



Synthesis and characterization of chain-extended and branched polyurethane copolymers as form stable phase change materials for solar thermal conversion storage

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ABSTRACT

In this work, polyethylene glycol (PEG) based polyurethane copolymer was synthesized using linear chain extension and branching methods. In linear chain extension, multiple PEG molecules were linked using urethane bonds. In branching, polyvinyl alcohol (PVOH) backbone was grafted with PEG molecules as branches and cross-linked to other PVOH molecules. 4,4'-Diphenylmethane di-isocyanate (MDI) was used as both chain extender and cross-linker. The resulting copolymers were characterized for chemical composition, microscopic morphology, crystalloid structure and thermal properties. Based on the results from characterizations, a detailed discussion on the phase change mechanism in polyurethanes is presented. ^1H NMR and FT-IR results confirmed the chain extension and branching. ^1H NMR spectra displayed characteristic signal of the urethane. DSC results revealed solid-solid phase change behavior of copolymers with high latent heat. Crystalline nature of spherulite lamellae structures was verified by observing birefringence using POM microscope and XRD peaks. Polyurethane copolymers had maximum latent heat absorption capacity of $144.14 \text{ kJ kg}^{-1}$ at melting temperature of $51 \text{ }^\circ\text{C}$ and had maximum heat release capacity of 117.5 kJ kg^{-1} at freezing temperature of $33 \text{ }^\circ\text{C}$. Polyurethane copolymers were thermally stable up to $200 \text{ }^\circ\text{C}$. Polyurethane copolymers satisfied all criteria for use as form stable solid-solid phase change material (SSPCM) in solar thermal conversion storage.

1. Introduction

Today, due to the rapid pace of development and increasing economic activities of mankind, demand for thermal energy has skyrocketed. Despite the abundant availability of clean and renewable energy sources like solar, wind, geothermal, etc. their contribution in satisfying this huge demand is a mere 2% [1]. This failure to tap clean and renewable energy sources is a direct consequence of lack of adequate number of TES systems. Hence, TES field deserves more attention in order to make the thermal energy systems easily available and cheaper to install and operate. The research into novel materials possessing excellent TES capabilities is one way to contribute to this purpose. One key application area for TES systems is providing thermal comfort in human life. In this domain, organic phase change materials (PCMs) are the most popular TES materials. Paraffin, fatty acids, esters, poly ethylene glycol, etc. are the main organic TES materials in use today [1]. The large latent heat capacity during the solid-liquid phase change process, make feasible all of them to achieve TES purpose. However, in liquid phase these materials present a problem of leakage necessitating a container to hold them. Different approaches have been

attempted to mitigate this issue as listed below:

- (1) Macro [2] and micro [3,4] encapsulation.
- (2) Form-stable PCM with polymer matrix using physical blending technique [5,6].
- (3) Form-stable PCM using chemical grafting technique [7–9].
- (4) Electrospun fiber [10,11].

Among these, the synthesis of a form-stable PCM through chemical grafting can be carried out by a simple technique where the PCM is bonded to a suitable polymer hard segment to give it the shape stability during the phase change process. Such materials undergo solid-solid phase change process with a high latent heat absorption or release. However, this technique requires suitable functional groups on both the PCM and the polymer molecular structures in order to be able to link them together. PCM like polyethylene glycol (PEG) and polymer like polyvinyl alcohol (PVOH) satisfy such criteria. Due to the presence of hydroxyl functional groups in their molecular structure, PEG and PVOH are best suited for the chemical grafting technique. A brief introduction of the material system used in this work is given below:

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1.1. Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is a synthetic polymer extensively used in biomedical field for tissue engineering, drug delivery, and biosensors, etc. It has a generic formula $H-(O-CH_2-CH_2)_n-OH$. PEG is available in various average molecular weights ranging from PEG400 to PEG100000. As the chain length and molecular weight of PEG increase, its melting point and latent heat of fusion also increase. For example, small molecular weight PEG400 has a melting point and latent heat of fusion of 4 °C and 117 kJ kg⁻¹. High molecular weight PEG1000000 has a melting point and latent heat of fusion of 70 °C and 174 kJ kg⁻¹ [1]. The high latent heat of fusion means that PEG has potential as a TES material. However, the most suitable melting temperature range for human thermal comfort is between 18 °C and 30 °C. The melting temperatures of most PEG (above the average molecular weight of 1000) are above 50 °C. That is slightly high for human thermal comfort applications. The backbone chain structure has a C-O-C linkage of ether with two terminal hydroxyl functional groups (-OH) on both ends of the molecular chain. The terminal hydroxyl functional groups and the presence of oxygen atom in ether linked (C-O-C) backbone make the PEG molecule polar in nature. PEGs are hydrophilic and they are partially soluble in water at room temperature due to their long chain-polymeric structure. PEG exhibits solid-liquid phase change behavior. PEG like other organic polymers undergoes lamellar crystallization during solidification. PEG has a high degree of supercooling and past studies have identified several influencing factors for PEG crystallization process, which is further discussed in POM section below.

The two terminal hydroxyl functional groups on PEG molecule can be used for linking it with other polymer molecular chains. PEG molecules have been grafted as branches to hard segment polymer backbones like poly(styrene-co-maleic anhydride) (SMA) [7] and polyvinyl alcohol (PVOH) [8], etc. In all these studies, PEG acted as a soft segment that provided latent heat and other polymers acted as hard segments that provided shape stability.

1.2. Polyvinyl alcohol (PVOH)

Polyvinyl alcohol (PVOH) is a synthetic polymer extensively used in food industry. It is used as a coating agent to maintain the quality of the foods like confectionary, dairy based deserts etc. PVOH coating protects the food from moisture, oxygen and other environmental factors. It is manufactured by polymerization of vinyl acetate into polyvinyl acetate and then followed by a partial hydrolysis. The hydrolysis is carried out through saponification reaction where the ester group in polyvinyl acetate is replaced with hydroxyl group from methanol in the presence of aqueous sodium hydroxide solution. The degree of hydrolysis may reach up to 89%. Therefore, polyvinyl alcohol is a copolymer with both hydroxyl functional groups (-OH) and a very small percentage of acetate functional groups (-O-(C=O)-CH₃) being present. The numerous hydroxyl functional groups (-OH) on the PVOH molecule backbone can be utilized for grafting other polymer chains as branches. The hydroxyl functional groups also can be used for cross linking with other PVOH molecules.

1.3. 4,4'-Diphenylmethane di-isocyanate (MDI)

4,4'-Diphenylmethane di-isocyanate (MDI) is the most popular diisocyanate used in the production of polyurethane. The molecular structure of MDI has two aromatic rings joined by a bridging methylene group (-CH₂-). The benzene rings of MDI are in para-substitution configuration. Each benzene ring has one isocyanate (N=C=O) group on position-4. With these two isocyanate groups MDI molecule has a functionality $f = 2$. The functionality ($f = 2$) and its symmetrical structure makes MDI molecule suitable coupling agent for linear chain extension of PEG molecule.

Presence of the urethane bond (-NH-(C=O)-O-) is the key identity

of a polyurethane polymer. Polyurethane copolymers are produced by the reaction of any di-isocyanate or poly-isocyanate with the polyols. Isocyanate group (N=C=O) reacts with hydroxyl group (-OH) to form the urethane link (-NH-(C=O)-O-) [12]. PEG with its two terminal hydroxyl groups is a diol.

There are many past studies on the application of polyurethane class of polymers to TES field. Such polyurethanes are normally PEG based. The long molecular chain of PEG soft segments provides the polyurethane copolymer with latent heat of solid-solid phase transition. In literature we find many works related to PEG based polyurethane copolymers. Alkan et al. [13] studied polyurethanes produced using three different diisocyanate coupling agents like hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and Toluene diisocyanate (TDI) with PEGs of three different average molecular weights. The effect of steric hindrance caused by the asymmetry of diisocyanate coupling agents (IPDI and TDI), was observed when the molecular weight of PEG was small. The steric hindrance resulted in a solid-liquid phase transition instead of solid-solid phase transition expected in polyurethanes. Cao et al. [14] studied the thermal energy storage potential of hyper branched polyurethane. Fu et al. [15] studied the performance of thermosetting polyurethane cross-linked using diethanol amine. This type of polyurethane had a lower latent heat, but had better mechanical properties and very high thermal stability compared to other polyurethanes. Wu et al. [16] prepared a composite of polyurethane with graphite foam. In this work, they reported a thermal conductivity of 0.31 W m⁻¹ K⁻¹ for PEG and 0.25 W m⁻¹ K⁻¹ for polyurethane material. The final composite with graphite foam had a high thermal conductivity of 10.86 W m⁻¹ K⁻¹. Meng et al. [17] synthesized polyurethane using IPDI as coupling agent. To achieve better mechanical properties, the hard segment was chain extended with 1,4-butanediol (BDO). They reported a plateau elastic modulus of 40 MPa for polyurethane in the region above the PEG phase melting transition and below 150 °C. Su et al. [18] synthesized PEG based polyurethane using 1,4-butanediol (BDO) as hard segment and 4,4'-diphenylmethane diisocyanate (MDI) as the coupling agent. Li et al. [19] synthesized PEG based polyurethane using pentaerythritol (PE) as hard segment and 4,4'-diphenylmethane di-isocyanate (MDI) as the coupling agent. Zhou [20] synthesized PEG based polyurethane using poly(vinyl alcohol) (PVA) as hard segment and 4,4'-diphenylmethane di-isocyanate (MDI) as the coupling agent.

In literatures, we also find works related to PEG based copolymers which are not polyurethane type polymers. Even such PEG based copolymers also exhibit solid-solid phase transition with latent heat. Li et al. [21] synthesized PEG based copolymer using melamine formaldehyde as hard segment. Sarier et al. [22] synthesized PEG based copolymer using poly(acrylonitrile) (PAN) as hard segment and maleic anhydride (MAH) as the coupling agent. Hu et al. [23] synthesized PEG based polyethylene terephthalate (PET) copolymer using the transesterification reaction between PEG of various molecular weights and dimethyl terephthalate (DMT). In this case, DMT acted as the hard segment and PEG as the soft segment. This work suggested that similar to PEG based polyurethane copolymers, even the PEG based polyethylene terephthalate (PET) copolymers also exhibit phase transition behavior with latent heat. In DSC analysis, they observed two melting peaks and two crystallization peaks in the heating and cooling cycles. The PEG soft segments had a phase transition at a lower temperature close to 50 °C and the DMT hard segments had a phase transition at a higher temperature close to 210 °C. However, the latent heat of these phase transitions was low at around 45 kJ kg⁻¹ for PEG phase transition and 25 kJ kg⁻¹ for DMT phase transition. Sari et al. [24] attempted grafting small molecular chain PCM soft segment branches on a polymer hard segment backbone. The PCM in this case is palmitic acid and it has a much smaller molecular chain when compared to PEG. The hard segment used was polystyrene. Similarly, Sari et al. [25] grafted another small molecular chain PCM like stearic acid to a hard segment of poly(styrene-co-allyl alcohol) copolymer. Alkan et al. [26] also grafted

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