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# Shape memory and physical properties of poly(ethyl methacrylate)/Na-MMT nanocomposites prepared by macroazoinitiator intercalated in Na-MMT

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## Abstract

A macroazoinitiator (MAI) containing a poly(ethylene glycol) (PEG) segment was intercalated in the gallery of sodium montmorillonite (Na-MMT) and this intercalated MAI was used in the preparation of Na-MMT/poly(ethyl methacrylate) (PEMA) nanocomposites via in situ radical polymerization of ethyl methacrylate. The X-ray diffraction pattern and the morphology observed with a transmission electron microscope showed that Na-MMT intercalated with a PEG segment was heterogeneously dispersed in the polymer matrix. Thus Na-MMT intercalated with a PEG segment effectively enhanced the mechanical properties of PEMA. Shape memory behavior and rheological properties showed that Na-MMT intercalated with a PEG segment performed its role as a physical crosslinker effectively even with 1.2 wt% of Na-MMT.
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## 1. Introduction

Shape memory polymer is a smart material that can be utilized in various applications such as medical devices or mechanical actuators. Compared to shape memory alloys or ceramics, shape memory polymers have advantages of lower density, lower cost, higher deformation, and easy control of recovery temperature and color variation [1–10].

Thermoresponsive shape memory polymers generally consist of two phases, a thermally reversible phase that becomes flexible and can be deformed elastically at temperatures above a thermal transition temperature ($T_S$) and a fixed phase for memorizing the original shape. Because the thermally reversible phase should show a large drop in elastic modulus and become flexible upon heating above $T_S$, the glass transition temperature ($T_g$) or melting temperature ($T_m$) are generally utilized as $T_S$ in the design of shape

memory polymers [11–14]. In the case where $T_g$ is used as $T_S$, if the shape memory polymer is deformed at the rubbery plateau above the $T_g$ and subsequently cooled below the $T_g$ under constant strain, the deformed shape is fixed because chains can barely move at this glassy state. Then, when the polymer is reheated above the $T_g$, the original shape can be recovered by entropy elasticity because, at this rubbery state, it is elastic and soft [2–4]. In this shape recovery process, the entanglement of polymer chains with their neighbors can do its roles as a fixed phase which memorizes the original shape, because it can prevent the irreversible sliding of deformed polymer chains. However, an unrecovered permanent deformation will increase as the number of the deformation at rubbery state is increased, because the polymer chains tend to disentangle and to slip off each other into new positions [2]. So, cross-linkage points, crystalline phase, or glassy phase are utilized as fixed phases in shape memory polymers, because the slippage or flow of polymer chains should be minimized to enhance the shape memory effect.

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A significant drawback of shape memory polymers is their low stiffness compared to shape memory alloys or ceramics. In macroscale composites of shape memory polymers, the mechanical weakness can be improved; however, the shape recovery effect can be damaged by the reinforcing fillers [15,16]. Some papers have shown that mechanical reinforcing can be achieved in nanocomposites reinforced with nano-size fillers without any decrease in their shape recovery effect [16,17]. In a polynorbornene nanocomposite, where the inorganic building block polyhedral oligomeric silsesquioxane (POSS) was included in the main chain of organic polymer, Mather et al. observed that shape recovery was improved compared to pristine polynorbornene [2,18]. Their result was explained as follows: the POSS groups aggregate to a certain extent, and this separated phase of inorganic moieties performs its role as a fixed phase to memorize the original shape because the physical interactions between inorganic moieties hinder the irreversible sliding of the organic main chain.

The poly(ethylene glycol) (PEG) segment can be easily intercalated in the sodium montmorillonite (Na-MMT) gallery. Na-MMT intercalated with PEG (Na-MMT/PEG) has high stability, because intercalated PEG cannot be replaced by organic compounds having a high affinity toward Na-MMT. And the maximum amount to be intercalated is quantitative, about 0.3 g-PEG/g-Na-MMT [19,20].

In this study, we intercalated macroazoinitiator (MAI), which has a PEG segment as shown in the chemical structure below, into the gallery of Na-MMT, and the Na-MMT intercalated with MAI was used in the polymerization of ethyl methacrylate to obtain nanocomposites. We examined the shape memory effect of the nanocomposites along with their mechanical and rheological properties because we anticipated that the Na-MMT/PEG building block linked to poly(ethyl methacrylate) can perform its role as a fixed phase in shape memory behavior as well as a moiety to enhance mechanical properties [21].
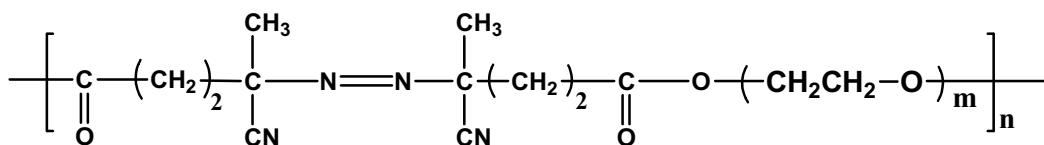
pentanoic acid) and PEG whose molecular weight was 4000. The molecular weight of MAI was in the range of 25,000–40,000 and its azo group content was 0.45 mmol/g. Ethyl methacrylate (EMA, Aldrich) was purified by a standard procedure [22]. Acetonitrile (Aldrich), methanol (Aldrich), dimethylformamide (DMF, Aldrich), and 2,2′-azobisisobutyronitrile (AIBN, Aldrich) were used as received.

Na-MMT intercalated with MAI (Na-MMT/MAI) was prepared using an acetonitrile/methanol mixture (1/1 by volume) as a solvent [19,20]. That is, 3 g of MAI was dissolved in 100 mL of solvent and the solution was stirred with 7 g of Na-MMT for 1 day at room temperature. The intercalated compound was separated with a centrifuge and repeatedly washed with acetonitrile and methanol to remove non-intercalated physisorbed MAI [20]. It was then dried at 25 °C for 48 h under vacuum before use. The amount of MAI intercalated at the gallery of Na-MMT, determined by thermogravimetry, was 0.22 g-MAI/g-Na-MMT.

The recipes for the preparation of poly(ethyl methacrylate) (PEMA)/Na-MMT nanocomposites are shown in Table 1. The DMF, EMA, Na-MMT/MAI, or AIBN were fed into the reactor and polymerization was carried out at 60 °C under a $N_2$ atmosphere for 24 h with stirring by a magnetic bar. The prepared PEMA/Na-MMT nanocomposites were crushed into powders and dried at 80 °C for 12 h under vacuum to remove the low molecular weight components. The characteristics of the nanocomposites are shown in Table 2.

## 2.2. Measurement

The number average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were measured at 43 °C with gel permeation chromatography (GPC, Waters M510) and the results are shown in Table 2. The nanocomposite was dissolved in tetrahydrofuran (THF) and the



## 2. Experimental

### 2.1. Materials

Na-MMT (Southern Clay) was used after drying at 60 °C under vacuum for 1 day. Macroazoinitiator (MAI, Wako Pure Chemical, VPE-0401) was used as received. The MAI was the condensation polymer of 4,4′-azobis(4-cyano-

solution was filtered with a 0.45 μm membrane filter before measurement. THF was used as an eluent.

To determine the content of Na-MMT in Na-MMT/MAI or nanocomposite, thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyzer (TA Instruments, TGA 2950) at a heating rate of 10 °C/min under an $O_2$ atmosphere using a 5 mg sample in a platinum crucible.