İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF PARAFFIN AND POLYETHYLENE GLYCOL BASED PHASE CHANGE MATERIALS FOR WHITE GOOD APPLICATIONS

M.Sc. THESIS

Nilüfer ERTUNÇAY

Department of Chemical Engineering

Chemical Engineering Programme

JUNE 2016

İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF PARAFFIN AND POLYETHYLENE GLYCOL BASED PHASE CHANGE MATERIALS FOR WHITE GOOD APPLICATIONS

M.Sc. THESIS

Nilüfer ERTUNÇAY
(506141038)

Department of Chemical Engineering

Chemical Engineering Programme

Thesis Advisor: Prof. Dr. F. Seniha GÜNER
Thesis Co-Advisor: Dr. Yusuf YUSUFOĞLU

JUNE 2016

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BEYAZ EŞYA UYGULAMALARI İÇİN PARAFİN VE POLİETHİLEN GLİKOL BAZLI FAZ DEĞİŞTİREN MALZEMELERİN HAZIRLANMASI VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Nilüfer ERTUNÇAY
(506141038)

Kimya Mühendisliği Anabilim Dalı

Kimya Mühendisliği Programı

Tez Danışmanı: Prof. Dr. F. Seniha GÜNER
Eş Danışman: Dr. Yusuf YUSUFOĞLU

HAZİRAN 2016

Name-surname, a M.Sc./a Ph.D. student of İTU Graduate School of Science Engineering and Technology student ID …....., successfully defended the thesis/dissertation entitled "THESIS TITLE", which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Name SURNAME** İstanbul Technical University	.....
Co-advisor :	**Prof.Dr. Name SURNAME** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Name SURNAME** Yıldız Technical University	.....
	Prof. Dr. Name SURNAME Boğaziçi University	.....
	Prof. Dr. Name SURNAME Gebze Institute of High Technology	.....
	Prof. Dr. Name SURNAME Şişli Etfal Teaching Hospital	.....
	Prof. Dr. Name SURNAME Bilkent University	.....

Date of Submission : 17 December 2014
Date of Defense : 21 January 2015

To my family,

FOREWORD

First of all, I express my sincere appreciation to my thesis supervisor Prof.Dr. F. Seniha GÜNER for her guidance, support and helpful critics throughout the progress of my thesis study. Also, I would like to express my deepest gratitude to my co-advisor Dr. Yusuf YUSUFOĞLU.
I would like specially thank to Gökçe UĞUR ERİNÇ for her full support and motivation.
I would like to thank to my company ARCELIK A.S. Central Research & Development Department Director Cem KURAL and Materials Technologies Manager Dr. Mustafa SEZER for supporting my research activities and offering an employment opportunity.
I would like to show gratitude to Kadir ERDOĞAN for his help during the measurements.
Finally, I would like to dedicate my thesis to my dearest family. I cannot ignore their motivating attitudes and guidance throughout my thesis and my life.

June 2016 Nilüfer ERTUNÇAY
(Chemical Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

PCM	**:** Phase Change Material
PEG	**:** Polyethylene Glycol
UTES	**:** Underground Thermal Energy Storage
TES	**:** Thermal Energy Storage

SYMBOLS

T_{cryst_S} **:** Beginning temperature of crystallization
T_{cryst_F} **:** Final temperature of crystallization
$T_{melting\_S}$ **:** Beginning temperature of melting
$T_{melting\_F}$ **:** Final temperature of melting

LIST OF TABLES

Page

LIST OF FIGURES

Page

PREPARATION AND CHARACTERIZATION OF PARAFFIN AND POLYETHYLENE GLYCOL BASED PHASE CHANGE MATERIALS FOR WHITE GOOD APPLICATIONS

SUMMARY

Nowadays, there is considerable demand for phase change materials (PCMs) within a wide temperature range to accomplish the energy efficiency in many areas. PCMs offer tremendous potential to fulfill the growing energy needs for cooling and heating applications across various industries including construction, commercial refrigeration, textiles, transportation packaging for temperature-sensitive products, several solar energy based systems, electronics and biomedical materials. The use of different PCM technologies is expected to improve the global efforts to conserve energy in the wake of fast depleting fossil fuels. However, effective integration of PCMs in end-products remains a challenging task. The increasing demand for energy-saving and ecologically friendly systems is driving the growth of the global PCM market. The paraffin-based PCM market commands the largest share of the overall PCM market in terms of value, while salt hydrate-based PCMs lead the market in terms of volume.

PCMs that are used for the storage of thermal energy as sensible and latent heats are an important class of modern materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. The storage of latent heat enables them to have considerably higher thermal energy storage densities with a smaller temperature difference between storing and releasing heat compared to sensible heat storage materials.

The basic operation principles of solid liquid PCMs is based on that PCMs absorb heat with increasing in temperature until phase change temperature, heat absorption at phase change from solid to liquid occurs at almost constant temperature and the same process repeats with release of heat during the cooling process and liquid completely converts into solid.

In this research, studies have been conducted in three different groups of which two are related with the development of suitable PCM formulations by using pure alkans and polyethylene glycols (PEGs) and other one is conserned with reducing the chemical usage and cost reduction by the way of making tetradecane/water emulsions.

According to the theoritical knowledge, organic phase change materials have more remarkable properties in terms of working life and performance. In the light of this notion, the choice of raw materials were evaluated taking account of the temperature of developed phase change materal which is desired between -20°C to 10°C.

Besides, the effects of preparation method on tetradecane and water emulsions have been observed. To achive the chemical structural integrity, the importance of the squence of added chemicals were investigated.

The findings from this study are introduced below:

- Tridecane – hexadecane formulations have shown two step melting and crystallization because of the pure tridecane's phase change characteristic. Due to the fact that, for refrigerator applications require more narrow operating temperature range, these formulations cannot be considered as suitable.
- In the case of tridecane – tetradecane mixtures, formulations demonstrate one step solid liquid phase change; moreover, because of the closeness of the melting and crystallization temperatures in between 0 - 5°C, this group of phase change materials are countenanced both fresh food cabined and crisper in refrigerator.
- When tetradecane – pentadecane mixtures are analyzed, single-phase change curves could not be seen for the formulations that contain low tetradecane weight percent (10%, 20% respectively). Beside this, developed other PCMs have shown phase change in between 3 - 8°C that exactly suit with the refrigerator operating temperatures.
- Within the context of this study, it observed that tetradecane – pentadecane mixtures become prominent for home appliances with low operating temperature.
- When DSC thermograms are investigated in detailed, both PEG300-PEG600 and PEG300-PEG1500 mixtures have shown the higher melting and crystallization temperatures above the operation conditions.
- Mixture of PEG300-PEG1500 phase change materials with relatively high phase change temperature (between 30 - 40°C) can be utilized as different white good applications such as in heating rinse water of dishwasher.
- Formulations which containe various amounts of PEG400 and PEG600 demonstrate solid liquid phase change in a wide range temperature - approxiametely in 10°C. Because of this situation, they cannot be used direct usage in refrigerator properly. However, especially PCMs with mixture of PEG400 and PEG600 can be utilized if they are frost utterly in freezer, they can be used in fresh food cabinet when power outage is exist; therefore, it can be extended the decay time of foods and beverages.
- As a result of the study that is examined the effects of the preparation method on the stabilization for tetradecane water emulsions, ıt has not seen a huge discrepancy between method 1 and method 3 in terms of the change in melting temperatures and enthalpy of fusion values.
- On the contrary, the beginning of the phase separation has been observed more significantly in PCM synthesized with method 2. That can be concluded that rather than the adding sequence of chemicals, the duration of interaction of materials all told is more effective.
- In performance measurement of PCM contains 70% PEG400 and 30% PEG600, fresh food compartment temperatures are kept under the upper limit temperature (10°C) more than 2.4 hours with the help of phase change materials.

- In addition to this result, by using the PCM includes 60% PEG400 and 40% PEG600 provides more than 3.5 hours cooling, if they are frost utterly in freezer and used in fresh food cabinet when power outage is exist; therefore, it can be extended the decay time of foods and beverages.

BEYAZ EŞYA UYGULAMALARI İÇİN PARAFİN VE POLİETİLEN GLİKOL BAZLI FAZ DEĞİŞTİREN MALZEMELERİN HAZIRLANMASI VE KARAKTERİZASYONU

ÖZET

Termal enerji depolama sistemleri arasında faz değiştiren malzemeler (FDM) son dönemde ön plana çıkmaktadır. Faz değiştiren malzemeler, ortam sıcaklığı maddenin erime sıcaklığına yükseldiğinde erimeye başlayan ve hal değişim prosesi boyunca ortamdan ısı absorbe edebilen, tam tersi durumda sıcaklık maddenin katılaşma noktasına kadar düştüğünde ise katılaşma prosesi boyunca depoladığı bu ısıyı ortama geri verebilen maddelerdir. Faz değişimlerini sabit sıcaklıkta gerçekleştirmeleri, -20°C ile +150°C gibi geniş bir aralıkta hem soğutma hem de ısıtma uygulamaları için kullanılabilir olmaları dikkat çeken özellikleridir.

Bu çalışmada beyaz eşya uygulamalarında kullanıma yönelik -20°C ile +10°C sıcaklıkları arasında faz değişimi gösteren faz değiştiren malzeme formülasyonlarının geliştirilmesi ve uygun olanların buzdolabı prototipi üzerinde uygulanması hedeflenmiştir. Faz değiştiren malzemelerin buzdolabı uygulamasında kullanılması, elektrik kesintisi durumunda sıcaklık kontrollerinin faz değiştiren malzemeler aracılığıyla yapılması, kabin içi sıcaklıklarını uzun süre uygun değerlerde tutulmasına ve böylelikle gıdaların raf ömrünün arttırılmasına olanak sağlayacaktır. Bunun yanı sıra özellikle elektrik enerjisinin pahalı olduğu saatlerde gerekli olan soğutma enerjisinin kabin içesinde bulunan FDM kullanılarak sağlanmasının müşteriye maliyet avantajı getireceği öngörülmüştür. Beyaz eşya uygulamalarında faz değiştiren malzemelerin kullanılmasıyla birlikte çeşitli elektronik cihazların sıcaklık kontrolü ayrıca evaporatör ve kompresör çevresinde açığa çıkan atık ısının geri kazanılmasıyla enerji verimliliği arttırılabilir.

Alternatif enerji kaynağı olarak yararlanılabilecek olan termal enerji depolama sistemleri, yenilenebilir ve atık ısı kaynaklarının mevcut olduğu zamanlarda enerjinin depolanmasına ve kaynakların kesintiye uğradığı zamanlarda kullanılmasına olanak vermektedir. Termal enerji depolama sistemleriyle ozon tabakasına zarar veren kloroflorokarbonlara gereksinim duymadan doğrudan soğutma-ısıtma yapılabilmektedir. Elektrik enerjisine duyulan gereksinim azalmakta ve elektriğin en çok kullanıldığı günlük periyotlarda, elektrik tüketimi engellenebilmektedir. Bu sistem, enerji santrallerine duyulan ihtiyacı ve fosil yakıt kullanımını azaltarak, çevreyi daha az kirleten çözümler sunmaktadır. Termal enerji depolama; binalar elektronik cihazların korunması, beyaz eşyalar gibi farklı alanlarda enerji verimliliğinin artırılması için kullanılabilir. Termal enerji depolama, duyulur ısı depolama, gizli ısı depolama ve termokimyasal ısının depolanması yollarıyla sağlanabilir. Duyulur ısı depolama yönteminde, ısı depolayan malzemenin sıcaklığının değişmesi sonucunda ortaya çıkan duyulur ısıdan yararlanılır. Bu malzemelerden ısı depolamak için geliştirilmiş olan teknoloji, etkin sistemlerin tasarlanması için uygundur. Bu yöntemle ısı depolamada, ısının depolanması ve geri kazanılması süresince depolama malzemesinin sıcaklığı değişir. Çok sayıda ısı

depolama ve geri kazanma çevriminin gerçekleştirilebilmesi, duyulur ısı depolama yönteminin önemli özelliklerinden birisidir. Gizli ısı depolama, istenilen sıcaklık aralığında eriyip katılaşarak faz değiştirebilen malzemelerde erime gizli ısısı şeklinde ısı depolamadır. Gizli ısı depolamada, katı-sıvı faz değişimi sırasında faz değiştiren malzeme tarafından soğurulan ve serbest bırakılan ısıdan yararlanılır. Gizli ısı depolamanın temel özelliği; duyulur ısı depolama yöntemine göre depolama kapasitesinin yüksek olmasıdır. FDM'nin sıcaklığını 1°C artırmak için gerekli ısı miktarı, katı malzemenin ergitilmesi için, FDM'nin birim ağırlığı başına gereken ısı miktarından azdır. FDM tamamen eritildikten sonra, eklenilen her fazla ısı FDM'nin sadece duyulur ısısını arttıracaktır. Gizli ısı depolama yönteminin duyulur ısı depolama yöntemine göre, ısı depolama kapasitesinin yüksek olması ve az miktarda malzeme kullanımından dolayı düşük ısı deposu hacmi kaplaması öne çıkan avantajlarındandır.

Faz değiştiren malzemeler arasında yüksek erime ısısına sahip organik ve inorganik yapılı malzemeler bulunmaktadır. Gaz fazı değişimi gösteren malzemeler, gaz fazının depolanması için basınç uygulanması gerektiğinden genellikle tercih edilmez. Katı-sıvı faz değişim malzemelerinin gizli ısı depolama sistemlerinde ısı depolama malzemesi olarak kullanılabilmesi için, termodinamik, kinetik ve kimyasal ve ekonomik yönlerden belirli özellikler göstermeleri gerekir. FDM seçiminde etkili değişik ölçütler aşağıdaki gibi sıralanabilir. Termodinamik özellikleri açısından FDM'nin ergime noktası istenilen çalışma aralığında ve birim kütlesinin ergime ısısı yüksek olmalıdır. Isıl iletkenliği, özgül ısısı ve küçük hacimdeki depolara yerleştirilebilmesi için yoğunluğu yüksek olmalıdır. Bunlara ek olarak faz değişiminde ısıl genleşme katsayısı düşük ve faz değiştirme sonucunda hacim değişimi az olmalıdır. FDM'lerin uygulama içerisinde yüksek performans gösterebilmesi için dikkat edilmesi gereken bir diğer öenmli özellik de donma sırasında çok az aşırı soğuma gösteriyor olmalarıdır. Kimyasal özellikleri değişmemeli, ayrışmamaya uğramamalı, korozif, yanıcı, zehirli ve patlayıcı olmamalıdır. İnorganik FDM'ler arasında tuz hidratları ön plana çıkmaktadır. Tuz hidratları, 0 - 150°C sıcaklık sınırlarında hacimsel ısı depolama kapasitelerinin yüksek olması nedeniyle inorganik FDM'lerin en önemli grubudur. İnorganik tuzların erime ısıları yüksektir, ısı depolama kapasiteleri 250 - 400 MJ/m3 arasındadır. Genellikle suda çözünebilen tuzlar ısı depolama amacıyla kullanılabilir. Isı depolama amacıyla kullanılabilen ve pahalı olmayan birçok tuz hidratı bulunmaktadır. Dezavantajları arasında ise faz ayrışması ve aşırı soğuma göstermeleri ile korozif etkiye sahip olmaları gösterilebilir. Organik bileşiklere göre daha düşük faz değişim entalpisi göstermeleri ile birlikte, ısı depolama malzemesi olarak çeşitli önemli özelliklere sahiptir. Bunlar arasında fiziksel ve kimyasal olarak kararlı yapıda olmaları, aşırı soğuma göstermemeleri ve korozif olmamaları ön plana çıkmaktadır. Organik faz değiştiren malzemeler içerisinde parafinler yaygın kullanıma sahiptir. Parafinler petrol türevleri olup, genel olarak C_nH_{2n+2} şeklinde belirtilen ve alkanlar olarak adlandırılan önemli bir bileşen içerirler. Saf parafinler, sadece alkanları içerir. Alkanların erime sıcaklığı karbon atomu sayısının artmasıyla artar. Karbon atomu sayısı 14 - 40 arasında olan alkanların erime sıcaklığı, 6 - 80°C aralığındadır. Parafinler alkan zinciri uzunluğuna bağlı olarak n-parafin veya izo-parafin seklinde olabilir. Doymuş hidrokarbonlar grubundan olan parafinler grubu içerisinde benzer özelliklerdeki bileşikler yer alır. Karbon atomu sayısı çift olan parafinler ucuz, bol ve kimyasal olarak kararlı olduklarından ısı depolama için tercih edilir. Parafinlerin katı durumdaki ısıl genleşme katsayıları tuz hidratlarına oranla düşüktür. Isıl genleşme katsayısının neden olduğu olumsuzlukları önlemek için ısı depolama ünitelerini

elastik malzemelerden tasarlamak ya da depolama ünitelerinde emniyet için gerekli hacim belirlemek katkı sağlayacaktır. Parafin olmayan organik materyaller arasında yağ asitleri ve polietilen glikol grupları ön plana çıkmaktadır. Yağ asitleri, genel olarak $CH_3(CH_2)2nCOOH$ seklinde belirtilir. Yağ asitlerinin erime ısıları parafinlerle karşılaştırılabilir değerlerdedir. Yağ asitleri; termodinamik, kinetik, ısıl ve kimyasal kararlılık, emniyet ve maliyet bakımından, tuz hidratları, parafin ve diğer kimyasal maddelere kıyasla üstün özelliklere sahiptir. Hiç aşırı soğuma olmadan donma özelliğine sahip olduklarından, FDM olarak uygun özelliklere sahiptir. En önemli olumsuzlukları, maliyetlerinin parafinlerden 2 – 2.5 kat daha yüksek olmasıdır.

Literatürde hem organik hem de inorganik faz değiştiren malzemelerin kullanıldığı pek çok çalışma bulunmaktadır. Bu çalışmalar genel olarak uygun FDM'nin seçimi, termal özelliklerinin iyileştirilmesi, sentezlenmesi ve ömür testlerinin değerlenririlmesi yönünde olmuştur.

Bu çalışmada, yüksek karbon zincirli alkanlar ile polietilen glikol (PEG) serileri kullanılarak hedeflenen çalışma aralığı içerisinde hal değişimi gösteren 33 farklı faz değiştiren malzeme formülasyonu geliştirilmiş, termal karaktrizasyonu ve ömür testleri yapılmıştır. Bunlara ek olarak, hem daha az kimyasal kullanılması hem de maliyet avantajı sağlamak amacıyla belirlenen bir formülasyon çerçevesinde farklı sentez methodları ile yağ su emülsiyonları hazınlanmış, hazırlama yönteminin emülsiyon stabilizasyonuna etkisi incelenmiştir. Faz değiştiren malzeme sentez çalışmaları temelde üç grupta yürütülmüştür.

İlk grupta, 13 karbon zincirinden 16 karbon zinciri uzunluğuna kadar 4 farklı alkan, katı sıvı faz değişim sıcaklıkları göz önünde bulundurularak tridekan-hekzadekan, tridekan-tetradekan ve tetradekan-pentadekan ikili grupları şeklinde toplamda 19 farklı faz değiştiren malzeme hazırlanmıştır.

İkinci grup çalışmada; PEG300 - PEG600, PEG300 - PEG 1500 ve PEG400 - PEG600 çifleri ile geliştirilen 14 farklı formülasyon incelenmiş, beyaz eşya uygulamalarına uygunluğu değerlendirilmiştir.

Son grup çalışmada ise yapılan literatür araştırması kapsamında parafin su emülsiyon çalışmaları incelenmiş, öne çıkan çalışmalar arasından uygun deney parametreleri belirlenmiştir. Parafin su emülsiyon sistemlerinde sentezlenen malzemenin zamanla faz ayrışması göstermemesi performans açısından büyük önem taşımaktadır. Yapılan çalışmalarda faz ayrışmasını engellemek için çeşitli yüzey aktif maddeleri kullanılması durumunda bile, sentez yönteminin stabilizasyona etkisi görülmüştür. Bu veriler ışığında temelde tetradekan su karışımı içeren formülasyon, 3 farklı yöntem uygulanarak hazırlanmıştır. Bu hazırlama yöntemlerinde temel olarak kimyasalların karışıma ilave edilme sırası değiştirilmiştir. Hızlandırılmış katı sıvı faz değişim programı uygulanarak ömür testine alınan FDM'lerin termal özellikleri 500 çevrim boyunca incelenmiştir.

Çalışmanın son kısmında ise buzdolabı taze gıda bölmesine uygulanabilecek PEG formülasyonu seçilerek, bunların performans ölçümleri yapılmıştır.

Değerlendirmeler:

Bu tez kapsamında yapılan çalışmalar aşağıdaki şekilde özetlenebilir;

- Yapılan detaylı literatür araştırması sonucunda organik kaynaklı faz değiştiren malzemelerin inorganiklere göre daha kararlı olduğu ve yüksek performans gösterdiği belirlenmiştir.

- Bu doğrultuda özellikle beyaz eşya uygulamalarında kullanabilecek -20°C ile +10°C sıcaklıkları arasında 33 farklı faz değiştiren malzeme geliştirilmiştir. Sentezlenen FDM'ler alkan ve PEG esaslıdır.
- Bunların yanı sıra tetradekan su emülsiyonlarına sentez methodunun etkisi incelenmiş, kullanılan yüzey aktif maddelerin tam olarak yapıda bağlanmayı sağlayabilmesi için, kimyasalların karışım içerisine ekleniş sırasının önemli olduğu belirlenmiştir.
- Alkanların kullanıldığı birinci grup çalışmalar kapsamında; tridekan - hekzadekan karışımlarında erime donma proseslerinin iki aşamada gerçekleştiği görülmektedir. Bunun sebebi tridekanın yapısıdır. Beyaz eşya uygulamalarında daha dar çalışma aralıklarında çalışılması gerektiğinden, katı sıvı faz değişiminin kademeli oluşu uygulanabilirlik açısından uygun bulunmamıştır.
- Tridekan – tetradekan karışımı içeren formülasyonlarında hem erime hem de donma tek basamakta gerçekleşmektedir. Bunun yanı sıra faz değişim sıcaklıklarının birbirine yakın olması ve 0 - 5°C aralığında bulunması, geliştirilen FDM'lerin buzdolabı taze gıda bölmesi ve sebzelik bölmelerinde uygulanabilirliğine işaret etmektedir.
- Tetradekan – pentadekan karışımları incelediğinde ise özellikle sırasıyla %10 ve %20 tetradekan içeren formülasyonlarda tek bir faz değişim sıcaklığı elde edilememiştir. Bunun yanısıra yine aynı grup içindeki geliştirilen diğer FDM'lerin faz değişimleri 3 - 8°C arasında ölçülmüştür.
- Alkan karışımları ile ilgili yapılan çalışmalarda buzdolabı uygulaması için tetradekan pentadekan karışımlarının öne çıktığı görülmektedir.
- Ölçüm sonuçları incelendiğinde hem PEG300-PEG600 hem de PEG300-PEG1500 karısımların erime sıcaklıklarının limit değerler üzerinde olduğu görülmüştür.
- Farklı oranlarda PEG300- PEG1500 içeren formülasyonların 30 - 40°C arasında faz değişimi göstermeleri sebebiyle bulaşık makinası gibi yüksek çalışma sıcaklıklarına sahip beyaz eşya uygulamalarında için kullanılabileği görülmüştür.
- PEG400-PEG600 karışımı içeren formülasyonlardan bazıları geniş aralıkta faz değişimi göstedikleri için buzdolabı uygulamalarında doğrudan kullanıma uygun değildir. Ancak geliştirilen bu malzemeler arasından özellikle %30-60 PEG400 içeren formülasyonların buzluk kısmında tamamen donması sağlandıktan sonra, elektrik kesintisi durumunda buzdolabı taze gıda bölmesine yerleştirilmesiyle gıdaların bozunma süresini uzatacağı öngörülmektedir.
- Tetradakan su emülsiyonlarında belirlenen formülasyon kapsamında tüm kimyasallların aynı anda eklenildiği method 1 ile uyumlu kimyasalların (su ile Tween60'ın, tetradekan ile Span 60'ın) kademeli olarak karıştırıldığı method 3 arasından entalpi ve faz değişim sıcaklıklarının değişimleri arasından büyük bir fark görülmemiştir.

- Method iki de ise zaman içerisinde faz ayrışması görülmüştür. Bunun sebebinin tüm karışım prosesi tamamlandıktan sonra homojenizasyon elde edilmiş olsa bile kimyasal bağlanmanın aslında tam anlamıyla tamamlanamamış olmasından kaynaklanmaktadır.

1. INTRODUCTION

In recent years, with the rapid consumption of fossil fuels, energy demand has increased incrementally. Moreover, this leads to environmental pollution and CO_2 emission in high quantitiy. This situation poses to new approaches for energy efficiency in many countries. With their share of 35%, buildings are existing leaders in energy consumption. Looking at currently consumption trends, building's energy demand will rise from 117 EJ in 2010, to 173 EJ by the year 2050. This means that global direct CO_2 emissions from all buildings will be 25% higher than today in 2050 and possibly reach 3.5 GT. In addition to this, domestic appliances and other electronics consumed nearly 2500 TWh of electricity in 2010 with an increase of 43% over the last decade that is about half of the total electricity consumption of homes [1].

Many countries are studying on the consumer awareness programs, standards, and new labels to reduce energy consumption by homes. Energy Star® the well known program of the U.S. has diminished 277 million tonnes of greenhouse gases in 2013 alone, providing over $10 billion USD in energy savings. In Europe, energy efficiency labels from A+++ to G are being used in appliances and with the help of a new and ambitious attempt for further increasing energy savings in appliances, more strict energy consumption levels that require manufacture of products with A+ or above are mandated. Because of this situation, appliance manufacturers have struggled to find new solutions and to make more efficient products [2].

Efforts to increase energy efficiency of white goods will directly reduce energy consumption in residential buildings. Under favour of phase change materials (PCMs) is a new approach to improve the performance of these appliances. PCMs which are used for the storage of thermal energy as sensible and latent heats are an important class of modern materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. The storage of latent heat enables them to have considerably higher thermal energy storage densities with a

smaller temperature difference between storing and releasing heat compared to sensible heat storage materials [3].

The basic operation principles of solid liquid PCMs is based on that PCMs absorb heat with increasing in temperature until phase change temperature, heat absorption at phase change from solid to liquid occurs at almost constant temperature and the same process repeats with release of heat during the cooling process and liquid completely converts into solid [4]. PCMs can be classified as organic, inorganic and eutectics; moreover, the selection of PCM varies according to the engineering application and its requirements [5].

The refrigerator is the one of the most crucial appliance that is in almost all households around the world today. The utalization of PCMs in refrigerator application can provide a number of benefits in terms of energy efficiency. Besides the usage of PCMs around the evaporator and/or condenser, they can also be used in fresh food cabinet and crisper. When power outage is existing, PCM starts the phase change in almost constant temperature and consequently the cabinet environment remains stable temperature; therefore, decay time of foods and beverages can be extended.

In this study, to obtain the energy efficiency in white good applications, preparation and thermal characterization of paraffine and polyethylene glycol based 33 different phase change materials are presented. Besides, the effects of sysnthesis method on tetradecane and water emulsions have been observed. To achive the chemical structural integrity, the importance of the squence of added chemicals are investigated.

2. BASIC CONCEPTS OF THERMAL ENERGY STORAGE

2.1 Thermal Energy Storage

Thermal energy storage (TES) is a technique that allows the storage of heat or cold to be used later. Thermal energy can be achieved by physical and chemical processes and stored in three forms: as sensible heat, as latent heat or as thermochemical energy. To be able to retrieve the heat or cold after some time, the method of storage needs to be reversible. Figure 2.1 shows some possible methods; they can be divided mainly into physical and chemical processes [6].

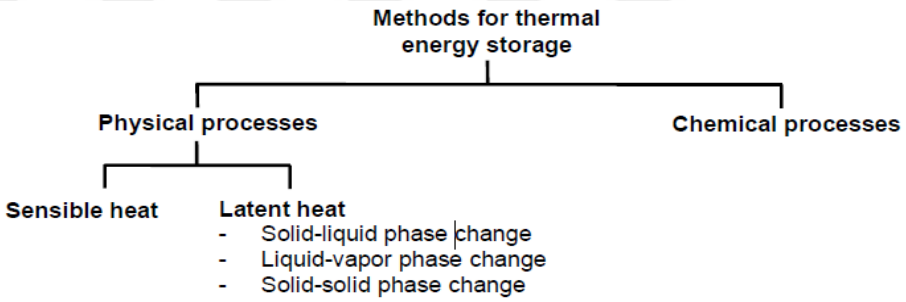

Figure 2.1 : Possible methods of reversible storage of heat and cold.

Long term and short term (night-day) storage can be done by using these methods for cooling and heating applications. The aim of long term storage is storing heat for seasonal such as in summer for heating in winter or storing winter cold for cooling in summer. Usually, underground thermal energy storage (UTES) is used for long term storage [7]. Sensible heat storage is suggested for long term applications whereas latent heat storage is suitable for short term applications [8].

2.1.1 Sensible heat storage

Sensible heat storage is one of the most well known method for storing thermal energy. With the help of high specific heat capacity or increasing the mass of storage material, high sensible heat storage in a limited temperature difference can be obtained. For this reason, as the medium of sensible heat storage materials like water or rocks are generally preferred. The most frequently used sensible heat storage material is water due to its remarkable properties like easy accessibility, low cost and

high specific heat capacity. For instance, hot water is used for heat storage in the floor structures or obtaining domestic hot water for our homes are some of the application areas of water in practice in the field of sensible heat storage. Gases are not generally used in sensible heat storage systems due to their low volumetric heat capacities. When compared to chemical or latent heat storage systems, by using sensible heat storage system heat storage and recovery cycles can be repeated many times without any problems. However, large storage volume requirement can be considered a substantial drawback for the system. Furthermore, they cannot be proper for the systems that have to work at a specific temperature because of the need for temperature difference to store the energy [9,10].

2.1.2 Thermochemical heat storage

″Any chemical reaction with high heat of reaction can be used for thermal energy storage if the products of the reaction can be stored and if the heat stored during the reaction can be released when the reverse reaction takes place.″ [6]. The schematic figure that shows the mechanism of the chemical heat storage process is shown in Figure 2.2.

$$AB + Heat \Longleftrightarrow A + B_{gas}$$

$$\text{Charge: } AB + Heat \Longrightarrow A + B_{gas}$$

$$\text{Discharge: } A + B_{gas} \Longrightarrow AB + Heat$$

Figure 2.2 : Storage with reversible chemical reaction.

Type of components that are involved in chemical reaction or produced after the chemical reaction and temperature at which the reaction takes place are two main issues have to be considered in these systems. Just like in the other storage methods, the temperature of the reaction has to be chosen according to the desired storage temperature; however, because of the nature of the chemical processes, sometimes this need cannot be achieved. In addition, if gases are used or produced in the chemical reaction, it is important to reserve necessary storage space [6].

Compared to physical processes, chemical heat storage has higher energy storage density. However, its application is limited due to the following problems: complicated reactor design needed for specific chemical reactions [11,12], corrosion and toxicity [13], wide working temperature ranges [14,15], strict requirements of

pressure vessels, weak long-term durability and reversibility [16], and weak chemical stability [17].

2.1.3 Latent heat storage

The latent heat is the energy needed for the phase change of a material. In latent heat storage systems which present higher energy density than sensible heat storage, the phase change between solid-liquid is presented as the most suitable due to the high energy density and the lack of problems related to volume expansions. In liquid - gas transformations are not practical due to the high pressures required to store the materials in the gas phase. Moreover, solid-solid phase change supplies low energy density [18].

2.2 Phase Change Materials

Phase Change Materials (PCMs) offer tremendous potential to fulfill the growing energy needs for cooling and heating applications across various industries, including construction, commercial refrigeration, textiles, transportation packaging for temperature-sensitive products, several solar energy based systems, electronics and biomedical materials [19]. The use of different PCM technologies is expected to improve the global efforts to conserve energy in the wake of fast depleting fossil fuels. However, effective integration of PCMs in end-products remains a challenging task. The increasing demand for energy-saving and ecologically friendly systems is driving the growth of the global PCM market. The paraffin - based PCM market commands the largest share of the overall PCM market in terms of value, while salt hydrate-based PCMs lead the market in terms of volume. Europe offers a lucrative market to PCM players because of its focus on energy security and therefore holds the largest share, 42.2%, of the global PCM market. Currently, the market players are focusing in development of new products and applications, which therefore accounted for the highest share of the total competitive developments in the global PCM market from 2007 to May 2010. Building and construction industries presently are the largest application market of organic PCMs due to the globally increasing requirement for cooling buildings, which in turn has arisen in consequence of the shift from heavy thermal mass design to lightweight architecture. This application contributed 22% to the global PCM market revenues in 2009. Textiles incorporated

with PCMs have been used in numerous products and applications from apparel, outdoor wear such as parkas, vests, thermals, snowsuits and trousers, underwear, socks, accessories and shoes to bedding, sleeping bags, blankets, duvets, mattresses and pillowcases. PCMs can even be found in specialty items, such as antiballistic vests, automotive, medical or special industrial applications. Industry participants with the most significant PCM incorporated product developments include BASF, Honeywell, Outlast Technologies and PCM Products. BASF, PCM Products and Outlast Companies are also collaborating with universities to conduct research and development on advanced PCMs in an attempt to increase market penetration of the PCM products [20].

Over the last 40 years several classes of materials, mainly hydrated salts, paraffin waxes, fatty acids, polymers and the eutectics of both organic and non-organic compounds have been considered as potential.

PCMs can be classified by type of phase transition: gas – liquid, solid – gas, solid – liquid and solid – solid systems see Figure 2.3. The applications of PCMs with a solid –gas or liquid – gas phase transition are limited due to the large volume expansion associated with the transition [8].

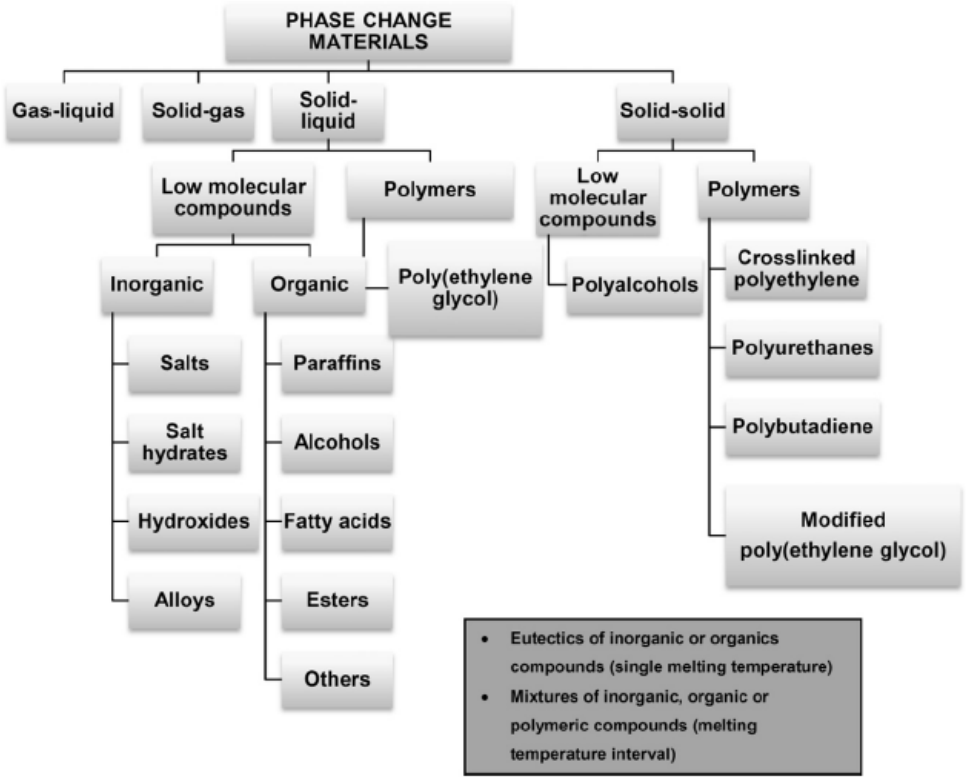

Figure 2.3 : Classification of PCMs.

Significantly smaller volume changes occur, usually 10% or less, with solid – solid and solid – liquid transformations. This makes them economically and practically attractive as materials for TES systems despite their smaller heat of phase transition [10]. Solid – solid PCMs employ the heat associated with the phase transition one to another crystalline form and can be considered as an alternative to solid–liquid PCMs [21]. Generally, the heat of phase transition for solid–solid PCMs is lower than that of solid – liquid PCMs [8,10,22].

Based on the temperature ranges PCMs can be divided into three main groups: low temperature PCMs with phase transition temperatures below 15 C which are usually utilized in air conditioning applications and the food industry, mid temperature PCMs with phase transition temperatures in between 15–90 C with solar, medical, textile, electronic and energy-saving applications in building design and high temperature PCMs with a phase transition above 90C developed mainly for aerospace and industrial applications [23,24].

2.2.1 Solid–liquid PCMs

Many different types of solid–liquid PCMs are employed for thermal storage applications for instance; water, salt hydrates, paraffins, selected hydrocarbons, polymers, selected hydrocarbons, polymers and metal alloys.

2.2.1.1 Inorganic PCMs

Salt hydrates

Salt hydrates are inorganic salts containing water of crystallization. During phase transformation dehydration of the salt occurs, forming either a salt hydrate that contains fewer water molecules or the anhydrous form of the salt. Depending on the melting behaviour, the salt hydrates can be classified as:

- salt hydrates with congruent melting behaviour
- salt hydrates with incongruent melting
- salt hydrates with semi-congruent melting [10].

Unfortunately, a great number of salt hydrates that could be considered as potential PCMs melt incongruently. For this reason, the amount of released water is insufficient to dissolve the crystalline salt formed during the dehydration process.

This leads to density differences, phase separation and sedimentation in containers causing serious technical problems in practical applications. With the help of adding gelling or thickening agents segregation and sedimentation of the heavier phase can be prevented. The addition of a gelling material to the salt creates the formation of a three-dimensional network to avoid salt sedimentation, while the addition of a thickening agent increases the viscosity of the salt hydrate and helps to hold the salt hydrate molecules together [25]. Another disadvantage of salt hydrates is their poor nucleating ability that causes significant supercooling. To avoid this problem, nucleating agents are added to PCM, or small amounts of crystals are retained in the system to act as nucleation sites [10]. Additionally, there are some corrosion problems of metallic components in energy storage installations [26]. However, despite these disadvantages, salt hydrates are generally considered as suitable materials for TES applications because they have large latent heat of fusion, appropriate phase transition temperature and they are very competitive in terms of economy and profitability to PCM, or small amounts of crystals are retained in the system to act as nucleation sites [10]. Additionally, there are some corrosion problems of metallic components in energy storage installations [27]. However, despite these disadvantages, salt hydrates are generally considered as suitable materials for TES applications because they have large latent heat of fusion, appropriate phase transition temperature and they are very competitive in terms of economy and profitability.

Alloys

Metallic alloys can be considered as high-temperature PCMs which offer high thermal reliability and repeatability [24]. The largest phase transition heat, on a mass or volume basis, has been found for binary and ternary alloys of the relatively plentiful elements Al, Cu, Mg and Zn, but not all of the potential materials are suitable for use in TES systems. Among other latent heat energy storage materials, eutectic aluminium alloys were principally investigated for use as PCMs in high temperature TES systems due to their convenient phase change temperature, high latent heat density and good thermal stability [28].

2.2.1.2 Organic PCMs

Organic PCMs comprise of a wide range of materials including paraffins, fatty acids and their eutectic mixtures, esters and other organic compounds.

Paraffins

The natural paraffins and paraffin waxes that are produced as by-product in crude oil refining correspond to the valuable product in comparison with pure alkanes for practical application. The paraffins are produced in large scale, they are relatively cheap and they have high heat of fusion. These characteristics of paraffins meet the requirements of phase change thermal energy storage materials. The paraffins produced in many countries are characterized as a rule by melting range and heat fusion whale other thermophysical properties required for practical application of paraffins as latent heat storage materials are not known [29].

Paraffins constitute the broadly used solid–liquid PCMs which possess a high latent heat storage capacities over a narrow temperature range and are considered as non-toxic and ecologically harmless. Paraffin waxes reveal moderate TES density, but a large surface area is needed as they have low thermal conductivity. This decreases their rate of heat charging and discharging during the melting and solidification cycles [30]. The latent heat of paraffins is molar mass-based and their various phase change temperatures give the flexibility to select an appropriate PCM for a specific LHTES application. They are economically viable and repeated cycling across the solid – liquid transition does not induce phase separation [31]. Paraffins between C5 and C15 are liquids with the higher analogs being waxy solids with melting temperatures ranging from 23 to 67C [8]. Commercial grade paraffin wax, which is a mixture of different hydrocarbons, is produced by the distillation of crude oil. In general, the longer the average length of the hydrocarbon chain, the higher the melting temperature and heat of fusion [32]. This relationship can be employed to design the PCM properties by mixing physically different paraffins. In fact, most paraffin PCMs are mixtures of saturated hydrocarbons with different numbers of carbon atoms in the molecules. The literature data show that after 1000 – 2000 cycles commercial grade paraffin waxes and other pure paraffins have stable properties and good thermal reliability. Paraffin waxes are safe, non-reactive and are compatible with metal containers as they do not promote corrosion. However, care must be taken when using plastic containers as paraffins' chemical similarity and affinity can lead to infiltrations and softening of some polymers, especially polyolefins [32].

The major problem with paraffins as PCM materials is that their thermal conductivity is too low to provide the required rate of heat exchange. Generally, an improvement of the thermal conductivity of a PCM by incorporating conductive particles results in a reduction in the energy storage capacity. It is important that new designs of paraffin-based TES systems increase the thermal conductivity but avoid a decrease in the ability to store energy [33].

Table 2.1 : Paraffins with potential for use as a PCM.

Paraffin	Number of carbon atoms in molecule	Melting temp. (°C)	Heat of fusion (J/g)	Density (g/cm^3)
n-Tetradecane	14	5.8–6.0	227–229	
n-Pentadecane	15	9.9–10.0	206	
n-Hexadecane	16	18.0–20.0	216–236	0.773
n-Heptadecane	17	22–22.6	164–214	0.778
n-Oktadecane	18	28.0–28.4	200–244	0.776
n-Nonadecane	19	32.0	222	0.785
n-Eicozane	20	36.6	247	0.788
n-Heneicozane	21	40.2	213	0.791
n-Docozane	22	44.0	249	0.794
n-Trikozane	23	47.5	234	0.796
n-Tetracozane	24	50.6	255	0.799
n-Pentacozane	25	53.5	238	0.801
n-Hexacozane	26	56.3	256	0.803
n-Heptacozane	27	58.8	235	0.779
n-Oktacozane	28	41.2	254	0.806
n-Nonacozane	29	63.4	239	0.808
n-Triacontane	30	65.4	252	0.775

Fatty acids

The interest in fatty acids as PCMs for energy storage has increased recently as they present desirable thermodynamic and kinetic characteristics for low temperature LHS. They exhibit a high latent heat of fusion, compared to that of paraffins, and reproducible melting and freezing behaviour, with little or no supercooling. However, fatty acids are more expensive than technical grade paraffins, are mildly corrosive and possess a disagreeable odour [10]. With an increasing number of carbon atoms in the fatty acids molecule, the melting and freezing points, the heat of melting and the degree of crystallization gradually increase. Carboxylic acids with an even number of carbon atoms in the structure possess higher values of thermal parameters than those with odd numbers of C - atoms. The former show a tendency for more regular alignment and a more dense crystalline lattice [34], arising from hydrogen bonding between the carboxylic acid molecules. The melting and boiling points of fatty acids are relatively high and the saturated fatty acids exhibit low phase transition volume changes with very little or no supercooling when freezing [34].

Esters

Fatty acid esters show a solid – liquid transition over a narrow temperature range and their mixtures can form eutectics, similar to numerous inorganic salt mixtures, with little or no supercooling. Most of the fatty acid esters are commercially available as large quantities are produced for the polymer, cosmetics, textiles industries and other applications [35,36]. Eutectic mixtures of methyl stearate – methyl palmitate, methyl stearate–cetyl palmitate and methyl stearate – cetyl stearate with a phase transition temperature close to room temperature, a high enthalpy of transition and low hysteresis become prominent [35]. Interestingly, commercial building materials, gypsum and bricks were impregnated with the selected molten esters by immersion. Compared to paraffin - based and fatty acids-based PCMs, EGDS has the advantages of greater energy storage capacity per unit mass, is less odorous and, since there are no acidic functional groups, less corrosive.

Polyethylene glycols (PEGs)

PEG, an OH-terminated poly (ethylene oxide), is a significant semi-crystalline polymer with a repeating unit of –CH2–CH2–O–. It is used in water paints, textile fibres, paper coatings, as a component of packaging materials and as a solubilising agent in drugs. A relatively new PEG application area is related to the TES – it can be used as a PCM as it has a large heat of fusion which is attributed to a high degree of crystallinity [37]. Molecular weight is the key issue for PEG's application as a material for TES seen in Table 2.2. The melting point of PEG is dependent on the molecular weight and may vary from 4 to 70 C, with the heat of fusion in the range of 117–174 J/g. An increase in the molecular weight of PEG causes an increase in the melting temperature and the heat of phase transition. The molecular weight also influences the degree of crystallinity which ranges from 83.8% to 96.4% [38].

Table 2.2 : Temperature and head of fusion for PEG with various molecular weights.

Polymer	Melting temperature (°C)	Heat of fusion (J/g)
PEG 400	4.2	117.6
PEG 600	12.5	129.1
PEG 1000	40.0	168.6
PEG 3400	63.4	166.8
PEG 10000	65.9	171.6
PEG 20000	67.7	160.2
PEG 35000	68.7	166.9
PEG 100000	67.0	175.8
PEG 1000000	70.0	174.0

The ideal PCM should meet a number of criteria related to the desired thermophysical, kinetic and chemical properties [10,39,40]:

Thermal properties:

- a melting temperature in the desired operating range,
- a high phase transition latent heat per unit volume,
- a high specific heat, to provide significant additional senbible heat storage,
- high thermal conductivity of both phases.

Physical properties:

- a small volume change on phase transformation,
- a low vapour pressure at the operating temperature,
- favourable phase equilibrium,
- congruent melting of the PCM,
- a high density.

Kinetic properties:

- no supercooling,
- a high nucleation rate,
- an adequate rate of crystallization.

Chemical properties:

- long-term chemical stability,
- a completely reversible freeze/melt cycle,
- compatibility with the construction materials,
- no corrosion influence on the construction materials,
- it should be non-toxic, non-flammable and non-explosive to ensure safety.

The PCM should be readily available in large quantities at low cost [40]. In practice, those criteria are not fully met by most PCMs. However, recent progress in the design and characterization of novel materials for energy storage, including

nanomaterials, has opened new possibilities for enhanced performance with extended lifetimes [10,39,40].

2.3 Literature Review

The study of PCMs, pioneered by M. Telkes and E. Raymond [41] in 1949, did not receive much attention until the 1970s. In 1971, D.V. Hale, M.J. Hoover and M.J. O'Neill did a pioneering study to design a PCM thermal protection system for the Lunar Roving Vehicle and Skylab [42]. Another significant study was published by W. Humphries and E. Griggs in 1977 [14]. These publications displayed how phase change thermal energy storage was applied for space crafts on a small scale, and then applied on a larger scale for buildings and solar energy systems toward the global energy crisis in the late 1970s [43,44]. Since then several research groups have conducted experimental studies for assessing the thermal behavior of latent heat storage systems. Most early studies of latent heat storage focused on the dehydration and hydration of inorganic salt hydrates, initially showing the greatest promise with their high energy storage density and high thermal conductivity. However, they had some obvious disadvantages, such as being corrosive, being incompatible with several materials, experiencing supercooling and segregation during phase transition under thermal cycling [39].

Depending on the type of applications, the organic PCMs should first be selected based on their phase change temperature. Materials that exhibit phase change below 15 ◦C are used in cooling applications, while materials that have phase change above 90 ◦C are used for absorption refrigeration. The organic PCMs and their mixtures that show phase change around 18–65 ◦C are suitable for the thermal comfort applications in textiles and in buildings [45]. Actually, over the last 25 years, more than 190 review articles have been published, considering a variety of literature related with PCMs. A. Abhat published one of the earliest reviews on PCMs [8]. He summarized the studies on PCMs for heat storage in the temperature range between 0 ◦C and 120 ◦C, classifying inorganic and organic PCMs as salt hydrates, paraffin waxes, fatty acids, and their eutectic mixtures. S.M. Hasnain reviewed the development of available thermal energy storage technologies, their individual advantages and disadvantages for space and water heating applications. He focused on the attempts of 1990s to utilize technical grade PCMs as storage media and

embedded heat exchange tubes or heat pipes with extended surfaces in order to enhance the heat transfer to and from a PCM [46]. B. Zalba et al. overviewed the history of thermal energy storage, focusing on the aspects of PCMs, heat transfer practices and applications. They listed over 150 materials used in research as PCMs, and about 45 commercially available PCMs [47]. M.M. Farid et al. reviewed the researches on latent heat storage and provided a detailed insight to the efforts for developing new classes of PCMs, focusing on their properties, encapsulation techniques and various applications [23].

F. Regin et al. summarized the development of available latent heat storage technologies, and the different aspects of heat storage, such as encapsulation methods, heat transfer applications and new technological innovations related with PCMs [48]. Sharma et al. appraised the investigation and analysis of the available thermal energy storage systems incorporating PCMs for use in different applications, such as heat pumps, solar systems and spacecrafts [10]. Agyenim et al. revised the development of latent heat storage systems, detailing various PCMs investigated over the last three decades, the heat transfer and enhancement techniques employed in PCMs to effectively charge and discharge latent heat energy [49].

L.F. Cabeza et al. reviewed the publications on the use of PCMs in buildings, compiling information about the classification of PCMs, requirements for the use of composites containing PCMs, problems and possible solutions on the application of such composite materials in buildings [50]. M. Delgado et al. gathered the information concerning the PCM emulsions and microencapsulated PCM slurries and the commercially available products [51]. C.Y. Zhao and G.H. Zhang overviewed the fabrication methods and characterization of microencapsulated PCMs (microPCMs) and their applications to textiles and building systems [52]. Z. Rao et al. reviewed the development and applications of PCMs and the environmental friendly materials for indoor thermal management and humidity control [53].

In all these studies, a number of criteria to be fulfilled by an ideal organic PCM candidate, has been listed as: exhibiting (i) high latent heat capacity to provide a high thermal storage density, (ii) small volume change during phase transition, (iii) repeatability of phase change, (iv) thermal stability in the course of numerous heating and cooling cycles, (v) high density to allow a small size of storage container, as well as being (vi) chemically stable, (vii) non-corrosive, (viii) non-toxic (ix)

nonflammable, (x) low in cost, and (xi) easily available. The limitations reported by many researchers are the low thermal conductivity possessed by many organic PCMs leading to low charging and discharging rates, supercooling effect in cooling cycles, and need for containers for preventing the leakage of PCMs [20].

3. MATERIALS AND METHODS

3.1 Materials

In this research, studies have been conducted in three different groups which two of them are related with the development of suitable PCM formulations by using pure alkans and polyethylene glycols (PEGs) and other one is conserned with reducing the chemical usage and cost reduction by the way of making tetradecane/water emulsions.

In first groups of experiment, 19 different higher alkanes' mixtures have been prepared by using four alkanes with sequential carbon number. Starting with 13 carbon number tridecane, mixtures have been synthesized taking into consideration their melting temperatures to remain in between desired working temperatures (-20/10°C) of developed PCMs, up to 16 carbon number n-hexadecane also called cetane. In addition to that, by using four forms of polyethylene glycols (PEGs), 14 varied blends have been investigated as alternative organic PCMs to screen out for white good applications. n-tridecane (>99%, Merck), n-tetradecane (>99%, Merck), n-pentadecane (>99%, Merck), n-hexadecane (>99%, Merck), PEG300 (>90%, Tekkim), PEG400 (>90%, Tekkim), PEG600 (>99%, Merck) and PEG1500 (>90%, Tekkim) were used without further purification. In addition to these as a surfactant, Tween 60 (Merck) and Span 60 (Merck) were utilised. Solid liquid phase change temperature and enthalpy values of pure alkanes are represented in Table 3.1. Materials generally show phase change in wide range temperatures; therefore, melting and crystallization temperatures are presented as ranges. $T_{melting\_0}$ represents the beginning temperature of melting and $T_{melting\_1}$ represents the final temperature of melting. In the same way, T_{cryst_0} and T_{cryst_1} symbolize the beginning and final temperatures of crystallization. Besides, some formulations have two step phase change and these values were presented in bottom rows of related formulation.

Table 3.1 : Solid liquid phase change temperatures and enthalpy of fusion for pure alkanes.

Material	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
n-tridecane	-17.83	-17.10	38.34	-18.77	-19.22	37.05
	-5.50	-3.96	141.00	-5.68	-6.74	144.10
n-tetradecane	5.87	8.07	225.10	-	4.13	225.70
n-pentadecane	-2.23	-1.52	41.61	-3.31	-3.73	39.16
	9.76	11.24	39.16	9.70	8.40	158.30
n-hexadecane	18.19	19.91	222.80	-	16.25	224.40

In Table 3.2, enthalpy and solid liquid phase change temperature values of PEG series are seen, among them, only PEG600 has two step crystallization which can be presented in the bottom row.

Table 3.2 : Solid liquid phase change temperatures and enthalpy of fusion for PEGs.

Material	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
PEG300	-31.69	-16.34	72.39	-32.42	-35.03	68.67
PEG400	-3.63	4.48	57.65	1.69	-0.30	50.86
PEG600	11.28	20.38	115.60	15.29	14.34	34.60
	-	-	-	10.48	9.32	20.75
PEG1500	39.11	47.48	152.80	32.65	28.94	150.10

Additionally, a group of tetradecane/water emulsion which provide less chemical usage and high cost advantage in industrial applications were prepared and the effect of preparation method have been examined. In emulsions, pure water and n-tetradecane were utilised, also to eliminate the phase separation occurance Tween 60 and Span 60 which have intercompatibility with each other were added.

3.2 Preparation of Higher Alkanes Mixtures

Higher alkanes mixtures were synthesized from different weight percent of tridecane, tetradecane, pentadecane and hexadecane which can be seen in Figure 3.1.

Figure 3.1 : Higher alkanes' formulations.

The compositions of mixtures are given in Table 3.3. were specified by taking into consideration the pure phase change temperatures of alkanes.

Table 3.3 : Higher alkanes' formulations.

Code	Composition(w%)
HA_1	10% tridecane - 90% hexadecane
HA_2	20% tridecane - 80% hexadecane
HA_3	30% tridecane - 70% hexadecane
HA_4	40% tridecane - 60% hexadecane
HA_5	50% tridecane - 50% hexadecane
HA_18	60% tridecane - 40% hexadecane
HA_19	70% tridecane - 30% hexadecane
HA_6	10% tridecane - 90% tetradecane
HA_7	20% tridecane - 80% tetradecane
HA_8	30% tridecane - 70% tetradecane
HA_9	10% tetradecane - 90% pentadecane
HA_10	20% tetradecane - 80% pentadecane
HA_11	30% tetradecane - 70% pentadecane
HA_12	40% tetradecane - 60% pentadecane
HA_13	50% tetradecane - 50% pentadecane
HA_14	60% tetradecane - 40% pentadecane
HA_15	70% tetradecane - 30% pentadecane
HA_16	80% tetradecane - 20% pentadecane
HA_17	90% tetradecane - 10% pentadecane

3.3 Preparation of Polyethylene Glycols Mixtures

Polyethylene glycols (PEGs) mixtures were prepared from different weight percent of PEG 300, PEG400, PEG600 and PEG1500. The compositions of mixtures are given in Table 3.4.

Table 3.4 : PEG formulations.

Code	Composition(w%)
PEG_3	30% PEG400 - 70% PEG600
PEG_2	40% PEG400 - 60% PEG600
PEG_1	50% PEG400 - 50% PEG600
PEG_4	60% PEG400 - 40% PEG600
PEG_5	70% PEG400 - 30% PEG600
PEG_6	80% PEG400 - 20% PEG600
PEG_7	90% PEG400 - 10% PEG600
PEG_8	40% PEG300 - 60% PEG600
PEG_9	30% PEG300 - 70% PEG600
PEG_10	20% PEG300 - 80% PEG600
PEG_11	10% PEG300 - 90% PEG600
PEG_12	50% PEG300 - 50% PEG1500
PEG_13	40% PEG300 - 60% PEG1500
PEG_14	30% PEG300 - 70% PEG1500

3.4 Preparation of Tetradecane - Water Emulsions

In this section, the effects of the preparation method on the stabilization of mixture were investigated. In determining the amount of materials in the formulation, study which was conducted by P. Schalbart et al. has been used as base. Three different methods were applied that mainly the order of addition of materials varies. During the preparation of emulsions, magnetic stirrer and Hielscher Ultrasonic Processor UP400S (with cycle: 0.5 and amplitute: 70%) were used.

Formulation;

- 74%w pure water
- 20%w n-tetradecane
- 4%w Tween 60
- 2%w Span 60

3.4.1 Method 1

Total amount of surfactants both Tween 60 and Span 60 was added the mixture of water and tetradecane. The mixture was firstly stirred with magnetic stirrer for 1.5 hours, after it was stirred 75 minutes by using ultrasonic processor contuniously. In Figure 3.2, situations of mixture at first instance (left) and after magnetic stirrer (right) can be seen.

Figure 3.2 : Method 1 mixing step.

3.4.2 Method 2

Total amount of Tween 60 was added on water and Span 60 was supplemented on paraffine. In Figure 3.3, views of mixtures before the mixing can be shown. Both mixtures were stirred with magnetic stirrer for 1.5 hours separately (Figure 3.4). After that, tetradecane-Span 60 mixture was poured to water – Tween 60 mixture and total blend was stirred 75 minutes by using ultrasonic processor contuniously.

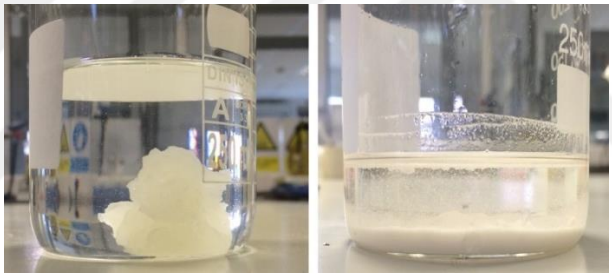

Figure 3.3 : Views of mixtures before the mixing.

Figure 3.4 : Mixtures after magnetic stirring.

3.4.3 Method 3

Solvents were added through the surfactants in three stages. In each step, one third of solvents were poured on the surfactants. Water-Tween 60 and tetradecane-Span60 mixtures were stirred with magnetic stirrer for 0.5 hours separately. Then, the mixture of water-Tween 60 was added into tetradecane-Span60 mixtures again in the

three stage. After the adding process, all of mixture was stirred 75 minutes by using ultrasonic processor. Applying the gradual adding process, achievement of longer stabilization is intended. In Figure 3.5 and 3.6 mixtures before the ultrasonic processor mixing step can be seen. After the 75 minutes sonication procedure homogenious mixture were obtained (Figure 3.7).

Figure 3.5 : Mixtures before the ultrasonic processor mixing.

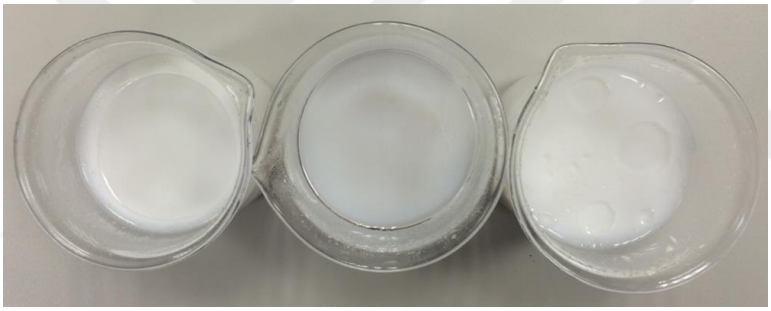

Figure 3.6 : Mixtures before the ultrasonic processor mixing (above).

Figure 3.7 : Mixtures after the ultrasonic processor mixing.

3.5 Characterization

3.5.1 Differential scanning calorimeter (DSC)

TA-Instruments DSC Q200 was used for thermal analysis of the PCMs. The measurements were carried out under inert nitrogen atmosphere at 50 ml/min flow rate. All the DSC thermal analyses of enthalpy were conducted at 2 °C /min heating and cooling rate and the temperature was changed generally in wide range scanned temperature interval (between -25°C and 25°C) for the thermal analyses of PCM formulations to achieve the well measurements. The heat flow calibration of the instrument was performed by indium reference and the temperature calibration was performed by indium and zinc references. Sapphire was used as an internal reference following the heat and temperature calibrations for the specific heat analyses. During the analyses, Tzero hermatic pan and lids were used; moreover thermal characterictis of PCMs were evaluated based on the second termal cycles of DSC programme.

Melting and freezing temperatures, latent heat of melting and freezing and the changes in thermal performance after accelerated cycling tests were determined with the help of DSC analyses at Arcelik A.S. Central Research & Development Materials Technologies Department. Every presented DSC result in this research is calculated according to the results of at least 2 individual analyses in order to minimize the uncertainity of the balance with four decimal digits.

3.5.2 Climatic chamber

ACS Challenge 250 climatic chamber (Figure 3.8) was utilized for performing both accelerated melting/freezing cycles and performance measurements.

Figure 3.8 : Climatic chamber.

In program for accelerated melting/freezing cycles, firstly all phase change materials are kept at -25°C in 1,5 hours to obtaine totally freezing than temperature of climatic chamber risen through the 25°C in 0,5 hours and 1,5 hours remain stable at this temperature.

3.6 Performance Measurements

Performance measurements are carried out to determine the effect of phase change materials on temperature changes of refrigerator fresh food compartment during power outages in Figure 3.9. In line with this purpose, PEG-4 and PEG-5 PCMs which represent the nearest phase change temperatures to fresh food compartment operating temperatures(3-8°C) among the developed PCMs are selected. Each formulation was prepared 2,580 grams and placed into 860 grams of material prepared in three different aluminum films for measurements that can be clearly seen in Figure 3.10. Dimensions of aluminum films are specified considering the dimensions of refrigerator shelves.

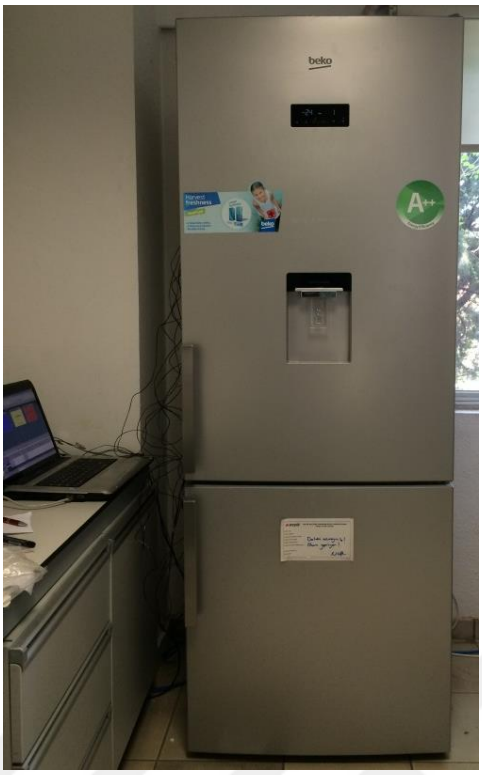

Figure 3.9 : Performance measurements refrigerator.

Figure 3.10 : Fresh food compartment.

Thermocouples are placed lower, middle and upper shelves of compartement and by using the data logger temperature values are recorded in each 30 seconds. Selected PCMs which represent the lover crystallization temperature than compartmet's operating temperature were frozen in the freezer (Figure 3.11).

Figure 3.11 : Freezer compartment.

Performance measurement is performed according to the steps which listed below;

- To simulate the power outage, refrigerator is pluged out when fresh food compartment reach the equilibrium temperatures.
- PCM packages are withdraw from freezer and then placed to the shelves as soon possible as.
- Temperature changes of three sections (lower, middle and upper) are observed.
- When all temperature values reach the 10°C, measurement is compliated.

Similar performance measurements and specification of phase change durations have also been measured by using the climatic chamber. During this test, HA-12 and PEG-5 PCMs are analyzed. Thermocouples are submerged into the PCMs and the program which was utilized for performing accelerated melting/freezing cycles is loaded to the climatic chamber is seen in Figure 3.12.

Figure 3.12 : Performance measurements inside the climatic chamber.

Again by using the data logger, temperature changes and phase change durations of PCMs are measured in Figure 3.13.

Figure 3.13 : Performance measurements in climatic chamber with data logger.

4. RESULTS AND DISCUSSIONS

4.1 Higher Alkanes Mixtures

In this study, 19 different formulation containing four higher alkanes' mixtures were prepared. In Table 4.1, solid liquid phase change temperature and enthalpy values of pure tridecane and hexadecane are presented.

Table 4.1 : Phase change data for higher alkanes mixtures.

Code	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
HA_1	13.65	17.18	159.2	13.70	13.19	153.20
HA_2	-7.33	-3.42	19.87	-5.44	-7.77	7.58
	10.99	15.21	111.4	11.57	11.25	108.50
HA_3	-7.50	-3.34	42.02	-4.80	-7.60	21.42
	8.09	13.17	86.26	8.84	8.29	82.52
HA_4	-7.22	-3.39	58.25	-4.63	-7.32	45.32
	4.53	10.96	100.6	6.52	5.90	74.06
HA_5	-7.51	-3.52	64.96	-5.76	-8.46	41.65
	3.86	8.07	29.72	2.33	1.54	27.55
HA_18	-7.68	-5.21	107.50	-6.04	-8.33	38.91
	2.19	5.07	22.83	-0.29	-1.17	17.63
HA_19	-7.46	-5.02	123.80	-3.51	-8.42	128.2

Due to the tridecane's phase change characteristic which is seen in Figure 4.1, formulations have two step melting and crystallization.

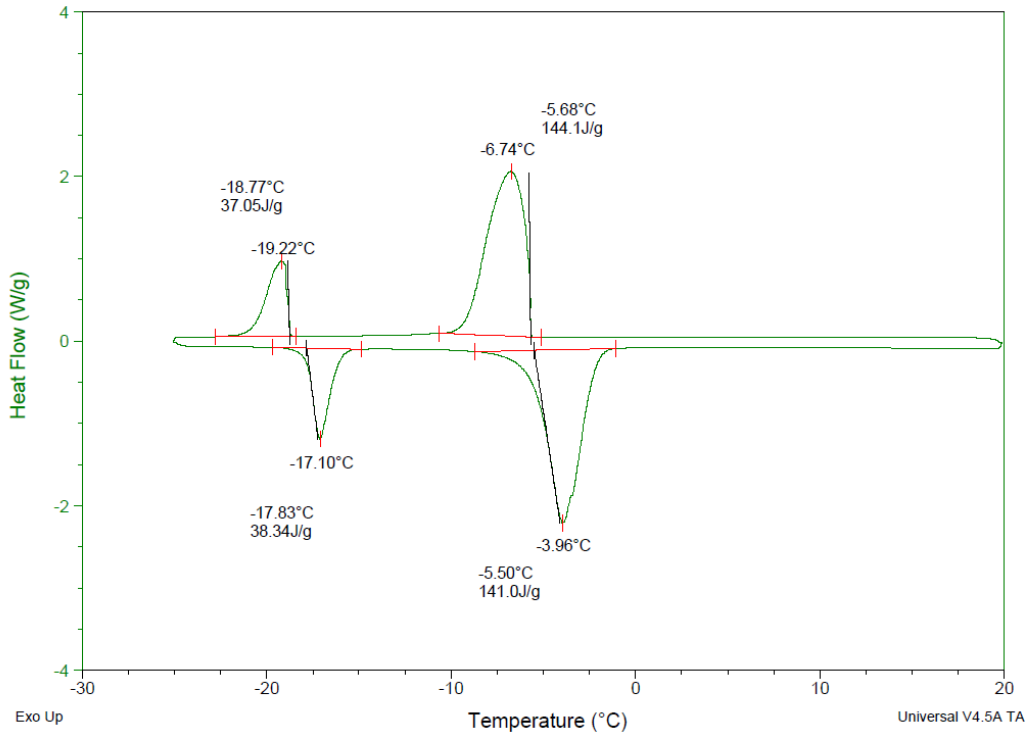

Figure 4.1 : Tridecan's DSC thermogram.

When Figure 4.2 is examined, solid liquid phase change cycles of HA_1 - HA_5 are observed between the -30°C and 25°C. Due to the temperature change in wide range, these formulations can be considered as not suitable for refrigerator applications.

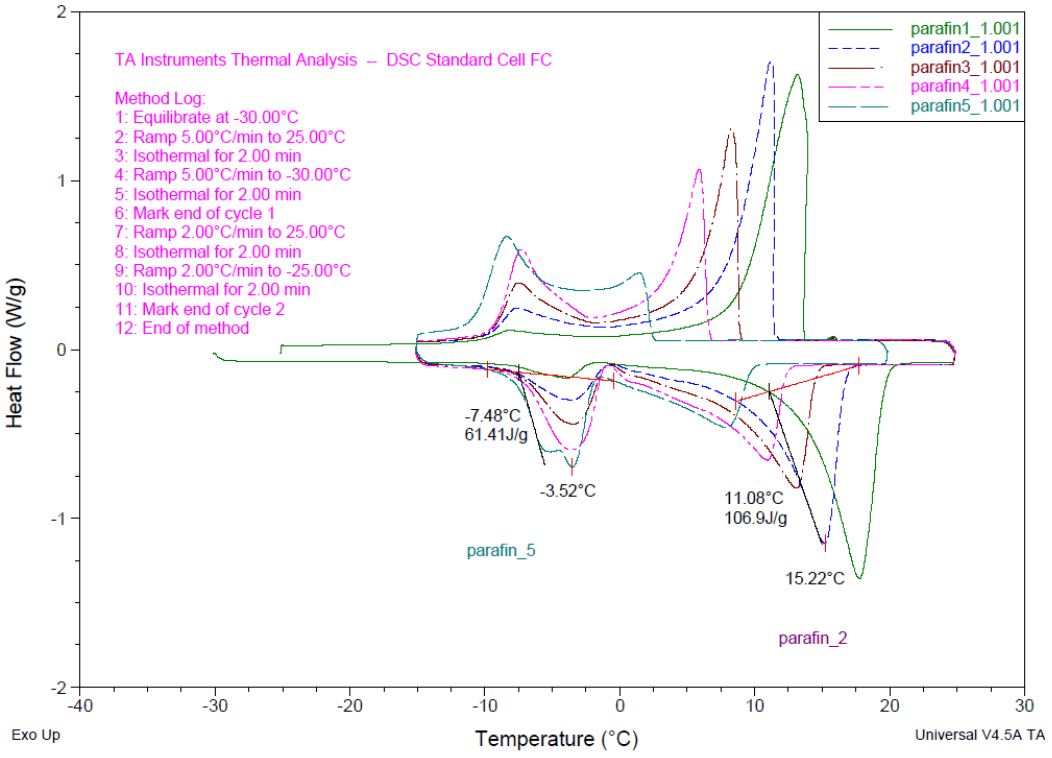

Figure 4.2 : Tridecane - hexadecane mixtures DSC thermograms.

As can be seen from the Figure 4.3 HA_18 and HA_19 have solid liqued phase transition between -8/-4°C to a large extent. Because of this reason, it can be said that these formulations cannot be proper for the home appliances in low temperature range.

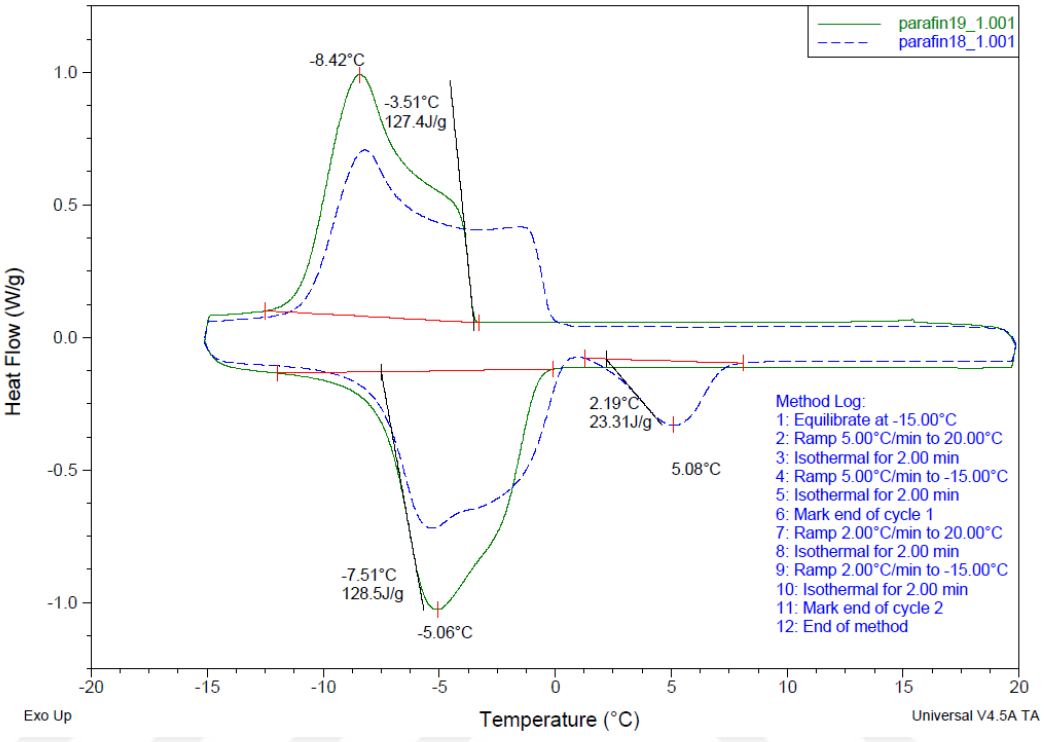

Figure 4.3 : Comparison of DSC thermograms of the HA_18 and HA_19 formulations.

In Table 4.2, tridecane - tetradecane mixtures' phase change values are represented and when Figure 4.4 is examined, one step solid liquid phase change curves are seen on the contrary tridecane- hexadecane mixtures.

Table 4.2 : Tridecane - tetradecane mixtures phase change data

Code	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
HA_6	2.65	5.38	197.70	n.a.	1.96	205.90
HA_7	-0.55	3.87	179.10	0.78	-1.32	171.30
HA_8	-2.17	0.50	162.40	-0.58	-1.83	123.90
				-5.37	-5.46	8.48

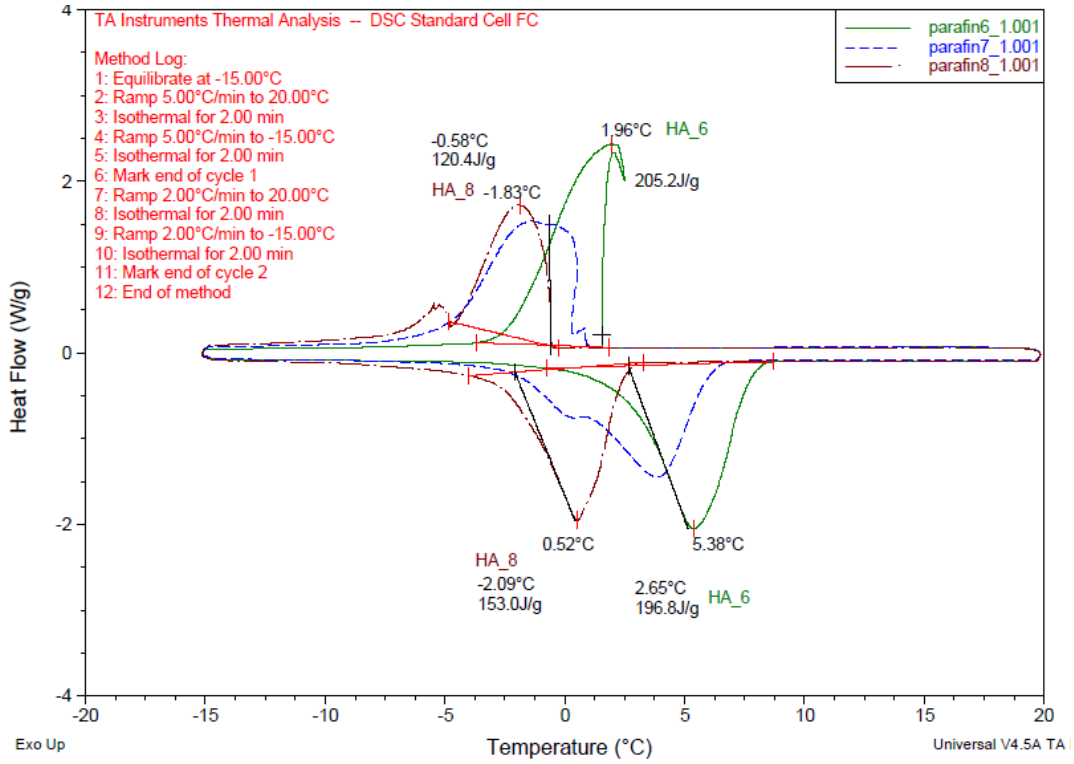

Figure 4.4 : DSC thermograms of tridecane - tetradecane mixtures.

In Table 4.3, solid liquid phase change temperature and enthalpy values of pure tetradecane and pentadecane are presented. HA_9 and HA_10 formulations have two step phase change and these values were presented in second row of related formulation.

Table 4.3 : Phase change data for tetradecane - pentadecane mixtures.

Code No	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
HA_9	-8.37	-7.05	24.45	-8.48	-8.90	20.17
	8.23	9.98	151.60	8.75	7.40	153.50
HA_10	-12.86	-11.58	8.50	-13	-13.36	9.74
	6.97	9.09	154.30	7.81	6.35	152.30
HA_11	5.75	7.90	147.60	6.86	5.40	149.20
HA_12	4.95	7.59	144.40	5.98	4.03	147.10
HA_13	4.17	6.55	141.40	5.12	3.35	146.10
HA_14	3.94	6.03	145	4.40	2.54	151.40
HA_15	3.60	5.17	147	3.80	2.37	153.80
HA_16	3.26	4.97	140	3.15	1.64	147.80
HA_17	3.11	4.94	146.90	8.84	1.16	149.30

Among this group, formulations with lower tetradecane ratios HA_9 and HA_10 (10%w and 20%w respectively) can be considered as not proper for the 0/10°C working region in refrigerator application (Figure 4.5).

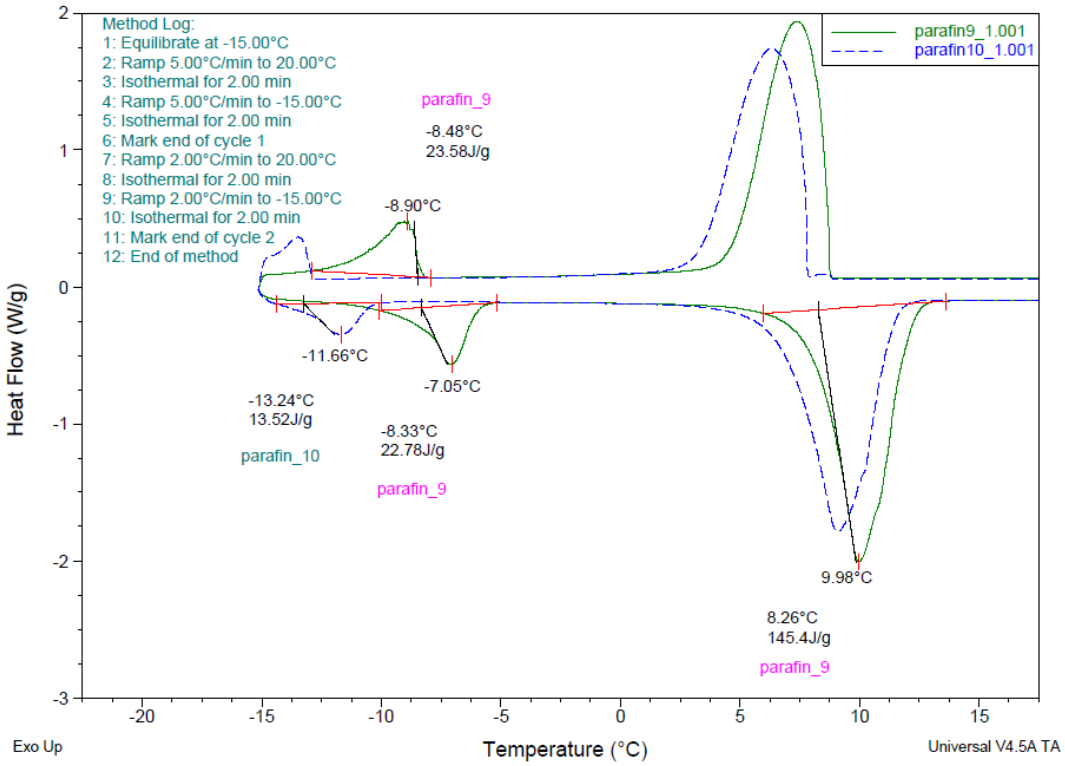

Figure 4.5 : Comparison of DSC thermograms of the HA_9 and HA_10 formulations.

As shown in Figure 4.6, it can be clearly indicated that most tetradecane-pentadecane combinations such as from HA_12 to HA_16 are suitable for the fresh food compartment and crisper. Also one step phase change, higher enthalpy values and having quite close melting and crsytallization temperatures are the main advantages for this usage purpose.

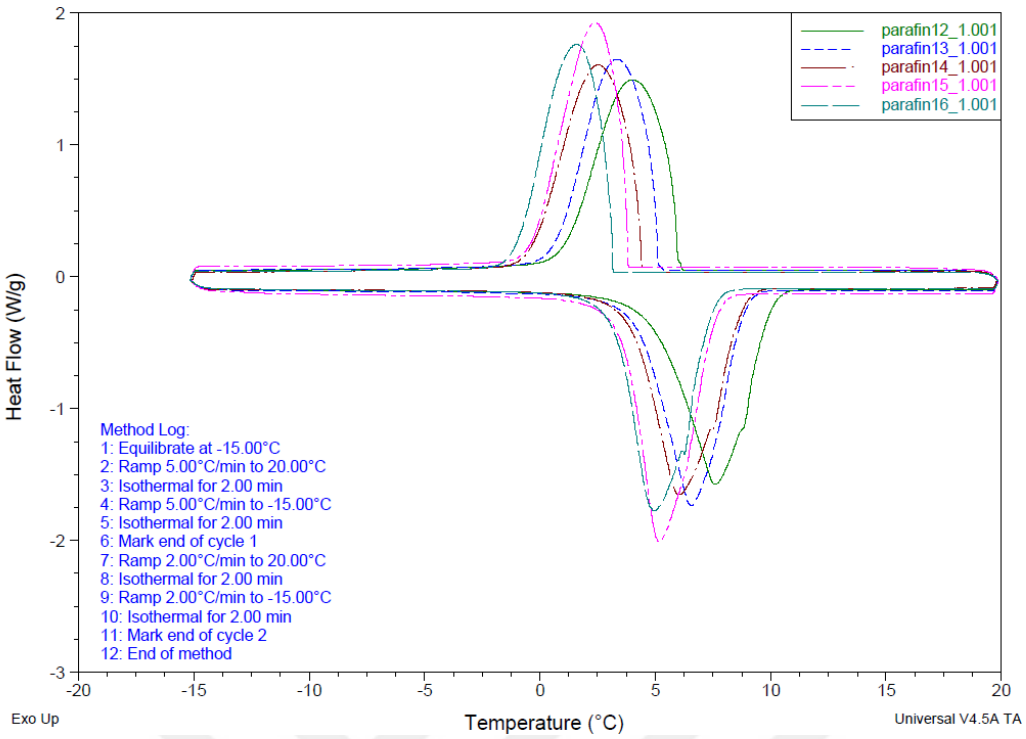

Figure 4.6 : DSC thermograms of tetradecane - pentadecane mixtures.

4.2 Polyethylene Glycol Mixtures

Solid liquid phase change temperature data and enthalpy values of binary combinations of PEG600 with PEG300 and PEG400 are given in Table 4.4. Because of that, pure PEG600 shows the two step crystallization, all formulations (except PEG_7) from PEG_1 to PEG_11 demonstare two different crystallization curves and temperature values are presented in second row.

Table 4.4 : Phase change data for polyethylene glycol mixtures.

Code	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
PEG_3	4.76	16.24	86.34	12.02	4.07	26.84
				10.66	3.56	15.99
PEG_2	2.07	12.66	71.33	9.77	1.49	23.87
				8.32	0.84	15.57
PEG_1	0.78	12.42	75.99	10.79	1.04	16.72
				8.7	0.22	20.64
PEG_4	-1.3	10.36	65.12	7.24	0.14	16.16
				6.13	0.05	25.1
PEG_5	-5.83	6.17	59.94	3.38	-2.91	11.38
				2.08	3.02	25.77
PEG_6	-8.5	2.91	50.81	-1.17	-5.33	4.8
				-2.31	-5.65	26.68
PEG_7	-8.31	3.06	51.12	-5.87	-6.71	61.68
PEG_8	1.42	12.78	59.5	1.71	-2.55	29.06
				6.41	-3.8	7.08
PEG_9	3.39	13.6	68.96	8.47	-1.63	33.64
				7.17	-2.77	8.64
PEG_10	1.6	16.43	80.49	11.43	2.27	32.74
				10.05	1.5	9.2
PEG_11	2.76	14.24	65.58	10.75	10.01	31.26
				2.28	1.47	12.63

PEG400-PEG600 mixtures' solid liquid phase change curves are represented together in Figure 4.7. When the start and end temperature points of both melting and crystallization curves are investigated, it can be clearly seen that phase changes take place between average 10°C tempertures. Also broad curves can be viewed in Figure 4.7.

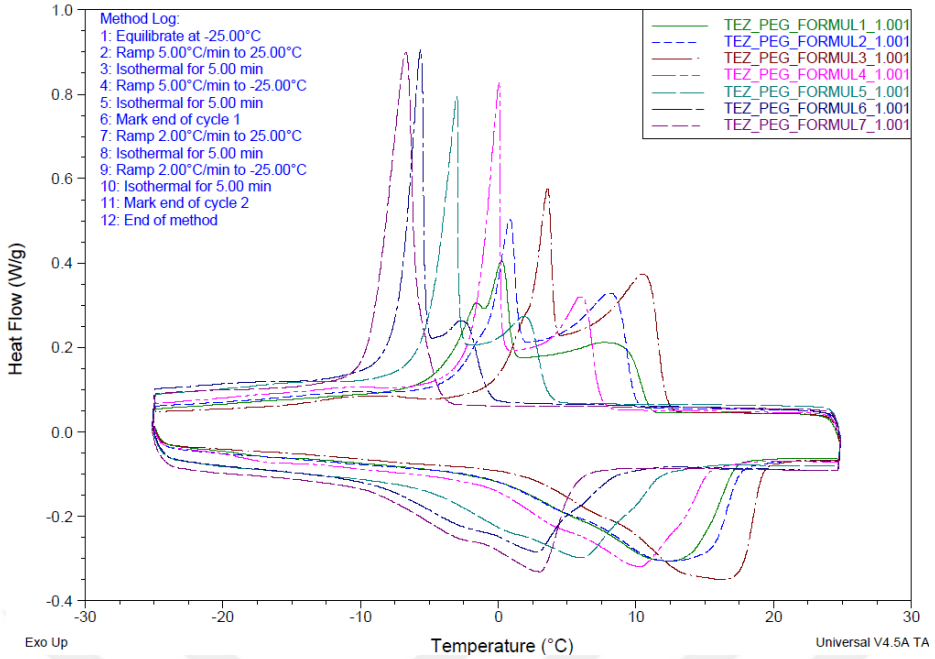

Figure 4.7 : DSC thermograms of PEG400 - PEG600 mixtures.

When PEG300-PEG600 mixtures which are represented as PEG_8, PEG_9, PEG_10 and PEG_11, it was found that the melting temperatures are above the limit value (10°C) and cannot be utilised properly in side the refrigerator cabinet, Figure 4.8.

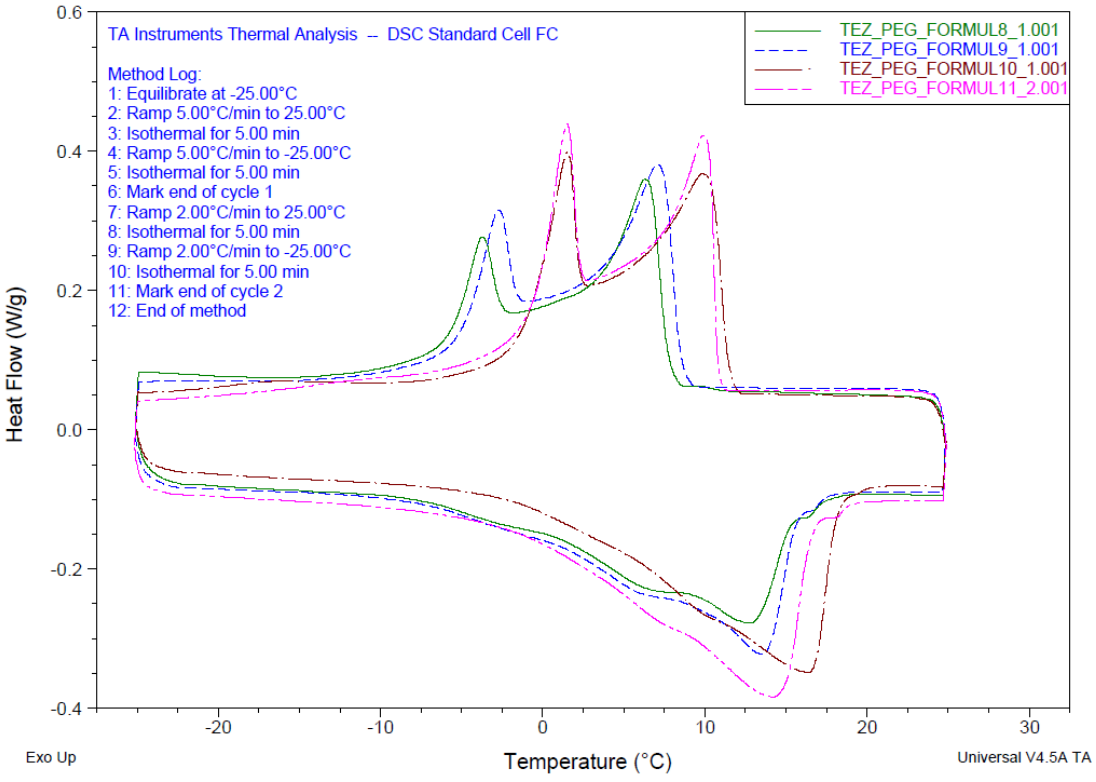

Figure 4.8 : DSC thermograms of PEG300 - PEG600 mixtures.

In Table 4.5, shows the solid liqid phase change data for PEG300 and PEG1500 mixtures and gradual melting curves can be seen also in Figure 4.9. Even if the PEG300 was used in the formulations, it was observed that metlting temperatures can not be lowered to the targeted temperature ranges.

Table 4.5 : Phase change data for PEG300 - PEG1500 mixtures.

Code	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
PEG_12	34.63	39.31	16.25	29.66	23.48	46.66
	40.84	41.99	4.87			
PEG_13	35.32	39.69	9.24	28.35	25.23	83.42
	41	42.91	16.12			
PEG_14	35.89	39.89	9.84	39.09	37.06	99.86
	41.56	44.21	22.47			

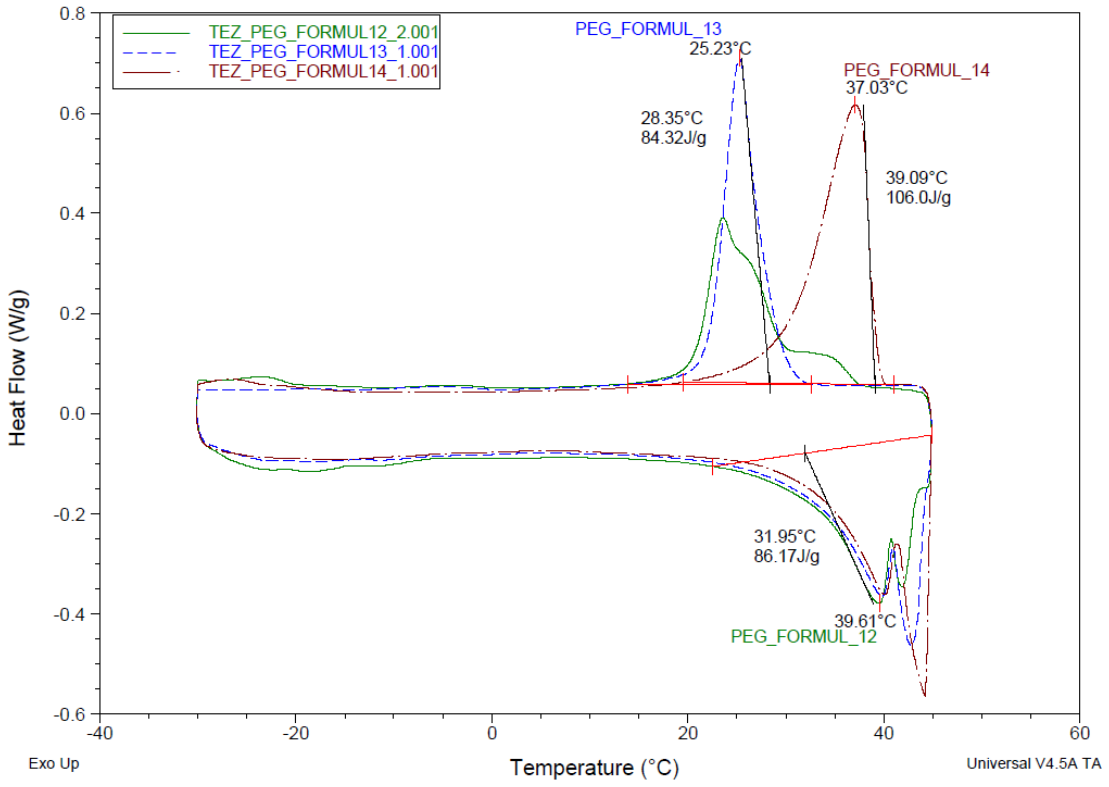

Figure 4.9 : DSC thermograms of PEG300 - PEG1500 mixtures.

4.3 Tetradecane/Water Emulsions

In this part of the work, solid liqid phase change temperature values and enthalies are presented with the accelerated melting/freezing cycle numbers in Table 4.5, 4.6 and

4.7. Enthalpy of crystallization values cannot be measured properly because of the supercooling effect.

Table 4.6 : The change of the phase change data for method 1.

method no	cycle	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
1	0	0.11	2.61	209.7	-16.45	-18.37	-
1	5	0.07	2	223.5	-14.38	-15.84	-
1	48	0.17	2.41	211.5	-16.2	-18.42	-
1	93	0.04	1.78	221.7	-12.61	-14.43	-
1	135	0.07	2.01	214.2	-15.44	-17.31	-
1	219	0.16	2.4	208.7	-15.79	-17.61	-
1	260	0.21	2.82	214.2	-16.55	-19.03	-
1	324	0.01	1.61	221.2	-16.66	-18.63	-
1	397	0.19	2.93	211.8	-16.66	-19.16	-
1	514	0.16	2.69	203.8	-12.93	-15.91	-

The comparison of DSC thermograms according to the cycles for method 1 is presented in Figure 4.10.

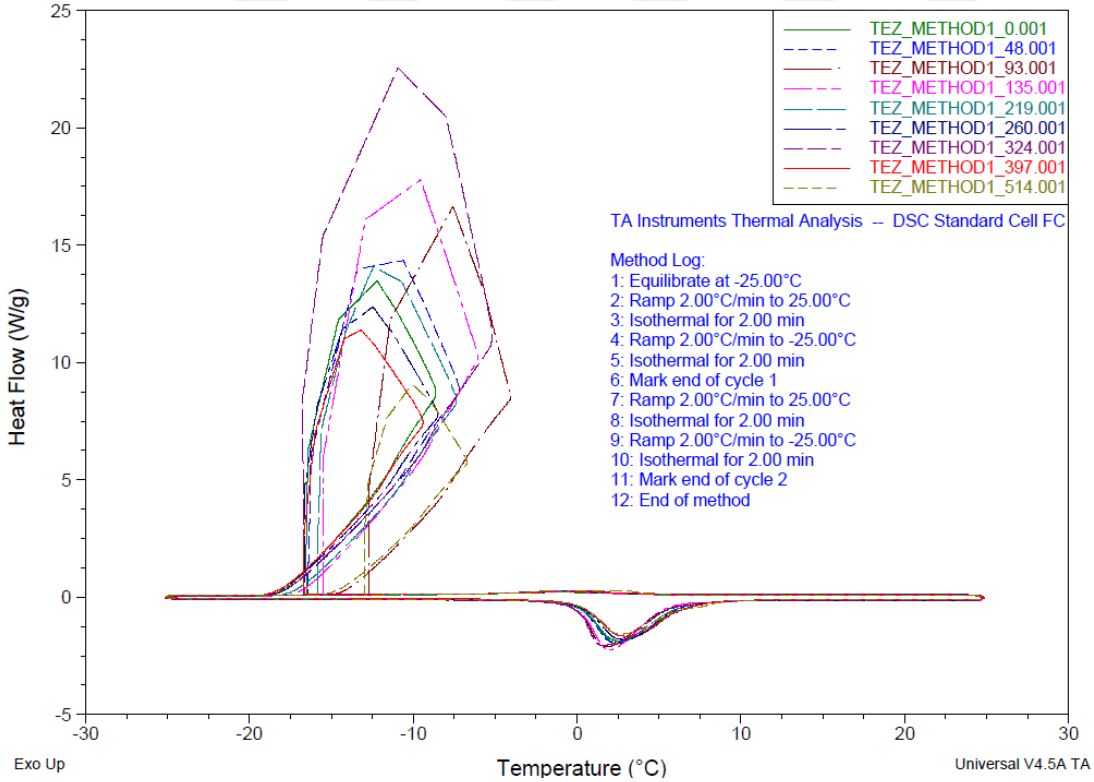

Figure 4.10 : Comparison of DSC thermograms of method 1.

Table 4.7 : The change of the phase change data for method 2.

method no	cycle	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
2	0	0.03	1.88	220.1	-12.81	-14.33	-
2	5	0.13	2.12	215.7	-16.5	-18.47	-
2	48	0.12	1.93	208.6	-15.48	-16.45	-
2	93	0.04	1.93	208.8	-15.29	-17.11	-
2	135	0.05	1.77	208.6	-20.19	-21.5	-
2	219	0.13	2.18	206.2	-20.49	-22.21	-
2	260	0.15	2.24	205	-14.78	-16.6	-
2	324	0.09	1.97	190.1	-21.05	-22.62	-
2	397	0.13	2.39	198.3	-19.8	-22.04	-
2	514	0.25	2.21	133.7	-19.85	-21.93	-

The comparison of DSC thermograms according to the cycles for method 2 is presented in Figure 4.11.

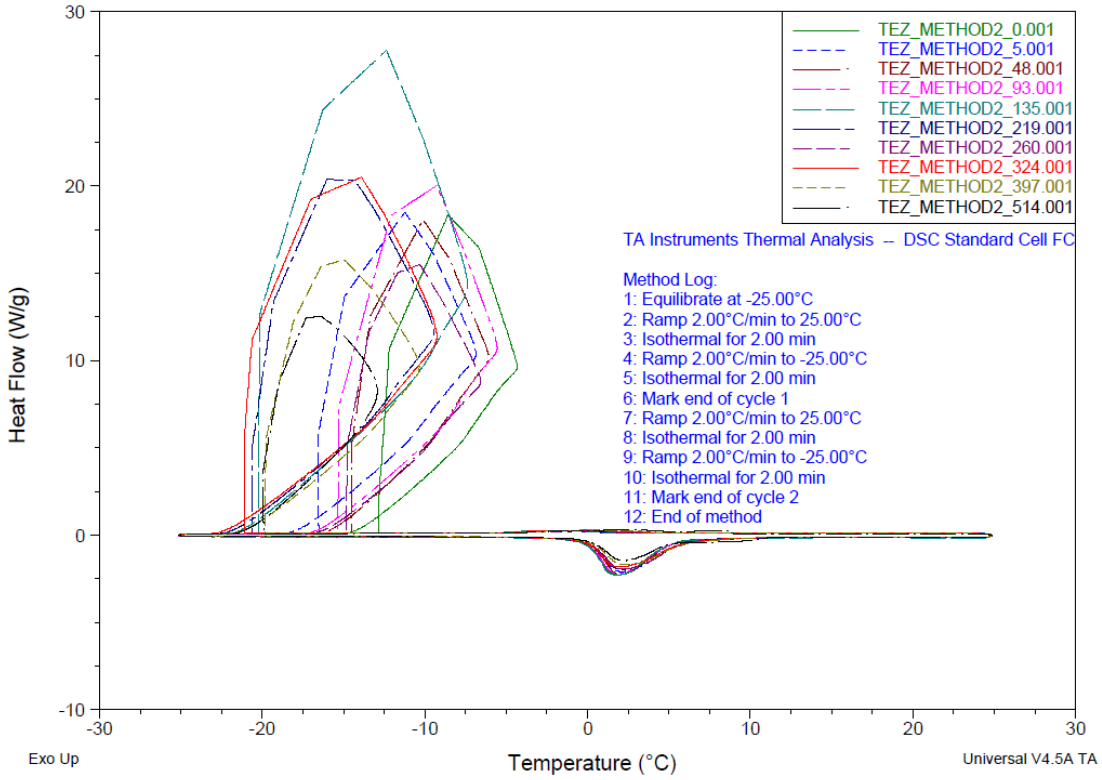

Figure 4.11 : Comparison of DSC thermograms of method 2.

Table 4.8 : The change of the phase change data for method 3.

method no	cycle	$T_{melting\_0}$ (°C)	$T_{melting\_1}$ (°C)	Enthalpy of Fusion (J/g)	T_{cryst_0} (°C)	T_{cryst_1} (°C)	Enthalpy of Cryst (J/g)
3	0	0.08	1.75	211.2	-17.61	-19.03	-
3	5	0.04	1.79	210.8	-17.51	-18.77	-
3	48	0.12	2.12	203.1	-10.69	-13.21	-
3	93	0.07	1.69	208.8	-17.06	-18.47	-
3	135	0.04	1.66	210.3	-15.54	-17.11	-
3	219	0.1	1.84	202.5	-20.49	-21.6	-
3	260	0.09	2.01	217.1	-16.25	-18.22	-
3	324	0.08	1.74	188.6	-17.41	-19.13	-
3	397	0.21	2.93	204	-18.63	-20.6	-
3	514	0.17	2.39	200.2	-15	-17.49	-

The comparison of DSC thermograms according to the cycles for method 3 is presented in Figure 4.12.

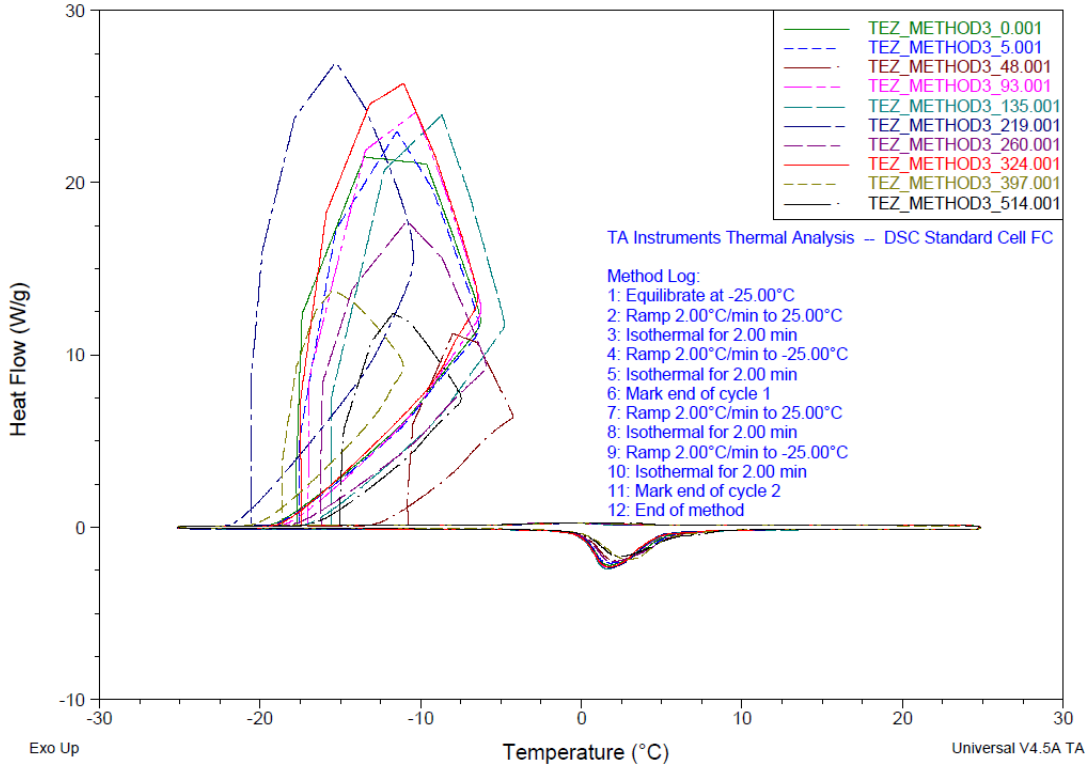

Figure 4.12 : Comparison of DSC thermograms of method 3.

According to the Figure 4.13, PCM which is synthesized by method 2 has the maximum change in melting point temperatures.

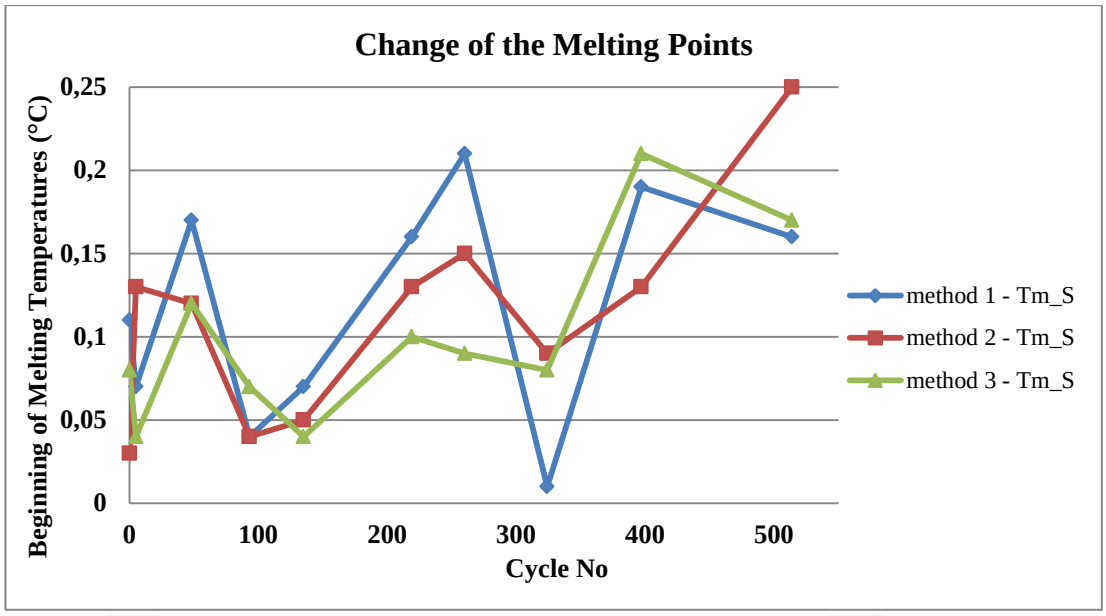

Figure 4.13 : Change of the melting points according to the cycles.

When the Figure 4.14 is examined it is clearly seen that, method 1 and method 3 show the similar change of fusion enthalpy.

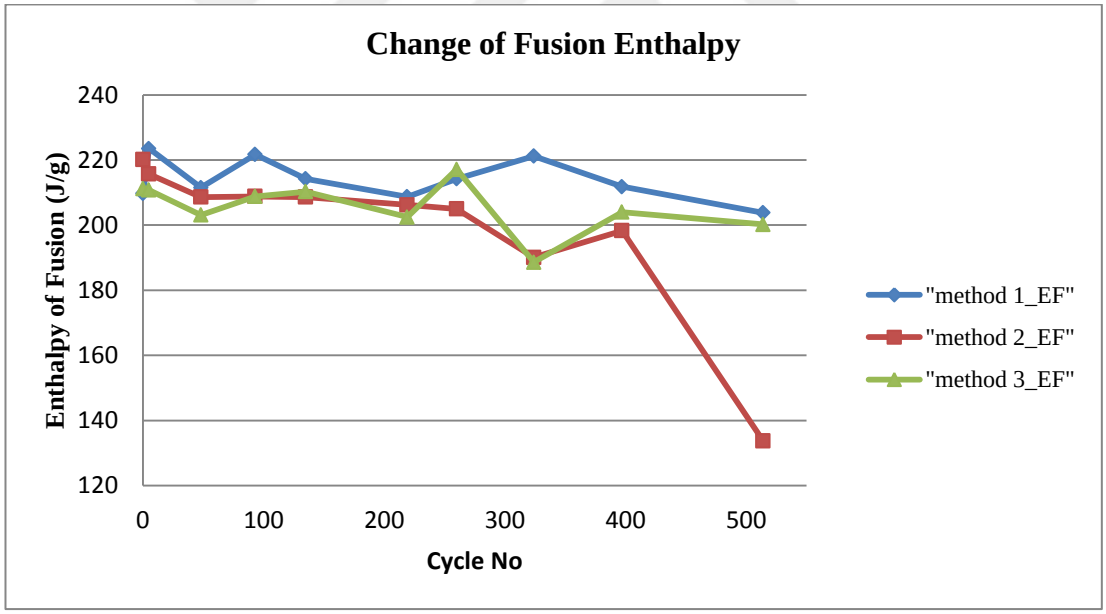

Figure 4.14 : Change of the fusion enthalpy values according to the cycles.

4.4 Accelerated Melting/Freezing Cycles

For higher alkanes formulations 1200 and for PEG mixtures 350 accelerated melting freezing cycles have been completed. Results of measurements will be supplemented. Related data about tetradecane/water emulsions are presented in section 4.3.

4.5 Performance Measurements

The comparative analyses of reference case and case which contains PCM packages are presented in Figure 4.15 and Figure 4.16. Both measurements that start at 3°C and proceed through the 10°C, middle section temperature changes have been shown.

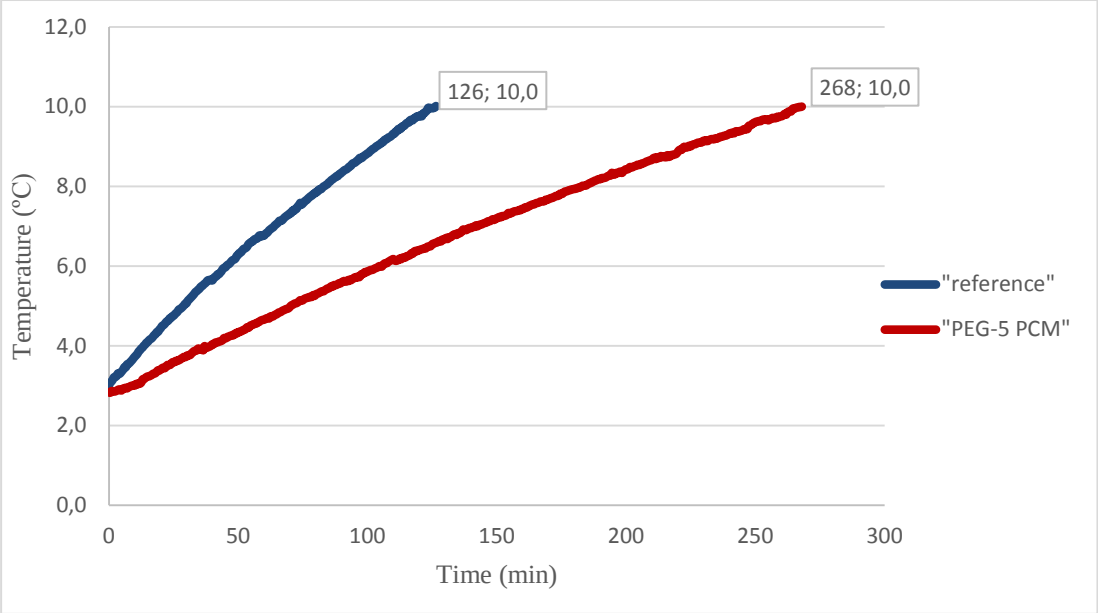

Figure 4.15 : Performance measurement of PEG-5 PCM

In performance measurement of PEG-5 PCM, with the help of phase change materials approxiametely fresh food compartment temperatures are kept under the upper limit temperature (10°C) more than 2.4 hours (Figure 4.15).

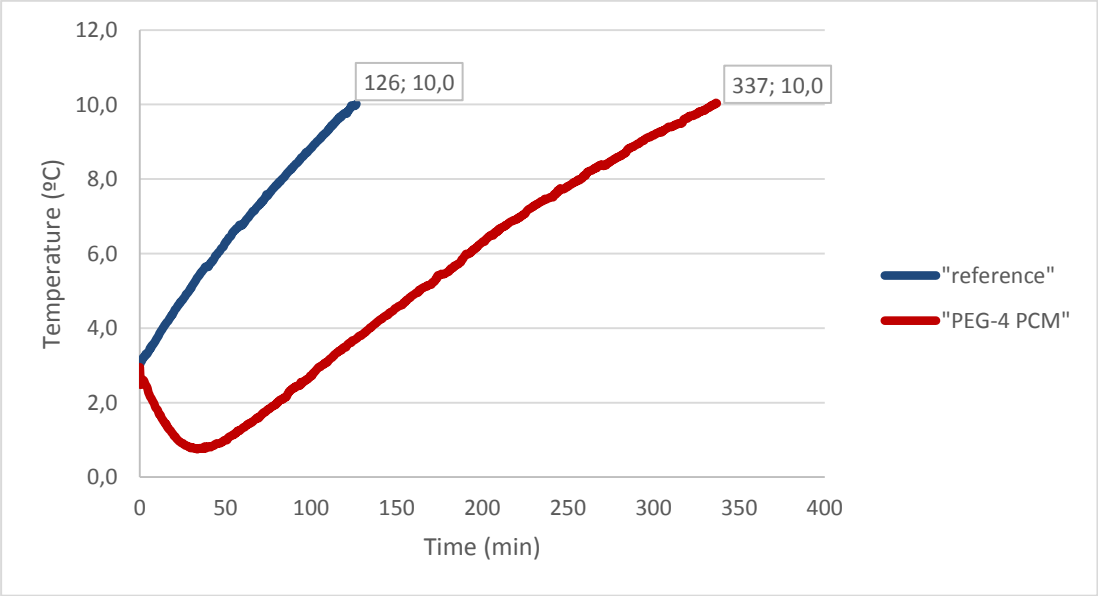

Figure 4.16 : Performance measurement of PEG-4 PCM

In addition to this,ıt can be clearly analyzed that, PEG-4 PCM provides more than 3.5 hours cooling (Figure 4.16). If they are frost utterly in freezer and used in fresh food cabinet when power outage is exist; therefore, it can be extended the decay time of foods and beverages.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study, to obtain the energy efficiency in white good applications, paraffine and polyethylene glycol based 33 different phase change materials were synthesized. According to the theoritical knowledge, organic phase change materials have more remarkable properties in terms of working life and performance. In the light of this notion, the choice of raw materials were evaluated taking account of the temperature of developed phase change materal which is desired between -20°C to 10°C.

Besides, the effects of sysnthesis method on tetradecane and water emulsions have been observed. To achive the chemical structural integrity, the importance of the squence of added chemicals were investigated.

The findings from this study are introdused below:

- Tridecane – hexadecane formulations have shown two step melting and crystallization because of the pure tridecane's phase change characteristic. Due to the fact that, for refrigerator applications require more narrow operating temperature range, these formulations can be considered as not suitable.
- In the case of tridecane – tetradecane mixtures, HA_6, HA_7 and HA_8 formulations demonstrate one step solid liquid phase change; moreover, because of the closeness of the melting and crystallization temperatures in between 0-5°C, this group of phase change materials are countenanced both fresh food cabined and crisper in refrigerator.
- When tetradecane – pentadecane mixtures are analyzed, single phase change curves could not be seen for the formulations HA_9 and HA_10 that contain low tetradecane weight percent (10%, 20% respectively). Beside this, developed PCMs from HA_12 to HA_16 have shown phase change in between 3 - 8°C that exactly suit with the refrigerator operating temperatures.

- Within the context of this study, it is observed that tetradecane – pentadecane mixtures become prominent for home appliances with low operating temperature.
- When DSC thermograms are investigated in detailed, both PEG300-PEG600 and PEG300-PEG1500 formulations have shown the higher melting and crystallization temperatures above the operation conditions.
- PEG_12, PEG_13 and PEG_14 phase change material formulations with relatively high phase change temperature (between 30-40°C) can be utilized as different white good applications such as in heating rinse water of dish washer.
- Formulations which containe various amounts of PEG400 and PEG600 demonstrate solid liquid phase change in a wide range temperature - approxiametely in 10°C. Because of this situation, they cannot be used direct usage in refrigerator properly. However, especially PCMs with PEG_1, PEG_2, PEG_3, PEG_4 and PEG_5 formulations can be utilized if they are frost utterly in freezer, they can be used in fresh food cabinet when power outage is exist; therefore, it can be extended the decay time of foods and beverages.
- As a result of the study that is examined the effects of the preparation method on the stabilization for tetradecane water emulsions, ıt has not seen a huge discrepancy between method 1 and method 3 in terms of the change in melting temperatures and enthalpy of fusion values.
- On the contrary, the beginning of the phase separation has been observed more significantly in PCM synthesized with method 2. That can be concluded that rather than the adding sequence of chemicals, the duration of interaction of materials all told is more effective.

For further studies, different types of paraffin waxes can be experienced instead of pure alkanes for white good applications. Besides, studies to reduce the wide phange change temperature range especially in PEG mixtures.

REFERENCES

[1] **IEA**, 2013. Transition to Sustainable Buildings, Strategies and Opportunities to 2050. Report.

[2] **Yusufoglu, Y., Apaydin, T., Yilmaz, S., & Paksoy, H. O**. (2015). Improving performance of household refrigerators by incorporating phase change materials. International Journal of Refrigeration, 57, 173-185.

[3] **Pielichowska, K., & Pielichowski, K.** (2014). Phase change materials for thermal energy storage. Progress in Materials Science, 65, 67-123.

[4] **Tyagi, V.V., et al.,** (2011). Development of phase change materials based microencapsulated technology for buildings: A review. Renewable and Sustainable Energy Reviews,. 15(2): p. 1373-1391.

[5] **Pendyala, S.** (2012). Macroencapsulation of phase change materials for thermal energy storage.

[6] **Mehling H., Cabeza L. F.,** (2008). Heat and cold storage with PCM, Springer Verlag Berlin Heidelberg, pp. 1, 5, 7, 11.

[7] **Bakema, G., Snıjders, A.L., Nordell, B.,** (1994). Underground Thermal Energy Storage-State of the Art Report. If Technology, Arhen, The Netherlands.

[8] **Abhat, A.,** (1983). Low Temperature Latent Heat Thermal Energy Storage: Heat Storage Materials. Solar Energy, 30(4): 313-332.

[9] **Lane, G.A**., (1983). Solar Heat Storage: Latent Heat Material, vol. II, CRC Press, p. 83.

[10] **Sharma, A., Tyagı, V.V., Chen, C.R., Buddhı, D.**, (2009). Review on Thermal Energy Storage with Phase Change Materails and Applications. Renewable and Sustainable Energy Reviews, 13: 318-345.

[11] **Zondag, A.H., Kalbasenka, A., Van Essen, M.,** (2008). First studies in reactor concepts for thermochemical storage. In: Proceedings of 1st International Conference on Solar Heating, Cooling and Buildings (Eurosun 2008), Lisbon, Portugal.

[12] **Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A.,** (2008). Analysis, synthesis and design of chemical processes. 3rd Edition, Prentice Hall, New Jersey, U.S.A.

[13] **Ervin, G.,** (1977). Solar heat storage using chemical reactions. J. Solid State Chem. 22, 51– 61

[14] **Kato, Y., Yamada, M., Kanie, T., Yoshizawa, Y.,** (2001). Calcium oxide/carbon dioxide reactivity in a packed bed reactor of a chemical heat pump for high-temperature gas reactors. Nucl. Eng. Des. 210, 1–8.

[15] **Kato, Y., Takahashi, R., Sekiguchi, T., Ryu, J.,** (2009). Study on medium-temperature chemical heat storage using mixed hydroxides. Int. J. Refrig. 32, 661–666

[16] **Hauer, A.,** (2007). Sorption theory for thermal energy storage. Chapter 24 in Book: Thermal energy storage for sustainable energy consumption. NATO Science Series, Springer, Netherlands, Volume 234, Part VI, 393–408.

[17] **Gil, A., Medrano, M., Martorell, I., Lázaro, A., Dolado, P., Zalba, B., Cabeza, L.F.,** (2010). State of the art on high temperature thermal energy storage for power generation. Part 1 –concepts, materials and modellization. Renew. Sust. Energ. Rev. 14, 31–55.

[18] **Gracia, Á. D.** (2013). Thermal analysis of a ventilated facade with phase change materials (PCM).

[19] **L. Ventola, T. Calvet, M.A. Cuevas-Diarte, V. Metivaud, D. Mondieig, H. Oonk,** (2002). From concept to application. A new phase change material for thermal protection at −11 ◦C, Mater. Res. Innovat. 6 284–290.

[20] **Sarier, N., & Onder, E.** (2012). Organic phase change materials and their textile applications: an overview. Thermochimica Acta, 540, 7-60.

[21] **Chandra D, Chellappa R, Chien W. (**2005). Thermodynamic assessment of binary solid-state thermal storage materials. J Phys Chem Solids;66:235–40.

[22] **Pillai KK, Brinkwarth BJ**. (1976). The storage of low grade thermal energy using phase change materials. Appl Energy;2:205–16.

[23] **Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S**. (2004). A review on phase change energy storage: materials and applications. Energy Convers Manage:1597–615.

[24] **Liu M, Saman W, Bruno F.** (2012). Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems. Renew Sust Energy Rev;16:2118–32.

[25] **Cabeza LF, Svensson G, Hiebler S, Mehling H.** (2003). Thermal performance of sodium acetate trihydrate thickened with different materials as phase change energy storage material. Appl Therm Eng;23: 1697–704.

[26] **Cabeza LF, Roca J, Nogues M, Mehling H, Hiebler S.** (2002). Immersion corrosion tests on metal–salt hydrate pairs used in latent heat storage in the 48 to 58 _C temperature range. Mater Corros;53:902–7.

[27] **Farrell AJ, Norton B, Kennedy DM.** (2006). Corrosive effects of salt hydrate phase change materials used with aluminium and copper. J Mater Process Technol;175:198–205.

[28] **Sun JQ, Zhang RY.** (2005). Review of thermal energy storage with metal phase change materials. Mater Rev;19:99–101.

[29] **Kenisarin, M. M**. (2014). Thermophysical properties of some organic phase change materials for latent heat storage. A review. Solar Energy, 107, 553-575.

[30] **Gong ZX, Mujumdar AS**. (1996). Enhancement of energy charge–discharge rates in composite slabs of different phase change materials. Int J Heat Mass Transfer;39:725–33.

[31] **Kaygusuz K, Sari A**. (2007). High density polyethylene/paraffin composites as form–stable phase change material for thermal energy storage. Energy Sources Part A;29:261–70.

[32] **Akgun M, Aydın O, Kaygusuz K.** (2007). Experimental study on melting/solidification characteristics of a paraffin as PCM. Energy Convers Manage;48:669–78.

[33] **Fukai J, Hamada Y, Morozumi Y, Miyatake O.** (2002). Effect of carbon-fiber brushes on conductive heat transfer in phase change materials. Int J Heat Mass Transfer;45:4781–92.

[34] **Pielichowski K, Flejtuch K.** (2003). Differential scanning calorimetry study of blends of poly(ethylene glycol) with selected fatty acids. Macromol Mater Eng;288:259–64.

[35] **Nikolic R, Marinovic-Cincovic M, Gadzuric S, Zsigrai IJ.** (2003). New materials for solar thermal storage—solid/liquid transitions in fatty acid esters. Sol Energy Mater Sol Cells;79:285–92.

[36] **Aydın AA.** (2013). Fatty acid ester-based commercial products as potential new phase change materials (PCMs) for thermal energy storage. Sol Energy Mater Sol Cells;108:98–104.

[37] **Pielichowski K, Flejtuch K, Pielichowski K.** (2004). Step-scan alternating DSC study of melting and crystallisation in poly(ethylene oxide). Polymer;45:1235–42.

[38] **Pielichowski K, Flejtuch K.** (2002). Differential scanning calorimetry studies on poly(ethylene glycol) with different molecular weight for thermal energy storage materials. Polym Adv Technol;13:690–6.

[39] **Khudhair AM, Farid MM.** (2004). A review on energy conservation in building applications with thermal storage by latent heat using phase change materials. Energy Convers Manage;45:263–75.

[40] **Tyagi VV, Buddhi D.** (2007). PCM thermal storage in buildings: a state of art. Renew Sust Energy Rev;11:1146–66.

[41] **M. Telkes, E. Raymond,** (1949). Storing solar heat in chemicals—a report on the Dover house, Heat Vent 46 (11) 80–86.

[42] **D.V. Hale, M.J. Hoover, M.J. O'Neill**, Phase Change Materials Handbook,

NASA CR-61363, Marshall Space Flight Center, AL, 1971

[43] **M. Pauken, N. Emis, B. Watkins,** (2007). Thermal energy storage technology developments, AIP Conf. Proc. 880 (1) 412–420.

[44] **D. Buddhi, R.L. Sawhney, P.N. Seghal, N.K. Bansal,** (1987). A simplification of the differential thermal analysis method to determine the latent heat of fusion of phase change materials, J. Phys. D: Appl. Phys. 20 1601–1605.

[45] **D. Feldman, M.M. Shapiro, D. Banu,** (1986). Organic phase change materials for thermal energy storage, Sol. Energ. Mater. 13 (1) 1–10.

[46] **S.M. Hasnain**, (1998). Review on sustainable thermal energy storage technologies. Part I: heat storage materials and techniques, Energ. Convers. Manage. 39 (11) 1127–1138.

[47] **B. Zalba, J. MaMarin, L.F. Cabeza, H. Mehling**, (2003). Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 251–283.

[48] **F. Regin, S.C. Solanki, J.S. Saini**, (2008). Heat transfer characteristics of thermal energy storage system using PCM capsules: a review, Renew. Sust. Energ. Rev. 12 (9) 2438–2458.

[49] **F. Agyenim, N. Hewitt, P. Eames, M. Smyth**, (2010). A review of materials heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS), Renew. Sust. Energ. Rev. 14 615–628.

[50] **L.F. Cabeza, A. Castell, C. Barreneche, A. de Gracia, A.I. Fernandez**, (2011). Materials used as PCM in thermal energy storage in buildings: a review, Renew. Sust. Energ. Rev. 15 (3) 1675–1695.

[51] **M. Delgado, A. Lazaro, J. Mazo, B. Zalba**, (2012). Review on phase change material emulsions and microencapsulated phase change material slurries: materials, heat transfer studies and applications, Renew. Sust. Energ. Rev. 16 (1) 253–273.

[52] **C.Y. Zhao, G.H. Zhang,** (2011). Review on microencapsulated phase change materials (MEPCMs): fabrication, characterization and applications, Renew. Sust. Energ. Rev. 15 (8) 3813–3832.

[53] **Z. Rao, S. Wang, Z. Zhang,** (2012). Energy saving latent heat storage and environmental friendly humidity-controlled materials for indoor climate, Renew. Sust. Energ. Rev. 16 (5) 3136–3145.

CURRICULUM VITAE

Name Surname **: Nilüfer ERTUNÇAY**

Place and Date of Birth **: İstanbul, 25.11.1991**

E-Mail **: nilufer.ertuncay@gmail.com**

EDUCATION **:**

- **B.Sc.** **:** 2014, İstanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Chemical Engineering Department