃ to 600℃, and the heating rate was 5℃/min. The tests with same condition were applied to both modified and unmodified microcapsules for comparison.
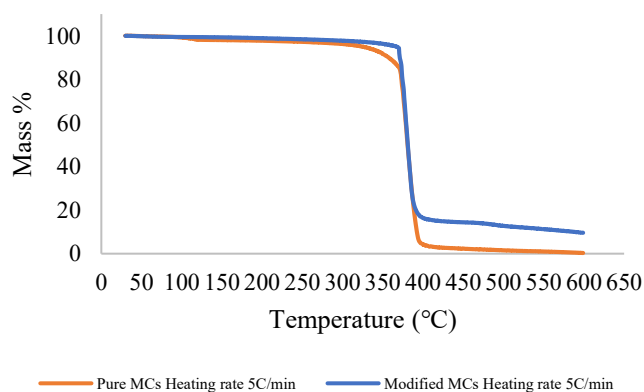
Figure 40 TGA for unmodified and modified microcapsules

4.3 Mechanical Properties of Modified Phase Change Composites

The original purpose of modify microcapsules was to enhance the poor bonding between the microcapsules and the matrix. Therefore, the uniaxial tension tests were applied to test if the tensile strength improves compared to reinforced phase change composites. According to Li, et al. the tensile strength of modified phase change composites will have around 15.2% improvement [25] (*Figure 41*).
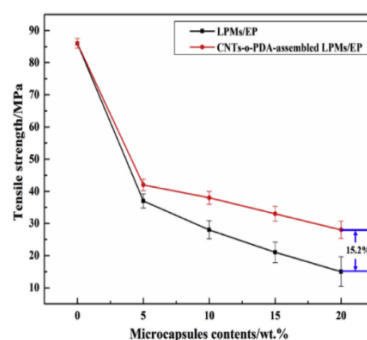
Figure 41 The tensile strength of modified and unmodified phase change composites [25]. Reprinted from

Composites Science and Technology, Vol 164, Haiyan Li,Yingjie Ma,Zhike Li,Yexiang Cui,Huaiyuan Wang,

Synthesis of novel multilayer composite microcapsules and their application in self-lubricating polymer

composites, 120-128., Copyright (2019), with permission from Elsevier

4.3.1 Standard of Tensile Test

The standard of cutting die and the dog-bone specimen of the tensile test applied to reinforced phase change composites were still based on the ASTM standard D-412. The cutting die and the dog-bone specimens were the same as the die and specimens used in simple PDMS-based phase change composites.

4.3.2 Equipment of Tensile Test

The equipment used in this tensile test was same as the equipment used for simple PDMS-based phase change composites. Their cross-section areas are measured multiple times from different positions of samples and averages were taken.

4.3.3 Setting of Tensile Test

To control variables, the setting of tensile test should keep the same with previous composites. The entire tensile tests were under the quasi-static condition (0.002 s^{-1}).

4.3.4 Tensile Results of Modified Phase Change Composites

The *Figure 42* shows the result of tensile test of modified phase change composites. The overall trend of the stress-strain curve was same as other composites. But, the tensile strength of modified phase change composites dropped to 2.4MPa, which is around 18.5% decrease (*Figure 43*). The result did not meet the expectation.
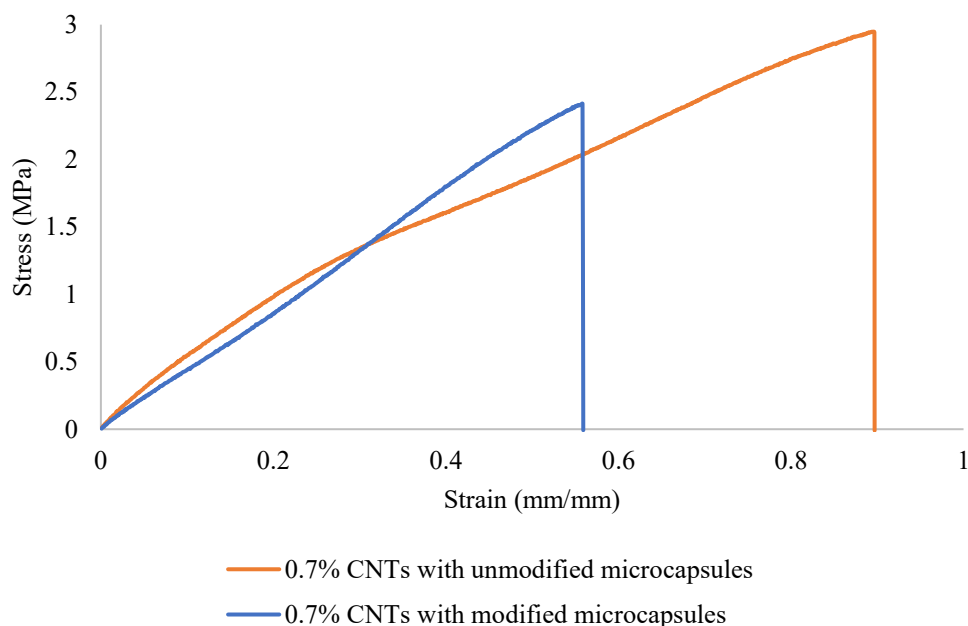
Figure 42 Stress-strain curve of modified and unmodified phase change composites
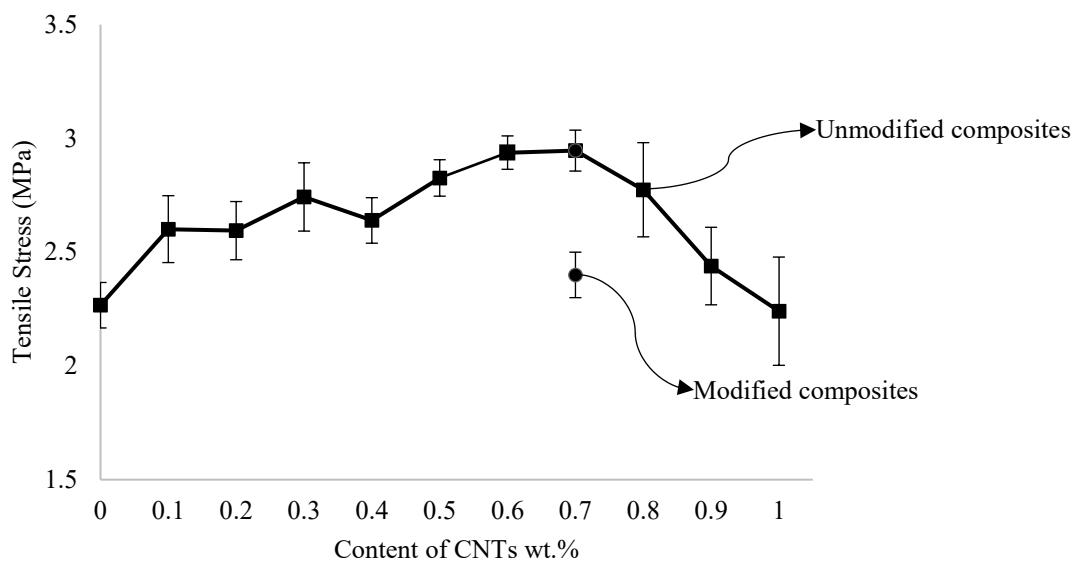
Figure 43 Comparison of tensile strength for modified and unmodified phase change composites

There could be multiple reasons of why the tensile strength decreased rather than increased. First, during the modification process, the magnetic stirring breaks the shell of microcapsules, and the remains of broken shell cannot be separated by suction filtration. So, they created defects inside the composites. Second, the high content of microcapsules would cause the solution to become more viscous. So, the mixing time was not enough to mix the particles uniformly. To improve the result, the stirring speed could be lowered to avoid the breaking shell of microcapsules, and the longer mixing time can be used to make the particles distributed uniformly.

4.4 Conclusion

The modification coated a CNTs-polydopamine film onto the surface of microcapsules. This film can increase the thermal stability of microcapsules by increasing the degradation temperature. But in the meantime, because some weight portion of microcapsules were

occupied by CNTs and polydopamine, the total amount of heat absorption decreased around 9%.   For the mechanical properties, although the stretchability of modified composites was drop to around 57%, they still have the high stretchability. The result of tensile strength was expected higher than reinforced phase change composites. However, since there were many defects inside the composites, the tensile strength decreased around 18.5%. To improve the tensile strength, the protection of shell of microcapsules and the high-power mixer should be applied to the fabrication process. Although, the stretchability and tensile strength were not increased as we expected, the increasing of thermal stability makes the modified composites could be used in some areas which require better thermal stability.

Chapter 5. Conclusion and Perspectives

5.1 Conclusion

The simple PDMS-based phase change composites have good thermal performance and stretchability. The strains of composites were usually higher than 100%. They have high tensile strength with lower content of microcapsules. However, when the content of microcapsules increased, the tensile strength dropped approximately linear. The drop of strength is caused by voids inside the composites.

Besides mechanical properties, the composites demonstrate a great ability of absorbing heat, the content of microcapsules has an increasing linear relationship with the amount of heat absorption. To keep the good thermal performance of composites, the content of microcapsules should be kept at a relative high-level concentration, but the tensile strength will drop. Thus, the reinforcement should be applied to the simple PDMS-based phase change composites so that the composites can have both good mechanical and thermal properties.

To improve the tensile strength, the CNTs are used to reinforce the composites. The

composites maintain good thermal performance and excellent stretchability. To keep high heat absorption amount, the microcapsules content was fixed at 35 wt.%, when the CNTs were added into the matrix, the tensile strength increased to reach the highest value at 0.7 wt.%, and after that the strength started to decrease. This is because broken capsules remaining inside the matrix, poor mixing and lack of degas. Thus, the 0.7 wt.% CNTs should be the optimal value of the reinforced phase change composites.

Indeed, when the CNTs were added into matrix, the strains were decreased (from 110% to 80%), but the tensile strength of all the samples were increased. However, the CNTs only enhance the matrix. The bonding between capsules and matrix was still poor. To achieve the best mechanical performance, the surface modification was used to enhance the bonding.

To enhance the bonding, the polydopamine surface modification was applied to both CNTs and microcapsules. By doing the modification, the microcapsules were successfully coated with a thin film onto the shell. This modification increased the thermal stability but decreased amount of heat absorption of the composites correspondingly.

The tensile strength was expected to be improved. However, due to the defects inside the composites, the tensile strength is lower than reinforced phase change composites.

5.2 Perspectives

The expectation of the modification was to optimize the tensile strength without lower or slightly decreases the thermal properties. Considering all the factors, to improve the tensile strength, the protection of shell of microcapsules and the high-power mixer should be applied to the fabrication process.

Although the tensile strength was not improved by modification, the simple PDMS-based phase change composites, reinforced phase change composites and modified phase change composites demonstrated the great stretchability, tensile strength and thermal stability respectively. The future work could be successfully reinforce the tensile strength of composites with high strain, and find the suitable applications for those composites.

Appendix

Table A1 Properties of MPCM 28D (microcapsuled) [29]

PROPERTIES

The MPCM 28D product exhibits the following general properties:

Typical Properties	
Appearance	White to slightly off-white color
Form	Dry Powder (≥97% Solids)
Capsule composition	85-90 wt.% PCM 10-15 wt.% polymer shell
Core material	Paraffin
Particle size (mean)	15 - 30 micron
Melting Point	28°C (82.4°F)
Heat of Fusion	180 - 190 J/g
Specific Gravity	0.9
Temperature Stability	Extremely stable – less than 1% leakage when heated to 250°C
Thermal Cycling	Multiple

Table A2 Properties of CNTs [30]

Multi Walled Carbon Nanotubes Doped Nano-powder Ag in Water Dispersion	15wt%
Multi Walled Carbon Nanotubes Purity	> 95%
Multi Walled Carbon Nanotubes Outside diameter	20-30nm
Multi Walled Carbon Nanotubes Inside diameter	5-10nm
Multi Walled Carbon Nanotubes Length	10-30um
Making Method	High-pressure Synthesis

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Curriculum Vitae

Boliang Wu was born in Hohhot, China on February 14th, 1995. He started his undergraduate study in Theoretical and Applied Mechanics at Sun Yat-sen University in Southern China in 2013. Then he transferred to Mechanical Engineering in Indiana University Purdue University Indianapolis as an undergraduate student in 2015. He received his Bachelor's degrees in Theoretical and Applied Mechanics from Sun Yat-sen University and Mechanical Engineering from Indiana University Purdue University Indianapolis in 2017. Then he became a MSE student at Mechanical Engineering in Johns Hopkins University in same year and will move to University of California, Los Angeles to pursue his PhD degree in Fall 2019. His research area in Johns Hopkins is focus on thermal energy storage and dissipation by using phase change materials.