Sakarya University Journal of Science

ISSN 1301-4048 | e-ISSN 2147-835X | Period Bimonthly | Founded: 1997 | Publisher Sakarya University |
http://www.saujs.sakarya.edu.tr/en/

Title: Synthesis And Characterization Of Maleic Anhydride Modified Poly (Ethylene Glycol) As Polymeric Solid-Solid Phase Change Materials

Authors: Tuğba GÜNGÖR ERTUĞRAL, Cemil ALKAN

Recieved: 2020-01-22 11:34:49

Accepted: 2020-08-04 18:43:55

Article Type: Research Article
Volume: 24
Issue: 5
Month: October
Year: 2020
Pages: 1023-1028

How to cite
Tuğba GÜNGÖR ERTUĞRAL, Cemil ALKAN; (2020), Synthesis And Characterization Of Maleic Anhydride Modified Poly (Ethylene Glycol) As Polymeric Solid-Solid Phase Change Materials. Sakarya University Journal of Science, 24(5), 1023-1028, DOI: https://doi.org/10.16984/saufenbilder.678545
Access link
http://www.saujs.sakarya.edu.tr/en/pub/issue/56422/678545

JOURNAL of SCIENCE
Sakarya University
Journal of Science
VOLUME: 24
ISSUE: 5
OCTOBER 2020
e-ISSN: 2147-835X

Sakarya University Journal of Science 24(5), 1023-1028, 2020

Synthesis and Characterization of Maleic Anhydride Modified Poly (Ethylene Glycol) as Polymeric Solid-Solid Phase Change Materials

Tuğba GÜNGÖR ERTUĞRAL*[1], Cemil ALKAN[2]

Abstract

In this study, a novel type of polymeric solid-solid phase change materials (SSPCMs) and Maleic anhydride (MA) modified poly (ethylene glycol) PEG. MAM-PEG polymers were synthesized from different moleculer weight PEG (Mw: 4000, 6000) .On the other hand two different catalyst system was used; para toluene sulfonic acid (PTSA) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU).The PEG bound to the backbone of the polymers formed crystalline regions responsible from latent heat storage with reversible crystalline to amorphous phase transition as linked unit prevented total melting of the structure. Also MAM-PEG polyester polymers acid and hydroxyl values were determined for number of average molecular weight (Mn) and calculated as 36232 and 49020. Characterization and thermal properties of SSPCMs were performed by using fourier transform infrared (FT-IR) spectroscopy and differential scanning calorimetry (DSC) techniques mainly. DSC results showed that solid-solid transitions 36-54 °C temperature range and 163-153 Jg^{-1} enthalpy. As a result, MAM-PEG polymers were found potential for thermal energy storage (TES) applications.

Key words: Thermal energy storage, maleic anhydride, PEG, PCM

1. INTRODUCTION

There are some important environmental problems that global warming, climate change and environmental pollution are emerging as a result of using coal, oil and natural gas, as an energy source of fossil fuels. Recently, the number of studies on cleaner and environmentally friendly renewable energy resources has increased significantly as a solution to these problems. Presence of different monomers in a polymer molecule can lead to production materials of commercial importance. One of the thermal energy storage methods is the latent heat storage method. Phase change materials (PCMs) are capable of storing and releasing latent heat energy reversibly during phase change. The latent heat is the amount of heat which changes the physical structure of the material (solid, liquid and

---

* Corresponding Author: tugbagungor@comu.edu.tr
[1] Çanakkale Onsekiz Mart University, Çanakkale School of Applied Sciences.
ORCID: https://orcid.org/0000-0002-1306-3399
[2] Gaziosmanpasa University, Department of Chemistry. E-mail: cemil.alkan@gop.edu.tr
ORCID: https://orcid.org/0000-0002-1509-4789

gaseous) [1], [2]. Solid-solid phase changes are preferred mostly small volume according to solid-liquid PCMs. PCMs and their eutectic mixtures have different uses in textiles, electronics, biomedical and biology and so on [3],[4],[5].

PEGs are non-toxic materials that have excellent thermal storage properties and they can maintain chemical stability during long-term use [6] and they have high fission energy [7] and MA is used in some applications such as artificial sweeteners, food enhancers, paper processing, water treatment chemicals.

SSPCMs can store highly latent heat at the time of conversion from crystal phase to amorphous phase. SSPCMs don’t produce toxic substances, pollute the environment and don’t need a different energy source as they perform latent heat storage through phase transition. Therefore, it was an environmentally friendly application [8] and so on SSPCM investigations with high TES characteristics include several PEG-based polymeric SSPCMs such as polyurethane-graft-PEG [9], cellulose diacetate-graft-PEG [10], polypropylene-graft-PEG [11], cellulose-graft-PEG [12], [13], poly(vinyl alcohol)-graft-PEG [14] and Poly(styrene-co-maleic anhydride)-graft-PEG [15] as SSPCMs have been prepared or modified by various methods [16], MAM-PEG was synthesized new SSPCM. MAM-PEG stores latent heat through the change from the crystalline to the amorphous phase of PEG bound. MA modified to PEG by ring opening reaction. MAM-PEG polyester polymers were synthesized by PTSA catalyst system and DBU and latent heat energy storage capacities compared PEG 4000 and PEG 6000. Fisher esterification method applied to synthesis. In this study, acid and hydroxyl values of polyester polymers were determined and the number of average molecular weight (Mn) was calculated. The effect of catalysts and molecular weight change in PEG on latent heat storage capacity was determined using DSC technique. As a result MAM-PEG polymer can be used as energy storage material for food packaging industry and especially for foods that need to be transported or stored in heat food as catering and process of factory fermentation units or incubation rooms.

2. MATERIAL AND METHODS

2.1. Materials

Maleic anhydride (MA), poly (ethylene glycol) PEG (Mw: 4000, 6000), p-toluenesulfonic acid (PTSA) and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) catalysts were purchased from Aldrich Company. Toluene solution, Potassium hydroxide (KOH), Phenolphthalein and Ethanol were purchased from Merck Company. All were used without further purifications.

2.2. Methods

2.2.1. Synthesis of MAM-PEG Polymers

MAM-PEG polymers have been synthesized by ring opening reaction of MA to connect PEG units each other as shown in Figure 1. The reaction was established in a nitrogen atmosphere containing a 500 ml dispenser apparatus system with reflux condenser and mechanical stirrer. First in reaction MA and PEG calculated 20:19 molar ratio and added at 300 ml toluene solution. Reaction system was catalyzed with 2–3 drops PTSA 160 °C temperature in 2 hours and 800 rpm. Furthermore, the same procedure was performed with DBU catalyst system at a 20:19 molar ratio.

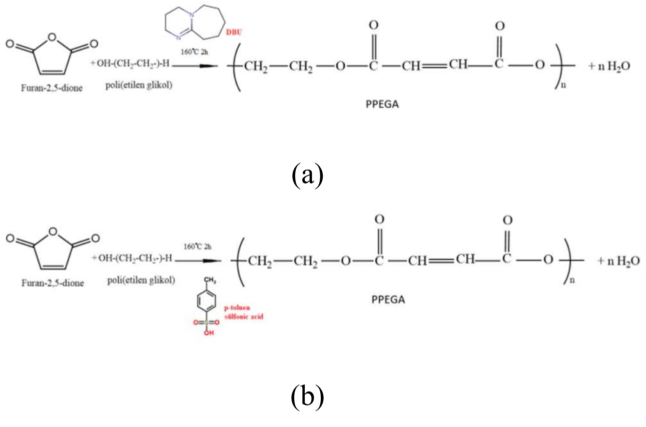

Figure 1 Synthesis of MAM-PEG Polymers Using (a) DBU catalyst and (b) PTSA catalyst

2.2.2. Number Average Molecular Weight (Mn) of MAM-PEG polymers

The acid and hydroxyl values were determined by standard methods described elsewhere and from these values the molecular weight of polyesters was estimated [17]. The acid value of the carboxyl-terminated ester was calculated by titration of product with ethanolic potassium hydroxide (KOH) solution. As known typical method, 1.3 g of sample was taken in a flask and 5 ml of water and 25 ml ethanol were added to flask. The mixture was stirred for 10–15 min until dissolved all of them. 2–3 drops of phenolphthalein indicator were added, followed by titration with 0.1 N ethanolic KOH. The turning point was determined as a change from colorless to pink and acid value was estimated [18]. MAM-PEG 4000 and MAM-PEG 6000 were number average molecular weight 36232 and 49020 as depicted in Table 1.

The number-average molecular weight (Mn) of polymers was calculated the following formula (1)[19].

$$Mn = 1 / (\text{Acid value} + \text{Hydroxyl value}) / (2 \times 56.1 \times 1000) \qquad (1)$$

Table1
M_n Analysis of MAM-PEG polymers

Compound	Acid value	OH value	M_n
MAM-PEG 4000	1.6	1.5	36232
MAM-PEG 6000	1.2	1.1	49020

2.3. Characterization

FT-IR spectra of SSPCMs were recorded with FT-IR spectrophotometer (JASCO 430 model) in 4000-400 cm^{-1} wavelength range and on KBr disks. Thermal energy storage characteristics were determined by using a Perkin Elmer Jade model DSC instrument in the range of -15 °C - 90 °C and at a heating-cooling ramp of 10 °C min^{-1}.

3. RESULTS AND DISCUSSION

3.1. FT-IR Spectroscopy Analysis of MAM-PEG Polymers

Ester and carboxylic acid groups of MAM-PEG 4000 polymer produced tensile vibration at 1710 cm^{-1} at FTIR spectra. It can be considered that decrease in O-H functional group with change in peak at approximately 3500 cm^{-1}. MA has characteristic peaks of 2923 and 2850 cm^{-1}, 1463 cm^{-1}, 1066 cm^{-1}, and 722 cm^{-1}. MAM-PEG 4000 polymer reduces O-H tensile vibration of MA in range of about 2500-3000 cm^{-1} and decrease in characteristic peaks of 1066 cm^{-1}. MA copolymerization FT-IR spectrums shown in Figure 2.

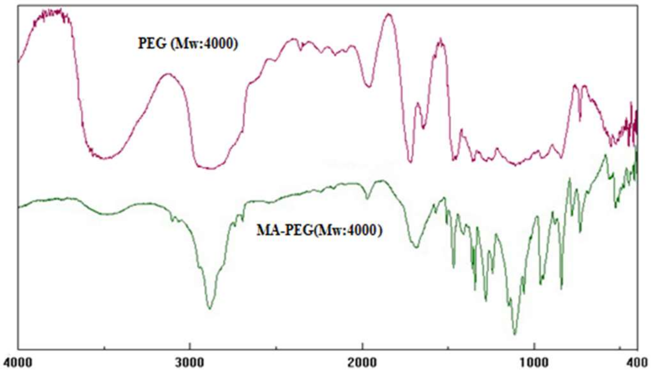

Figure 2 FT-IR spectra of PEG 4000 and MAM-PEG 4000 polymer (produced using DBU catalyst)

3.2. Thermal Reliability of MAM-PEG Polymers

When the DSC curve of MAM-PEG 4000 polymer produced using PTSA catalyst was examined, melting and solidification temperature difference was measured as 18.6 °C and melting and solidification enthalpy difference as 7.6 Jg^{-1} and overcooling observed at 33.4 °C (Figure 3), DSC curve of DBU catalyst, melting and solidification temperature difference was 14.8 °C and enthalpy difference of melting and solidification was 10.2 Jg^{-1} (Figure 4). It was close to the phase change temperature of PEG 4000 with a melting point of 55.6 °C. MAM-PEG 6000 polymer produced using PTSA as a catalyst, melting and solidification temperature difference was 13 °C and the enthalpy difference of melting and solidification was 16 Jg^{-1} with the effect of the catalyst, energy storage capacity increased and the melting point decreased and overcooling observed at 33.6 °C (Figure 5). DSC curve of DBU as a catalyst was examined melting and solidification temperature difference was 13.6 °C and the enthalpy difference of melting and solidification was 0.4 Jg^{-1} (Figure 6). DSC analysis results of SSPCMs was showed in Figure 3, 4, 5, 6 and Table 2 respectively.

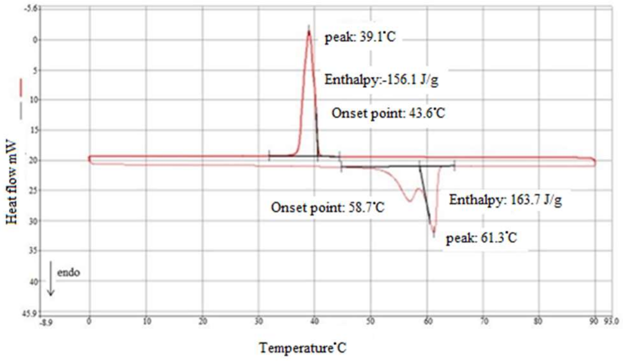

Figure 3 DSC curve of MAM-PEG 4000 polymer produced using PTSA catalyst

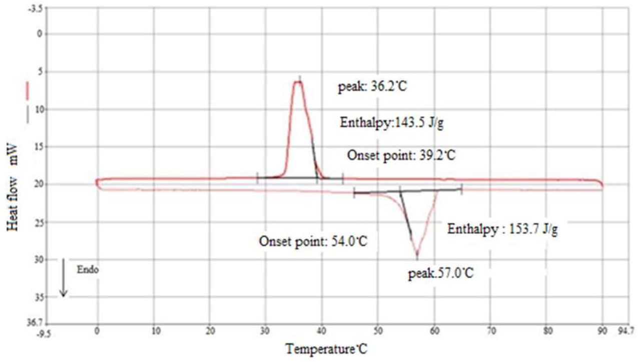

Figure 4 DSC curve of MAM-PEG 4000 polymer produced using DBU catalyst

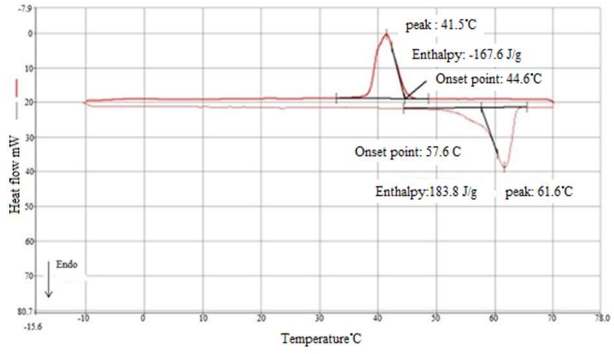

Figure 5 DSC curve of MAM-PEG 6000 polymer produced using PTSA as a catalyst

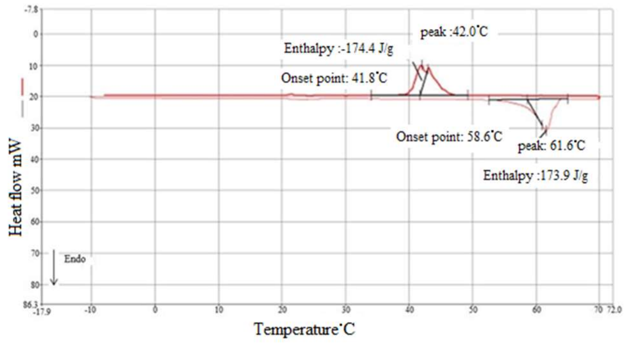

Figure 6 DSC curve of MAM-PEG 6000 polymer produced using DBU as a catalyst

Table 2
The latent heat thermal energy storage specifications of pure PEGs and SSPCMs

	Heating period		Cooling period		
	$T_{s\text{–}s}$ (°C)	**$\Delta H_{s\text{–}s}$ (J g^{-1})**	**$T_{s\text{–}s}$ (°C)**	**$\Delta H_{s\text{–}s}$ (J g^{-1})**	
PEG 4000	40.5	171.5	53.9	174.2	[15]
MAM-PEG 4000 (DBU)	54	153.7	39.2	143.5	
MAM-PEG 4000 (PTSA)	58.7	163.7	43.6	156.1	
PEG 6000	42.3	190	59.9	196.3	[15]
MAM-PEG 6000 (DBU)	58.6	173.9	41.8	174.4	
MAM-PEG 6000 (PTSA)	57.6	183.8	44.6	167.6	

Ts-s: Solid-solid heating and cooling temperature

4. CONCLUSIONS

MAM-PEG polymers were synthesized as thermally protecting food packaging materials. MAM-PEG polymers gained latent heat storage feature from the crystalline phase to semi crystalline phase. MAM-PEG 4000 polymer reduced tensile vibration at 3453 cm^{-1} –O-H absorption peaks and 2867 cm^{-1} for –C-H stretching, decreased in the characteristic peak 1066 cm^{-1} of MA by modification. Ester and carboxylic acid group of MAM-PEG produced tensile vibration at 1710 cm^{-1}. DSC curve of MAM-PEG 4000 polymer was examined, melting and solidification temperature difference was measured as 18 °C and melting and solidification enthalpy difference was measured as 8 Jg^{-1}

(Figure 3), DSC curve of the MAM-PEG 4000 polymer synthesized using DBU as a catalyst, melting and solidification temperature difference was 14.8 °C and enthalpy difference of melting and solidification was 10.2 Jg^{-1} (Figure 4) and it was close to the phase change temperature of PEG 4000 with a melting point of 55.6 °C. Melting and solidification temperature difference 13 °C and enthalpy difference 16 Jg^{-1} with effect of catalyst so that energy storage capacity increased and melting point decreased. DSC measurements shows that PEG chains attached to main chain so copolymers have phase transition temperatures of 40-58 °C and high latent heat storage capacity in the range of 153-183 Jg^{-1}. The synthesized MAM-PEG polymer usable TES material for food packaging and storage industry (ready food industry, fast food etc.).

Acknowledgements

The authors thank the anonymous reviewers for constructive suggestions, which improve the quality of the paper.

Funding

The author received no financial support for the research, authorship, and/or publication of this paper.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

T.G.E synthesized Maleic Anhydride Modified Poly (Ethylene Glycol), calculate average molecular weight and C.A made polymer characterization. This study was produced from the corresponding author's PhD thesis.

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

REFERENCES

[1] B. Zalba, J.M. Marin, L.F. Cabeza, and H. Mehling, “Review on thermal energy storage with phase change: materials, heat transfer analysis, and applications,” Appl. Therm. Eng., vol. 23, no. 3, pp. 251–283, 2003.

[2] M. Kenisarin and K. Mahkamov, “Solar energy storage using phase change materials,” Renew. Sust. Energy Rev., vol. 11, no. 9, pp. 1913–1965, 2007.

[3] C. Chen, L. Wang, and Y. Huang, “Crosslinking of the electrospun polyethylene glycol/ cellulose acetate composite fibers as shape-stabilized phase change materials," Mater. Lett., vol. 63, no. 5, pp. 569-571, 2009.

[4] C. Chen, L. Wang, and Y. Huang, “Morphology and thermal properties of electrospun fatty acids/polyethylene terephthalate composite fibers as novel form-stable phase change materials,” Sol. Energ. Mater. Sol. Cells, vol. 92, no. 11, pp. 1382-1387, 2008.

[5] M. Li, Z. Wu, and H. Kao, “Study on preparation and thermal properties of binary fatty acid/diatomite shape-stabilized phase change

materials," Sol. Energy Mater. Sol. Cells, vol. 95, no. 8, pp. 2412–2416, 2011.

[6] Y. Wang, A. Yuan, Y. Zhao, Q Liu., and J. Lei, "Phase change material with flexible crosslinking for thermal energy storage," J. Appl. Polym. Sci., vol. 137, no. 13, pp. 48497, 2020.

[7] S. Sundararajan, A.B. Samui, and P.S. Kulkarni "Versatility of polyethylene glycol (PEG) in designing solid-solid phase change materials (PCMs) for thermal management and their application to innovative technologies," J. Mater. Chem.A, vol. 5, no. 35, pp. 18379-18396, 2017.

[8] L. Liu, L. Kong, H. Wang, R. Niu, and H. Shi, "Effect of graphene oxide nanoplatelets on the thermal characteristics and shape-stabilized performance of poly(styrene-co-maleic anhydride)-g-octadecanol comb-like polymeric phase change materials," Sol. Energ. Mater. Sol. Cells, vol. 149, pp. 40-48, 2016.

[9] X. Fu, W. Kong, Y. Zhang, L. Jiang, J Wang., and J. Lei, "Novel solid–solid phase change materials with biodegradable trihydroxy surfactants for thermal energy storage," RSC Adv., vol. 5, no. 84, pp. 68881–68889, 2015.

[10] Y. Jiang, E. Ding, and G. Li, "Study on transition characteristics of PEG/CDA solid–solid phase change materials," Polymer, vol. 43, no. 1, pp. 117–122, 2002.

[11] Y.N. Zang and E.Y. Ding, "Energy storage properties of phase change materials prepared from PEG/CPP," Chin. Chem. Lett., vol. 16, no. 10, pp. 1375–1378, 2005.

[12] X.H. Liang, Y.Q. Guo, L.Z. Gu, and E.Y. Ding, "Crystalline–amorphous phase- transition of a poly(ethylene glycol) cellulose blend," Macromolecules, vol. 28, no. 19, pp. 6551–6555, 1995.

[13] X.P. Yua and E.Y. Ding, "Synthesis and characterization of storage energy materials prepared from nano-crystalline cellulose/polyethylene glycol," Chin. Chem. Lett., vol. 17, no. 8, pp. 1129–1132, 2006.

[14] M. Zhang, Y. Na, and Z.H. Jiang, "Preparation and properties of polymeric solid–solid phase change materials of polyethylene glycol (PEG)/poly(vinyl alcohol) (PVA) copolymers by graft copolymerization," Chem. J. Chin. Univ., vol. 26, no.1, pp. 170–174, 2005.

[15] A. Sarı, A. Biçer, and C. Alkan, "Thermal energy storage characteristics of poly(styrene-co-maleic anhydride)-graft-PEG as polymeric solid–solid phase change materials," Sol. Energ. Mater. Sol. Cells, vol. 161, pp. 219–225, 2017.

[16] X. Huang, J. Guo, Q. An, X. Gong, Y. Gong, and S. Zhang, "Preparation and characterization of di-hexadecanol maleic/triallyl isocyanurate cross-linked copolymer as solid–solid phase change materials," J. Appl. Polym. Sci., vol. 133, no. 40, pp. 44065, 2016.

[17]W.R. Sorenson and T.W. Campbell, "Preparative Methods of Polymer Chemistry, Interscience Publishers," New York, pp. 130-154, 1968.

[18] S. Sundararajan, A. Kumar, B.C. Chakraborty, A.B.Samui, and P.S. Kulkarni, "Poly(thylene glycol) (PEG)-modified epoxy phase-change polymer with dual properties of thermal storage and vibration damping," Sust. Energ. Fuels, vol. 2, no. 3, pp. 688-697, 2018.

[19] Liu H.J., L.H. Lin, and K.M. Chen, "Preparation and Properties of Water-Soluble Polyester Surfactants. III. Preparation and Wetting Properties of Polyethylene Glycol–Polydimethylsiloxane Polyester Surfactants," Appl. Polym. Sci., vol. 88, no. 5, pp. 1236 –1241, 2003.