

**SYNTHESIS, CHARACTERIZATION AND ENCAPSULATION OF
PHASE CHANGE MATERIALS AND THEIR INCORPORATION IN
ASPHALT PAVEMENTS**

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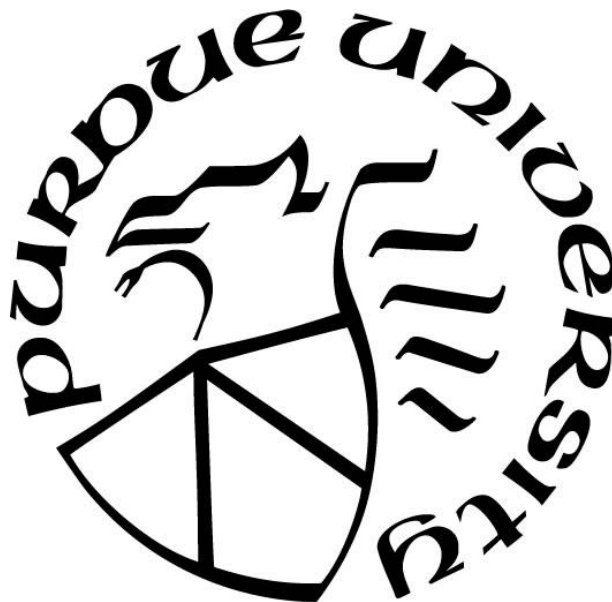
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Dedicated to my family.

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ABSTRACT

This document summarizes the research conducted on organic phase change materials, from the synthesis, characterization, and encapsulation of biobased FAAs for PCM applications to the incorporation of commercially available PCM microcapsules in asphalt pavement to regulate its temperature and potentially prevent or mitigate rutting and the urban heat island (UHI) effect.

The first chapter presents the synthesis of bio-based fatty acid amides for PCM applications. Fatty acid amides (FAAs) were successfully synthesized from commercial vegetable oils and primary alkyl amines. The chemical structures of the samples were characterized through FTIR, ^1H -NMR and ^{13}C -NMR while their thermal properties were studied using DSC and TGA. Results show the potential of FAAs synthesized from corn and sunflower oils to be used as phase change materials, which exhibited single transitions over narrow temperature ranges upon cooling/heating even when no fractionation or separation of the material was carried out. The melting temperature of the FAAs increased with the length of the precursor amine and a similar trend was observed for latent heat except for FAAs from hexadecylamine. Latent heats of the synthesized materials were as high as 141 kJ/kg, and all the FAAs were thermally stable under 200 °C.

The second chapter focuses on the encapsulation of biobased FAAs in core-shell UV curable polyester capsules fabricated using a coaxial needle. Capsules were dripped from the needle tip into a collection bath where they were exposed to UV light to cure the polyester shell. The addition of rheology additives to the shell resin was proven successful in improving the capsules' shape and the stability of the generating process. Capsule production parameters such as core and shell flow rates were varied and their effect on the process stability and the capsules' size and core content were studied. Thermal properties were also assessed with results indicating that the FAAs retain their PCM potential after encapsulation. Furthermore, the capsules were determined to be thermally stable under 190 °C. The general trend observed from compression test results was the decrease of the capsules' mechanical performance when the core content was increased; however, it was also discovered that their failure response is highly dependent on the uniformity of the capsule's shell. It was concluded that the thermal properties of the capsules can be improved by adding fillers with high thermal conductivities to the shell; similarly, the failure

behavior can be enhanced by reducing the level of core off centeredness with changes in the shell formulation or addition of higher density particles to the FAAs. Results from this investigation are expected to lay the groundwork for the commercial use of biobased FAAs and potential replacement of petroleum derived PCMs currently in the market.

The third and last chapter of this document presents efforts made to incorporate commercially available PCM microcapsules in asphalt pavements in order to prevent them from reaching high temperatures that can promote rutting and the UHI effect. First, the thermal properties and stability of the capsules were characterized using DSC and TGA analysis. They exhibited high latent heats (200 J/g) and were thermally stable under 400 °C. Next, the ability of the capsules to withstand compression forces and high temperatures typical of asphalt processing was assessed by milling them at a high temperature (<145 °C) for 20 minutes. Results from visual inspection indicate that approximately 90% of the capsules endured the experiment. Microcapsules were then added to asphalt mixtures in 10 and 20 vol% and thermal cycling experiments were conducted to study the effect of the PCMs on the temperature of the samples. As the specimens were heated and they approached the melting point of the PCM, the temperature of those containing 10 vol% and 20 vol% PCM were 5 °C and 10 °C lower than that of the control specimen, respectively. Similarly, when the mixtures were cooled down from 62 °C to room temperature, specimens with 10 and 20 vol.% PCM were 2.9 and 5.4 °C hotter than the control when their temperatures were just below the melting point of the PCM. However, the dynamic modulus of control and PCM containing mixtures was also studied and results indicate that the addition of the microcapsules resulted in a reduction of this property which could decrease the pavement's rutting resistance.

1. INTRODUCTION

Phase change materials (PCMs) are substances that can be used for thermal storage and thermal managing applications due to their high latent heats [1]. They have the ability to absorb significant amounts of energy from their surroundings when they melt while remaining at a relatively constant temperature; similarly, when the transition is reversed the energy is released as the material crystallizes [2]. The absorbed or released energy can be used to cool or heat any system where the PCM is incorporated. PCMs find applications in a wide range of fields including buildings, where they are added to walls to reduce temperature fluctuations during the day that result in high heating and cooling demands [3]. Textiles [4], electronics [5], and heat exchangers [6] are also found among the different systems where PCMs are commonly used.

Since PCMs are required to transition from the solid to the liquid state to perform their task, they need to be contained to avoid their leakage during the liquid phase [7]. The two most popular methods used for PCM containment are encapsulation and shape stabilization. In the former, PCMs are enclosed within a structure that provides a physical barrier between the PCM and the outside; Usually, the size of the containment structure is below 1000 μm (microencapsulation) [8] but PCMs have also been packed in larger encasements such as capsules of a few millimeters in diameter [9] and aluminum panels as wide as 45 cm (macroencapsulation) [10], [11]. On the other hand, in shape stabilization the PCM is contained in the matrix of generally porous materials by capillary forces [12].

Ideally, in order to use a material as a PCM it should exhibit certain characteristics being the most important the following ones: a melting point in the practical range of operation, high latent heat per unit volume, a high thermal conductivity, no supercooling and long-term chemical stability [13]; however, most substances do not fully meet this criteria. Phase change materials can be classified according to their chemical composition in metals, inorganic and organic [7]. Metals and metal alloys comprise the least popular type of PCMs, primary due to their high densities and low latent heats of fusion [7]. Inorganic PCMs include salt and salt hydrates which are mostly used when extremely high melting temperatures are required. Other than that, their application is limited due to their chemical instability, corrosive nature, and supercooling problems [7], [14]. The most

commonly used PCMs are the organic ones which are composed mainly by paraffins and the fatty acids family [15]. This type of PCM are generally preferred since they are unexpensive, easy to work with and can be mixed together to obtain specific melting temperatures [7], [15]. Additionally, they present many other advantages including high latent heats, narrow operating temperature range, stability over thermal cycling, and compatibility with a wide range of materials without corroding or attacking them [3]. However, the main disadvantage of organics PCM is their low thermal conductivity, typically ranging from 0.1 to 0.7 W/m K [16].

Among organic PCMs, paraffins obtained as byproducts of petroleum refining are the most popularly used in the market today [17], mainly due to their low cost and their wide variety of substances with different melting points [18]. In order to find renewable alternatives that are less polluting to the environment, several authors have suggested the obtention of PCMs from natural sources including animal fats [19], oils [20] and marine microalgae [21]. For instance, Ravotti et al. [17] studied the potential of esters derived from different carboxylic acids commonly found in fats and oils as PCMs. They determined these materials exhibit high enthalpies (190 J/g) with melting points in the 20 °C – 50 °C range making them potential candidates for low-medium temperature applications. Similarly, Kenar et al. [22] analyze the thermal properties of different oleochemical carbonates that can be obtained from renewably derived fatty alcohols; these materials exhibited melting points and latent heats ranging from -2.2 °C to 51.6 °C, and 144 to 229 J/g, respectively. Even when these biobased alternatives have the potential to replace petroleum-based paraffins, they require the hydrolyzation of fats and oils to obtain mixtures of fatty acids that need to be subsequently fractionated, purified and derivatized to be used as PCMs [22]. Costs associated to these processes make it difficult for renewably based PCMs to compete with unexpensive paraffins available in the market.

In order to simplify the production of biobased PCMs and make them more affordable, the first chapter of this document reviews a new approach to obtain these substances from natural oils without the need for hydrolysis nor fractionation. Mixtures of fatty acid amides (FAAms) with high latent heats (up to 140 J/g) and melting temperatures ranging from 7.8 °C to 61.7 °C can be obtained from commercially available vegetable oils by direct amidation with different alkyl amines. A thorough chemical and thermal characterization of these materials was conducted, confirming their full conversion from triglycerides to FAAms and their potential for PCM

applications. Analysis of different green chemistry metrics showed promising results even when the production process had not been optimized. Due to the simplicity and mild conditions of the synthesis reaction, the method here presented could be easily adapted for the industrial production of unexpensive biobased PCMs.

Since PCMs need to be contained before they can be incorporated in any system, the second chapter of this document is dedicated to the encapsulation of biobased FAAs in core/shell capsules using UV-curable resins and a coaxial needle. The stability of the generation process along with the capsules' size and PCM core content were studied as a function of flow rates. The transition temperature, latent heats and thermal stability of the capsules were assessed through DSC and TGA analysis. Results show that this method can be successfully used to encapsulate biobased FAAs and that the thermal properties of these materials remain unchanged after encapsulation, making them suitable for PCM applications.

The third and last chapter of this document is focused on the implementation of PCM technology in a very specific field: asphalt pavements. Due to binder's viscoelastic behavior, asphalt performance changes greatly with temperature variations which constitutes an important problem especially in regions subject to seasons or abrupt changes in temperature throughout the day [23]. At high temperatures, the binder's viscosity decreases along with the adhesion among aggregates, lowering its stiffness and making it prone to large permanent deformation under repeated loading, a distress known as asphalt rutting [23], [24]. Conversely, at low temperatures, the binder undergoes volumetric changes that are restricted by the base layers and can induce tensile stresses in the pavement, resulting in another distress denominated low-temperature cracking [25]. The use of phase change materials could help regulate the pavement's temperature and keep it from reaching the high and low temperatures at which these temperature-related distresses take place.

Research on the incorporation of PCMs in asphalt has been previously reported [26]–[28], and while it has proven that these materials are effective at regulating the temperature of the system, their incorporation had detrimental effects on the pavement's mechanical properties [26], [29], preventing this technology from being implemented. Often, this weakening effect is caused by the breakage of capsules which are not sufficiently strong and released the PCM material to the

pavement. Another problem commonly encountered is the low thermal conductivity of the encapsulated PCMs, which can counteract their heating or cooling effect [30]. The work here documented proposes to address these issues by using mechanically strong commercial PCM capsules with high thermal stability and large surface area. The first stage of this investigation consisted in the thermal and mechanical characterization of the capsules to assess their suitability for asphalt applications. The second stage studied the incorporation of the PCM microcapsules in the pavement and their temperature regulating effect along with its impact on the dynamic modulus of the asphalt mixtures.

2. SYNTHESIS AND CHARACTERIZATION OF FATTY ACID AMIDES FROM COMMERCIAL VEGETABLE OILS AND PRIMARY ALKYL AMINES FOR PHASE CHANGE MATERIAL (PCM) APPLICATIONS

All lab-work in this chapter was performed by Daniela Betancourt. All analysis and writing was performed by Daniela Betancourt with guidance by Dr. Carlos Martinez and Dr. Jeffrey Youngblood.

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2.1 Introduction

As the world looks into reducing CO₂ emissions and using energy more efficiently, the use of phase change materials (PCMs) has become popular. PCMs absorb significant amounts of energy when they melt and release it back to their surroundings once they solidify[7]. This feature makes them excellent candidates for applications where thermal energy storage is desired, or the temperature of a certain system needs to be regulated. Perhaps the most widely known use of PCM is in the construction industry[31], [32] but these materials also find applications in other fields including textiles[4] and electronics[5], and research is being conducted to expand their applications to solar energy systems[33], heat exchangers[6] and road materials[8], [9].

PCMs can be classified as organic or inorganic, with the former the most used due to their high thermal cycling stability, low degree of supercooling, non-corrosiveness, and low cost[34]. However, these are generally derived from petroleum. To reduce their environmental effect, some efforts have been done to make bio-based versions of organic phase change materials. For instance, Suppes et al. [35] investigated FAEs derived from natural oils and their potential use as PCMs. While some of the FAE mixtures studied exhibited high heats of fusion (up to 181 J/g) and single transitions, most mixtures of FAEs from different fatty acids exhibited at least two peaks, making them less appealing candidates as PCMs. This investigation[35] concluded that mixtures exhibiting single transitions are not found naturally in any large-volume oil feedstocks and FAEs need to be separated into highly pure single acid derivatives for them to perform well as PCMs. In

other words, only a small fraction of the feedstocks would be useful, making the production of these biobased PCMs non-profitable and preventing them from reaching the market.

Although not popular, other fatty acid derivatives such as amides can exhibit thermal properties suitable to be used as PCMs. That is the case for acetamide, which has a latent heat of 263 kJ/kg and a melting temperature of 82 °C[36], an ideal candidate for applications at high temperatures. Some of the advantages that amides offer over FAEs include more stability and higher resistance to hydrolysis and other degradation mechanisms[37]. Just as seen for FAEs, fatty acid amides (FAAms) can also be derived from natural sources such as oils and fats. Furthermore, due to similarities in their chemical structures, some of their mixtures could exhibit high latent heats and melt over narrow ranges of temperature. Nonetheless, despite their potential, little previous research exists on the potential of these biobased materials for PCM applications.

The present work investigated the synthesis and characterization of biobased FAAms obtained by direct amidation of different vegetable oils with primary alkyl amines. The effect of amide length on the thermal properties of the resulting FAAms were studied through DSC and TGA. Results obtained show that some FAAms exhibited high latent heats (up to 141 J/g) and transitions over narrow temperature ranges. Additionally, their transition temperatures can be tailored to meet a temperature range by changing the precursor amine or oil. Overall, the results verify that FAAms are a promising alternative to paraffins and FAEs for PCM applications.

2.2 Experimental Section

2.2.1 Materials

Butylamine (99.5%), dodecylamine (98%), hexadecylamine (synthesis grade) and DABCO (1,4-diazabicyclo [2.2.2] octane) were all purchased from Sigma-Aldrich. Octylamine ($\geq 99\%$) was acquired from Alfa Aesar. Ethyl alcohol (200 Proof, anhydrous) was ordered from Decon Labs, Inc. Corn oil (food grade) and sunflower oil (food grade) were bought from Kroger, Inc., while palm oil (food grade) was purchased from Essential Depot. All the chemicals were used without further purification. All the water used was deionized and purified with a Barnstead Nanopure system (Thermo Scientific).

Oils are typically a combination of different triglycerides which are esters that consist of a glycerol molecule bound to three fatty acid molecules[38]. The specific fatty acid composition of the triglycerides in the oils used in this work was initially unknown, however, compositions found in literature are shown in Table 2.1 and were used as a reference to estimate the molecular weight of the oils and resulting fatty acid amides.

Table 2.1 Fatty acids contents for corn oil, sunflower oil and palm oil [39]–[41]

Oil	Fatty acid content (wt.%)						
	Literature values				Experimental values		
	Saturated		Unsaturated		Saturated	Unsaturated	
	C16:0	C18:0	C18:1	C18:2	C16:0 + C18:0	C18:1	C18:2
Corn oil	12.7	2	27.5	53.2	15	30.2	54.8
Sunflower oil	3.2	4.4	83.3	7	7.6	73.5	18.9
Palm oil	42.7	4.6	39.4	10.6	55.4	35.9	8.7

Palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), and linoleic acid (C18:2).

2.2.2 Synthesis of the FAAs.

All fatty acid amides were synthesized by reacting 4.0 grams of oil (~14 mmol) with 3 times molar excess amine (~126 mmol) and 20 mg of DABCO (~0.2 mmol). The reaction was carried out at 60 °C during 72 h with magnetic stirring. The purification step varied depending on the amine used during synthesis; for FAAs synthesized from butylamine or octylamine, the product was rinsed twice with deionized water and recovered using a separatory funnel. Lastly, the product was subjected to high vacuum until the pressure stabilized (approximately at 300 mTorr) to evaporate any remaining water and unreacted amine. In the case of FAAs synthesized from dodecylamine or hexadecylamine, the product was dissolved in ethanol (20 ml/g), recrystallized at –10 °C and 0 °C, respectively, and vacuum filtered to remove the ethanol with the unreacted amine and byproducts. This process was repeated twice. Next, the purified product was dried in a vacuum oven at 100 °C for 2 hours to remove any remaining ethanol.

2.2.3 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FT-IR)

The chemical composition of the obtained FAAMs was analyzed through FT-IR using an ATR accessory with a Spectrum Q100 spectrometer (Perkin Elmer). Each analysis was conducted in a 4000-600 cm^{-1} wavelength range under 10 scans. The background signal was subtracted, and the baseline was flattened for all the spectra.

2.2.4 ^1H and ^{13}C Nuclear Magnetic Resonance (^1H and ^{13}C NMR)

NMR analysis was also conducted to further study the chemical composition of the FAAMs. Each FAAM was dissolved in deuterated-chloroform and analyzed using a Bruker AV-III-400-HD spectrometer. The instrument is equipped with a 5 mm BBFO Z-gradient probe. Analysis was conducted at 400 Hz, and 8 and 512 scans for ^1H and ^{13}C , respectively.

2.2.5 Differential scanning calorimetry (DSC)

Melting and crystallization temperatures along with latent heats for both transitions were determined using Q2000 DSC analyzer (TA Instruments). Heating and cooling rates were 10 $^{\circ}\text{C}/\text{min}$ and analysis was conducted over a $-100\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ temperature range in a nitrogen atmosphere.

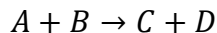
2.2.6 Thermogravimetric Analysis (TGA)

Thermal stability of the FAAMs was assessed using a 50Q thermogravimetric analyzer (TA Instruments). Each sample was ramped at 15 $^{\circ}\text{C}/\text{min}$ from room temperature to $600\text{ }^{\circ}\text{C}$ in a nitrogen atmosphere.

2.2.7 Green chemistry metrics

The sustainability of the synthesis process was assessed using different metrics widely accepted in the scientific community such as atom economy (AE), the environmental factor or E factor (EF) and the EcoScale [42], [43]. The AE measures the efficiency of the reaction in terms of how much of the reactants are incorporated into the desired product. This parameter is

determined by dividing the molecular weight of the desired product by the sum of the molecular weight of the reactants. For a generic stoichiometric chemical reaction where A and B are the reactants, C is the desired product and D is a byproduct, AE is given by Eq. 2.1 [43].



$$\% AE = \frac{MW_C}{MW_A + MW_B} \times 100 \quad \text{Equation. 2.1}$$

Where MW_C , MW_A and MW_B are the molecular weights of C, A and B, respectively. Note that the chemical equation needs to be properly balanced before calculating AE. This parameter finds its highest value (100%) in the ideal case where the totality of the reactants remains in the desired product (no byproducts are generated). Since %AE does not consider any other materials besides the reactants and does not contemplate the use of some of them in excess quantities, this metric is only a good indicator of the intrinsic waste associated with the reaction [43].

A much broader perspective can be obtained by calculating the E factor (EF), which accounts for the actual amount of reactants used in the organic preparation and other materials involved such as reagents and catalysts[44]. As a matter of fact, all substances used in the synthesis and generate waste should be considered in the E factor calculation. However, some ambiguity exists in the literature about the need to include water and any materials that can be recovered and/or recycled [43]–[45]. To avoid reporting any misleading results, two EF values proposed by Roschangar et al[45] were calculated in this study, the simple E factor (sEF) and the complete E factor (cEF). As seen in Eq. 2.2 [45], the former only considers the reactants and reagents used, leaving water and any solvents out of the calculation:

$$sEF = \frac{\Sigma m(\text{Reactants}) + \Sigma m(\text{Reagents}) - m(\text{Product})}{m(\text{Product})} \quad \text{Equation. 2.2}$$

Where m is the mass (in Kg) of each substance. Alternatively, the complete E Factor takes into account all the reactants, reagents, catalysts, solvents, and water used for both synthesis and workup/purification even when some of these could be partially or totally recovered or recycled [45]:

$$cEF = \frac{\Sigma m(\text{Reactants}) + \Sigma m(\text{Reagents}) + \Sigma m(\text{Solvents}) + \Sigma m(\text{Water}) - m(\text{Product})}{m(\text{Product})} \quad \text{Equation. 2.3}$$

Note that in both cases, the E factor is the ratio of waste generated respect to the amount of product obtained. Lower values of EF are preferred since they indicate a more efficient use of the materials, being 0 the ideal value (no waste). If reliable data exists about how much of the substances can be treated and/or recycled, these amounts can be subtracted from the numerator in Eq. 2.3 to determine the “true” E factor [45]. The cEF and the sEF then represent the upper and lower bounds of the amount of waste generated for any given synthesis, respectively.

Since metrics discussed so far only base the sustainability of the process on its intrinsic and extrinsic waste, Van Aken et al.[46] proposed the use of the EcoScale, a semiquantitative tool that takes into consideration other aspects of the organic preparation. The EcoScale goes from 0 to 100, where 100 represents the ideal green synthesis and lower values translate into less eco-friendly settings. This tool is based on a penalty system that subtract points from the preparation according to the yield %, price of reaction components, safety of the materials, experimental setup, reaction conditions and ease of workup and purification. The amount of points subtracted according to each category will not be discussed here since they can be found elsewhere [46].

2.3 Results and Discussion

2.3.1 FAAs synthesis

The synthesis method used in this work was previously reported by Bilyk et al. [47]. This reaction is carried out without the addition of organic solvents, in the presence of oxygen, at room pressure and with mild heating (60 °C). The reaction scheme is provided in Figure 2.1 The mechanism starts by the nucleophilic attack of the catalyst on the carbonyl of the glyceride, causing the displacement of the alkoxide and formation of the alcohol by addition of a proton from the media. Subsequent nucleophilic attack of the cationic quaternary amide by the primary alkyl amine displaces and reforms the catalyst. Since alkoxide is known to be a poor leaving group [47], 3 times molar excess amine and mild heating were used to increase the conversion rate. While this amount of excess is not feasible at scale, the purpose was to synthesize enough FAAs at a high enough purity to test thermal response, not to optimize the reaction. In this work, DABCO was chosen as catalyst due to its eco-friendly nature, low toxicity and high reactivity[48].

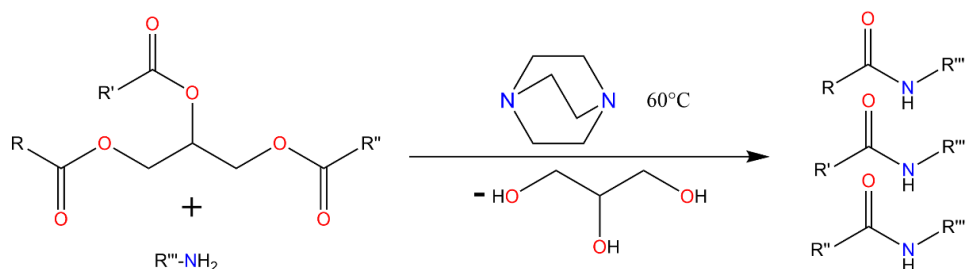


Figure 2.1 Scheme of the chemical reaction taking place in the synthesis of FAAM from vegetable oils and primary amines.

Three oils and four amines were used to synthesize a total of 12 different FAAMs. Due to differences in fatty acid composition (Table 2.1), FAAMs from each oil are expected to exhibit different thermal properties. The amines used had 4, 8, 12 and 16 carbon chains in their backbones, respectively. These amines were chosen to study the effect of hydrocarbon length in the transition temperatures and latent heats of the resulting amides. The purification step varied depending on the reactants used for synthesis since higher molecular weight amines (dodecylamine and hexadecylamine) are not water-soluble and water rinsing was not an effective approach for their removal. Conversely, ethanol rinsing was not suitable for FAAMs from amines with lower molecular weights (butylamine and octylamine) since the recrystallization temperatures of those were too low.

The molecular weight of the resulting FAAMs were estimated from the oil compositions presented in Table 2.1 and the molecular weight of the amines used. The theoretical weight of FAAMs were determined based on the amount of oil used for synthesis and full conversion of this reactant was assumed. Equation 2.4 was then used to calculate the yield of each reaction relative to the oil and results are listed on Table 2.2.

$$Yield (\%) = \frac{W_P}{W_T} \times 100 \quad \text{Equation 2.4}$$

Where W_P corresponds to the amount of FAAM recovered after purification and W_T is the theoretical amount of synthesized FAAM. The yield for each FAAM was above 70%, which is high considering that part of the product was lost during purification. It must be noted that in some cases partial solidification of the products was observed before the reaction ended. For this reason,

it is believed that the synthesis could have been completed in less than 72 h, especially for FAAs where longer amines were used. This theory is based on the work of Bilyk et al.[47] where shorter reaction times were observed for higher molecular weight amines. Nonetheless, the effect of reaction time on yield was not studied and is recommended for future work.

Table 2.2 Reaction yields after purification

Oil	Amine	Yield %
Corn oil	Butylamine	70
	Octylamine	85
	Dodecylamine	72
	Hexadecylamine	78
Sunflower oil	Butylamine	77
	Octylamine	81
	Dodecylamine	74
	Hexadecylamine	81
Palm oil	Butylamine	80
	Octylamine	83
	Dodecylamine	70
	Hexadecylamine	83

2.3.2 Chemical Characterization

Figure 2.2 shows the FTIR spectra of corn oil and its FAAs derivatives. In the corn oil spectrum, the stretching of the =C-H bonds (in linoleic and oleic segments) and the C-H bonds (in methylene groups) are observed around 3010 cm^{-1} and $2900\text{--}2800\text{ cm}^{-1}$, correspondently. Also, bands associated to the stretching of both the C=O and C-O bonds in the ester groups are found around 1744 cm^{-1} and 1160 cm^{-1} , respectively. Lastly, bands corresponding to the scissoring and rocking of methylene groups are observed at 1460 cm^{-1} and 722 cm^{-1} [41], [49].

The conversion of corn oil to FAAs is confirmed by the appearance of the N-H stretching band of the amide group at 3300 cm^{-1} . Also, the C=O stretching band shifted to lower frequencies (around 1630 cm^{-1} instead of 1744 cm^{-1}) due to the presence of the amide group. New bands are also found around 1550 cm^{-1} and 690 cm^{-1} , caused by N-H bending and N-H wagging, respectively. It can also be noted that the C-O stretching band of the ester group is not present in any spectra of the FAAs, confirming once more the successful synthesis of the amide.

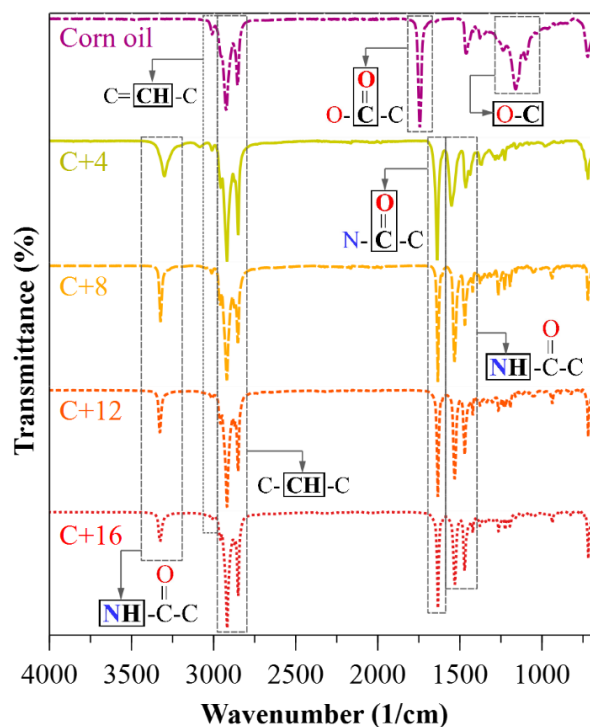


Figure 2.2 FT-IR spectra of pure corn oil and fatty acid amides (FAAMs) from: corn oil and butylamine (C+4), corn oil and octylamine (C+8), corn oil and dodecylamine (C+12) and corn oil and hexadecylamine (C+16).

Since all the FAAMs from corn oil have the same functional groups in their chemical structures, their spectra were very similar despite being synthesized from different amines. However, when longer amines were used, more methylene units were introduced into the chemical structure of the resulting FAAM, reducing the ratio of amide to methylene groups and decreasing the intensity of the signals of N–H, and C=O vibrations.

As seen in Figure 2.3 and Figure 2.4, the FT-IR spectra of both sunflower and palm oils show most of the characteristic bands observed for corn oil since they all have similar chemical structures. The only significant difference is the absence of the =C–H stretching band for palm oil ($\sim 3010\text{cm}^{-1}$), which is explained by the decreased amount of unsaturated bonds contained in its structure. Conversion of sunflower oil and palm oil to FAAMs was also evidenced from FTIR analysis.

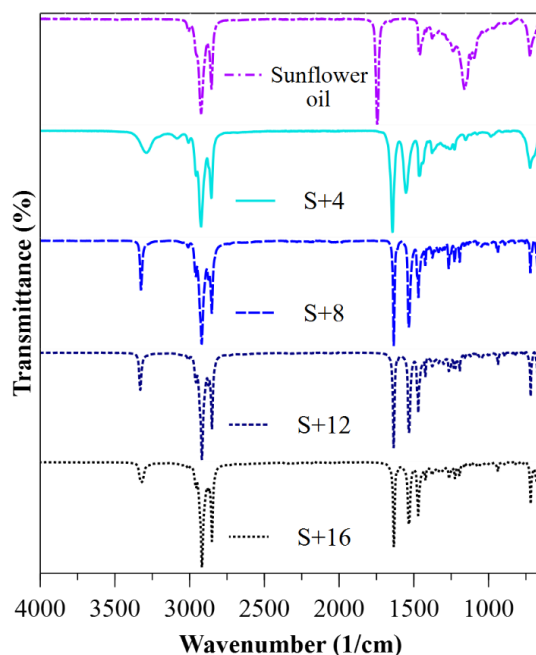


Figure 2.3 FT-IR spectra of sunflower oil and fatty acid amides (FAAMs) from: sunflower oil and butylamine (S+4), sunflower oil and octylamine (S+8), sunflower oil and dodecylamine (S+12) and sunflower oil and hexadecylamine (S+16).

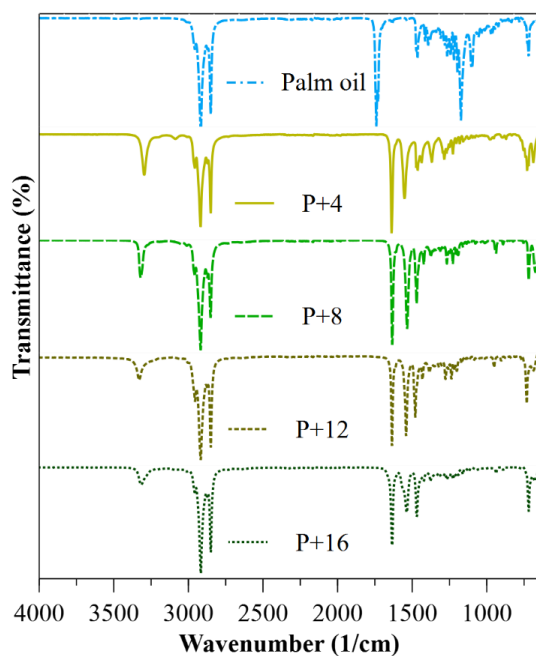


Figure 2.4 FT-IR spectra of palm oil and fatty acid amides (FAAMs) from: palm oil and butylamine (P+4), palm oil and octylamine (P+8), palm oil and dodecylamine (P+12) and palm oil and hexadecylamine (P+16).

^{13}C NMR spectra of pure core oil along with its FAAMs derivatives are shown in Figure 2.5. The peaks at 173 ppm corresponds to carbons in the carbonyl groups of the triglycerides. The series of peaks found in the 125-135 ppm region appear as a result of the carbon-carbon double bonds found in the oleic and linoleic segments. Peaks at 69 ppm and 62 ppm correspond to carbons forming the ester groups. The peak found around 34 ppm corresponds to carbons adjacent to the carbonyl group in the ester. Lastly, peaks found in the 32-10 ppm region correspond to methyl and methylene groups [50].

^{13}C NMR spectra of the FAAMs from corn oil and the amines are very similar and they show two main differences when compared to pure corn oil. First, no peaks in the 55-70 ppm region are found, indicating that no ester groups exist in the chemical structure of the synthesized FAAMs. Second, new peaks are found around 39 ppm and 37 ppm, which corresponds to carbon bonded to nitrogen atoms and carbon adjacent to carbonyl groups in the amide group, respectively. Also, the height of the peaks resulting from both carbon-carbon double bonds and the amide group decrease as the precursor amine gets longer, which results from the introduction of a larger number of methylene groups into the structure.

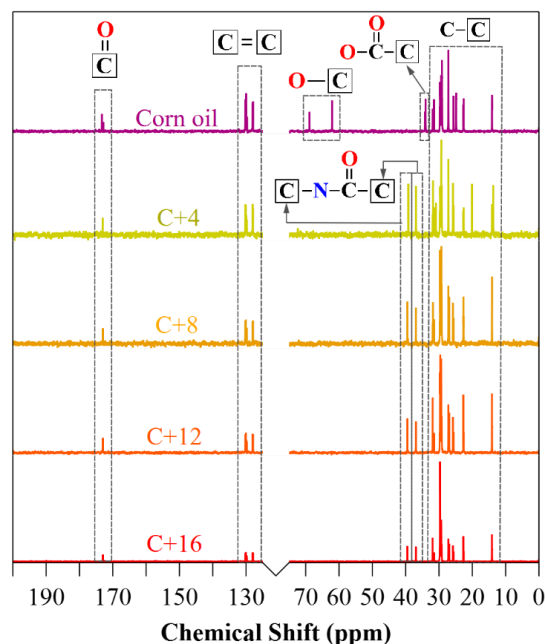


Figure 2.5 ^{13}C NMR spectra of corn oil and fatty acid amides from: corn oil and butylamine (C+4), corn oil and octylamine (C+8), corn oil and dodecylamine (C+12) and corn oil and hexadecylamine (C+16).

^{13}C NMR results for sunflower oil, palm oil and their FAAs derivatives are presented in Figure 2.7 and Table 2.7. Both spectra presented the same characteristic peaks observed for corn oil with some variations in their magnitudes which are attributed to differences in their triglyceride profiles (see Table 2.1). The spectra of FAAs from palm oil and sunflower oil corroborate once more the full conversion of the triglycerides into amides.

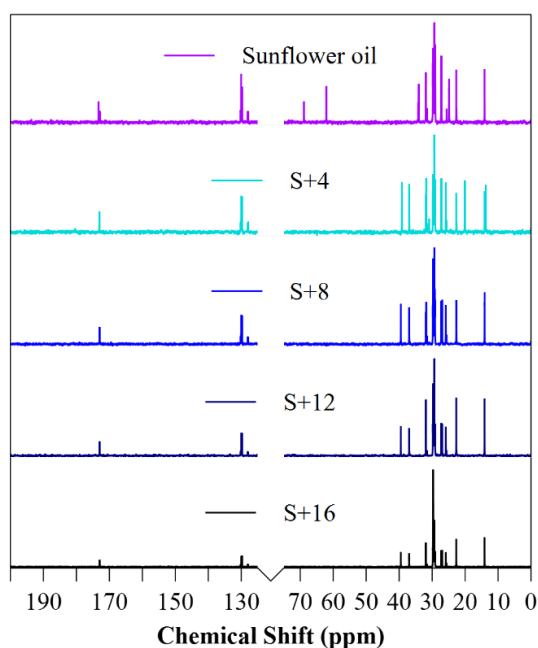


Figure 2.6 ^{13}C NMR spectra of sunflower oil and fatty acid amides from: sunflower oil and butylamine (S+4), sunflower oil and octylamine (S+8), sunflower oil and dodecylamine (S+12) and sunflower oil and hexadecylamine (S+16).

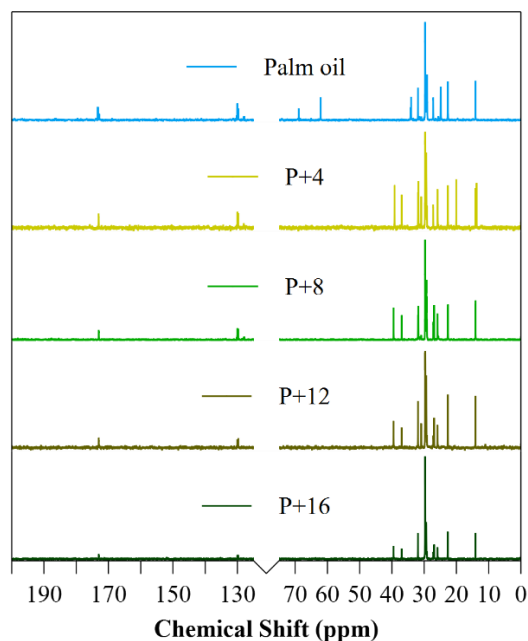


Figure 2.7 ^{13}C NMR spectra of palm oil and fatty acid amides from: palm oil and butylamine (P+4), palm oil and octylamine (P+8), palm oil and dodecylamine (P+12) and palm oil and hexadecylamine (P+16).

The proportion of the different acyl groups contained in corn, sunflower and palm oil was determined from their ^1H NMR spectra following the procedure described by Guillen et al[51]. Figure 2.8 shows the ^1H NMR spectra of these oils where the signals observed were numbered and assigned to hydrogen atoms in the different functional groups detailed in Table 2.3.

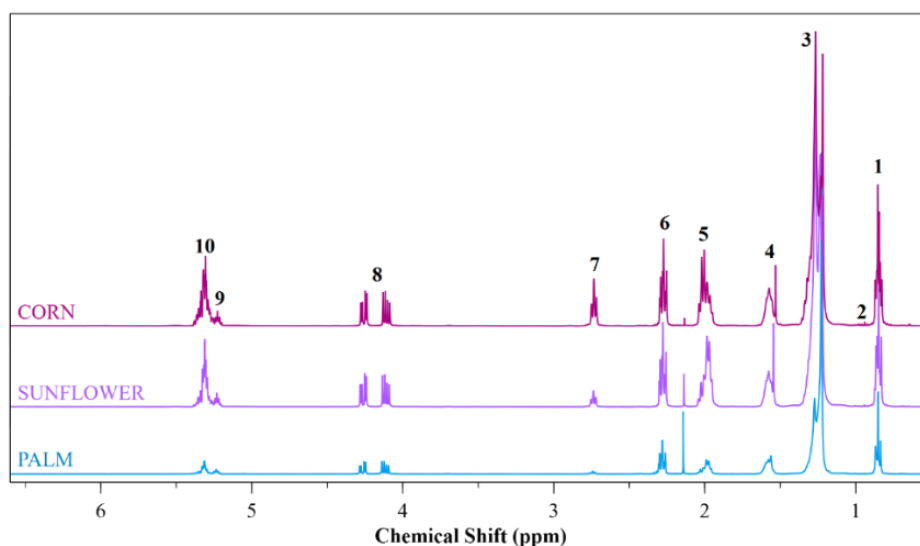


Figure 2.8 ^1H NMR spectra of corn, sunflower, and palm oil samples. Signal numbering corresponds to that in Table 2.3.

Table 2.3 Assignment of ^1H NMR signals to hydrogen atoms in different functional groups found in the triglyceride molecules of corn, sunflower and palm oil

Signal	Chemical shift [ppm]	Functional group	Segment of the triglyceride containing the functional group
1	0.80-0.87	$-\text{CH}_3$ groups	Saturated, oleic and linoleic acid segments
2	0.93-1.03	$-\text{CH}_3$ groups	Linolenic acid segments
3	1.21-1.36	$-\text{CH}_2$ groups in β positions or further respect to olefinic groups ($-\text{C}=\text{C}-$) and $-\text{CH}_2$ groups in γ positions or further respect to carbonyl groups ($-\text{C}=\text{O}$)	All acid segments
4	1.53-1.60	$-\text{CH}_2-$ in β positions respect to carbonyl groups ($-\text{C}=\text{O}$)	All acid segments
5	1.95-2.05	$-\text{CH}_2-$ in α positions respect to a single olefinic group ($-\text{C}=\text{C}-$)	Oleic, linoleic and linolenic acid segments
6	2.24-2.34	$-\text{CH}_2-$ in α positions respect to carbonyl groups ($-\text{C}=\text{O}$)	All acid segments
7	2.72-2.76	$-\text{CH}_2-$ in α positions respect to two olefinic groups ($-\text{C}=\text{C}-$)	Linoleic and linolenic acid segments
8	4.08-4.29	$-\text{CH}_2-$ groups	Glycerol segment
9	5.21-5.27	$-\text{CH}-$ groups	Glycerol segment
10	5.27-5.39	$-\text{CH}=\text{CH}-$ groups	Oleic, linoleic and linolenic acid segments

The signal numbers agree with those in Figure 2.8.

The magnitude of the signals in the spectra is proportional to the number of hydrogen atoms conforming each functional group. Since some of these functional groups are only present in certain fatty acid segments, their signals can be integrated to determine the fatty acid profile of the oils. For example, hydrogen atoms in methyl groups ($-\text{CH}_3$) will exhibit different chemical shifts depending on which acid segment they are part of. In the case of linolenic segments, this signal is observed around 0.93-1.03 ppm [51] (signal 2) while for all the other acid segments (saturated, oleic and linoleic) the signal is shifted downward to 0.83-0.93 ppm (signal 1 in Figure 2.8). It must be noted that all acid segments independently of their unsaturation degree contain three hydrogen atoms in their methyl groups, contributing equally to this group's signal. Hence, the fraction of linolenic acid segments (L_n) with respect to the total amount of acid segments can be determined by Eq. 2.5, where A_1 and A_2 are the areas under signals 1 and 2, respectively.

$$L_n = \frac{A_2}{A_1 + A_2} \quad \text{Equation 2.5}$$

As illustrated in Figure 2.8, signal 2 is not clearly observed for any of the oils studied. Guillen et al.[51] reported that this specific signal can only be detected when the fraction of linolenic acid segments is above 0.4%. The absence of signal 2 in these spectra indicates that the amount of linolenic acid segments in corn, sunflower and palm oils is very small or nonexistent. This result matches well with compositions found in literature and reported in Table 2.1.

Once the fraction of linolenic acid is known, the percentage of linoleic acid segments can be determined. Signal 7 corresponds to hydrogen atoms in *bis*-allylic positions or, in other words, hydrogen atoms in α positions respect to two olefinic groups. *Bis*-allylic protons are only found when two or more unsaturations exist, i.e., in linoleic and linolenic acid segments. Knowing that linolenic acid has two times the number of bis-allylic protons of linoleic acid, the fraction of linoleic acid segments (L) is given by:

$$L = \left(\frac{A7}{A6} \right) - 2Ln \quad \text{Equation 2.6}$$

Where A6 and A7 are the areas under signals 6 and 7, respectively. Note that signal 6 corresponds to protons in α positions respect to carbonyl groups (C=O), which are found in the same quantity for all acid segments independently of their degree of unsaturation. Then, the second term in Eq. 2.6 (A7/A6) represents the fraction of linolenic plus linoleic acid segments in the sample.

As shown in Table 2.3, signal 5 corresponds to hydrogen atoms in α positions respect to a single olefinic group, also known as allylic protons. Any acid segments with unsaturations contributes to this signal equally since all of them have 4 protons of this type in their structures. Knowing the fractions of linoleic (L) and linolenic acid (Ln), the percentage of oleic acid segments (O) can be determined using the following equation:

$$O = \left(\frac{A5}{2A6} \right) - (L + Ln) \quad \text{Equation 2.7}$$

Where A5 is the area under signal 5 in Figure 2.8. Note that in Eq. 2.7, A6 is multiplied by 2 since the number of allylic protons (4) is twice the number of protons in α -positions to carbonyl

groups (2) for each unsaturated acid segment contained in the sample. Finally, the percentage of saturated (S) acid segments can be calculated using Eq.2.8:

$$S = 1 - \left(\frac{A5}{2 A6} \right) \quad \text{Equation 2.8}$$

The area under each signal was determined by integrating the ^1H NMR spectra using the software TopSpin 3.6.2 by Bruker BioSpin. The obtained values are presented in Table 2.4 and were used along with Equations 2.5 to 2.8 to determine the fatty acid profile of the oils.

Table 2.4 Area of the signals of the ^1H NMR spectra of corn, sunflower and palm oils

Oil	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Corn oil	0.0889	0	0.5184	0.0686	0.1011	0.0595	0.0326	0.0402	0.0139	0.0768
Sunflower oil	0.0831	0	0.5618	0.0686	0.1044	0.0565	0.0107	0.0385	0.0110	0.0613
Palm oil	0.0829	0	0.6213	0.0673	0.0512	0.0574	0.005	0.0398	0.0100	0.0302

The experimentally determined fatty acid compositions of the oils are very similar to those reported in the literature (Table 2.1). Small differences exist which are to be expected considering factors such as sowing date, water regime, growing location and climate conditions have an influence on the oil composition [40], [52]. Also, small variations in the integration values of the ^1H NMR signals can significantly affect the fatty acid profile obtained, introducing an error in the measurements[53].

The composition of each FAAs was also determined to ensure that the initial proportion of the fatty acids was maintained after the synthesis reaction. The ^1H NMR spectra of the FAAs synthesized from corn, sunflower and palm oil are presented in Figure 2.9, Figure 2.10, Figure 2.11, respectively. The signals were numbered and assigned to the different hydrogens found in the samples according to Table 2.5.

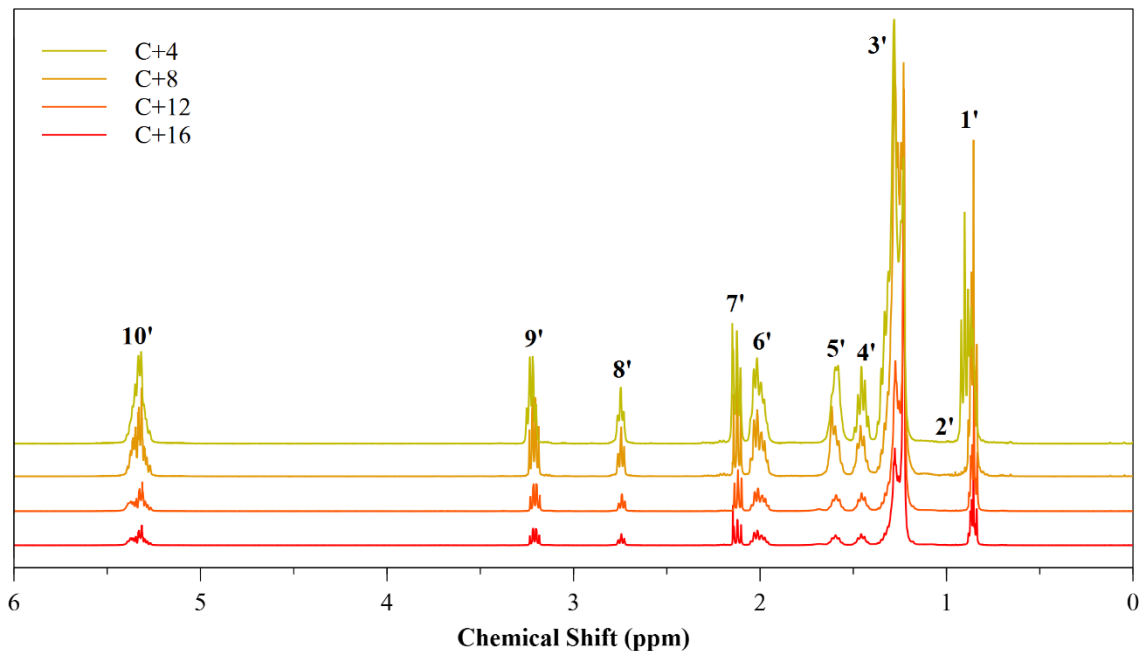


Figure 2.9 ^1H NMR spectra of FAAs synthesized from: corn oil and butylamine (C+4), corn oil and octylamine (C+8), corn oil and dodecylamine (C+12) and corn oil and hexadecylamine (C+16). Signal numbering corresponds to that in Table 2.5.

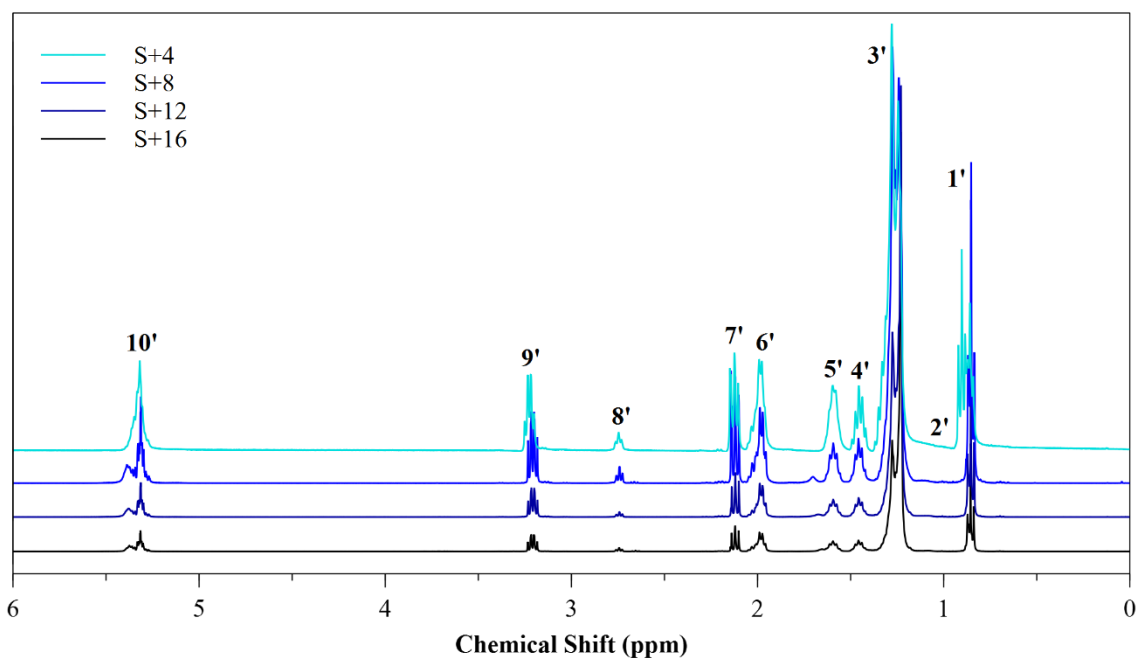


Figure 2.10 ^1H NMR spectra of FAAs synthesized from: sunflower oil and butylamine (S+4), sunflower oil and octylamine (S+8), sunflower oil and dodecylamine (S+12) and sunflower oil and hexadecylamine (S+16). Signal numbering corresponds to that in Table 2.5.

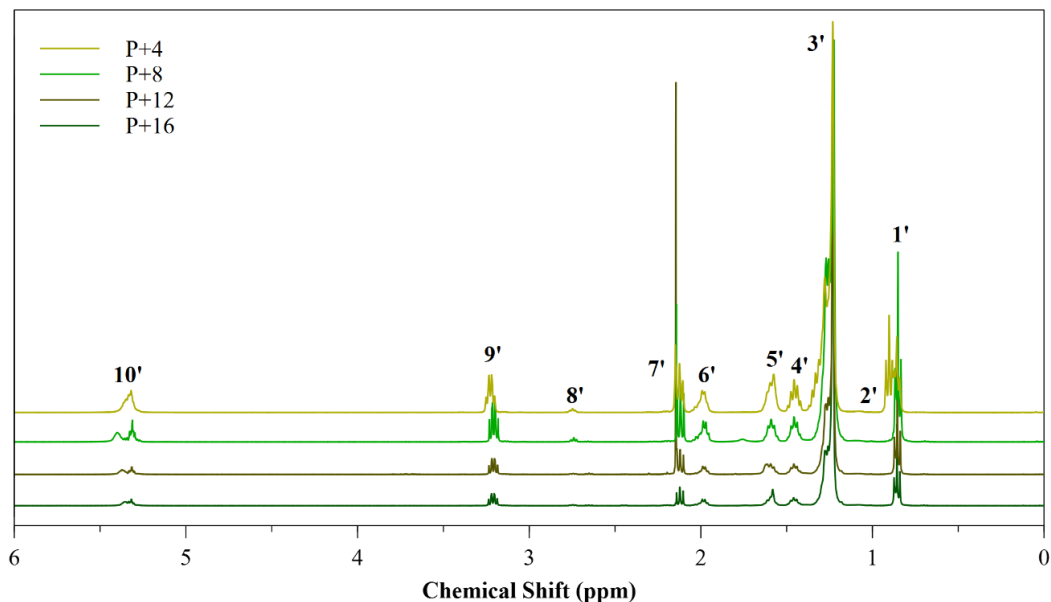


Figure 2.11 ^1H NMR spectra of FAAs synthesized from: sunflower oil and butylamine (S+4), sunflower oil and octylamine (S+8), sunflower oil and dodecylamine (S+12) and sunflower oil and hexadecylamine (S+16). Signal numbering corresponds to that in Table 2.5.

Table 2.5 Assignment of ^1H NMR signals to hydrogen atoms in different functional groups present in FAAs synthesized from corn, sunflower and palm oil

Signal	Chemical Shift [ppm]	Functional group	Segments containing the functional group
1'	0.83-0.92	$-\text{CH}_3$	Saturated, oleic and linolenic segments
2'	~ 1.09	$-\text{CH}_3$	Linolenic segments
3'	1.22-1.35	$-\text{CH}_2-$ in γ positions or further respect to double bonded carbons ($-\text{C}=\text{O}$ or $-\text{C}=\text{C}-$)	All segments
4'	1.41-1.49	$-\text{CH}_2-$ in β positions respect to olefinic groups ($-\text{C}=\text{C}-$)	Oleic, linoleic and linolenic segments
5'	1.55-1.62	$-\text{CH}_2-$ in β positions respect to amide group ($-\text{NH}-\text{C}=\text{O}$)	All segments
6'	1.95-2.00	$-\text{CH}_2-$ in α positions from olefinic groups ($-\text{C}=\text{C}-$)	Oleic, linoleic and linolenic segments
7'	2.09-2.14	$-\text{CH}_2-$ in α positions from carbonyl groups ($-\text{C}=\text{O}$)	All segments
8'	2.72-2.77	$-\text{CH}_2-$ in α positions respect to two olefinic groups ($-\text{C}=\text{C}-$)	Oleic, linoleic and linolenic segments
9'	3.18-3.25	$-\text{CH}_2-$ in α positions respect to $-\text{NH}-$ groups	All segments
10'	5.26-5.40	$-\text{CH}-$ in olefinic groups	Oleic, linoleic and linolenic segments

The signal numbers agree with those in Figure 2.9, Figure 2.10, Figure 2.11.

All the samples independently of their precursor amine or oil exhibited the same characteristic signals. Nonetheless, variations in their relative magnitudes were observed due to differences in their compositions. The fatty acid profile of each FAAM was determined after making some slight changes to the procedure described in the previous section. First, the fraction of linolenic segments (Ln) in the sample was calculated from the signals corresponding to methyl ($-CH_3$) groups in the same way it was done for the oils:

$$Ln = \frac{A_{2'}}{A_{1'} + A_{2'}} \quad \text{Equation 2.9}$$

Where $A_{1'}$ and $A_{2'}$ are the areas of signals 1' and 2', respectively (Figure 2.9, Figure 2.10, Figure 2.11). It must be noted that signal 2' is not observed in any of the spectra. This was to be expected since the precursor oils for these FAAMs do not have linolenic segments in their compositions. Next, the percentage of linoleic acid was computed by calculating the fraction of segments with 2 or more unsaturations and then subtracting the fraction of linolenic acid segments:

$$L = \left(\frac{A_{8'}}{A_{9'}} \right) - 2Ln \quad \text{Equation 2.10}$$

Where $A_{8'}$ and $A_{9'}$ are the areas under signals 8 and 9, respectively. Note that signal 8' corresponds to *bisallylic* protons, which are only found on segments with two or more unsaturations (linolenic and linoleic). Signal 9' corresponds to protons in α positions respect to N-H bonds, which are found in the same quantity for all acid segments independently of their degree of unsaturation. Then, second term in Eq. 2.10 ($A_{8'}/A_{9'}$) represents the fraction of bisallylic protons respect to all acid segments in the sample. Two times the fraction of linolenic segments is then subtracted since linolenic segments have twice as many bisallylic protons as their linoleic counterparts.

All unsaturated acid segments have 4 allylic protons in their structure; hence, once the fractions of linolenic and linoleic acid segments are known, the percentage of oleic acid (O) can be determined using Eq. 2.11:

$$O = \frac{A_{6'}}{2 A_{9'}} - (L + Ln) \quad \text{Equation 2.11}$$

Where $S_{6'}$ is the area under signal 6'. Note that $A_{6'}$ is divided by 2 since for any unsaturated segment there are twice as many allylic protons as there are α -protons respect to -NH- groups. Finally, the fraction of saturated segments (S) is calculated using Eq. 2.12:

$$S = 1 - \left(\frac{A_{6'}}{A_{9'}} \right) \quad \text{Equation 2.12}$$

The fatty acid profile of the synthesized FAAm was then determined from Eq. 2.9 to 2.12 and values in Table 2.6.

Table 2.6 Area of the signals of the ^1H NMR spectra of FAAMs synthesized from corn (C), sunflower (S) and palm oils (P) and butylamine (4), octylamine (8), dodecylamine (12) and hexadecylamine (16)

FAAm from:	A1'	A2'	A3'	A4'	A5'	A6'	A7'	A8'	A9'	A10'
C+4	1.6525	0.0000	5.4141	0.6001	0.8586	0.9637	0.7122	0.3159	0.5399	1.0000
C+8	0.1124	0.0000	0.5407	0.0416	0.0574	0.0622	0.0374	0.0189	0.0365	0.0661
C+12	1.0000	0.0000	6.2273	0.3674	0.3557	0.5486	0.3355	0.1660	0.3385	0.5832
C+16	0.0879	0.0000	0.6646	0.0320	0.0324	0.0499	0.0287	0.0157	0.0292	0.0532
S+4	0.1370	0.0000	0.5065	0.0489	0.0480	0.0845	0.0478	0.0095	0.0453	0.0725
S+8	0.1158	0.0000	0.5798	0.0431	0.0408	0.0709	0.0444	0.0075	0.0381	0.0597
S+12	1.0045	0.0000	6.5835	0.3734	0.3684	0.6084	0.3483	0.0466	0.3364	0.5000
S+16	0.0864	0.0000	0.6943	0.0339	0.0323	0.0523	0.0289	0.0049	0.0282	0.0438
P+4	2.9324	0.0000	12.0714	1.0906	1.6194	0.9230	1.4499	0.1151	1.0206	1.0000
P+8	0.1175	0.0000	0.6430	0.0428	0.0414	0.0347	0.0388	0.0036	0.0388	0.0394
P+12	0.0979	0.0000	0.6875	0.0365	0.0523	0.0235	0.0386	0.0016	0.0329	0.0293
P+16	0.0840	0.0000	0.7097	0.0304	0.0458	0.0231	0.0281	0.0017	0.0282	0.0259

Results presented in Table 2.7 show slight changes in the fatty acid profile of the FAAMs depending on the precursor amine used. Nonetheless, no trends that could indicate that any amine is more likely to react with a specific fatty acid segment are observed. Hence, differences in composition are believed to have been introduced during the purification process.

Table 2.7 Experimentally determined fatty acid composition (wt.%) of the FAAMs

FAAM from: Oil	Amine	Saturated C16:0 + C18:0	Unsaturated	
			C18:1	C18:2
Corn oil	Butylamine	10.8	30.7	58.5
	Octylamine	14.8	33.4	51.8
	Dodecylamine	18.2	32.0	49.0
	Hexadecylamine	14.6	30.7	54.7
Sunflower oil	Butylamine	6.7	72.3	21.0
	Octylamine	7.0	73.4	19.7
	Dodecylamine	9.6	76.6	13.8
	Hexadecylamine	7.3	75.4	17.4
Palm oil	Butylamine	54.8	33.9	11.3
	Octylamine	55.3	35.4	9.3
	Dodecylamine	64.3	30.9	4.9
	Hexadecylamine	59.0	34.9	6.0

2.3.3 Thermal characterization

Thermal properties of the as-purchased corn, sunflower and palm oils were assessed through DSC and their respective thermograms are presented in Figure 2.12. As it can be noted in the plot, each oil exhibited very different thermal profiles. In the case of corn oil, two broad overlapping peaks are observed for both crystallization and melting transitions. The presence of multiple peaks in oils is attributed to their complex composition consisting of a mixture of numerous triglycerides with different fatty acid segments. Generally, triglycerides with a higher content of saturated acids melt and crystallize at higher temperatures than triglycerides richer in the unsaturated versions [54].

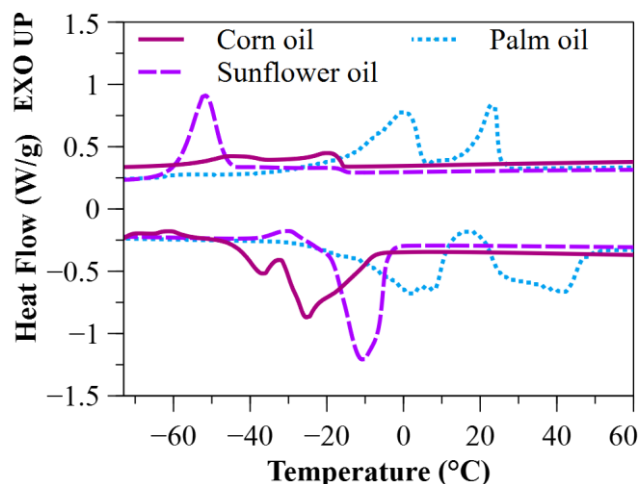


Figure 2.12 DSC diagram of corn, sunflower and palm oils.

The behavior observed for sunflower oil was quite different, exhibiting only one peak for both crystallization and melting transitions. This behavior has been reported before for highly unsaturated oils and indicates that the different triglycerides interact with each other during the cooling process and are able to co-crystallize into the same structure. This is possible due to the similarity of the triglyceride components, which for sunflower oil are mostly oleic and linoleic acid [55]. The small exothermic peak found right before the melting transition indicates that some recrystallization took place during the heating step of the experiment. Due to their polymorphic nature, triglycerides can form different crystalline structures depending on several factors including the nature of the fatty acid segments, the purity of the sample and the crystallization procedure[56]. It has been reported[55] that when oil samples are heated, some triglycerides can rearrange and recrystallize in more stable polymorphs which appears as an exotherm in the heating curve of the DSC thermogram.

For palm oil, two exotherms were obtained after cooling the sample from the melt. This was expected since approximately 45 wt.% of the sample is rich in unsaturated acids (linoleic and oleic) (refer to Table 2.1) that crystallize at lower temperatures, while the other triglycerides are mainly made of saturated segments (palmitic and stearic) and typically exhibit higher crystallization temperatures. The high content of both types of triglycerides and their marked difference in degree of saturation makes it unlikely for them to interact and co-crystallize into the same structure, hence producing more than one peak upon cooling.

Based on the previous discussion of their thermal properties none of the as-received oils exhibit the right characteristics to be used as PCMs. The latent heat of melting and crystallization for each of these oils is around 52-76 J/g (see Table 2.8), which is lower than those of commercial organic PCMs usually ranging between 86-340 kJ/kg [57]. Additionally, they are prone to exhibit polymorphism and they melt and crystallize over wide temperature ranges, making them unsuitable materials for thermal management applications.

Table 2.8 Latent heat of melting and crystallization for corn oil, sunflower oil, palm oil and their FAAM derivatives

Material	T _m (°C)	ΔH _{fusion} (kJ/kg)	T _c (°C)	ΔH _{crystallization} (kJ/kg)
Corn oil	-24.6 ± 0.3	52 ± 1	-22 ± 1	52 ± 1
C+4	7.8 ± 0.1	94 ± 3	2.6 ± 0.1	94.1 ± 0.2
C+8	25.6 ± 0.2	114.5 ± 0.8	20.6 ± 0.1	112 ± 1
C+12	46.0 ± 0.1	128.5 ± 0.6	38.0 ± 0.1	123 ± 1
C+16	59.8 ± 0.2	125.3 ± 0.9	53.5 ± 0.2	123.0 ± 0.9
Sunflower oil	-9.8 ± 0.2	61 ± 1	-44.8 ± 0.1	57.5 ± 0.4
S+4	21.5 ± 0.2	106 ± 1	10.5 ± 0.4	100 ± 1
S+8	30.1 ± 0.1	117.8 ± 0.7	22.0 ± 0.3	117.6 ± 0.2
S+12	49.3 ± 0.2	139.5 ± 0.9	37 ± 1	136.8 ± 0.9
S+16	61.7 ± 0.1	126.6 ± 0.3	55.8 ± 0.1	125.8 ± 0.2
Palm oil*	1.5 ± 0.1, 26.8 ± 0.6	76 ± 1	0.9 ± 0.1, 23.2 ± 0.6	66 ± 1
P+4*	19.2 ± 0.2, 58.3 ± 0.1	100 ± 2	13.6 ± 0.1, 51.5 ± 0.5	95.5 ± 0.9
P+8*	31.6 ± 0.1, 61.4 ± 0.1	136 ± 1	24.2 ± 0.1, 51.2 ± 0.1	134 ± 1
P+12*	47 ± 1, 69.4 ± 0.2	141 ± 3	40.1 ± 0.1, 64.0 ± 0.2	127 ± 2
P+16*	60.1±0.1, 83.1±0.1	133 ± 2	53.5 ± 0.3, 78.1 ± 0.2	132 ± 1

FAAMs from: C= corn oil, S= sunflower oil, P= palm oil, 4=butylamine, 8=octylamine, 12=dodecylamine, 16=hexadecylamine. *Two transitions are observed for both cooling and heating.

As it can be seen in Figure 2.13(a), the thermal properties of corn oil drastically change after reaction with any of the amines. The most significant difference is that some of the obtained FAAMs exhibit only one peak for each transition. Additionally, all FAAMs melt and solidify over narrow temperature ranges when compared to corn oil. The two FAAMs that did not show single peaks were the ones synthesized from butylamine and dodecylamine. However, the FAAM from dodecylamine shows one large peak overlapped with a small one upon cooling and the temperature

range in which this amide crystallizes might still be narrow enough to be considered a good candidate for PCM applications. Note that all DSC experiments were conducted at high cooling and heating rates (10 °C/min), which are known for broadening the peaks and shifting them to lower temperatures in cooling and to higher temperatures in melting [58]. This effect worsens in materials with poor thermal conductivities; hence it is possible that these FAAs exhibit sharper peaks at lower rates. However, the effect of cooling and heating rates on the thermal behavior of the FAAs is out of the scope of this work.

The appearance of single peaks in some corn oil derived FAAs is remarkable considering that these materials consist of a mixture of amides derived mostly from triglycerides of oleic, linoleic and palmitic acids. Results shown in Figure 2.13(a) suggest that even though these amides have different chemical structures, they interact with each other and either solidified into the same crystalline structure or into several crystalline structures with similar melting points. Possible factors that could be promoting co-crystallization is that despite their differences, these FAAs have similar numbers of methylene units in their structures (C16 or C18), are linear, and the ratio of $-CH_2$ groups to unsaturations and amide groups is large. Also, it is possible that hydrogen-bonding of the amide group diminishes the role that unsaturation differences play during crystallization, making the amides pack in similar ways. Nonetheless, it is believed that the ratio of $-CH_2$ groups to unsaturations and amide groups dominates over hydrogen bonding interactions. FAAs from butylamine which have the smaller number of methylene groups in their structures, were the only ones to exhibit three individual crystallization events upon cooling. A possible explanation is that unsaturations are not as “diluted” in the structure of these FAAs and play a more significant role, impeding co-crystallization.

Results also indicate that the proportion of saturated and unsaturated segments in the sample have the larger effect on co-crystallization. As mentioned before, FAAs from dodecylamine exhibited one main peak overlapped by a small one during the cooling segment, a different behavior than that observed for FAAs from octylamine and hexadecylamine. The presence of this small overlapping peak is believed to be caused by the slightly increased concentration of saturated acid segments in the sample, which could be promoting the formation of a new crystal structure at a higher temperature.

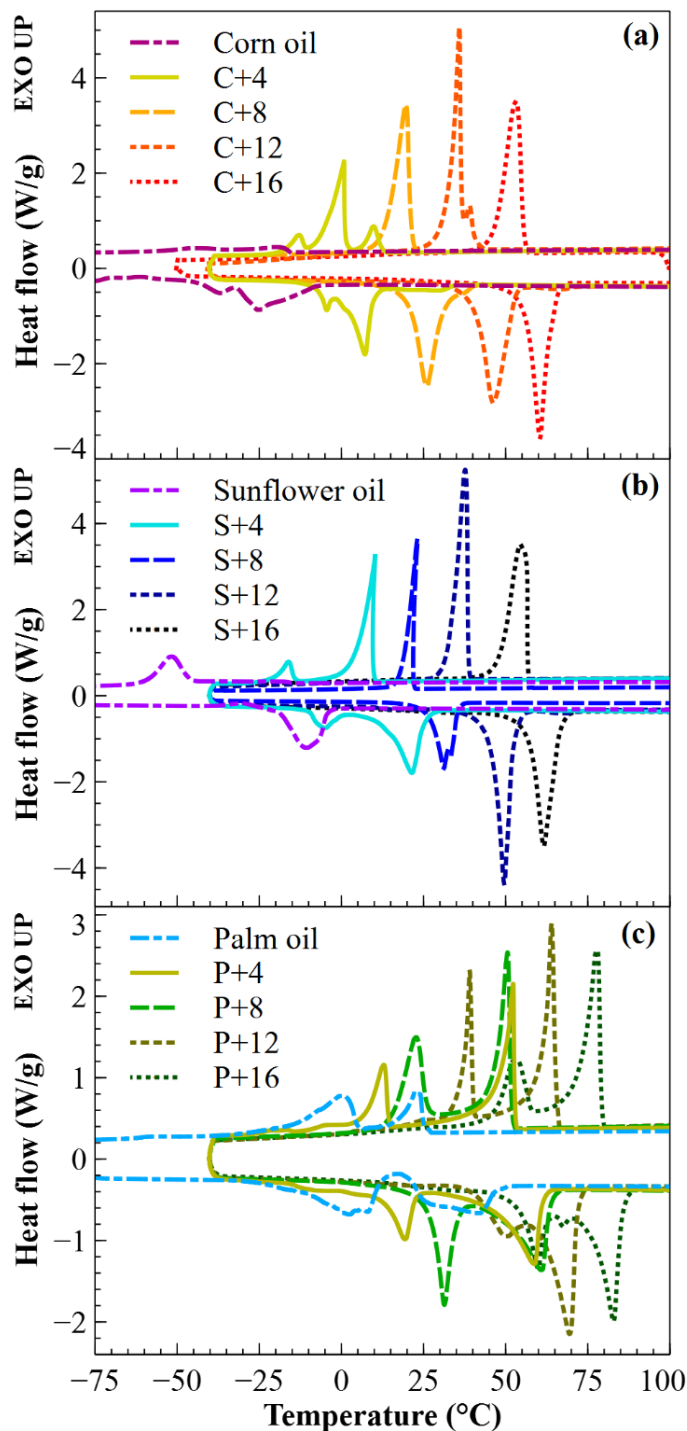


Figure 2.13 DSC diagram of (a) FAAMs from corn oil, (b) FAAMs from sunflower oil, and (c) FAAMs from palm oil. C= corn oil, S= sunflower oil, P= palm oil, 4=butylamine, 8=octylamine, 12=dodecylamine, 16=hexadecylamine.

Figure 2.13 (a) also shows that the melting point of the FAAM increases with the length of the amine used. This was expected since linear organic compounds of the same kind increase their

melting points with molecular weight [59]. The magnitude of the peaks (i.e., latent heat) also increases with the molecular weight of the amine, except for the case where hexadecylamine was used (refer to Table 2.8). Latent heat is an inherent property of the molecule and when a first-order transition is taking place is given by [60], [61]:

$$\Delta H = T\Delta S \quad \text{Equation 2.13}$$

where ΔH is the enthalpy or latent heat, T is the temperature and ΔS is the change of entropy associated with the transition. The latent heat of fusion of a substance is directly proportional to its melting point, which explains the continuous increase of latent heat observed for FAAs from butylamine, octylamine and dodecylamine. However, this is not true for FAAs from hexadecylamine which have the highest melting temperature of all the amides but a lower latent heat than C+12. It is believed that in this case, the entropy of fusion of the C+16 FAAs is significantly lower, and this surpasses the effect of having a higher melting point, ultimately causing an overall enthalpy reduction.

Thermal properties of FAAs from sunflower oil were also studied and results are presented in Figure 2.13 (b). The changes observed in sunflower oil after reaction with the amines are the same reported for corn oil. This was somewhat expected considering that both oils consist mostly of unsaturated fatty acids. It can be stated that increasing the number of methylene groups in the molecule promotes co-crystallization of the FAAs. The most relevant evidence of this is the change in thermal behavior of FAAs synthesized from octylamine, which showed one peak for crystallization and two overlapping peaks for melting in contrast to FAAs from butylamine that presented two distanced peaks in both cases.

The DSC diagrams of FAAs synthesized from palm oil are presented in Figure 2.13 (c). All the amides from palm oil exhibited two melting and crystallization peaks instead of one. It must be noted that FAAs from palm oil have high contents of both saturated and unsaturated acid segments (59% and 41%, respectively). It is possible that since both groups were present in similar proportions, segregation during cooling was promoted causing the saturated FAAs to crystallize at higher temperatures, followed later in the process by the unsaturated FAAs at lower temperatures. This segregation was not seen in FAAs from corn and sunflower oils since even

when these two groups also existed, their proportions were very different, with unsaturated amides constituting about 75-80 wt.% of the product. In these cases, since the content of saturated FAAs was small, they were “diluted” in the unsaturated amides and interacted with them during the cooling process instead of segregating, making it possible for them to co-crystallize into the same structures.

Except for exhibiting two peaks instead of one, FAAs from palm oil showed the same trends observed for those derived from corn and sunflower oils. Based on results presented in Table 2.8, the two transitions observed in the FAAs from palm oil grow closer by approximately 10 °C every time the length of the amine is increased by four methylene units starting at 4 (butylamine) and ending at 12 (dodecylamine). It is possible that as more $-\text{CH}_2$ units are introduced into the FAAs, the effect of unsaturations on crystallization becomes less significant and the crystalline structures formed are more similar, shortening the distance between the transitions. However, the effect of increasing the number of methylene units is limited considering that when it is increased from 12 to 16 (hexadecylamine), the distance between the two transitions remains unchanged (around 20 °C).

TGA results of the FAAs from the three different oils are shown in Figure 2.15. The diagrams show that the weight of all the FAAs remains constant at temperatures below 200 °C and that the evaporation temperature increases as the amine used for synthesis gets longer, independently of the precursor oil. The boiling point is directly proportional to molecular weight which explains why the FAAs have higher evaporation temperatures as their length is increased. The FAAs also have higher evaporation temperatures than other PCMs with similar melting points. For example, FAAs from corn oil and butylamine (C+4) which melt around 7 °C evaporate about 100 °C above methyl laurate, a PCM material with a melting point of 5 °C (Figure 2.15). This feature can be particularly advantageous in applications where the PCM material will be subjected to high temperatures.

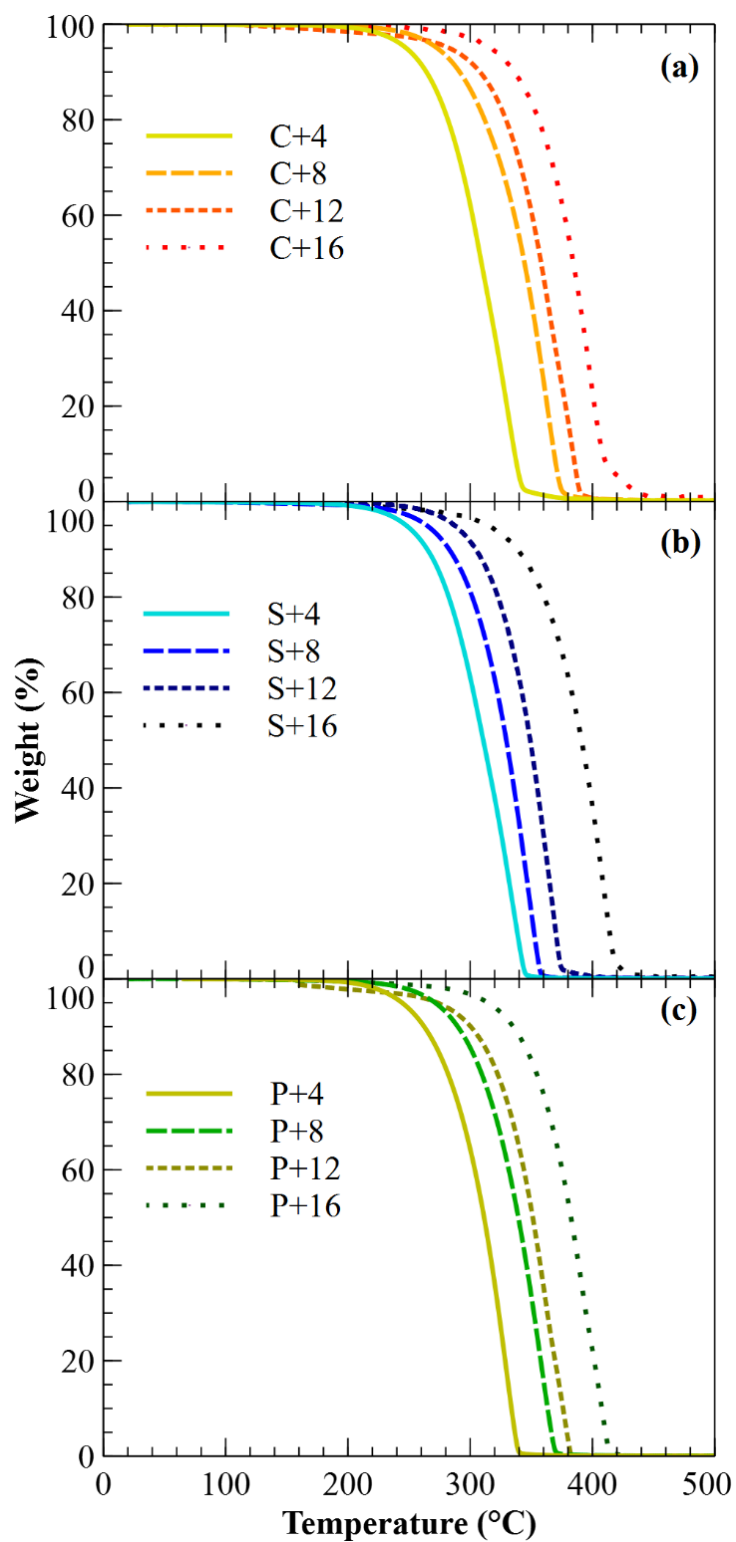


Figure 2.14 TGA diagram of FAAs. (a) FAAs from corn oil, (b) FAAs from sunflower oil, and (c) FAAs from palm oil. C= corn oil, S= sunflower oil, P= palm oil, 4=butylamine, 8=octylamine, 12=dodecylamine, 16=hexadecylamine.

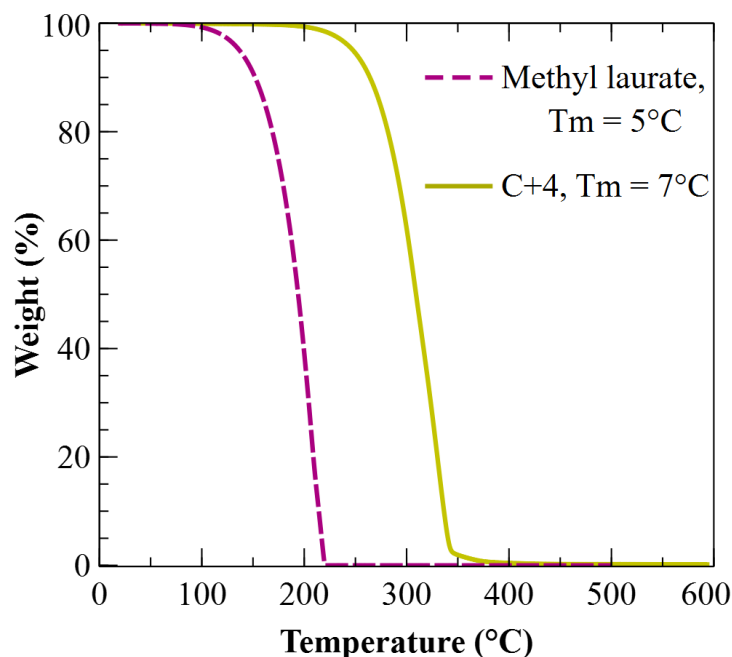


Figure 2.15 TGA diagram of methyl laurate and FAAMs from corn oil and butylamine (C+4).

2.3.4 Green chemistry metrics

Results of the atom economy, E factor and EcoScale are presented in Table 2.9. %AE results obtained are above 91.7% for all the FAAMs, which are high despite the fact their synthesis results from a substitution reaction where byproducts are generated. Fortunately, the molecular weight of glycerol is considerably lower than that of the FAAMs, which makes possible that these syntheses present such high values of %AE. Another fact that greatly contributed to the results obtained is that the chosen synthesis route consists of only one step. As mentioned before, high %AEs such as the ones obtained for the FAAMs are desired since they indicate low amounts of waste are associated to the reaction's mechanism. Selecting a synthesis route with a high %AE is the first step to design a green organic preparation [42]–[44].

Table 2.9 Green metrics results for each of the FAAMs

Product	%AE	sEF	cEF	EcoScale
C+4	91.70	1.22	44.18	69.00
C+8	92.80	1.06	36.20	76.50
C+12	93.60	1.06	44.82	72.00
C+16	94.30	0.67	41.30	80.00
S+4	91.70	1.00	40.03	72.50
S+8	92.80	1.17	38.26	74.50
S+12	93.60	1.03	43.86	73.00
S+16	94.30	0.61	39.43	81.50
P+4	91.70	0.95	38.42	74.00
P+8	92.80	1.12	37.27	75.50
P+12	93.60	1.16	46.49	71.00
P+16	94.30	0.59	38.51	82.50

As mentioned in the experimental section, two values of EF were determined to define the lower and upper bounds of the waste generated in the production of the FAAMs. Results obtained for the sEF were around 0.6-1.22. It must be noted that these values were significantly affected by two factors: the yield of each reaction and the use of excess reactants in large quantities. The decreased yields obtained for each FAAM are associated to product losses introduced during purification and not to reaction conversion, hence, they can be increased by improving the purification methodology. Additionally, reactants were used up to 3 times in excess to ensure the full conversion of the oils to amides. If these reactions were optimized, their sEF values could be lowered. For example, in the conservative case where the amount of reactants were decreased from 3 to 1.5 times excess and the yield were increased to 90%, the sEF would range from 0.34-0.47, a significant decrease from the current values.

The cEF results ranged from 36.2 to 46.49, a notable increase when compared to obtained sEF values. The main difference between these two parameters is that water and ethanol used in the purification steps were included in the calculation of cEF. However, it must be noted that due to differences in the boiling points of ethanol and the reactants and byproducts, the first can be recovered using a rotary evaporator. Recycling the ethanol will significantly lower the real EF of FAAMs synthesized from dodecylamine and hexadecylamine, bringing it to values close to those of sEFs.

The biobased PCMs here produced are a potential alternative to petroleum-derived paraffins, a non-renewable source widely known for having an important environmental impact. The environmental factor of paraffins was not found in the literature, nevertheless, values of EF of less than 0.1 have been reported for the oil refining industry [44]. One possible explanation for such a low EF is that virtually all the byproducts of gasoline production are commercialized for different applications and are not considered waste. An important factor that needs to be accounted for before drawing any conclusions is that EF values reported in this work correspond to a laboratory synthesis that has not been optimized. EF values found in the literature often correspond to highly optimized industrial settings that use sophisticated techniques for solvent recovery and water treatment. This results in waste minimization and translates into very low EF values. Therefore, it would be unfair to compare the EF of oil refining industry to the values here reported. Again, there is plenty of room for optimization of the FAAs production process including decreasing the amount of solvents used in the purification steps or using other purification methods that do not required the use of large amounts of solvents. These changes could drastically lower the EF of FAAs, allowing them to compete with paraffins. Regardless, unlike paraffins which are completely petroleum derived, and therefore depleting, FAAs are partially to totally renewable (depending on the source of amine), which is an inherent improvement in sustainability.

The EcoScale results ranged from 72.5 to 82.5. These high values result from the relative low toxicity of the reactants, low cost of the materials, simplicity of the experimental setup and high yields obtained. Note that these reactions could score even higher EcoScale values if their yields are increased. EcoScale results obtained are encouraging since they shed light on other aspects that contribute to the greenness of this preparation such as the use of inexpensive plant feedstocks, use of nontoxic biodegradable solvents for purification, mild reaction conditions and simplicity of the reaction.

2.4 Summary

The synthesis of FAAs from different commercial vegetable oils and primary alkyl-amines was carried out and their chemical and thermal properties were studied. Based on the obtained results these materials have the potential to be used as PCMs. Although the latent heats of these amides are in the low end for PCM applications (around 100-140 kJ/kg) they present a series of

advantages that might let them compete against other organic PCMs. First, they are derived from abundant and inexpensive plant feedstocks, contrary to most commercial organic PCMs which are petroleum derived. Additionally, their synthesis is simple, not requiring the use of inert atmospheres, high pressures, or toxic catalysts. These aspects were reflected by the high EcoScale values obtained for the FAAs, which ranged from 72.5 to 82.5. Another positive feature is that amides with different transition temperatures can be obtained depending on the amine chosen as a precursor, allowing for the design of a PCM for a specific application. Most importantly, even when these FAAs consist of a mixture of amides of different lengths and degree of unsaturations, in most cases they exhibited only one effective transition, eliminating the need for separation or fractionation after production. Even in the case of palm oil where fractionation would be necessary, it is expected to be an uncomplicated process since only two phases exist and their melting points are far apart from each other. All these factors have the potential to make the industrial production of the presented FAAs easy, bringing cheap biobased PCMs to the market.

3. ENCAPSULATION OF BIOBASED FATTY ACID AMIDES FOR PHASE CHANGE MATERIAL APPLICATIONS

All lab-work in this chapter was performed by Daniela Betancourt with assistance from Brandon Wells. All analysis was performed by Daniela Betancourt with assistance from Brandon Wells and guidance by Dr. Carlos Martinez. All writing was performed by Daniela Betancourt with guidance and editing by Dr. Carlos Martinez.

3.1 Introduction

Phase change materials or PCMs consist of substances with high latent heats that can be used for thermal storage or thermal managing applications [62]. They are generally classified according to their nature in organics, inorganics, and metals [7]. Among these, organic PCMs are the most popular and frequently used due to their low toxicity, high latent heats, thermal cycling stability, and broad range of transition temperatures [63]. Generally, commercially available organic PCMs consist of paraffins obtained as a byproduct from petroleum refining[18], [64]. This raises an environmental concern since not only these materials are not renewably sourced and petroleum extraction and refining processes are polluting to water, air, and soil [65].

In recent years, several studies [66] have been carried out to find bioderived PCM alternatives. Floros et al.[67] studied the thermal properties of commercially available biobased waxes such as carnauba wax, soy wax and beeswax as possible replacements for petroleum waxes; unfortunately these materials exhibit broad melting and crystallization transitions which makes them less than ideal for PCM applications. In a different approach, O'Neil et al.[21] evaluated the use of alkenones extracted from marine microalgae as PCMs. The resulting alkenones display tall and narrow melting peaks in their DSC thermograms with high latent heats (200 J/g) at a melting temperature of 65 °C. Even when these results are encouraging, the extraction of alkenones implicate the use of toxic solvents such as hexane and dichloromethane; also, the obtained alkenones can only replace paraffin PCMs with similar melting points.

Other researchers have successfully obtained esters [17], diesters [68], and diamides [69] with high latent heats from different fatty acids that are widely found in animal fats and vegetable oils. Nonetheless, for these materials to exhibit desirable PCM properties they need to be

synthesized from a single, pure carboxylic acid. Natural fats and oils then need to be hydrolyzed and fractionated into high purity single fatty acids before they can be used for PCM synthesis [70]. These extra steps have the potential to increase production costs and make it hard for these biobased PCMs to compete with the inexpensive paraffins available in the market.

With a simpler approach, Betancourt-Jimenez et. al [71] were able to obtain potential PCMs from grocery store vegetable oils without the need of fractionating the fatty acids. Fatty acid amides (FAAms) with high latent heats (up to 140 J/g) and single melting and crystallization events were produced by reacting primary alkyl amines with sunflower and corn oils without the use of toxic catalyst or solvents. The transition temperature of the resulting FAAms were tuned by changing the precursor oil and/or amine, making it possible to synthesize a variety of PCMs that can be used in different applications. Due to the simplicity of the synthesis process carried out at moderate temperatures (60 °C) and atmospheric pressure and the fact that natural oils can be used as purchased, FAAms have the prospect of becoming real contenders to petroleum derived PCMs. However, in order to promote their use, more studies need to be conducted to study if they are suitable for thermal management applications.

Before any material can be used as a PCM, they need to be contained so they do not leak into the system they are being incorporated to during their liquid phase. Different methods for containment exist including shape stabilization and encapsulation. The former involves the use of generally porous materials to retain the PCM by capillary forces even when it is in its molten state. In the latter, these materials are enclosed in core-shell structures where the shell acts as a barrier that isolates and protects the PCM from its surroundings and the environment. Typically, encapsulation methods use polymers for the shell which is formed around the PCM core through interfacial or suspension polymerization [72]. However, these processes produce small PCM capsules (generally with diameters below 100 μm) with broad size distributions and work only for specific polymer chemistries such as polyurea-urethane, melamine formaldehyde and urea formaldehyde, among others. Characterizing the properties and the shell structure of capsules obtained with these methods can be difficult due to their small size, a very important step when developing new encapsulated PCMs. For this reason, a simple method that allows to produce monodisperse capsules a few millimeters (3 mm) in diameter was used in this study to conduct the first efforts to encapsulate biobased FAAms for their use as PCMs. Polyester capsules were

successfully produced using a coaxial needle and UV curable resins and the influence of process parameters on capsule's size and core content will be discussed along with the capsules' thermal and mechanical properties. The use of UV-curable polyester resins has been reported for the encapsulation of pigments [73] and microsensors [74] but no literature was found for their use with PCMs. This fact motivated the selection of these materials for the production of FAAs capsules.

3.2 Experimental Section

3.2.1 Materials

Sunflower oil (food grade) was bought from Kroger, Inc. Octylamine ($\geq 99\%$) was purchased from Alfa Aesar. EBECRYL 1885 (radiation curable polyester resin) and EBECRYL P104 (radiation curable diacrylated amine resin) samples were provided by Allnex; TMPTMA (trimethylolpropane trimethacrylate, technical grade), 2-Hydroxy-2-Methylpropiophenone (97%), DABCO (1,4-diazabicyclo[2.2.2]octane), Sudan Blue II (98%) and Sudan red III (technical grade) were all purchased from Sigma Aldrich. A sample of Claytone-40 was provided by BYK USA INC. Finally, heavy mineral oil was acquired from VWR.

3.2.2 Synthesis of the FAAs

FAAs were synthesized from commercial edible sunflower oil and octylamine following the procedure developed by Betancourt-Jimenez et al. [71]. Briefly, sunflower oil was reacted with 3 times molar excess octylamine and 0.2 mmol of DABCO at 60 °C for 3 days. The product was rinsed three times with deionized water to remove excess reactants and byproducts. Last, to evaporate any traces of octylamine and water, the product was subjected to high vacuum until the pressure stabilized (at approximately 300 mTorr).

3.2.3 Formulation of the shell material

Polyester was selected to formulate the shell material due to its ability to rapidly cure under UV light exposure. Also, the large variety of commercially available monomers and resins makes it easy to combine them to prepare different formulations and tailor the properties of the cured product based on the desired application. The formulation of the resin used for the capsules' shell

consisted of UV-curable materials in the following proportions: 73 wt.% EBECRYL 1885, 10 wt.% EBECRYL P104, 10 wt.% TMPTMA, 5 wt.% 2-Hydroxy-2-Methylpropiophenone (will be referred as photoinitiator or PI from this point on) and 2 wt.% CLAYTONE-40 (rheology additive). Physical properties of these materials can be found in Table 3.1. The mixture was homogenized using a planetary centrifugal mixer (DAC 400.1 FVZ, Flacktek Inc.) for 10 minutes at 1500 rpm. Rheological measurements of the formulated resin with and without Claytone-40 were conducted using a Bohlin Gemini HR Nano Rheometer (Malvern Instruments). All measurements were conducted in continuous rotation using a cone and plate configuration; the apparent viscosity of the formulations was determined by performing a shear rate sweep (0.1 to 2000 s^{-1}) and their thixotropic properties were assessed by carrying out three interval thixotropy tests (3ITT) with 60 second intervals and low and high shear rates of 0.1 s^{-1} and 1000 s^{-1} , respectively.

Table 3.1 Physical properties of the materials in the shell formulation [75]–[79]

Property	EBECRYL 1885	EBECRYL P104	TMPTMA	Photo initiator	CLAYTONE-40
Dynamic viscosity at 25 °C, Pa·s	±34	0.007 – 0.013	-	-	-
Density, g/cm ³	1.19	1.01	1.06	1.08	1.80
Molecular weight, g/mol	1350	298	338.40	164.20	-
Young Modulus, MPa	18.3*	-	-	-	-

*when cured

3.2.4 Encapsulation

The process of making capsules via droplet dripping was chosen due to its simplicity and possibility to create capsules with reproducible properties (diameter and core content) to study the behavior of encapsulated FAAs for phase change materials applications. The set-up depicted in Figure 3.1 was used for the encapsulation of the PCM. In detail, a red dye (Sudan Red III, 2000 ppm) was added to the FAAs to change their color to and provide better visualization of the core during the generation process. The FAAs were later transferred to a 10 ml glass syringe (Hamilton Gastight, model 1010 TLL) which was heated by winding up a heating cord around it (Briskheat HTC451005) connected to a PID Temperature controller (AUBER SYL-2352). Heating

was necessary in order to keep the FAAs in the liquid state. The syringe was connected to PTFE tubing (1/16" inner diameter) and aluminum tape was used to attach the tubing to a heating tape (Briskheat BIH051020L). The temperatures of both the syringe and the tubing were kept between 70-75 °C during the experiments. Lastly, the other end of the tubing was connected to the inner channel of a coaxial needle (Ramehart 23-18 Custom) with outer needle diameters of 1.24 mm (outer) and 0.84 mm (inner) and inner needle diameters of 0.635 mm (outer) and 0.330 mm (inner). The shell fluid was transferred into a 20 ml stainless steel syringe (Cole-Parmer EW-74044) connected to PTFE tubing covered with aluminum tape to avoid exposing the resin to light. The other end of the tubing was then connected to the outer channel of the coaxial needle. Identical syringe pumps (Harvard Apparatus PHD 2000) were used to flow the FAAs and the polyester resin, respectively. Capsules were generated by ranging the core and shell flow rates from 2 ml/h – 7 ml/h and 3 ml/h – 6 ml/h, respectively. The capsules were collected in a graduated cylinder filled with heavy mineral oil at 50 °C and were cured as they descended through the fluid with two fiber optic broad spectrum light sources (X-Cite 120Q by Lumen Dynamics, wavelength 350-600 nm). The coaxial needle tip was placed 8 cm above the collecting oil surface while the lights were positioned 11 cm and 13 cm below it, respectively. Once cured, the capsules were removed from the oil and pat dried with paper towels.

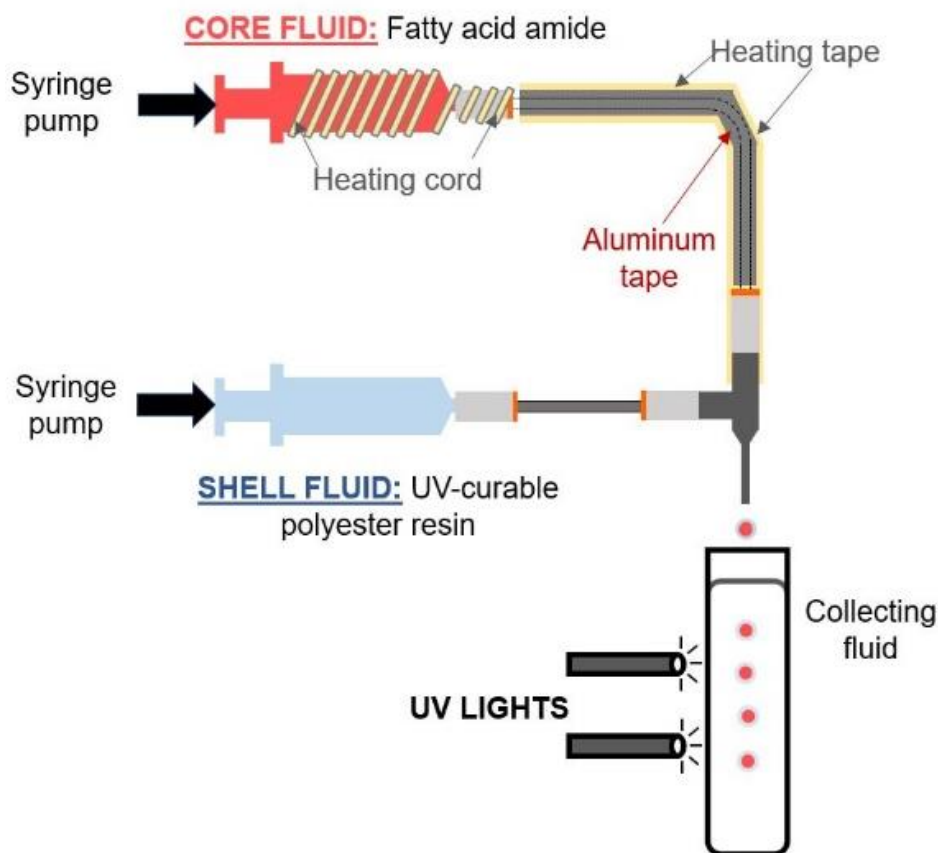


Figure 3.1 Experimental set-up for the generation of PCM-containing capsules.

3.2.5 Characterization methods

Capsule size and core percent

Digital photographs of the capsules were taken using a D3200 Nikon Camera with a Nikon AF-S Micro-Nikkor lens (105 mm 1:2.8 G ED VR). These images were processed with ImageJ to determine their size, core roundness and core volume percentage from the capsule's projected cross section following the procedures detailed in the Appendix A.

Thermal properties

A Q2000 DSC analyzer (TA Instruments) was used to determine melting and crystallization temperatures along with the latent heats of each transition. At least three capsules were tested for each parameter combination of interest to calculate average values with their respective standard deviation. Tests were conducted at cooling/heating rates of 5 °C/min in a nitrogen atmosphere.

The capsules' PCM content was calculated using data collected from DSC Analysis. First, the core weight percentage was determined from the capsules' latent heat values compared to those of the bulk FAAs. Next, the density of the cured polyester resin was measured from 1 cm x 1 cm x 2 mm bulk samples using the Archimedes density measuring method [80]. Conversely, the density of the liquid FAAs was determined using a Densito 3PX Density meter (Mettler Toledo). Once the densities of both the shell material and the FAAs were known, the weight percentages were converted to core volume percentages.

The thermal stability of the capsules was studied using a Q50 thermogravimetric analyzer (TA Instrument) by ramping the samples at 15 °C/min from room temperature to 600 °C in air.

Mechanical properties

The capsules' deformation and load at break in compression were measured using a laboratory-made micromechanical tester. 10 to 12 capsules generated with each parameter set of interest were tested to calculate average values with standard deviations. Compression tests were conducted at a strain rate of 50 $\mu\text{m/s}$ and pictures of the broken capsules' cross section were taken using a stereoscope (Meiji SMD-5TR) and a Basler camera (model: acA1920-155uc). Shell thickness measurements were obtained from the images using ImageJ.

3.3 Results and Discussion

3.3.1 Formulation of the shell material

Polyester was selected to formulate the shell material due to its ability to rapidly cure under UV light exposure. Also, the large variety of commercially available monomers and resins makes it easy to combine them to prepare different formulations and tailor the properties of the cured product based on the desired application. EBECRYL 1885 was selected as the main constituent of the formulation (73 wt.%) due to its high flexibility and excellent abrasion resistance. EBECRYL 1885 consists of an undiluted polyester acrylate oligomer with a theoretical molecular weight of 1350 g/mol [75] and its relatively high viscosity makes it difficult to flow through the coaxial needle used to generate the capsules. For this reason, two other components were added to the formulation: EBECRYL P104 (10 wt.%) and TMPTMA (10 wt.%). The former is composed of

diacrylated amines that not only helps reduce the viscosity but also provides a rapid UV cure response [76]. Likewise, the latter promotes a reduction in viscosity and was chosen due to its short structure and trifunctionality, which is expected to act as a crosslinker and increase the modulus of the final resin [81]. Last of all, 5 wt.% of 2-Hydroxy-2-Methylpropiophenone and 2 wt.% of CLAYTONE-40 were added to serve as photoinitiator and rheology modifier, respectively. CLAYTONE-40 is based on an organophilic phyllosilicate that promotes thixotropic flow behavior and was introduced in the formulation after some issues were encountered during the generation of capsules which will be discussed later.

Since the FAAMs had to be synthesized and purified, they were replaced by sunflower oil during the first encapsulation attempts to save material as it has similar viscosity and density to the sunflower oil derived FAAM. These trials were conducted at room temperature to tune and improve the experimental set-up and the formulation before moving on with the FAAMs. To help differentiate capsules containing sunflower oil, Sudan Blue (200 ppm) were added to the substance before encapsulation. The initial formulation (without CLAYTONE-40) was able to flow through the needle and form core-shell capsules, however, these capsules exhibited deformed and significantly off-centered cores (Figure 3.2.(a)). This is a result of the density difference between the core and the shell (0.86 g/cm^3 and 1.1 g/cm^3 , respectively), which causes the core to move upward due to buoyancy (creaming) and deforms the shell before the capsule is cured [82]. As can be seen in Figure 3.2.(b) these issues improved considerably after 2 wt.% CLAYTONE-40 was introduced in the formulation. To better understand the effect of this additive on the flow properties of the resin, rheological tests were performed and results are presented in Figure 3.2.

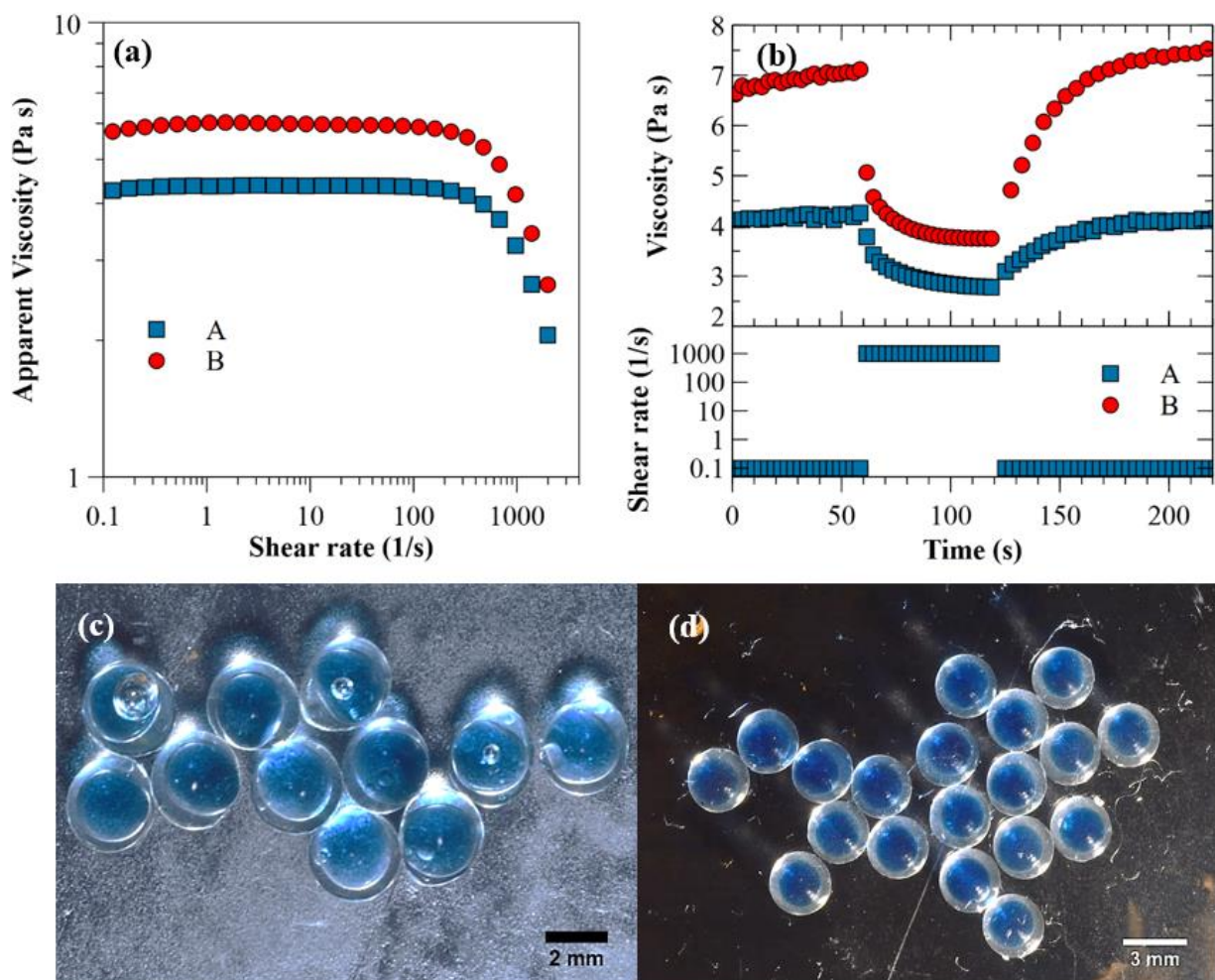


Figure 3.2 (a). Apparent viscosity as a function of shear rate, and (b) three interval thixotropy test for polyester formulations (A) without CLAYTONE-40, and (B) with 2 wt.% CLAYTONE-40; Sunflower oil capsules made using a polyester formulation (c) without CLAYTONE-40, (d) with 2 wt.% CLAYTONE-40.

Figure 3.2 (c) shows the resins behave as Newtonian fluids at low to moderate shear rates which is expected due to the low molecular weight of the formulations' components. However, at higher shear rates ($>400 \text{ s}^{-1}$) both formulations exhibit shear thinning behavior which is attributed to the chain alignment of polyester oligomers contained in EBECRYL 1885 [83]. The addition of CLAYTONE-40 does not change the viscosity-shear rate dependency, probably due to its low content; however, 2 wt.% is enough to cause an increase in viscosity ($\sim 47\%$) as a result of flow hindrance by the organoclay particles [84], [85]. Additionally, Figure 3.2(d) shows how the viscosity of both formulations decrease as a function of time when subjected to high shear rates and gradually recovers once the shear is reduced; nevertheless, this effect is significantly more

pronounced for the formulation containing CLAYTONE-40. As the formulation's components are mixed, the organoclay can experience two different processes: intercalation and exfoliation. During intercalation, the space among the phyllosilicate layers is filled with the polymer precursors causing the particles to swell. Conversely, exfoliation happens when these layers become completely detached from each other and are individually dispersed within the mixture. In either case, the resulting mixture contains highly anisotropic layered silicate particles or stacks of silicate layers, or most commonly, a combination of both [86]. The marked difference in how the viscosity of both formulations change is caused by the organoclay particles/platelets, which align when subjected to high shear rates reducing their flow hindrance effect [87]. As soon as the shear stress is removed or decreased, the particles return to their unaligned configuration and the viscosity recovers in time to its initial value. This enhancement on the resin's thixotropy is believed to aid in the formation of more uniform and centered capsules. The shell fluid is subjected to shear for prolonged times as it flows from the syringe to the needle tip which results in a lowered viscosity and a more uniform flow rate. Nonetheless, as the resin exits the needle and surrounds the core fluid it is no longer subjected to shear and the viscosity starts to recover. By the time the uncured capsule detaches from the needle's tip the viscosity of the shell has increased, slowing down the creaming of the core and allowing them to be more centered by the time the shell is cured (approximately 3 to 5 seconds after droplet detachment), which translates into more uniform capsules.

3.3.2 Encapsulation process

As mentioned before, the process of making capsules via droplet dripping was chosen due to its simplicity and possibility to create capsules with reproducible properties (diameter and core content). Additionally, if successful, the UV-curable polyester/FAAms system can be easily transitioned to industrial production. The FAAms selected for encapsulation have a melting point of approximately 30 °C, making it necessary to heat them in order to flow them through the tubing and the needle. Both the syringe and the tubing were heated well above the T_m of the FAAms (30 °C) due to 2 reasons: first, the set temperatures were those of the equipment's point of contact with the heating elements and not the fluid's, which is probably lower due to the poor thermal conductivity of PTFE and the high surface area of the tubing. Second, the needle was not heated,

and they core needed to be sufficiently hot so it would not cool and solidify before forming the capsule.

Since the available UV light sources were not intense enough to cure the capsules falling in air, they were collected in a high viscosity fluid to slow their fall and expose them to the UV for long enough to fully polymerize the shell. Heavy mineral oil was chosen as the collecting fluid due to its high molecular weight, so that a high viscosity even at 50 °C (~40 mPa.s) is attained; also, its lack of miscibility with the shell material ensured the capsules kept their spherical shape without any adverse interactions taking place between these two substances. The collecting oil was heated to avoid the core solidifying before the capsules were cured. The drawback of using a high viscosity fluid for collection is that the capsules' droplets deform significantly after they impact the oil-air interface. Hence, the UV lights had to be placed several centimeters below the oil's surface to give the capsules enough time to recover their spherical shape, which was promoted by the high interfacial tension between the shell and the mineral oil.

Capsules were made varying the flow rates of both the core and the shell. The shell flow rate was ranged from 3 ml to 6 ml; these limits were imposed by the capacity of the syringe pump which could not pump the shell uniformly through the needle below these values and would stall above them. The starting point for the core flow rate was 1 ml/h lower than that of the shell and was increased by 1 ml/h as long as core-shell capsules were still obtained. Figure 3.3 shows the stability of the generation process for the different parameter combinations tried. Whenever the core flow rate was the same or 1 ml/h below the shell's flow rate, the generation was mostly stable, meaning that at least 90% of the droplets dripped from the nozzle were successfully cured into core-shell capsules. However, when the rate of the core was higher than the shell's the process became sometimes unstable: approximately 25% of the droplets would release the core before they could be cured. Last, when the core flow rate was further increased most of the droplets (close to 60 %) would not have any FAAMs in the core by the time they were cured. The general trend observed is that the generation process became unstable when the core to shell flow rates were equal or higher than 4:3; Also, instability issues were aggravated for ratios higher than 7:6. An increased in core content translated into less resin surrounding it and higher buoyancy forces within the droplet, making it more likely for the core to break through the shell and be released to the collecting fluid. Added to this, it was noticed from visual inspection that the core is not always

centered within the droplet when it forms at the needle tip. It is hypothesized that temporary flow instabilities resulted in the shell being thinner in some areas of the droplet, decreasing their chance of survival when they impact the surface of the collecting oil. It is expected that this issue would play a bigger role as the core to shell ratio becomes larger, causing the generation process to be more unstable. Figure 3.4 shows how the capsules look after collection. In all the cases, they exhibited spherical shapes with slightly off-centered cores, which is attributed to the significant density difference between the core and the shell materials as seen in the work of Lee et al. [88].

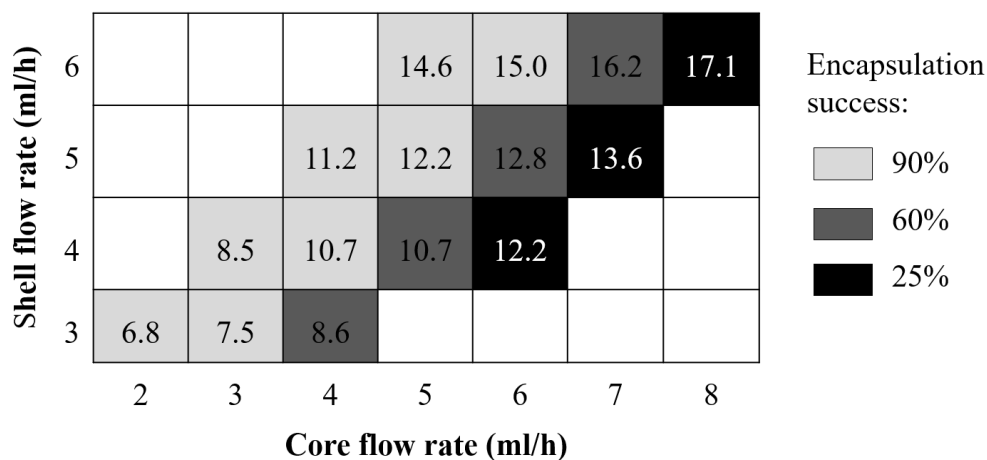


Figure 3.3 Stability of the generation process at different parameter combinations. Numbers in the cells indicate the production rate (in droplets per minute).



Figure 3.4 Capsules containing FAAMs generated with core and shell flow rates of 2 ml/h and 3 ml/h, respectively.

3.3.3 Capsule's size and core content

Image processing was chosen as a simple and fast method to analyze variations in the capsules' size, core content and shape for each parameter set tested. As shown in Table 3.2 all capsules exhibited outer diameters of approximately 3 mm and core roundness values around 0.96 (in a scale from 0 to 1, where 1 corresponds a mathematically perfect circle). Results then indicate that the size and shape of the resulting capsules seem to be independent from flow rates. This is explained by the fact that in a dripping setup like the one used in this work the outer diameter of the capsules only depend on the needle's diameter and the interfacial tension and density of the material being dripped as described by Equation 3.1:

$$D = \left(\frac{6d_o\sigma_o}{\rho g} \right)^{1/3} \quad \text{Equation 3.1}$$

Where D , d_o , σ_o , ρ represent the drop diameter dripping from the needle, the needle's outer diameter, the initial surface tension, the material's density, and the gravity constant, respectively [89]. The surface tension of the shell resin is unknown, however, literature values reported for commonly used polyester monomers indicate this property can range from 36.0 mN/m to 39.1 mN/m [83]. In order to estimate the capsules' outer diameter using Equation 3.1, an average value of 37.5 mN/m was taken for the surface tension and the density of the droplet fluid was approximated to 1.02 g/cm³ using the rule of mixtures and assuming a 50 vol.% core content. Theoretical results then indicate the droplet size should be around 3.03 mm which is in good agreement with experimental values obtained and presented in Table 3.2.

Table 3.2 Characteristics of capsules generated at a constant shell flow rate of 4 ml/h and variable core flow rates.

Parameter	Shell flow rate (ml/h)	Core flow rate (ml/h)					
		2	3	4	5	6	7
Diameter (mm)	3	2.97 ± 0.04	3.03 ± 0.04	3.01 ± 0.03	-	-	-
	4	-	2.92 ± 0.03	3.00 ± 0.04	3.03 ± 0.05	3.04 ± 0.05	-
	5	-	-	2.99 ± 0.03	3.01 ± 0.03	3.05 ± 0.04	3.05 ± 0.04
	6	-	-	-	2.97 ± 0.04	2.99 ± 0.03	2.99 ± 0.04
Core content (vol.%)	3	$(63 \pm 12) \%$	$(63 \pm 7) \%$	$(64 \pm 9) \%$	-	-	-
	4	-	$(42 \pm 9) \%$	$(56 \pm 5) \%$	$(63 \pm 9) \%$	$(64 \pm 5) \%$	-
	5	-	-	$(55 \pm 6) \%$	$(53 \pm 4) \%$	$(64 \pm 5) \%$	$(63 \pm 3) \%$
	6	-	-	-	$(63 \pm 9) \%$	$(55 \pm 6) \%$	$(64 \pm 6) \%$
Core roundness	3	0.89 ± 0.05	0.94 ± 0.03	0.96 ± 0.02	-	-	-
	4	-	0.97 ± 0.02	0.96 ± 0.02	0.93 ± 0.03	0.95 ± 0.03	-
	5	-	-	0.93 ± 0.03	0.95 ± 0.02	0.94 ± 0.02	0.97 ± 0.01
	6	-	-	-	0.94 ± 0.04	0.96 ± 0.02	0.97 ± 0.02

Conversely to what was observed with the capsules' outer diameter, the one thing that was expected to change with the process parameters was core content. It was anticipated that the capsules' FAAs content would increase with core flow rate for a constant shell flow rate; however, the large error values of the measurements make it difficult to state that this trend was observed in all the cases. Core content values obtained from this method ranged from 42 to 64 vol%. It must be mentioned that none of the parameter combinations tested yielded perfect capsules. As observed in Figure 3.4 neither the shell nor the core of the capsules are perfectly spherical, and the core is not precisely centered. It is believed that the projected cross section captured in the images might are not a good representation of the real core and shell volume fractions within the capsules which caused the large dispersion in the measurements. Additionally, any light variations for capsules in different areas of the same picture could have resulted in different threshold adjustments during the measurement and led to wrong estimations of core content.

Since it was determined that the size nor the shape of the capsules were affected by the generation parameters, the subset of capsules made with a 4 ml/h shell flow rate and varying core flow rates was selected to conduct the analysis of thermal and mechanical properties. This specific subset was chosen above all the others since they were the only ones where the increase of core content with flow rate was seen despite the large variability of results.

3.3.4 Thermal properties

DSC thermograms of the capsules made at 4 ml/h shell rates and variable core flow rates are presented in Figure 3.5. All capsules exhibited melting and crystallization events at temperatures similar to those of the bulk FAAs, proving that they are able to retain their PCM potential after encapsulation. The magnitude of the capsules' peaks is proportional to their PCM content, where a capsule with 100% PCM should match the PCM curve in the thermogram.

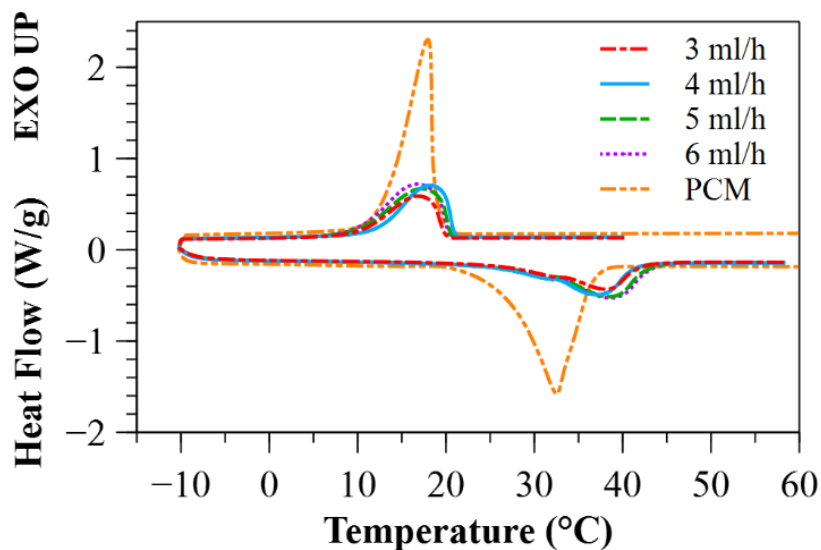


Figure 3.5 Comparison of DSC thermograms of capsules made with a constant shell flow rate (4 ml/h) and different core flow rates against bulk FAAMs sample.

Detailed values of latent heats and transition temperatures for each sample are presented in Table 3.3. As expected, the latent heats of fusion and crystallization become larger with the core flow rate, which translates in capsules with higher contents of FAAMs. No relevant changes are observed in the crystallization temperature of FAAMs when encapsulated, however, the melting temperature does shift to higher values (from approximately 32 °C to 38 °C). It is believed that the low thermal conductivity of the polyester shell ($\sim 0.13 \text{ W/m.K}$ [90]) combined with the fast heating rate ($5 \text{ }^{\circ}\text{C/min}$) caused a thermal lag in the measurement that manifested as a higher melting point. It is expected that if these measurements were repeated at a sufficiently slow heating rate, the capsules would exhibit melting points that coincide with that of the bulk FAAMs. The poor thermal conductivity of the shell is detrimental to the PCM's performance and the addition of particles with a higher thermal conductivity (such as CNCs [91] and nano-graphite [92], [93]) is recommended for future work to improve this issue.

Table 3.3 Transition temperatures and latent heats values for capsules generated at different core flow rates and a constant shell flow rate of 4 ml/h.

Core flow rate (ml/h)	T _c (°C)	ΔH _{Cryst} (J/g)	T _m (°C)	ΔH _{Fusion} (J/g)
3	17.3 ± 0.5	36.2 ± 0.9	37.7 ± 0.7	36 ± 1
4	18.0 ± 0.1	43.3 ± 0.3	37.2 ± 0.1	42.3 ± 0.4
5	16.9 ± 0.4	48 ± 1	38.6 ± 0.4	47 ± 1
6	16.7 ± 0.6	52.3 ± 0.9	38.5 ± 0.6	51.3 ± 0.9
Bulk FAAs	17.92 ± 0.3	113 ± 0.7	32.54 ± 0.3	112.1 ± 0.8

Core volume fractions were determined from latent heat values and are compared to those obtained from image processing in Figure 3.6. It was then determined that capsules made with a 4 ml/h shell flow rate reached minimum and maximum volume percentages of approximately 40% and 54% when the core flow rates were 3 ml/h and 6 ml/h, respectively. Figure 3.6 shows that in most cases, results from DSC do not fall in the range of the measurements obtained from image processing and that this method significantly overestimated the amount of PCM in the capsules. This is believed to be caused by a combination of the low density of the FAAs and the off centeredness of the cores, with the latter resulting in areas where the shell is thicker, and the capsule is locally heavier. It is likely that when the capsules were placed in the mineral oil for imaging, they rotated to accommodate these denser regions at the bottom and the lighter cores at the top. Since the images were taken from the top, the heavier sections of the shells were hidden behind the cores and were not visible in the projected cross sections used for the volumetric analysis.

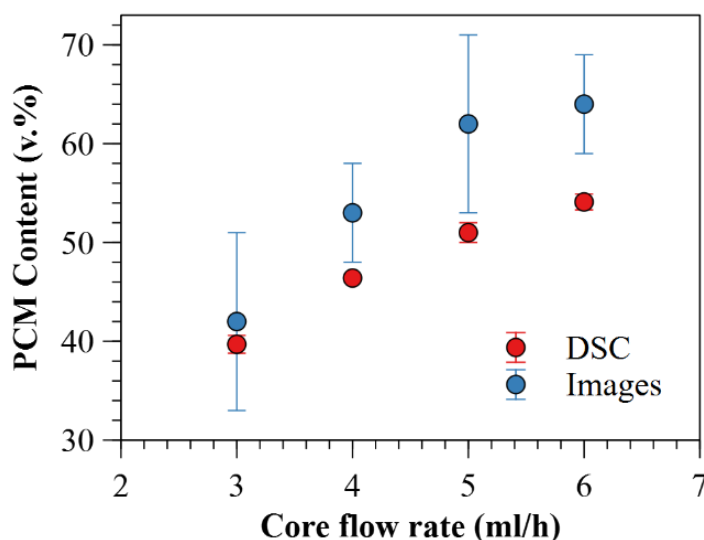


Figure 3.6 Comparison of PCM content (vol.%) values obtained from DSC data and image processing. Shell flow rate was 4 ml/h in all the cases.

To study the thermal stability of the capsules, only those with the higher core contents (54 vol.%) were tested. Figure 3.7 shows that these capsules lose approximately 53 wt.% around 200 °C. Since the cores for these capsules account only for ~ 46% of their weight, it is possible that any unreacted monomers or photo initiator degraded at this temperature, compromising the integrity of the capsule, and leading to the evaporation of the FAAs. The thermogram also shows that rest of the polymerized shell degraded gradually over a wide range of temperatures (215 – 500 °C). The capsules are then thermally stable under approximately 195 °C which should be sufficiently high considering that these capsules are expected to be used in temperature ranges around their melting temperature (40 °C).

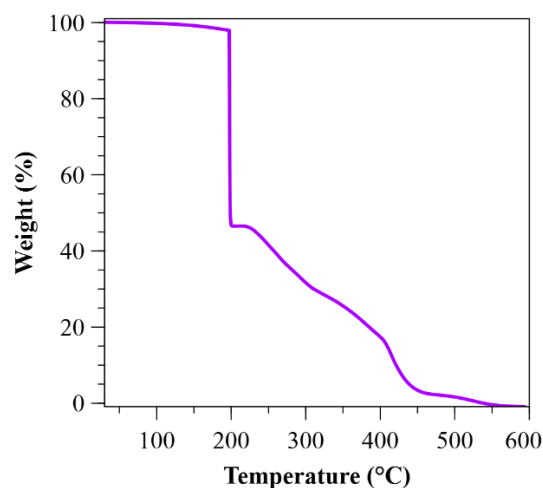


Figure 3.7 TGA thermogram of a capsule generated with shell and core flow rates of 6 ml/h and 4 ml/h, respectively.

3.3.5 Mechanical properties

The capsule system consists of two materials: the FAAs in the core which at room temperature have the consistency of a soft wax, and the polyester resin, which behaves as a flexible rubber. Due to the nature of these two materials, the shell's properties are expected to dictate the mechanical response of the capsules. Table 3.4 shows the load and deformation at break values in compression for capsules generated at different core flow rates and a shell flow rate of 4 ml/h; also, the load vs deformation curves are presented in Figure 2.8(a). The general trend observed is the decrease of both load and deformation at break when the core flow rate is increased, which was expected since this variation results in thinner shells and hence, less material that can bear the load. However, this reduction does not seem to be gradual and is debatable when the core flow rate was

decreased from 5 ml/h to 6 ml/h. It is then assumed that the decline in mechanical properties is not only affected by the overall shell thickness, but that any variations in this parameter plays an important role as well.

Table 3.4 Mechanical properties of the capsules as a function of core flow rate. The shell flow rate was 4 ml/h in all the cases

Core flow rate (ml/h)	Load at break (N)	Deformation at break
3	29 ± 3	0.68 ± 0.03
4	20 ± 3	0.60 ± 0.03
5	14 ± 1	0.58 ± 0.03
6	13 ± 2	0.54 ± 0.04

As previously mentioned, each capsule was cut open with a razor blade following the crack formed during the compression test and images of their cross sections were taken (see Figure 3.8(c), (d), (e), and (f)). These images show that the thickness is not uniform throughout the capsules as a result of the off-centered cores; the thinnest sections of the shells are believed to act as weak points and govern the failure response. In order to prove this theory, the minimum thickness of each capsule was divided by the capsule's radius, and this ratio ($t_{\min}/r$) was plotted against the load at break for all the samples tested (Figure 3.8(b)). This graph shows that higher $t_{\min}/r$ ratios translate into higher loads at break. These results are in good agreement with those reported by Hennequin et al.[94] and Edwards-Levy and Levy [95], where capsules with thicker shells broke at higher forces. It is possible that the position of the thinnest section of the shell respect to the applied force also had an influence on the mechanical response of the capsules, which would explain the dispersion in the results. Nonetheless, the study of this variable was not in the scope of this investigation and is advised for future work. Figure 3.8(b) shows that $t_{\min}/r$ consistently falls as the core flow rate is increased from 3 to 4 and then to 5 ml/h; however, capsules made at 5 and 6 ml/h show $t_{\min}/r$ values within the same range, explaining the very similar load at break values seen for these capsules in Table 3.4.

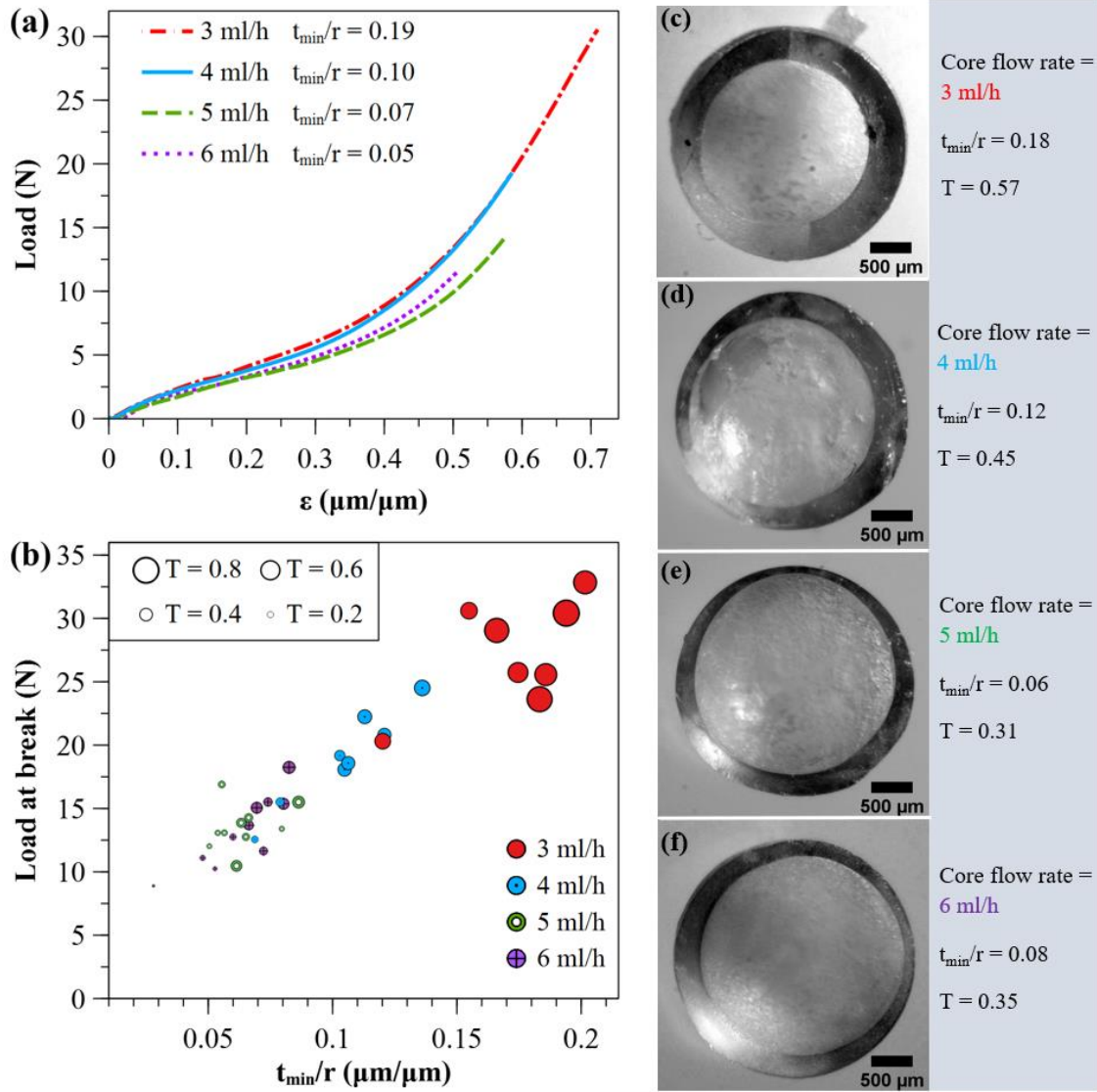


Figure 3.8 Mechanical properties of capsules generated at a shell rate of 4 ml/h and variable core flow rates. (a) Load vs deformation curves of the capsules; (b) Load at break as a function of the thinnest thickness/capsules' radius ratio ($t_{\min}/r$), where T = thinnest shell thickness/thickest shell thickness; (c), (d), (e) and (f) are images of the capsules' cross section after the compression test

The size of the markers in Figure 3.8(b) are proportional to T, which is defined as the ratio of the minimum to the maximum shell thickness measured from the capsule's projected cross section. In other words, the more uniform the shell is, the larger the marker will be (T reaches a maximum value of 1 when the shell is perfectly uniform). Once again, variations in shell thickness result from the core not being perfectly centered so it could be said that T indirectly measures the degree of off centeredness of the capsule. As with $t_{\min}/r$, T also decreases as the core flow rate is

increased within the 3 to 5 ml/h range, but no relevant variations in the marker sizes are observed when this parameter is further increased: capsules made with core flow rates of 5 ml/h and 6 ml/h exhibit both a wide range of $t_{\min}/r$ and significantly smaller T values than the rest capsules. In other words, these capsules are considerably more off-centered than the others, which is a consequence of their higher PCM content. As mentioned before, there is a considerable density difference between the FAAMs and the polyester resin which drives the core to move upward within the capsule due to buoyancy forces. The organoclay added to the formulation helps delay the movement of the core but when the PCM content increases, so do the buoyancy forces and the amount of shell material available to counteract them is reduced, which translates into capsules with more off centered cores. Capsules with comparable T and $t_{\min}/r$ values exhibited similar mechanical properties, independently of the flow rates used during generation; this finally explains why there was not a change in the mechanical properties when the core flow rate was increased from 5 to 6 ml/h.

It is anticipated that any changes in the system resulting in more centered cores would improve the stability of the generation process and the mechanical properties of the capsules. This could be achieved by adding other rheological additives to the shell formulation that promote a viscoelastic behavior with a yield stress capable to keep the core in place despite the high buoyancy forces. Another alternative would be to decrease the level of density mismatch between the FAAMs and the polyester by selecting polyester monomers with lower densities; also, small quantities of solvents could be added to the shell formulation to decrease its density; last, small quantities of high-density nanoparticles could be suspended in the FAAMs to increase its overall density.

3.4 Summary

Polyester capsules containing FAAMs for PCM applications were successfully produced using a coaxial needle. Capsules were generated by varying both the core and the shell flow rates and the generation rate was limited by the syringe pump, which stalled above 6 ml/h due to the high viscosity of the shell. The generation process was the most stable when the core flow rate was lower or equal to the shell flow rate and became more unstable as the core flow rate was further increased. All capsules were approximately 3 mm in diameter and no changes in shape or size were observed when varying the process parameters. Core content measurements obtained from

image processing were inconclusive due to the large variation of the results. Since only the core to shell flow rate ratio seem to be producing changes in the capsules, the subset of capsules generated at a 4 ml/h shell rate was selected above the others to continue with the analysis.

Thermal analysis showed that the FAAs retained their properties and PCM potential after encapsulation. Nonetheless, due to the poor thermal conductivity of polyester, the capsules exhibited higher melting temperatures than the bulk FAAs. The addition of thermally conductive fillers to the shell formulation is recommended to improve this issue in the future. The latent heat of the capsules increased with core flow rate and these values were used to determine the capsules' core content. Capsules generated with shell and core flow rates of 4 ml/h and 6 ml/h, respectively, exhibited the highest core content (54 vol.%) with a heat of crystallization of 51.3 J/g.

It was determined from compression test results that the mechanical response of the capsules was proportional to their shell to diameter ratio ($t_{\min}/r$). Capsules generated with shell and core flow rates of 3 ml/h and 4 ml/h, respectively, presented the highest load (29 N) and deformation at break (68%) values. Images from the capsules' cross section allowed to corroborate that the cores were not perfectly centered which resulted in variations in the thickness throughout the capsules. It was also determined that higher core flow rates resulted in more off centered cores, less uniform thicknesses and lower load and deformation at break values. Core off centeredness is caused by the density mismatch between the polyester resin and the FAAs and any measures taken to reduce these differences are expected to improve the stability of the generation process and the mechanical properties of the capsules.

4. STUDYING THE FEASIBILITY OF INCORPORATING PHASE CHANGE MATERIAL (PCM) MICROCAPSULES IN ASPHALT PAVEMENT TO REGULATE ITS TEMPERATURE

All lab-work in this chapter was performed by Daniela Betancourt Jimenez and Miguel Montoya. All analysis and writing was performed by Daniela Betancourt Jimenez with guidance by Dr. Carlos Martinez, Dr. Jeffrey Youngblood, and Dr. John Haddock.

4.1 Introduction

Thanks to its many advantages, asphalt concrete or asphalt pavement is the most widely used material for road construction nowadays: close to 95% of the roads in the United States are made of asphalt. When compared to concrete pavement, asphalt is less expensive, recyclable, easier to maintain and its installation is simpler and faster, reducing the amount of time roads are closed during construction [96]. However, due to asphalt binder's viscoelastic behavior, performance changes greatly with temperature variations constituting one of its major drawbacks [23]. This represents an important problem especially in regions subject to seasons or abrupt changes in temperature throughout the day.

Since conventional asphalt pavement is black, it has a strong heat-absorbing capacity [24] and can reach temperatures as high as 70 °C during peak sunlight conditions [97]. The air temperature in urban cities is higher when compared to rural areas because of the high volumetric heat capacity and reduced evapotranspiration of concrete and asphalt, the two main materials used in buildings, roads, and parking lots. This phenomenon is known as the urban heat island (UHI) effect and has many environmental and health issues [98]. Areas that suffer from UHI have higher water and energy consumption and contribute to the acceleration of smog production [99], [100]. Furthermore, when asphalt reaches high temperatures, the binder's viscosity decreases along with the adhesion among aggregates. This results in a lower asphalt mixture stiffness that can lead to large permanent deformation under repeated loading, a distress commonly known as asphalt rutting [23], [24].

Several methods to lower the temperature of asphalt during the summer have been considered, such as spraying water on the pavement and using porous pavement, however, they

have not been effective or practical [101]. A novel and different approach that could be used to prevent asphalt pavements from reaching such high temperatures is the use of phase change materials (PCMs). PCMs are substances that absorb significant amounts of energy from their surroundings when they melt, while remaining at a constant or approximately constant temperature [2]. This energy that is absorbed is known as latent heat of fusion and it is transferred back to the surroundings when the material goes back to the solid state [7]. This particular property of PCMs make them suitable materials to be incorporated in asphalt to help regulate its temperature and decrease the UHI effect and avoid/delay rutting.

PCMs can be used in many applications related to thermal energy storage and management such as in textiles [4], buildings[102], and solar energy storage systems [103]. However, since these materials need to transition from the solid to the liquid state to fulfill their function, they must to be contained to avoid their leakage during the liquid phase [7]. The use of PCMs in asphalt pavements poses a series of challenges that are not encountered in other applications. Perhaps the most difficult one is to find a containment system that is able to keep the PCM from leaking at the high temperatures and mechanical loadings typical of asphalt processing. Partially successful results have been obtained in studies where the PCMs were shape stabilized using porous aggregates as carriers [104]. However, it was found that PCMs in these systems are prone to evaporate at asphalt processing temperatures. This issue has been addressed by coating the carrier aggregates using polymeric resins [105]. Nonetheless, this decreases the overall PCM content in the aggregate along with their thermal conductivity. Another alternative for PCM containment is the microencapsulation of these materials in core-shell structures made of polymeric materials. The use of PCM microcapsules in this way is popular in building walls, however, only a few investigations have been conducted to incorporate them in asphalt pavements. This is likely due to the fact that most polymeric materials do not perform well at high temperatures, making these capsules incompatible with asphalt processing conditions. This work here studies the feasibility of adding PCM microcapsules with high thermal stability and robust walls to asphalt pavements to decrease their peak temperatures which could potentially alleviate issues such as UHI effect and rutting.

4.2 Experimental Section:

4.2.1 Materials

Nextek 43 (PCM microcapsules) were purchased from Microtek Labs. Premixed hot mix asphalt (HMA) materials obtained in the field were provided by the Indiana Department of Transportation (INDOT). Limestone sand aggregates of different sizes were purchased from US Aggregates and asphalt binder PG 64-22 was bought from Seneca Petroleum Co Inc.

4.2.2 Thermal characterization of the PCM microcapsules

A Q2000 DSC analyzer (Q2000 DSC TA Instruments) was used to determine the transition temperatures and latent heats of the capsules. Experiments were conducted under a nitrogen atmosphere with cooling and heating rates of 10 °C/min. Thermogravimetric analysis (Q50 TGA, TA Instruments) was also conducted to study the thermal stability of the capsules at asphalt processing temperatures. Samples were ramped at 15 °C/min from room temperature to 600 °C. Isothermal experiments at 165 °C for 3 hours were carried out as well.

4.2.3 Ball milling experiments

0.7 g of microcapsules and 14 g of tungsten carbide balls (3 mm in diameter) were added to a 25 ml glass vial and then put inside an oven at 145 °C for 2 hours. Next, the vial was taken out of the oven, capped, and immediately milled using a wheel mixer (30 rpm) for 20 minutes at room temperature.

4.2.4 Imaging

Photographs of the capsules were taken using both optical (Z16 APO, Leica) and scanning electron (Phenon, FEI Company) microscopes. Capsules photographed with SEM were previously mounted and coated with a thin layer of platinum (~10 nm) using a sputter coater (K550X, Emitech) for 30 seconds.

4.2.5 PCM Load analysis

The amount of PCM required to change the temperature of asphalt pavement by 1 °C was roughly estimated using Equation 4.1 [106]:

$$Q = m \cdot C \cdot \Delta T \quad \text{Equation 4.1}$$

Where Q is the amount of heat (in J) required to produce a temperature difference or ΔT (in °C), m is the mass of the sample undergoing the temperature change (in Kg), and C is the specific heat capacity of the sample (in J/Kg °C). The amount of heat required to decrease the temperature by 1 °C of a 2 inch thick asphalt slab with a length and width of 1 meter with a mass of 115.6 Kg was estimated to be –110.88 KJ (for an asphalt sample with $\rho = 2,276 \text{ Kg/m}^3$ and $C = 959 \text{ J/Kg } ^\circ\text{C}$ [107]). The minimum amount of PCM needed to achieve this temperature change would be 0.55 Kg (for a PCM with a latent heat of 200 KJ/Kg), assuming there are no heat losses in the system and no heat is being transferred from or to the asphalt pavement and its surroundings. 0.55 Kg of PCM would then be the equivalent to 1.2 vol.% of the slab. It must be noted that these calculations are not expected to be representative of the actual amount of PCM needed to induce the mentioned temperature change since several variables such as heat losses in the system, and the thermal conductivity and diffusivity of the materials were not considered. This theoretical value was used to determine the order of magnitude in which the PCM must be added. To ensure that the thermal regulation action of the PCM would be seen in the thermal cycling tests, the PCM microcapsules were added in 10 vol.% and 20 vol.% to the asphalt mixtures.

4.2.6 Preparation of HMA Specimens

HMA specimens used for the thermal cycling tests were prepared from premixed HMA materials produced by Milestone Contractors; the technical sheet with the mixture's specifications can be find in Appendix B. Premixed HMA materials were used in order to save time associated with the design of the mixture and rapidly assess if the PCM microcapsules were able to actually endure asphalt processing conditions. To prepare each specimen, approximately 2,680 g of premixed HMA were heated at 145 °C for 2 hours. Next, they were removed from the oven and PCM microcapsules were added in different volume fractions (0, 10 and 20 vol.% which were equivalent to 0, 4 and 8 wt.%, approximately). The capsules were dispersed in the HMA by

manually mixing everything together using a large metal spoon and encircling movements. Next, the mixture was returned to the oven at 130 °C for 20 minutes before being compacted into 4-inch diameter specimens at 50 gyrations using a Superpave Gyratory Compactor (SGC). After 10 minutes, the mixtures were demolded and allowed to cool down at room temperature for at least 24 hours. Specimens were subsequently trimmed to 2 inches in height and a small hole was drilled radially into the specimen at 1-inch from the bottom. Thermocouples were placed on the top, the bottom and in the middle hole of the specimen. The HMA samples were then insulated from the bottom and the sides using a 2-inch-thick insulation board.

The HMA mixture used to make the dynamic modulus specimens was prepared in the lab instead of using the premixed HMA materials. This was done to make some alterations in the mixture design that could not be done if premixed materials were used. This changes included the substitution of some fine aggregates with the PCM microcapsules to reduce the amount of small size particles ($>300\text{ }\mu\text{m}$) in the mixture and hopefully decrease the impact of the PCM addition on the mechanical performance of the pavement. The mixture design of the HMA materials was taken as a reference (gradation, asphalt content, etc.) and some other changes were made: no reclaimed asphalt pavement (RAP) was used; since all the binder added to the new mixture was virgin, the actual binder content was decreased from 6.1 wt.% to 5.2 wt.%. The final gradation of the control mixture is presented in Table 4.1.

Table 4.1. Gradation of the lab-made control HMA mixture

	DMF Mass
%Pass 12.5 mm	100.0
%Pass 9.5 mm	95.2
%Pass 4.75 mm	59.8
%Pass 2.36 mm	34.0
%Pass 1.18 mm	18.8
%Pass 600 μm	10.2
%Pass 300 μm	4.9
%Pass 150 μm	2.1
%Pass 75 μm	0.9
Binder, actual, %	5.2
Bag House Fines, DMF %	1.5

4.2.7 Thermal cycling experiments

The samples were placed inside an environmental chamber (Darwin Chambers Company) and were left to stabilize at room temperature for 24 hours. After this, the chamber was set to increase the temperature to 62 °C in 6 hours, stabilized for 25 hours, and then cool down to room temperature. J type thermocouples were used to read the temperature of the specimens and the chamber and a data logger (CR1000, Campbell Scientific) was used to record the data.

4.2.8 Dynamic modulus analysis

The dynamic modulus of control and PCM-containing specimens was determined using an asphalt mixture performance tester (Model B200P115, Pavetest). Experiments were conducted at different temperatures (4 °C, 20 °C and 40 °C) and frequencies (0.1, 0.5, 1, 5, 10, and 25 Hz). All specimens were conditioned at the experiment temperature for 4 hours before conducting the measurements. The specimens were 1.45” in diameter and 4.25” in height.

4.3 Results and Discussion

4.3.1 PCM material selection and characterization

Nextek 43, a commercially available microencapsulated PCM, were selected for this study due to their high thermal stability (less than 1% leakage when heated to 250 °C) and their robust capsule walls [108]. These features are expected to help the capsules withstand asphalt processing conditions and allow them to perform their thermal management role. Another advantage of these capsules is their high latent heat of fusion (220-230 J/g) and small size which translates into high surface area to improve heat transfer, helping counteract the low thermal conductivity typical of these materials [3]. As seen in Figure 4.1, the capsules presented spherical shapes and a wide size distribution (2 μm – 25 μm). Interestingly, most capsules have dents on them. It must be noted that this micrograph was taken at room temperature, hence, the PCM cores are expected to be in the solid state. It is highly possible that the dents were produced by volumetric changes experienced by the core during their phase change from liquid to solid, which for paraffins can be around 10% [109]. However, even when most capsules look dented, they do not seem have cracks, indicating that the shell is sufficiently strong and flexible to sustain these volumetric changes

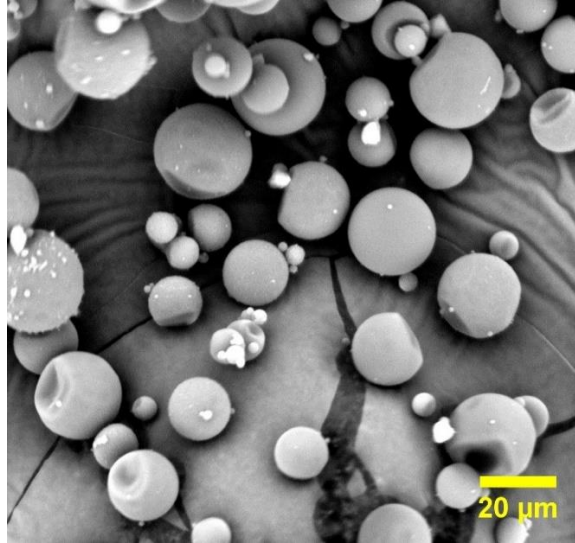


Figure 4.1 SEM micrograph of the PCM microcapsules

Before adding the capsules to asphalt pavement samples, their thermal properties such as melting temperature, latent heat and thermal stability values were analyzed by DSC and TGA. As seen in the thermogram presented in Figure 4.2, the microcapsules exhibited two separate events for both melting and crystallization transitions; the first and minor melting event takes place around 5 °C with a latent heat of approximately 9.6 J/g. The second and main melting event has an onset around 36.5 °C and reaches its peak at ~45 °C. It is possible that the difference between the experimental melting point and that reported by the manufacturer (43 °C) was a consequence of the fast heating rate (10 °C/min) used during the experiment. The heat of fusion was ~200 J/g which is 20-30 J/g below the manufacturers' specification. However, these differences in melting point and latent heat are not significant for the project and should not affect the PCM's ability to regulate the asphalt's temperature. Figure 4.2 also shows that each transition event shows two humps or overlapping peaks. It is possible that the PCM contained in this capsule is based on a blend of two or more paraffins which were mixed to tune the melting temperature of the resulting substance [3], [110].

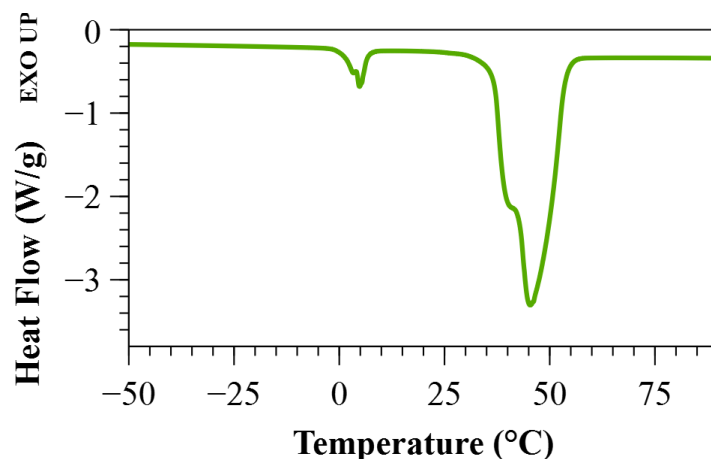


Figure 4.2 DSC thermogram of PCM microcapsules

The thermal stability of the capsules was studied by performing two different experiments. In the first one, the capsules' temperature was increased at a constant rate (15 °C/min) from room temperature to 500 °C. Results presented in Figure 4.3(a) show that the capsules degrade at approximately 410 °C when they lose most of their mass (~90 wt.%) due to PCM evaporation. To simulate asphalt processing conditions, the second experiment consisted of increasing the capsules' temperature to 165 °C and keeping it constant for three hours. The thermogram in Figure 4.3(b) indicates that the sample only lost 4% of its weight during this test. This weight loss probably corresponds to the PCM evaporation of inherently imperfect capsules in the production batch. Considering how small these weight losses are, results then confirm that the microcapsules are stable at asphalt processing temperatures (140 – 160 °C).

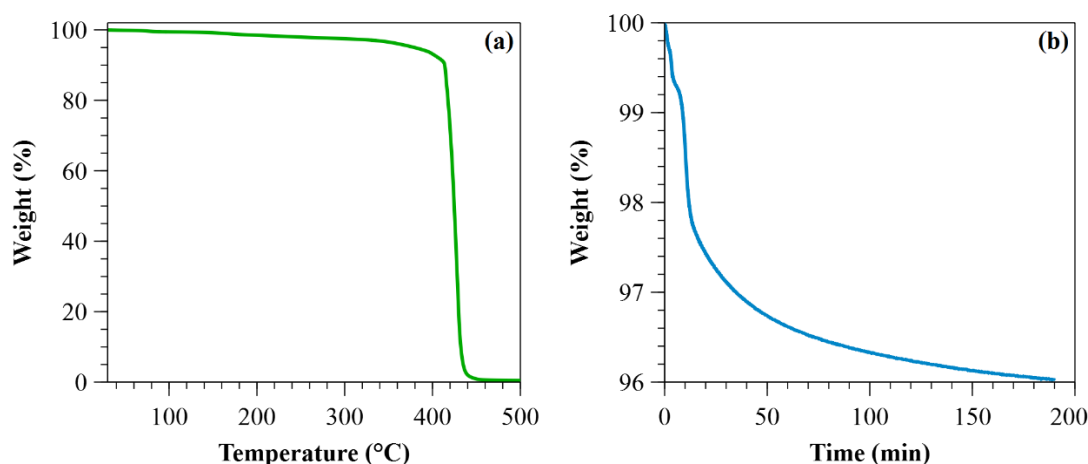


Figure 4.3 TGA thermograms of microcapsules (a) temperature ramp from room temperature to 400 °C (15 °C/min), and (b) Isothermal at 165 °C.

To implement these PCM microcapsules in asphalt pavements they not only need to be thermally stable but must be able to withstand compression and shear stresses typical of the mixing and compacting stages of HMA pavements. To assess the mechanical performance of the microcapsules, ball milling experiments were also conducted followed by a visual inspection using an optical microscope. As described in the experimental section, both the capsules and the milling media were heated to 145 °C before being immediately milled for 20 minutes. Micrographs of the capsules taken after the experiment are presented in Figure 4.4. Unfortunately, it was not possible to precisely determine the ratio of broken capsules for several reasons: first, agglomerates formed during test and could not be broken up entirely to assess the capsules' integrity individually. Second, the micrographs only allow imaging of a partial section of the capsules, hence even when they may look whole from the top they could be broken on the bottom. However, to obtain a rough estimate all those capsule that still exhibited a circular contour after the test (despite being dented) were considered whole while those with irregular shapes and flat appearance were counted as broken (signaled by black arrows in Figure 4.4). Based on this analysis roughly 10% of the capsules broke, or in other words, close to 90% of the capsules survived the ball milling experiment. This survival rate is high considering that the capsules are made of polymers (unknown composition due to proprietary rights) which usually soften and underperform at high temperatures. Nonetheless, even if only 10% of the capsules break this could translate in a significant amount of PCM being released and will most likely have a detrimental effect on the mechanical properties of the pavement [111].

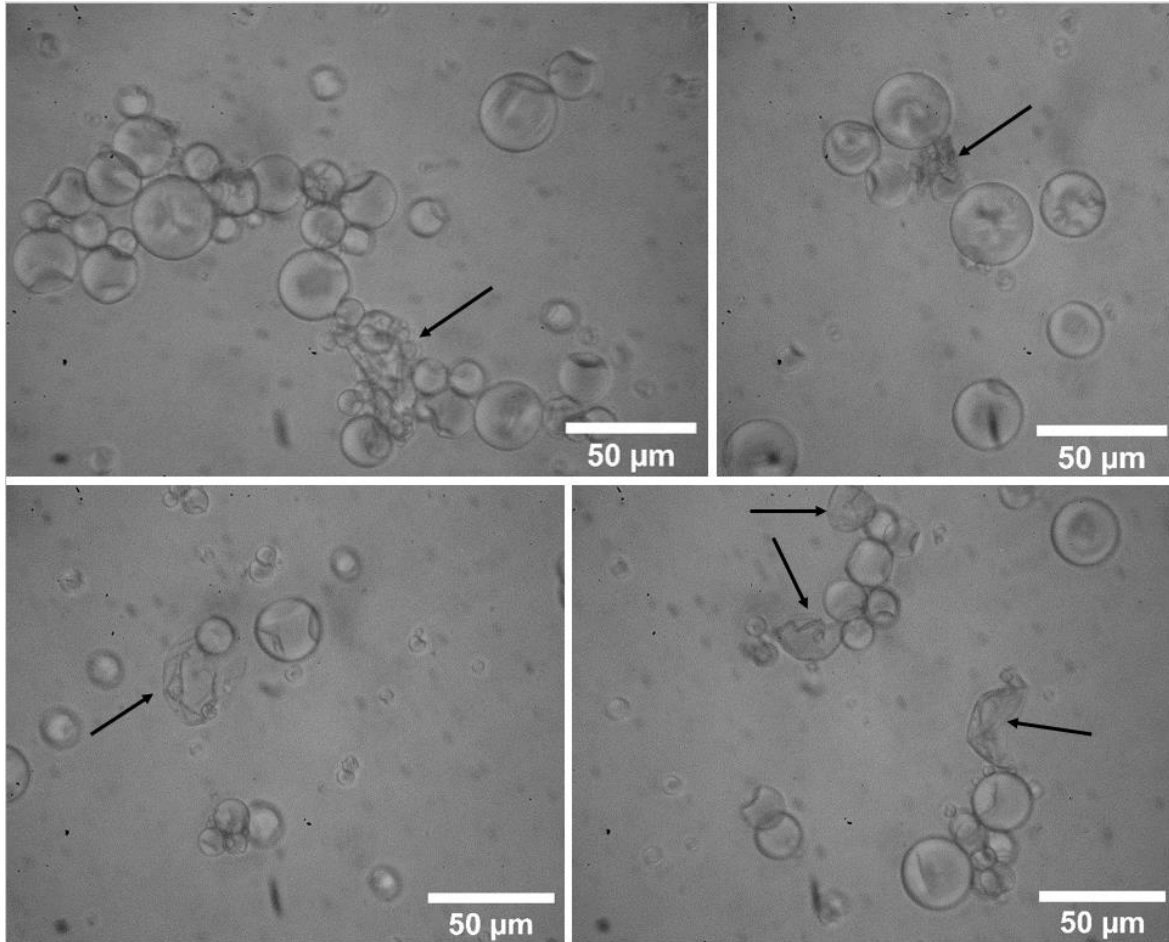


Figure 4.4 Optical micrographs of microcapsules after the ball milling experiment.

4.3.2 Thermal cycling experiments

Specimens were prepared using premixed HMA materials to save time in the mixture design and preparation. This was done to quickly assess if the capsules would survive the fabrication process and perform their thermal managing function. Since results from ball milling experiments showed that the capsules are susceptible to leaking PCM at processing conditions, the HMA mixing process was modified to try to maximize the capsules' survival rate. The capsules were not preheated and were added only after the asphalt mixture was heated for 2 hours at 140 °C. Also, the capsules were dispersed by manually mixing everything together using a large metal spoon instead of an asphalt mixer; this was done to hopefully decrease the stresses generated in the mixing process. Once the capsules were dispersed, the mixture was briefly placed in the oven to increase its temperature (130 °C for 20 min) and was subsequently compacted in the SGC.

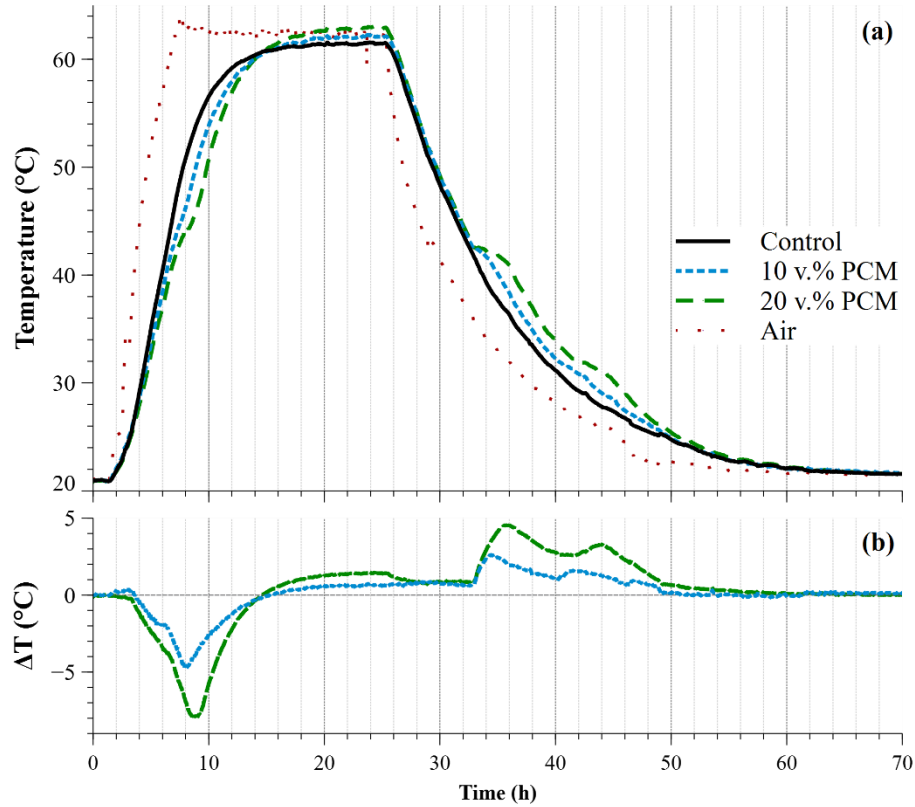


Figure 4.5 (a) Temperature profile of specimens and the environmental chamber during thermal cycling experiments. (b) Temperature gradient of PCM-containing capsules respect to the control mixture as a function of time.

Figure 4.5.(a) shows the change in temperature on the specimens' top surface as a function of time. The dotted curve (air) corresponds to the reading of a loose thermocouple inside the chamber and indicates the temperature profile during the experiment. As seen in the plot, the temperature of the environmental chamber was first increased from room temperature (~ 21 °C) to 62 °C in a period of 6 hours (~ 6.8 °C/h or ~ 0.1 °C/min). Next, the temperature was held at 62 °C for 20 hours to allow for the specimens to reach equilibrium. Last, the chamber was cooled down back to room temperature (~ 22 °C). Unfortunately, the environmental chamber used in the experiment did not have a cooling unit and was not capable of controlling the cooling rate. For this reason, the cooling rate was considerably slower (from 62 °C to 22 °C in approximately 24 hours) than the heating rate (from 21 °C to 62 °C in 6 hours).

As seen in the plot (Figure 4.5.(a)), all the specimens were at the same temperature when the experiment started ($\sim 21^\circ\text{C}$); as the heating step began, the specimens' temperature increased linearly with time until they reached $\sim 40^\circ\text{C}$. During this segment of the experiment, the curve corresponding to the control sample exhibited the steepest slope, followed by the 10 vol.% PCM and the 20 vol.% PCM samples, respectively. In other words, the control specimen heated up slightly faster than the others and the heating rate decreased the higher the PCM content. For instance, the control reached 35°C 18 min (0.3 h) and 32 min (0.5 h) faster than the 10 vol.% PCM and 20 vol.% samples, respectively. These differences in heating times result from a reduction in the effective thermal diffusivity of the asphalt mixture caused by the introduction of the PCM microcapsules [30]. Thermal diffusivity measures how fast heat is propagated through a material when it is subjected to changes in temperature [112]. Conventional asphalt mixtures typically exhibit thermal diffusivity values among 0.45 and $0.80\text{ mm}^2/\text{s}$ [107], [113] while paraffin waxes similar to the PCM contained in the microcapsules exhibit values that are several orders of magnitude lower ($1.7 \times 10^{-7}\text{ mm}^2/\text{s}$ [114]), which explains the decrease in the effective thermal diffusivity of the asphalt mixture containing PCM microcapsules. Figure 4.5(a) also shows that the temperature of the control sample keeps increasing smoothly after it hits 42°C and reaches equilibrium at 61.4°C and 19.3 hours. However, a different behavior is observed for the PCM-containing samples; Once they read $43\text{--}45^\circ\text{C}$, the data shows one little step moving the curves further away from that of the control and increasing the time gap among the three specimens at a given temperature. For example, the 10 vol.% and 20 vol.% PCM samples take 48 min (0.8 h) and 110 min (1.8 h) longer than the control to reach 48°C . This delay results from the heat absorbed by the PCMs as they start to melt around 40°C which causes a temporary temperature “stall” in the PCM specimens causing them to lag the control. However, once the transition ends, the curves of the PCM-containing samples eventually catch up with that of the control at 60.6°C and 14.7 hours. After this point, their temperatures surpass that of the control sample and stabilize at 62.0°C and 62.9°C for the 10 vol.% and 20 vol.% PCM specimens, correspondingly. The fact that each sample stabilized at a different temperature was probably caused by variations in temperature within the chamber.

As the samples start to cool down from $60\text{--}62^\circ\text{C}$, their temperatures decrease in a relatively linear fashion until they hit $\sim 43^\circ\text{C}$. Within this range, samples containing PCMs presented curves

with slightly less steep slopes than the control due to their diminished apparent thermal diffusivities as explained earlier. However, when the temperature decreased from 43 °C to 24 °C, the cooling curves of both PCM-containing mixtures exhibited two peaks which delayed the cooling of the specimens with respect to the control sample. The onset of the first peak coincides with the crystallization temperature of the PCMs (~43 °C) and results from the heat released from the microcapsules as they solidify. The second peak observed around 32 °C corresponds to the smaller apex of the transition as seen in the DSC thermograms (Figure 4.2). As expected, the peaks are more pronounced in samples with higher PCM contents. The presence of two peaks instead of one step (as seen in the heating segment of the experiment) is explained by the difference in cooling and heating rates. As mentioned before, the samples were heated significantly faster than they were cooled; hence, the amount of time it took for the mixtures to go from the temperature of the first peak to the second was considerably shorter and the heat absorption was displayed as only one hump. Once the phase transition ended, the time gap between the PCM-containing samples and the control started decreasing until they finally caught up and stabilized at ~21.6 °C.

Figure 4.5.(b shows the temperature gradient between the control and the PCM-containing samples as a function of time. This parameter is negative when the temperature of the PCM specimen is below that of the control, or positive when it is above it. Any temperature gradients observed before the samples hit ~36 °C (onset of the melting transition as observed in Figure 4.2) are attributed to the lower thermal diffusivity of the mixtures containing PCM microcapsules. However, when the specimens reach this temperature, the gradient increases in magnitude at a higher rate due to the heat absorbed from the PCM during its phase change increasing the apparent thermal diffusivity. The gradients reached minimums of -4.6 °C (8.2 h) and -10.1 °C for the 10 vol.% and 20 vol.% PCM samples, respectively, after which they started to progressively decrease. Finally, the temperature gradient of both PCM-containing samples stabilized at 0.6 and 1.4 °C during the isothermal step of the experiment. Positive gradients exist even after the samples stabilized due variations in temperature within the chamber; it is possible that PCM containing samples were located in warmer areas, causing them to reach higher temperatures than the control mixture.

Figure 4.5(b also shows that shortly after the cooling step started (~26 h) the temperature of the samples with PCMs started decreasing, promoting a reduction of the gradient. This parameter

remained relatively constant for both samples until the time in the experiment was around 33 hours and the specimens' temperature were close to 43 °C; from this point on, the gradient started increasing as the samples' got warmer from the heat released during the PCM during solidification. The gradient exhibited two maximums during the cooling step since the PCMs' heat is released over a range of temperatures and peaks at two different points within this range (Figure 4.2). Once the transition ended, the gradient progressively decreased until it reached zero once all the samples stabilized after 60 hours.

Figure 4.6 show the change in the temperature gradient between PCM-containing samples and the control mixture as a function of temperature at the three different locations where thermocouples were placed. The general trend observed is that the largest temperature gradients are achieved in the middle and on the bottom surfaces of the samples. This was expected since they are insulated from all sides except the top and hence, this area heats up and cools down faster than the others by convection. During the heating step, specimens with 10 vol.% and 20 vol.% PCM content exhibited the largest temperature gradients respect to the control mixture at 44 °C ($\Delta T = -6.1$ °C and -10.1 °C, respectively). Conversely, the temperature gradient of these samples reached its highest value during the cooling step at 41-42 °C, when the 10 vol.% and the 20 vol.% PCM were 2.9 and 5.4 °C below the control mixture. Differences in the magnitude of the gradients experienced in each step are related to the disparity between the cooling and the heating rates. Since the samples were heated significantly faster than they were cooled, the PCMs experienced the phase transition quicker, absorbing all the heat needed from their surroundings over a short period of time and resulting in a more significant temperature difference that decreased shortly after the transition was over. However, at lower cooling rates, the PCM released the heat slowly and the temperature of the sample was gradually increased over longer periods of time.

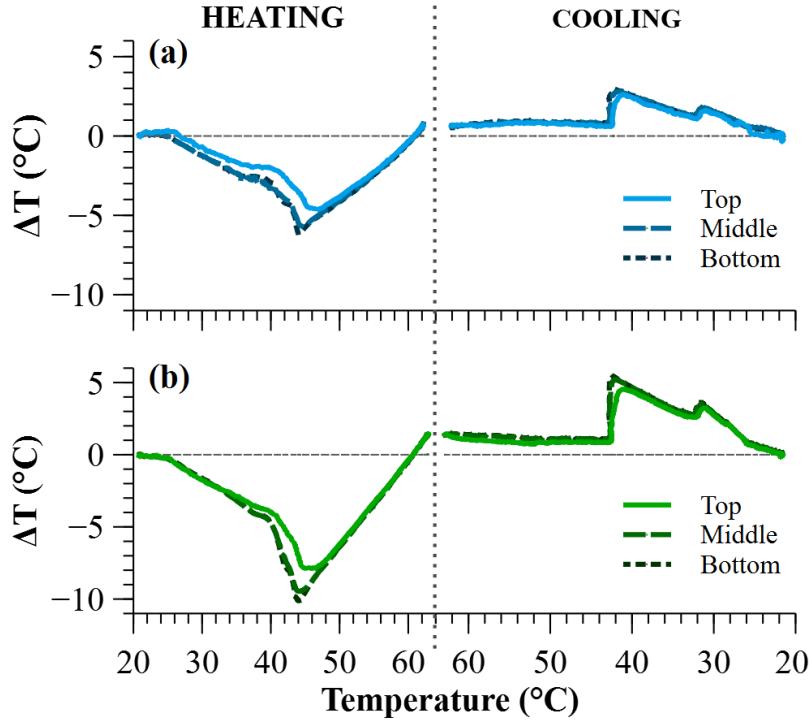


Figure 4.6 Temperature gradient between PCM-containing specimens and the control mixture as a function of temperature at three different locations within the specimens: (a) 10 vol.% PCM and (b) 20 vol.% PCM.

4.3.3 Dynamic Modulus

Figure 4.7 shows the dynamic modulus of the control (Figure 4.7(a)) and the PCM-containing mixtures (Figure 4.7(b)) as a function of frequency. In both cases, this property increases with frequency as a consequence of the viscoelastic behavior of the binder. Asphalt binder or bitumen is an amorphous material that consists mainly of a mixture of high and low molecular weight hydrocarbon molecules classified in asphaltenes and maltenes, respectively [115], [116]. At lower frequencies, these molecules have the ability to rearrange and flow under the imposed stress, deforming at lower loads and decreasing the modulus. However, at higher frequencies, the time given for molecular motion is reduced, increasing the stress needed to induce deformation and hence, the materials' stiffness.

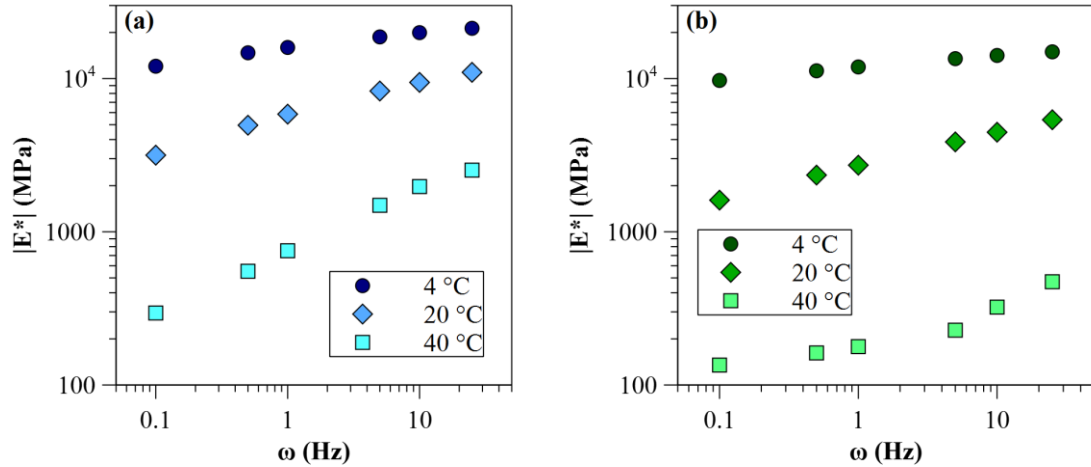


Figure 4.7 Dynamic modulus as a function of frequency for: (a) control mixture, and (b) mixture containing 4 wt.% PCM.

Figure 4.7 and show the modulus also decreased when the temperature of the experiment was raised. Again, this is related to the binder's nature; at higher temperatures there is more free volume between the molecules, making it easier for them to move under stress and decreasing the resistance to flow [117]. The general trend observed is that independently of frequency or temperature, PCM-containing samples exhibited a lower modulus than the control mixture. Several factors could be contributing to the detriment of this property; First, the sample with PCM contains a large number of microcapsules (~10 vol.% of the mixture) that are significantly smaller than the rest of the aggregates. Thus, by adding the microcapsules the gradation of the mixture was changed and this is expected to affect its mechanical performance [118], [119]. Birgisson and Roque [119] noticed that a gradual increase in the percentage of passing of fine aggregates as the sieve opening size gets larger leads to mixtures with higher dynamic modulus. In other words, a variety of fine aggregates with a wide size distribution exist within the mixture. However, for the PCM containing specimens, most of the fine particles are constituted by PCM microcapsules that are less than 75 μm in diameter and aggregates that are retained in 600 μm sieves or larger. No particles with sizes between 75 and 600 μm exist, causing an abrupt change between gradation bands and explaining the decrease in the dynamic modulus for PCM containing mixtures [119].

Additionally, the microcapsules have a considerably lower density than the aggregates and mineral fillers used in the HMA mixtures (0.9 g/cm^3 vs $\sim 2.8 \text{ g/cm}^3$) and are expected to exhibit significantly lower modulus as well, which probably contributed the most to the decrease in modulus. Second, as determined from TGA and ball milling tests, some among of capsules broke

when the samples were prepared causing some PCM leaking into the mixture. Since this PCM is paraffin-based it is expected to mix readily with the asphalt binder and affect its composition. Thus, the leaked PCM would increase the fraction of maltenes in the binder, which are known to promote a lower modulus [115]. If PCM leakage is causing the decrease in modulus, this issue could be corrected by improving encapsulation. It must be mentioned that the capsules used in this study are for general use and were not designed to be used in asphalt pavements specifically.

Several studies have reported that mixtures with higher dynamic modulus at low frequencies (0.1 Hz) and high temperatures ($< 40\text{ }^{\circ}\text{C}$) are associated with a better performance against rutting [120], [121].

Figure 4.8 shows that PCM-containing samples showed a 54% reduction in the modulus when compared to the control mixture under said conditions which could indicate that adding PCM microcapsules to HMA mixtures worsens their rutting resistance. However, as seen in results from thermal cycling experiments, the PCM microcapsules can lower the rate at which asphalt heats up, decreasing the maximum temperature reached by the pavement during the day and potentially reducing rutting. Since the degree of rutting is not only dependent on modulus but also on temperature variations, more studies are needed to determine the impact of PCM microcapsules addition in rutting performance of asphalt pavements.

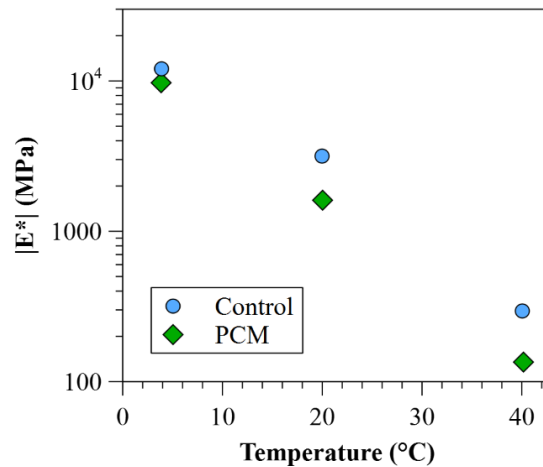


Figure 4.8 Dynamic modulus measured at 1.0 Hz as a function of temperature for the control mixture and the mixture containing 4 wt.% PCM.

4.4 Summary

PCM microcapsules were characterized to study the feasibility of incorporating them in HMA mixtures. The microcapsules exhibited a melting temperature of 45 °C, a high heat of fusion (200 J/g) and were thermally stable under 300 °C. Also, results from ball milling tests conducted at high temperatures (< 140 °C) showed that approximately 90% of the capsules survived the experiment, indicating that capsules have the potential to sustain asphalt processing conditions. PCM microcapsules were then incorporated to premixed HMA materials in ~10 and ~20 volume percentages. Thermal cycling experiments were conducted, and results suggest that the addition of PCM microcapsules reduces the thermal diffusivity of the HMA mixtures. During the heating step of the test, once the mixtures reached the PCM's melting point, their temperatures were 5 °C and 10 °C lower with respect to the control when the content of PCM microcapsules added was 10 and 20 vol.%, respectively. On the other hand, during the cooling step, the cooling rate of the PCM-containing specimens decreased around the melting point of the PCM: mixtures with 10 and 20 vol.% PCM exhibited temperatures that were 2.9 and 5.4 °C higher than the control. Variations in the magnitude of the thermal gradients experienced at the different steps of the experiment are attributed to disparities between cooling and heating rates. Results here obtained prove that PCM microcapsules can be successfully added to asphalt pavements to regulate their temperature. Nonetheless, dynamic modulus measurements indicate that the addition of PCM microcapsules lowers the modulus of the capsules which is attributed to changes in the mixture's gradation and the low density of the capsules. Future studies are suggested to optimize the gradation of PCM containing mixtures to improve their mechanical performance.

5. CONCLUSIONS AND FUTURE WORK

Results from this work indicate that mixtures of fatty acid amides obtained from vegetable oils can exhibit high latent heats of fusion and melt congruently, making them suitable materials for PCM applications. It was determined that the fatty acid composition of the precursor vegetable oil plays an important role in the thermal properties of the resulting FAAs; FAAs derived from oils that were rich in unsaturated fatty acids exhibit lower transition temperatures than those with higher contents of saturated species. Also, mixtures synthesized from oils with small ratios of saturated to unsaturated fatty acids are more likely to melt and crystallize congruently than those where both types of acids are in similar proportions. It was observed that the melting point of the FAAs increased with the molecular weight of the alkyl amine used for their synthesis; a similar trend was observed for the heat of fusion and crystallization, except in the case where hexadecylamine was used. Lastly, all FAAs synthesized were thermally stable under 200 °C. The synthesis of FAAs from other varieties of natural oils such as soybean oil is recommended for future work along with the preparation of mixtures of FAAs obtained from different alkyl amines to study their thermal properties and determine if their melting points can be tailored using this method.

Furthermore, it was concluded that the encapsulation of FAAs in polyester shells do not affect their PCM potential. FAAs capsules can be successfully produced using a coaxial nozzle and a UV-curable polyester resin. The PCM content of the capsule can be varied by changing the flow rates used during generation, however, these parameters do not affect the capsules' diameter which was always around 3 mm for the coaxial needle used. The maximum PCM content achieved by this method was 54 vol% when the capsules exhibited a latent heat of 51 J/g. The capsules produced were thermally stable under 150 °C which is expected to be high enough for most PCM applications. Also, results from mechanical properties indicate the capsules are able to withstand forces and deformations of up to 29 N and 68%, respectively, before breaking. Their mechanical performance, however, is highly dependent on their minimum thickness to outer diameter ratio which can be significantly affected by the off centeredness of the core. The development of new methods to keep the core centered within the capsules is recommended to improve their mechanical performance and the stability of the generation process. Possible alternatives to address this issue

include the addition of other rheology modifiers to the shell formulation that induce shear thinning behavior or to increase the density of the core material by suspending denser particles in it. The addition of thermally conductive particles to the shell formulation is also advised to increase the thermal conductivity of the capsules. The study of other methods for encapsulation such as interfacial polymerization

Last, it can be concluded that the use of PCM microcapsules to regulate the temperature of HMA asphalt pavements is feasible. Results from the mechanical and thermal characterization of the PCMs indicate that approximately 90% of the microcapsules survive high temperatures and compressive forces that are similar to those experienced at asphalt processing conditions. Thermal cycling experiments demonstrated that adding PCM microcapsules can in fact decrease the temperature of pavements when heated once they reach their melting point. Unfortunately, the dynamic modulus of the mixtures was reduced after the addition of PCM microcapsules which could worsen the rutting performance of the pavement even if its maximum temperature is decreased. Then, it is important to determine if the decrease in loss modulus is only caused by changes in the mixture's gradation or if the lower density and the spherical shape of the PCM microcapsules are also playing an effect. This could be done by replacing the PCM microcapsules by particles of similar sizes but with a higher density (close to 2.8 g/cm^3). If the PCM microcapsules are deemed to be responsible for the reduced modulus, different alternatives can be studied to increase the rutting performance of the pavement including the addition of modifiers such as multi-walled carbon nanotubes, crumb rubber or KTL anti-rutting additives [122].

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APPENDIX A

Image processing procedure for the determination of the core volume fraction of polyester/FAAms capsules

All photographs were taken with the same camera and lighting setup, which allowed for the same procedure to be followed when analyzing all the capsules generated. All the image files were opened in Image J 1.53e software where first step was to set the pixel to mm scale (183.96 pixels/mm). Next, images were converted to 16 bit (grayscale) and the contrast was enhanced to 35% saturation. The auto threshold function was then selected to isolate the core of the capsules from the shells. The “analyze particle” function was used to measure the core’s area, ferret diameter, circularity, roundness, and aspect ratio. Note that the minimum diameter and circularity values were set to 1 mm and 0.2, respectively, to reduce the noise in the measurements. Additionally, the capsules’ outside diameters were measured by manually outlining the shell with the “oval” tool and measuring the area of each capsule using the “measure” function. The outside diameters were then estimated using these area values and the area of a circle formula. The average outside diameter of the capsules was calculated for each set of generating parameters; this value, along with the area of the core determined in previous steps were then used to calculate the core volume percentage assuming that both the capsule and the core shapes were perfectly spherical.

Technical sheet of premixed HMA materials used to make specimens for the thermal cycling experiments.

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