



Polyurethane/graphite nano-platelet composites for thermal energy storage



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ABSTRACT

In this work new polyurethane-based phase change materials containing segments of poly(ethylene glycol) with average molar mass of 8000 g/mol with and without chain extender and modified with graphite nano-platelets have been fabricated and characterized. Structure, morphology and phase behaviour of these solid-solid phase change materials were investigated, as well as the thermal stability and conductivity. The heat of phase transition was in the range of 118.0–164.5 J/g for polyurethane without chain extender and 128.0–148.5 J/g for polyurethane with chain extender. The highest heat of phase transition and crystallinity were found for system modified with 0.3% of graphite nano-platelets in polyurethane without chain extender. Modulated differential scanning calorimetry results showed some changes in the phase transition behaviour and the crystallinity of the polyurethane matrix due to graphite nano-platelets confinement effect. Enhancements in the thermal stability in polyurethane modified with graphite nano-platelets, attributed to the barrier effect, were found based on thermogravimetric analysis data. The thermal conductivity increased with an increase of graphite nano-platelets content for both polyurethane systems, with and without chain extender, which is important for modern thermal energy storage applications.

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1. Introduction

Thermal energy storage in the form of latent heat is one of the most efficient methods for thermal energy storage. Due to high storage density and almost constant temperature during phase transition phase change materials (PCMs) are widely used for storing thermal energy [1,2]. Poly(ethylene glycol) (PEG) is considered as one of the most promising PCMs as it is characterized by high phase change enthalpy, non-corrosiveness, adjustable phase change temperature and ease of chemical modification [3]. Properties of PEG for application as a PCM depend on average molecular weight and its crystallization behaviour. Depending on average molecular weight the melting point of PEG may vary from 1 to 69 °C, whereby the heat of melting lies in the range of 165–189 J/g. Generally, PEG is a semi-crystalline thermoplastic polymer containing in the solid state both amorphous and crystalline regions in different proportions, depending upon the synthesis and thermal history [4]. However, the main problem with application of PEG as

PCM is leakage above its melting temperature due to solid-liquid phase transition. To avoid this problem, different methods of PEG shape stabilization were described in literature. Ding and co-workers modified PEG with cellulose diacetate (CDA) by chemical reaction and physical blending methods and they concluded that chemically linked materials were solid-solid PCMs while blended materials were solid-liquid PCMs [5]. Guo et al. [6] investigated systems obtained by mixing of PEG with CDA in acetone and detected the solid-solid phase transition when the PEG fraction within the composite was less than 85%. Cellulose-graft-poly(ethylene glycol) copolymers showed solid–solid phase-transition behaviour with a high thermal storage density and good thermal stability too [7]. In other cellulose or cellulose derivative blends with PEG solid-solid phase transitions have been also observed at some concentrations [8,9], as well as in shape-stabilized PEG-based PCMs with polysaccharides, such as potato starch [10]. Shape stabilization effect was also observed in numerous copolymers of vinyl monomers with PEG such as poly(decaglycerol-co-PEG) [11], poly(styrene-graft-PEG) [12], poly(glycidyl methacrylate)-co-PEG [13] or PEG/poly(methyl methacrylate) blend [14] and PEG/epoxy composites [15]. An alternative approach is chemical linking of PEG

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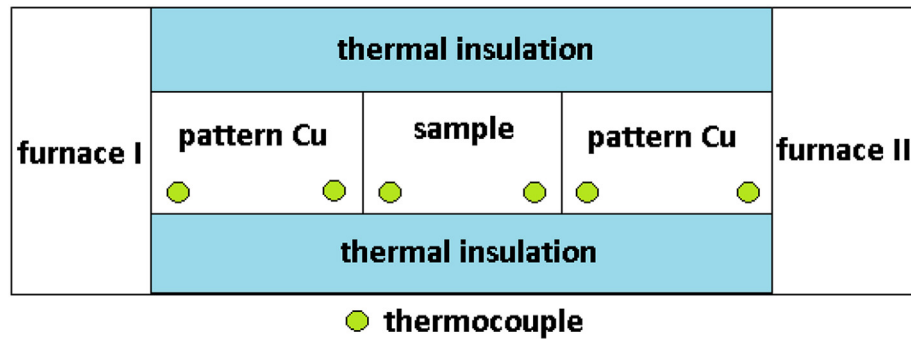


Fig. 1. Scheme of thermal conductivity measurement unit.

with polyisocyanates to obtain polyurethanes (PU) offering advantageous performance properties and ease of processing. The PU chains are composed of hard and soft segments arranged alternately. The hard segments are made of structures derived from diisocyanates, urethane oligomers obtained from diisocyanates and low-molecular weight hydroxyl chain extenders, or urea oligomers produced with the use of diisocyanates and water or amino chain extenders. The soft segments are composed of oxyethylene groups or oxypropylene groups, in particular oxytetramethylene polyester polyols or polyesters – which make linear polyurethane more flexible [16]. Poly(ethylene glycol) is one of the possible substrates for soft segments synthesis and its chemical incorporation in PU chains makes it possible to obtain PCMs with solid–solid phase transition. Hence, Su and Liu [17] synthesized polymeric

solid–solid PCM composed of high molecular weight PEG as soft segment, 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as a chain extender. Their results indicated solid–solid phase transition, suitable transition temperature, high transition enthalpy and good thermal stability. Li and Ding prepared solid–solid PCM via the condensation reaction of PEG 10000 with tetrafunctional pentaerythritol isocyanate [18].

On the other hand, carbon-based materials and nanomaterials were used in PCMs to improve thermal conductivity and for shape stabilization. Form-stable composite PCMs were prepared by vacuum impregnation of paraffin within graphene oxide (GO) sheets and thermal conductivity of the composite PCM was considerably improved from 0.305 to 0.985 W/mK [19]. In the work by Qi [20] GO sheets were introduced to PEG to obtain shape stabilized PCM. Authors found that a maximum weight percentage of PEG was 96% without any leakage and the heat of phase transition of the composite obtained was 142.8 J/g.

In this paper new polyurethane/graphite nano-platelet composites displaying solid–solid and solid-liquid transitions were prepared by one step bulk polymerization method using PEG with average molar mass 8000 as a soft segments and MDI as a diisocyanate. Polyurethanes have been synthesized with or without 1,4-butanediol as chain extender and subjected to differential scanning calorimetry (DSC), modulated differential scanning calorimetry (TOPEM DSC), thermogravimetry (TG), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and optical microscopy (OM) investigations. The influence of graphite nano-platelets (GNP) on the thermal conductivity of PU composites has been investigated, too.

2. Experimental part

2.1. Materials and synthesis

Polyurethane PCMs were obtained by a one-step bulk polymerization process. Poly(ethylene glycol) (PEG) with average molecular weight 8000 was used as a soft segment, 1,4-butanediol (BDO) as a chain extender and 4,4'-diphenylmethane diisocyanate (MDI) as a hard segment component in stoichiometric amounts. For the PUPEG samples molar ratio PEG:MDI was 1:1, for PUPEG_BDO samples molar ratio PEG:MDI:BDO was 1:2:1. All reagents were supplied from Sigma-Aldrich and were used as received without further purification. Graphite nano-platelets were supplied from Graphene Supermarket, USA; Grade AO-4 with the following producer specification: specific surface area <math>< 15 \text{ m}^2/\text{g}</math>, purity 98.5%, average flake thickness 60 nm and particle lateral size ~ 3–7 microns. Poly(ethylene glycol) was dried under vacuum at the temperature of 110 °C for 2 h. Graphite nano-platelets were introduced to the dry and melted PEG and dispersed by sonication. MDI

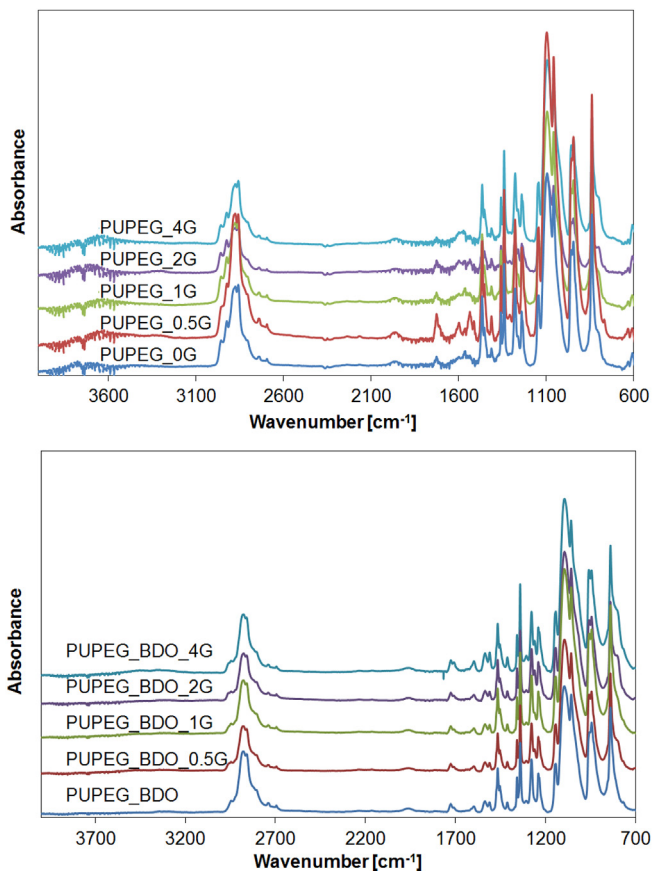


Fig. 2. FTIR spectra of PUPEG and PUPEG_BDO with different GNP content.

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