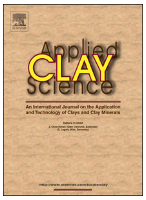
Applied Clay Science 102 (2014) 41–50

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

The effect of organoclay addition on the properties of an acrylate based, thermally activated shape memory polymer

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ARTICLE INFO

Article history:
Received 21 July 2014
Received in revised form 15 October 2014
Accepted 18 October 2014
Available online xxxx

Keywords:
Shape memory polymer
Nanocomposite
Organoclay
Polyacrylate

ABSTRACT

Shape Memory Polymers (SMPs) exhibit the intriguing ability to change back from an intermediate, deformed shape back to their original, permanent shape. In this contribution a systematic series of t-butylacrylate-*co*-poly(ethyleneglycol) dimethacrylate (tBA-*co*-PEGDMA) polymers have been synthesised and characterised prior to incorporation of organoclay. Increasing the poly(ethyleneglycol) dimethacrylate (PEGDMA) content in increments of 10% increased the storage modulus from 2005 to 2250 MPa, reduced the glass transition temperature from +41 to −26 °C and reduced the intensity of the associated tan δ peak. The tBA-*co*-PEGDMA crosslinked networks displayed useful shape memory properties up to PEGDMA contents of 40%. Above this PEGDMA percentage the materials were prone to fracture and too brittle for a realistic assessment of their shape memory capability. The system containing 90% t-butylacrylate (tBA) and 10% PEGDMA was selected as the host matrix to investigate how the incorporation of 1 to 5 mass% of a benzyl tallow dimethylammonium-exchanged bentonite (BTDB) influenced the shape memory properties. X-ray diffraction data confirmed that BTDB formed a microcomposite in the selected matrix and exerted no influence on the storage modulus, rubbery modulus, glass transition temperature, T_g, or the shape or intensity of the tan δ peak of the host matrix. Therefore, it was anticipated that the presence of BTDB would have no effect, positive or negative, nor on the shape memory properties of the host matrix. However, it was found that the incorporation of clay, especially at the 1 mass% level, significantly accelerated the speed, compared with the clay-free SMP, at which the microcomposite returned to the original, permanent shape. This accelerated return to the permanent shape was also observed when the microcomposite was coated onto a 100 μm PET film.

1. Introduction

Shape memory polymers (SMPs) have the ability to store a permanent shape and be deformed into a temporary shape by applying an external stress and temperature. This temporary shape is stored by cooling into the dormant shape, in which it remains, until it is encouraged to return to its original, permanent shape (Fig. 1). The transformation from the stressed temporary shape back to the permanent, stress-free shape is usually triggered by thermal (Liff et al., 2007), electrical (Liu et al., 2009), or other environmental stimuli e.g. UV or visible radiation (Jiang et al., 2006). This change from temporary to permanent shape is essentially driven by the elastic strain stored in the dormant shape during the initial deformation into the temporary shape (Liu et al., 2007).

The most common SMPs are thermally-responsive, which means that the material is deformed into its temporary shape, at one temperature and a second thermal change is required to initiate the return to its original, permanent, shape. The temperature at which this change in shape occurs is referred to as the transition temperature, T_{trans}, and is typically the glass transition temperature, T_g, or melting transition temperature, T_m, of the polymer. The unique, 'tunable' properties of SMPs make them attractive for a number of potential applications in almost every avenue of life, ranging from self-repairing car bodies (Ikematu et al., 1993), kitchen utensils (Lendlein and Kelch, 2002), switches to sensors (Liu et al., 2009), intelligent packaging (Behl et al., 2010), toys (Ikematu et al., 1993) and tools (Tong, 2004). A significant number of studies have focussed on the use of SMPs in biomedical applications including sutures (Lendlein and Langer, 2002), stents (Venkatraman et al., 2006), catheters (Liu et al., 2007), micro-actuators (Maitland et al., 2002) and tissue scaffolds (Migneco et al., 2009). More recently, the focus has moved towards SMPs with two temporary shapes which

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http://dx.doi.org/10.1016/j.clay.2014.10.010

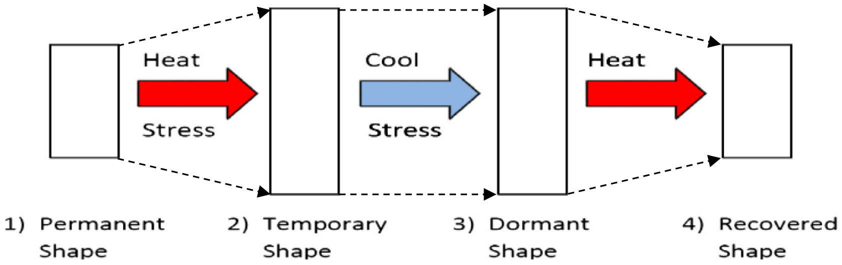

Fig. 1. Schematic depiction of the unconstrained shape memory effect (SME) of a thermally activated SMP.

transform in response to two different stimulus events (Behl et al., 2010; Ge et al., 2013; Tao, 2010).

Two commonly adopted approaches to improve and expand the applications of SMPs are 1) optimise the polymer system's mechanical, thermal and shape memory properties for the intended application and/or, 2) incorporate nanomaterials into the optimised polymer to provide additional property enhancements. The knowledge that the incorporation of 1 to 5 mass% of well dispersed clay can increase both the tensile properties and the storage modulus of the host polymer (Annabi-Bergaya, 2008; Utracki, 2010) means that a clay polymer nanocomposite (CPN) has the potential to increase the energy stored within the temporary shape of a SMP; giving it the ability to exert a stronger physical force when returning to the original shape and/or transform at a faster rate. Despite their potential to improve shape memory properties, clays have not been extensively studied. Most reports focus on their positive influence on polyurethanes (PU) at organoclay (OC) levels of 0.5 to 2 mass% (Cao and Jana, 2007; Chung et al., 2011; Haghayegh and Sadeghi, 2012) although larger quantities of calcined attapulgite (Xu et al., 2009) and grafted bentonite (Wu et al., 2013) were required. Rezanejad and Kokabi (2007) established that adding 12 mass% of Cloisite 15A (a dihydrogenated tallow dimethyl ammonium-bentonite) increased the recovery stress by 200%. Finally, OC have been used to improve the shape memory properties of epoxy CPN (Liu et al., 2011) and nanofoams (Quadrini et al., 2012).

Acrylate polymers represent an ideal system for SMP/clay studies since the copolymerization of linear acrylates (mono-functional monomers) with acrylate cross linkers (multifunctional monomers) yields SMPs with tuneable properties that can be optimised for specific applications (Safranski and Gall, 2008; Voit et al., 2010). Previous investigations by Ortega et al. (2008), Yakacki et al. (2008) and Yang et al. (2007) have shown that tert-butylacrylate-*co*-poly(ethylene glycol) dimethacrylate (tBA-*co*-PEGDMA) networks have shape memory ability with thermal and mechanical properties that can be readily tailored. In this particular example a transition temperature near 40 °C was required.

To our knowledge the enhancement of tBA-*co*-PEGDMA networks via incorporation of OC has yet to be reported, thus this contribution represents a benchmark study designed to explore the impact of clay on the properties of an optimised acrylate based SMP system. It aims to identify the influence of the OC loading on a UV polymerised polyacrylate system, of selected stoichiometry, and the effect on the resulting physical properties. The features under investigation are; the OC loading required to influence the shape memory effect of self-supporting polymer films (and when coated onto a PET substrate); the effect of OC loading on the storage moduli, the glass transition temperature, and, in particular, macroscopic effects including the shape fixity, the extent of shape recovery as well as the time required to return to the original, permanent shape.

2. Experimental

2.1. Materials

The mono-functional acrylate tert-butyl acrylate (tBA), the di-functional acrylate poly(ethylene glycol) dimethacrylate (PEGDMA), with an average molecular weight of 750 g mol^{-1}, the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and accelerator ethyl-4-(dimethylamino) benzoate (EDB) were purchased from Sigma-Aldrich and used as received. The purity of tBA was 98%, while the purities of the other reagents were ≥99%. The Cloisite 10A (C10A), is a bentonite in which the resident Na^{+}-cations have been replaced by quaternary benzyl hydrogenated tallow dimethylammonium ions, and was supplied by Rockwood Specialties Inc., UK. The substrate material used in the coating studies was a 100 μm thick polyethylene terephthalate (PET) film (HiFi Films Ltd.).

2.2. Pre-treatment of commercial organoclay

Initial attempts to fully polymerise the tBA-*co*-PEGDMA systems in the presence of as-received C10A were unsuccessful and the excess surfactant present on C10A was identified as the cause. The excess organomodifier was removed, prior to use, by dispersion in water while stirring at 80 °C for 1 h, then filtered and washed with propan-2-ol. This was repeated 6 times before drying at 70 °C for 4 h. The fully washed material is subsequently referred to as benzyl tallow dimethylammonium-bentonite (BTDB).

2.3. Preparation of polymers and PCN

2.3.1. tBA-co-PEGDMA

A series of polymer networks were prepared using selected ratios of the monomers (Table 1). The tBA, PEGDMA, DMPA and EDB were weighed out and added together in a glass vial, wrapped in foil and the solution was magnetically stirred for 30 min at ca. 22 °C. The solution was then sonicated for an additional 30 min before photopolymerisation (see Section 2.3.3 below).

2.3.2. tBA-co-PEGDMA/BTBD

The tBA90/PEGDMA10 polymer network was used as a host matrix for selected quantities of BTBD (Table 1). The procedure was similar to that described above except that the mixture was stirred for 24 h at ca. 22 °C, before sonication and photopolymerisation (Decker et al., 2005).

2.3.3. Polymer photopolymerisation

Photopolymerisation of stirred and ultrasonicated mixtures was carried out in a mould constructed using two ultraviolet (UV) clear glass slides, $100 \times 100 \times 1$ mm^3, to which UV clear PET film liners, $12 \times 12 \times 0.1$ mm^3 were attached so that the reaction mixture was only in contact with the PET film and the 500 μm spacer. The reaction mixtures were injected into the reaction cavity and the entire mould was placed in a UV chamber (model CL-1000 ultraviolet cross-linker, $\lambda = 254$ nm, output energy $= 200$ mJ/cm^2). The mould was turned over every 5 min for ca. 30 min to promote an even cure on both surfaces of the mould.

In order to polymerise the tBA90/PEG10 mixture, with and without BTBD, onto the PET film it was applied using a metre bar, producing a ca. 30 μm thick film. The coated film was placed into a nitrogen gas filled