Thermal Property Analysis and Characteristic Study of Poly Ethylene Glycol with Diverse Molecular Weight for Thermal Energy Storage Material

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Abstract. In this study, the investigation on thermal property and characteristic analysis of Poly Ethylene Glycol (PEGs) material by varying the molecular weights is examined. In this context, the study on thermal energy material storage is explored by using the different techniques such as Differential Scanning Calorimetry (DSC) for persistent heating rate and Thermal Gravity Analysis (TGA) for determining the amount of change of mass of the material in addition to the function of increasing temperature. Subsequently, the characterization of PEGs with different molecular weight is carried out to explore the property and insight of the material by using the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) by examining the surface topology, crystallography in addition to this the X-Ray Diffraction (XRD) techniques for catch a glimpse of the crystal structure is studied. As an outcome, in the DSC techniques the results made known when the molecular weight increases, correspondingly the melting temperature and solidification temperature similarly increases however, the heat of fusion during the freezing cycle increases. In the TGA techniques, similarly specified increases in the volume of PEG with different molecular weight has resulted in an increase in the temperature. Subsequently, in the characterization of the PEGs, the SEM has shown an enormous amount of insignificant sphere-shaped crystal-like structures which are joined together and impinging on their neighbour’s which paved the way for the formation of a multi-layered lamellar structure in due course activated rise in the solidification temperature in its molecular weight. Henceforth, from the analytical studies, it’s been evident that the molecular weight greatly influences the mechanical and thermal properties of PEGs. In this concern, the PEGs blends are a potential benefit to replace pure components.

1. Introduction
The energy conservation is the most essential measure for thermal energy storage applications in which energy can be stored in the form of sensible heat, latent heat, and heat storage due to physical transition. Although PCMs can store energy, there are three major problems in using traditional PCMs. Namely, in the case of inorganic salt hydrates and heir mixtures does not melt uniformly and during melting a new solid (of different composition) forms. Super cooling liquid salt hydrate earlier
towards freezing, this is headed by the poor nucleating properties. High packing and maintenance cost elsewhere, short service lives led by poor corrosion properties. [1,2]. In this concern, significant importance on emerging novel polymeric materials should be developed which be able to end result commencing an enhanced property than traditional PCMs. In this context, the compound like polyethylene oxide has a significantly large heat of fusion, consistent melting behaviour, non-corrosiveness as well as an extensive range of melting point [3,4,5] In this aspect, a new polymeric material that can be applied is polyethylene (PE) due to its properties [6]. An analytical study by using the Diffraction Scattering Calorimetry (DSC) by varying the diverse molecular weight of polyethylene glycol (PEG) is carried out in particular on the behaviour on phase transition and as an outcome from his research, the material for thermal energy storage is an important concern [7]. As a result, by utilizing the DSC technique the thermal characteristics behaviour can be explored and the potential use of material at the phase transitions related to different temperature can be attained. The phase transition and the evolution of compositional homogeneity is the valuable information which can be obtained by using a profile of thermal signal. This research works objective is to define the thermal properties and thermal analysis by using the different techniques such as Diffraction Scattering Calorimetry (DSC), Thermal Gravity Analysis (TGA) of persistent heating, phase transitions and morphological studies with diverse molecular weight of PEG for Thermal Energy Storing Materials TESMs.

2. Experimental Work

2.1. Materials Preparation
The illustrations on PEG by means of diverse molecular weight used as a cutting-edge in this research work is shown in the table 1 which are taken into account as a result of six different molecular weight of PEGs. In this context, the PEG of six different molecular weight available in which two remain pure PEGs Xi Plus and left over four remains normal PEGs. The composites of PEGs are equipped by means of mixed with the polymeric constituents in the melt (melting temperature as made known in the table 2) which is monitored through successive solidification processes.

| Sl. No | PEG and PEG Exi Plus | Molecular Weight |
|--------|----------------------|-----------------|
| 1      | 3350 PEG Exi Plus    |                 |
| 2      | 4000                 |                 |
| 3      | 6000 PEG Exi Plus    |                 |
| 4      | 6000                 |                 |
| 5      | 20000                |                 |
| 6      | 9000                 |                 |

2.2. Techniques

2.2.1. Differential Scanning Calorimetry (DSC)
By means of persistent heating/cooling rate (active method) is employed. Samples of different molecular weight (2-4mg) are weighed and employed in the aluminium pans. The heating system amounts from 1, 2.5, 5, 10 and 20 K/min be a functional parameter is enforced. The inert gas as argon was used with the flow rate of 30 cm$^3$/min. Subsequently, the calorimeter was regulated by mercury and indium standards. In this aspect, cooling process to be initiated and the liquid nitrogen of 50 ml/min is utilized as a cooling medium.

2.2.2. Thermal Gravity Analysis (TGA)
The TGA samples thermos-gravimetric investigation were carried out by means of concurrent DTA-TGA thermal analyser device (Shimadzu DTG-60H). Samples of different molecular weight (6-
15mg) are weighed and employed in the platinum pans then heated upon 900°C at a rate of 10°C/min under nitrogen purge (60mL/min).

2.2.3. Microscopy
Characterization of samples during the crystallization (Cooled Down) process carried out for the polyethylene glycol with diverse molecular weight. However, the blends of samples are prepared in a successive step for microscopy analysis. In this context, the characterization techniques such as Scanning Electron Microscopy (SEM) as well as Transmission Electron Microscopy (TEM) investigations are carried out for exploring the properties of the surface topology as well as crystallography of the material. In sequence, X-Ray Diffraction (XRD) techniques is used for spotting the crystal structure of Poly-ethylene Glycol (PEG) material.

3. Results and discussion
Experimental study on different molecular weight PEG samples are measured and their melting temperature and heat of melting (ΔH_m) is shown in the table 2. In deep, thermal history of the samples is discussed and the consequence of temperature sustainability is determined for the better understanding for the further use of PEG in diverse applications as heat storage materials. The different molecular weights of PEGs effect on high temperature as well as heat of melting. In this framework, when the molecular weight increases, in parallel the heat of melting moreover increases therefore, molecular weight plays a significant role which results an increases in the melting temperature.

Table 2. Temperature as well as Heat of Melting (ΔH_m) of PEG Samples

| Molecular Weight | Heat cycle | Melting point (°C) | ΔH_m (J/g) |
|------------------|------------|--------------------|------------|
| PEG 3350         | 1          | 54.47              | 214.6      |
| PEG 4000         | 1          | 49.71              | 212.3      |
| PEG 6000         | 1          | 54.78              | 231.5      |
| PEG 6000         | 1          | 57.56              | 217.6      |
| PEG 9000         | 1          | 55.72              | 221.9      |
| PEG 20000        | 1          | 62.08              | 235.6      |

Figure 1. Diffraction Scanning Spectroscopy curves of Different molecular weight PEGs
As an outcome, DSC experiment is conducted in a sequence of six different molecular weight PEGs. In which two polymers are purity PEGs called as Exi-plus other four are normal PEGs. Two set of PEGs having different melting points in the direction of increasing molecular weight. In which Exi-plus PEGs has maximum melting point of (58.15˚C & 59.48˚C) and normal PEGs has (56.40, 60.56, 61.14, 66.59˚C), drawn in the figure 1 these melting points (Temperature) remain increased as soon as a molecular weight increases as shown in the figure 2 in the meantime, the heat of melting correspondingly increases. Phase transition properties determined through melting peak temperature and transition enthalpy. It has apprehended by DSC technique; temperature range from (-90 to 396.70˚C) at 19.99˚C/min heat only. The transition properties are determined from curve. Maximum melting point increases with molecular weight increase in normal polymer and in exi-plus polymer. exi-plus PEG3350 attain high melting point parallel to normal PEG 4000 as shown in the figure 3.

![Figure 2. Temperature of melting and heat of melting with respect to PEG of different molecular weight.](image)

![Figure 3. DSC technique; temperature range from (-90 to 396.70˚C) at 19.99˚C/min heat.](image)
Superior polymer like exi-plus is better than normal polymer. Good phase transition area in exi-plus PEG 6000 (231.5 J/g) better than high range of molecular weight in normal PEG 9000(221.9 J/g) and 6000 (217.6 J/g) as shown in the figure 4. Phase transition properties are not affected by refined PEGs.

![Figure 4. Transition properties Heat flow versus Temperature](image)

Crystallization formation is stronger when the molecular weights of the PEGs are higher (Increased). Meanwhile crystallization degree moreover higher (expect. PEG 4000) [8]

The crystallinity degree $X_c$ is determined using the formula.

$$X_c = \frac{\Delta H - \Delta H_a}{\Delta H_m^O} = \frac{\Delta H_m}{\Delta H_m^O}$$

Where,

- $\Delta H_m^O$ Heat of melting % crystalline polymer (196.8 J/g) [8]
- $\Delta H_m$ Heat of melting of polymer (PEGs)

In the table 3, figure 5, the results of the crystallinity degree of PEG by means of diverse molecular weights through the DSC techniques are made known. As a consequence, when the molecular weight of the PEGs increases which results an increase in development of crystalline phase associated with the lower segmental mobility, feasible and a suitable geometrical orientation. In the meantime, PEGs with different heating rate is experimented as an effect. In this context, heating rate takes place on melting temperature as well as heat of melting which has resulted an increase in the heat rate which increases the melting temperature as shown in the figure 6 and table 4. In addition, the effect of crystallization process is studied by means of diverse molecular weight of PEGs. As an effect, from the figure 7 and table 5 it is evident that when a molecular weight of PEGs increases the solidification temperature similarly increases.

| Table 3. Crystallinity Degree of PEG (as a result of DSC Method) |
|---------------------------------|
| Molecular Weight | $X_c$ (%) |
| PEG 3350 Exi-plus | 100.9 |
| PEG 4000 | 100.2 |
| PEG 6000 Exi-Plus | 107.2 |
PEG 6000 100.8
PEG 9000 102.8
PEG 20000 109.9

Table 4. Melting Temperature as well as PEG Heat of Melting on Diverse Heating Rates

| Melting Point (°C) ( ΔH_m) (J/g) | 1       | 2.5     | 5       | 10      |
|----------------------------------|---------|---------|---------|---------|
| PEG 3350                         | 61.94   | 61.96   | 62      | 62.3    |
|                                  | 234.3   | 234.3   | 234.3   | 234.4   |

Figure 5. Crystallinity Degree of PEG (as a result of DSC Method)

Figure 6. Effect of heating rate of melting temperature as well as heat of melting
Thermal Gravimetric Analysis is carried out for the characteristic study on decomposition patterns on polymeric materials. Eventually to study the thermal stability such as the polymer melting or degradation before 200°C. In these point of view, TGA curve in the Figure 8 shown that the thermal decomposition temperature ranges from 176°C to 437°C of PEGs. The different molecular weight PEGs the decomposition temperatures takes place largely in the large molecular weight than the smaller molecular weight PEGs. These PEGs results are similar thermal characteristic from Karman et al [9] (except 6000 PEG). From the result, it is clear that the PEG samples remain thermally stable in the heat capacity measurement region below 126°C are similar when compared with the yan kou et al study [10]. Iragorri et al [11] studied the dynamics of the crystalline structures by their behavior of the PEGs. In this context, plentiful small spherical crystalline structures are joined together and influenced the adjacent and subsequent formation of multilayer lamellar texture. Katiem et al [12] on the other hand exposed from his characterization study that there is on no account of reduction on growth rate with respect to time unless it impacts or influence additional growing spherules.
Figure 8. TGA curve on thermal decomposition temperature ranges from of PEGs

Lisowski et al [13] research work on polyethylene glycol material by carrying out an investigation on its microstructure arrangement such as lamellar structure as well as bulk crystallinity development process by using \( MW = 1.81 \times 10^5 \) which in sequence with a result of time-resolved synchrotron wide-ranging as well as small-angle X-ray scattering by the side of 45,48,50 and 52°C. Talibuddin et al [14] conducted his research on Time-resolved (TR) Small-Angle X-ray (SAXS) and explored his results on the development of microstructure and crystallinity. In this context, commencing from his fallouts, it is explored that the \( lc \) increase intentionally with an increase in \( T_c \). On the other hand, in the initial phase the crystallization time decreases at all values of \( T_c \) by means of lamellar thickness with the moderate lengthy-term, in addition, it is persisted continuously all the way through the crystallization period [15,16].

3.1. Scanning Electron Microscopy

The thermal transition figures are reinforced by using the Scanning Electron Microscopy and X-ray Diffraction method by diverse molecular weight of PEGs samples are examined for the better understanding from end to end crystallography structure and its behaviour. PEGs with different molecular weight is examined by the scanning electron microscopy and their surface topography is exposed in the form the microstructure analysis. As shown in the figure 9 the PEG samples of higher molecular weight has an enormous amount of small sphere-shaped crystal-like arrangements which remains to have a fused together as well as impinging on their neighbor’s which paved the way for the formation of a multi-layered lamellar structure. As a result, by an increase in the molecular weight of PEG the temperature of solidification increases.
3.2. Transmission Electron Microscopy

The technique which is used to determine the insight of the very small specimens is Transmission electron microscopy (TEM) technique. In this technique, the electrons are accelerated by a beam of light with which the electron passes from end to end in a very thin sample in the direction towards for the observation of topographies such as structure and morphology with a higher magnification and resolution as shown in the figure 10. The microstructure analysis of the polyethylene glycol with a molecular weight of 3350 has shown a better property such as the voids alike air bubble with a nanometre range of 200 whereas in the 500 nanometre range it is evident that the voids is observed which may be caused due to the improper mixing and also the heating rates with respect to temperature variation. Correspondingly, the exi-plus 6000 PEG has shown spherical shaped voids such as air bubbles at range of 200 nm as shown in the figure below. In this context, both the 3350 and exi-plus 6000 PEG has as air bubble when a resolution is increased for the observation of surface topography. As a result, the exi-plus has shown a more potential voids which may be caused by the heating rates and heat of fusion of particles.

Figure 9. Microstructure analysis of 3350 and 6000 Exi plus.
**Figure 10.** Microstructure analysis of 3350 and 6000 Exi-Plus

**X-Ray Diffraction:** The most common and important logical technique utilized for the identification of the crystal-like materials is the X-Ray Diffraction method. In this context, from the outcomes, as shown in Figure 11, the normal PEGs such as PEG 20000 (4666.67) cps attained higher intensity when
compared to other PEGs concerning different molecular weight. On the other hand, Exiplus samples have less intensity which is in the range of (3133.33 for Exi plus 3350 and 4160.00 for exi plus 6000).

XRD result reveals that the intensity of PEG samples decreases gradually with their molecular weight decrease. Two diffraction peaks are present in XRD cures at about $2\theta=19.3^\circ$ to $23.6^\circ$ for PEGs considered in this study. Y.Kou et al [10] results on the aspect of diffraction peaks shown angle $2\theta=19.2^\circ$ to $23.4^\circ$. In the meantime, the intensity ratio increases, as a result, the molecular weight increases in a regular interval. Subsequently, the crystal thickness of the polyethylene glycol increases which tends towards an increase in an average molecular weight increase. Which has a high-intensity value that contains more density, as a result, high-intensity PEG had structure quality as shown in figure 11.

![X-Ray Diffraction of Different Molecular weight of PEG](image)

**Figure 11.** X-Ray Diffraction of Different Molecular weight of PEG

In this Context, from the outcomes as shown in the figure 11, the normal PEGs such as PEG 20000 (4666.67) cps attained higher intensity when compared to other PEGs with respect to different molecular weight. On the other hand, Exiplus samples has less intensity which is in the range of (3133.33 for Exi plus 3350 and 4160.00 for exi plus 6000). XRD result reveals that the intensity of PEG samples decreases gradually with their molecular weight decrease. Two diffraction peaks are present in XRD cures at about $2\theta=19.3^\circ$ to $23.6^\circ$ for PEGs considered in this study. Y.Kou et al [10] results on the aspect of diffraction peaks shown similar angle $2\theta=19.2^\circ$ to $23.4^\circ$. In the meantime, the intensity ratio increases as a result, the molecular weight increases in a regular interval. Subsequently, the crystal thickness of the polyethylene glycol increases which tends towards an increases in an average molecular weight increases. Which have high intensity value that contain more density, as a result high intensity PEG had structure quality as shown in the figure 11.
4. Conclusions
A Cutting-edge effort on thermal analysis, thermal stability, and phase change property of the PEGs with different molecular weight such as 3350 Exi-plus, 6000 Exi-plus, 4000, 6000, 9000 and 20000 are taken for the study and their thermal properties and its potential are investigated and compared within PEG of different molecular weight of the samples and the potential one for the heating applications is resulted. As an outcome, the melting point varies from (50 to 66) °C by means of PEGs using different molecular weight. Subsequently, the heat of melting ranged from the (215 to 236.2) J/g. The degree of crystallinity is influenced by the molecular weight in which it ranges on or after (100 to 109.9) %. Henceforth, from the conclusions, it’s been evident that the diverse molecular weight of polyethylene glycol are significantly influences the mechanical properties characteristically by means of an increase in polyethylene glycol with different molecular weight. In this concern, the PEGs blends are a potential benefit to replace pure components which are mainly associated with the materials by means of probability of varying with the temperature series as well as heat associated through melting. However, the thermal properties as well as facts encompassed a cutting-edge in this effort would remain technically essential, in addition to this it is desirable for theoretical study which would lay concrete for the thermal energy based applications by utilizing polyethylene glycol as phase change materials.

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