



# The influence of chain extender on properties of polyurethane-based phase change materials modified with graphene



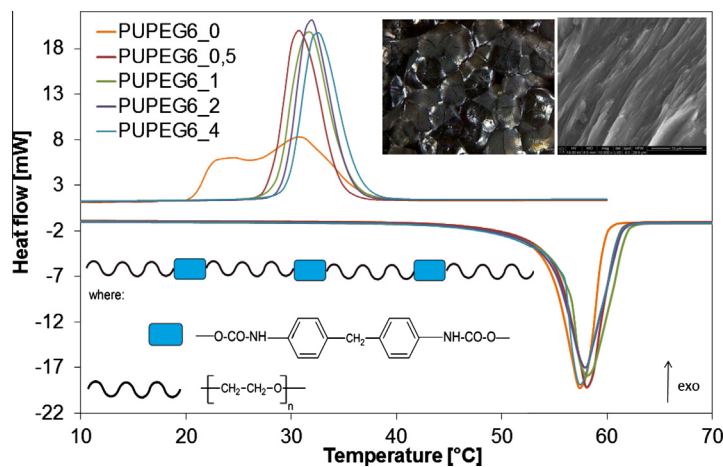
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## HIGHLIGHTS

- Polyurethane/graphene composites with solid–solid phase transition were obtained.
- PEG incorporated as a soft segment acts as PCM with high heat of phase transition.
- The influence of chain extender on PU PCMs properties was investigated.
- Graphene introduction caused an increase in thermal stability and conductivity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper polyurethane-based phase change materials (PCMs) modified with graphene for thermal energy storage were obtained *in situ* using a one-step bulk polymerization method. Polyurethanes (PUs) have been synthesized with 1,4-butanediol as a chain extender or without a chain extender. FTIR-ATR, DSC, TGA, SEM, OM and ultrasonic techniques were used for characterization of the obtained composites containing up to 4 wt.% of graphene. FTIR-ATR analysis confirmed PU structure and proved that there was no chemical reaction between polyurethane and graphene. The highest heat of phase transition and crystallinity were found for PU system synthesized without the chain extender and modified with 1.0 wt.% of graphene. Microscopic observation results indicated spherulite structures typical for poly(ethylene glycol) (PEG) which was used to form soft segments, with regions of lamellar crystal bundles radiating from the center of a spherulite. Thermal cycling tests were done by 50 and 100 heating/cooling cyclings in air and nitrogen atmosphere for verification of the thermal reliability and chemical stability – it has been found the heat of phase transition was generally not diminished. Importantly, the thermal conductivity of the PCMs was improved after modification with graphene. Generally, PUPEG without chain extender exhibited higher heat of phase transition, higher thermal stability and better thermal reliability.

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## 1. Introduction

Phase change materials (PCMs) with high storage density at nearly isothermal conditions have attracted considerable interest in numerous solar energy heating and cooling applications, but they are also applied in many different applications like buildings, food transport and packing, medicine, automotive or textiles [1,2]. One of the widely investigated PCMs is poly(ethylene glycol) (PEG) which displays large heat of melting, congruent melting behavior, resistance to corrosion and melting point suitable for low-temperature applications [3–5]. However, there are some difficulties in using PEG for latent heat storage like solid–liquid phase transition and low thermal conductivity [6]. To avoid leakage of molten PCM different strategies have been applied, such as encapsulation, which is also used to increase the surface area for heat transfer, as the thermal conductivity is low [7], shape stabilization with inorganic materials, e.g. vermiculite, silica [8,9] or expandable graphite [10], chemical crosslinking using cellulose and its derivatives [11], or crosslinking *via* hydrogen bonds with the use of polysaccharides [12]. However, leakage-free polyurethanes characterized by solid–solid phase transition have received an increased attention as PCMs in the recent years [13–15].

Hence, Alkan et al. [15] synthesized a series of polyurethanes for thermal energy storage applications showing solid–solid phase transition by using three different kinds of diisocyanate (hexamethylene diisocyanate, isophorone and toluene diisocyanate) and PEGs with three average molecular masses (1000, 6000, and 10,000 g/mol). The highest heat of phase transition of 169 J/g was found for polyurethane based on isophorone and PEG 10000. In the work by Xi and co-workers [14] thermoplastic form-stable polyurethane solid–solid phase change material with the heat of phase transition 137 J/g was described. The soft segments were synthesized from poly(ethylene glycol), the hard segments were made of 4,4'-diphenylmethanediisocyanate (MDI) and tetrahydroxy dicarbamate-based compound was used as a crosslinking agent. Linear polyurethane-based PCM with solid–solid phase transition ( $\Delta H = 152$  J/g) was obtained by Chen and co-workers [16] who applied PEG with average molar mass 6000 and 10,000, 4,4'-diphenylmethanediisocyanate (MDI), N-methyldiethanolamine (MDEA) and 1,3-propane sulfonate (PS).

Generally, as it was summarized in Ref. [2] polyurethane-based PCMs have been synthesized and studied with or without chain extender. However, no systematic discussion about the influence of the structure of polyurethane chain on the thermal properties and thermal energy storage ability was presented in the literature. In polyurethane synthesis, the chain extender essential functions are increasing the chain length of the urethane hard segments and increasing the overall molecular weight of the polyurethane produced. The presence of chain extender cause an increase of phase separation in polyurethane and enhances crystallization of soft or hard segments [17].

Hence, in our work we have synthesized using the same substrates polyurethanes with and without chain extender and investigated the influence of polyurethane chain structure on its thermal properties.

On the other hand, one of the major problems PCMs are suffering is the low thermal conductivity. To overcome this disadvantage conducting fillers are incorporated into the phase change material matrix, such as carbon nanoadditives – short and long multi-walled carbon nanotubes, carbon nanofibers, and graphene nanoplatelets (GNPs). Interestingly, the greatest relative enhancement in thermal conductivity of paraffin-based PCMs was observed for graphene nanoplatelets and it was attributed to their two-dimensional planar structure that leads to reduced filler/matrix thermal interface resistance. Graphene is a one-atom-thick planar sheet of  $sp^2$  bonded carbon atoms densely packed in a honeycomb

crystal lattice that has very large specific surface area with outstanding thermal, electrical and mechanical properties [18]. The potential use of graphene and graphene-based products to improve thermal and electrical conductivity of PCMs has drawn much interest recently. Hence, Qi et al. [19] introduced graphene oxide (GO) sheets to stabilize the shape of polyethylene glycol (PEG) during the solid–liquid phase change process. There was no leakage up to temperature of 150 °C, far above the melting temperature of PEG. In the work by Mehrali and co-workers [20] paraffin-based PCM was prepared by impregnation method with graphene oxide (GO) as supporting material. Authors found that the highest mass percentage of paraffin found was 48.3% in the composite to avoid leakage and latent heat of composite PCM was *ca.* 65 kJ/kg.

This kind of materials can be broadly used in energy-related applications. For instance, hybrid passive thermal management systems using phase change materials have been applied as effective systems to prevent overheating of lithium ion batteries [21]. Other potential application area are free air cooling systems that combine phase change material with a natural cold source (i.e., cold air) to reduce the space cooling energy consumption in telecommunications base stations [22], electronics [23], in concentrated solar thermal power plants [24] and in photo-thermal energy conversion systems [25].

In this paper polyurethane-based solid–solid and solid–liquid PCMs were obtained by a one-step bulk polymerization method using two PEGs with average molar mass 3000 and 6000, and MDI as a diisocyanate component. Polyurethanes have been synthesized with 1,4-butanediol as a chain extender or without a chain extender and studied by differential scanning calorimetry (DSC), differential scanning calorimetry with stochastic temperature modulation (TOPEM DSC), thermogravimetry (TG) Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermal conductivity measurements.

## 2. Materials and synthesis

Polyurethane based phase change materials were obtained in a one-step bulk polymerization procedure. Poly(ethylene glycol) (PEG) with average molecular weight 3000 and 6000 was used as a soft segment, and 4,4'-diphenylmethane diisocyanate (MDI) in stoichiometric amount. 1,4-butanediol (BDO) was used as a chain extender. All reagents were supplied from Sigma–Aldrich and were used as received without further purification. Poly(ethylene glycol) were dried under vacuum at the temperature of 110 °C for 2 h. Graphene was supplied from Graphene Supermarket, USA; Grade AO-4 with producer specification: specific surface area <15 m/g<sup>2</sup>, purity 98.5%, average flake thickness 60 nm and particle lateral size ~3–7 μm. Graphene was introduced to melted PEG and dispersed by sonication. MDI were introduced to PEG/graphene (or PEG/graphene/BDO) system and stirred. In the samples with chain extender BDO was introduced to the melted PEG just before synthesis. Next, the reaction mixtures were put on Petri dish, degassed, and heated for two hours at the temperature 100 °C and for 8 h at 80 °C. Description of the obtained samples and their chemical structure are presented in Table 1 and in Scheme 1.

**Table 1**  
Description of the obtained samples.

Sample	PEG average molar mass	Molar ratio PEG: MDI:BDO	Graphene content (wt.%)
PUPEG3	3000	1:2:1	0; 0.5; 1; 2; 4
PUPEG3_BDO		1:1:0	
PUPEG6	6000	1:2:1	
PUPEG6_BDO		1:1:0	

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