

Synthesis and shape memory performance of polyurethane/graphene nanocomposites



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ABSTRACT

Small amounts of allyl isocyanate modified graphene (iG, 0–2.5 phr) were incorporated into acrylate terminated polyurethane (PU) by UV curing. The effects of this incorporation on the morphological, mechanical, thermal and shape memory properties of the nanocomposites were examined. The iG nanoparticles incorporated into the PU chains acted as both multifunctional crosslinkers and reinforcing fillers, and the effects were most pronounced at 1.5 phr iG. Consequently, the glassy and rubbery state moduli, yield strength, glass transition temperature (T_g), shape fixity and shape recovery ratios were increased by adding up to 1.5 phr iG. Above the loadings, most of the above properties decreased due to aggregation and the auto-inhibition reaction of allyl compounds.

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1. Introduction

Polyurethanes (PUs) are a most versatile engineering material which is synthesized by a simple polyaddition reaction of polyol, isocyanate and chain extender. They find a variety of industrial applications including coatings, adhesives, sealants, elastomers, primer, sports goods, medical devices, textile finish aside from the various foam products [1–3].

Shape memory polymers (SMPs) are a class of smart materials that respond to external stimuli, typically heat, and their applications have expanded steadily [4–8]. Potential applications have also opened for biomedical devices using biocompatible polymers, such as PU and space materials with enhanced mechanical performance [9–11]. Among the many SMPs, shape memory polyurethane (SMPU) has found the broadest applications because of their ample degree of freedom in property design. Design variables include various types and molecular weights of soft segment (polyol), type of hard segment, and soft segment/hard segment composition. Depending on the molecular design, SMPU could be crystalline or amorphous showing the actuation temperature in a broad range of –20 to 150 °C.

Mechanical reinforcement and functionalization are largely achieved by the hybridization of SMPs with fillers in the form of particles, fibers, platelets or tubes [12–15]. Generally, chemical hybridization on the nanoscale is superior to physical blending

on the macro-scale due to the fine dispersion and improved interface between the polymer and filler. Chemically-incorporated fillers provide multifunctional crosslinks that augment the rubber elasticity and strain recovery [16–18].

Graphene is a fascinating two-dimensional nanomaterial with superior thermal and electrical conductivity and modulus. It is essential to highly exfoliate the graphite into layers to significantly enhance the mechanical and electrical properties of composites at extremely small loading [19–21]. Oxidative exfoliation of natural graphite by acid treatment has been a most efficient method. However, the damage to graphene's sp^2 carbon network would severely affect the properties of graphene, such as mechanical [22], electrical [19], thermal properties [23]. This can be solved by reducing graphene oxide (GO) which can restore sp^2 carbon network [24,19].

GO carries some oxygen containing groups, which can be used for chemical modification. Chemically-modified graphene oxide can be incorporated into a polymer by covalent bonding, where graphene is expected to act as a multifunctional crosslinker as well as a conventional reinforcing filler [25]. As a multifunctional crosslinker, it would augment the rubber elasticity and strain recovery, as well as cyclic hysteresis, which are important properties for shape memory materials. On the other hand, little has been evolved from the literature survey for the use of graphene as shape memory materials.

Presently, GO was prepared and modified chemically with allyl isocyanate (iGO) and reduced by N,N-dimethylhydrazine(allyl modified graphene, iG) after mixing with PU. We assume that in

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reduction procedure, iG will be not aggregated because allyl group exists on graphene surface, although oxygene groups on graphene surface will be removed and PU can prevent the agglomeration of iG. iG was reacted with the hydroxyethyl acrylate termini of PU at various compositions by UV curing to synthesis PU/iG nanocomposites. The effects of graphene and chemical hybridization were analyzed in terms of the particle dispersion, mechanical, thermal and shape memory properties of the nanocomposites. We emphasize that the fine dispersion of iG in PU matrix is critical to effectively reinforce the matrix at high iG loading.

2. Experimental

2.1. Raw materials

Polypropylene glycol ($M_n = 600$ g/mol, KPX, Korea) and 1,3-butanediol (Aldrich) was dried and degassed at 80 °C under vacuum for 3 h prior to use. 4,4'-methylene diphenyl diisocyanate (BASF), 2-hydroxyethyl acrylate (Aldrich), N,N-dimethylhydrazine (Aldrich) and dibutyltin dilaurate (Aldrich) were used as received.

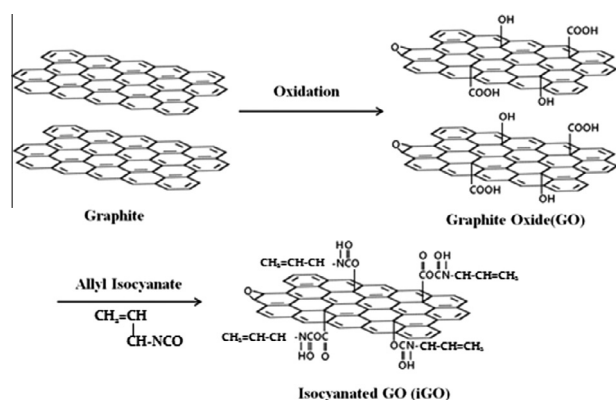
2.2. Preparation of GO and allyl isocyanate modified GO (iGO)

GO was prepared following the Hummers' method [26–28]. Ten grams of graphite and 7.5 g of NaNO_3 were placed in a flask. To this mixture, 621 g of H_2SO_4 was added and stirred in an ice water bath. Then, 45 g of KMnO_4 was gradually added over about 1 h. Cooling was done in 2 h, and the mixture was allowed to stand for 5 days at 20 °C with stirring smoothly. The liquid obtained was added to 1 L of 5 wt.% H_2SO_4 aqueous solution for 1 h with stirring. Then, 30 g of 30 wt.% H_2O_2 aqueous solution was added and stirred for the next 2 h. Finally, the mixture was purified by repeating the following cyclic procedure 15 times; centrifugation, removal of the supernatant liquid, addition of a mixed aqueous solution of 3 wt.% H_2SO_4 /0.5 wt.% H_2O_2 , and shaking to redisperse it. Sample was dried by lyophilization.

Scheme 1 shows the procedure to prepare iGO [29]. GO (2.1 g) was loaded into a 500-mL round-bottom flask equipped with a stirrer under nitrogen. Anhydrous dimethyl formamide (DMF, 210 mL) was added to create a suspension. Allyl isocyanate (7.0 g) was then added and stirred for 7 days. Subsequently, the reaction mixture was poured into methylene chloride (2.1 L) to coagulate the product, which was filtered, washed and dried by lyophilization.

2.3. Synthesis of PU/iG nanocomposites

Table 1 and Scheme 2 show the formulation to prepare the PU/iG nanocomposites and overall reaction scheme to prepare



Scheme 1. Overall reaction scheme to modify graphene oxide.

Table 1

Formulations to prepare polyurethane/iG nanocomposites (Molecular weight = 9000 g/mole, number is the weight in grams, total solid = 30 g).

Series	Polyurethane				iGO (phr)
	PPG600	MDI	1,3-BD	HEA	
PG00	15.80	7.42	1.59	0.77	–
PG10					1.0
PG15					1.5
PG20					2.0
PG25					2.5

the PU/iG nanocomposites, respectively. Polypropylene glycol ($M_n = 600$ g/mol) and 1,3-butanediol was placed in a 500-mL round-bottom flask with a mechanical stirrer, thermometer and condenser with a drying tube. The reactions were carried out in a constant temperature oil bath. Molar excesses of 4,4'-methylene diphenyl diisocyanate were reacted in DMF at 70 °C until the theoretical isocyanate values were obtained. The isocyanate terminated PU was end capped with HEA at 50 °C to obtain PU with a molecular weight of approximately 9000 g/mol. Then, the iGO particles dispersed in DMF (concentration; 2.0 mg/mL) were fed into the PU solutions at various compositions, as listed in Table 1. To improve the dispersion of iGO particles in DMF, the particles were added to DMF in a vial and ultrasonicated for 2 h at 40 °C before adding the mixture to the polymer solution. Reduction of the dispersed material was carried out with N,N-dimethylhydrazine (0.95–2.37 g) at 80 °C for 24 h with stirring. The nanocomposite solution was then added dropwise to room-temperature methanol (800–2500 mL) with stirring [30]. Coagulated product was isolated by filtration and washed with methanol (400–800 mL). Composite was redissolved in DMF with stirring and sonication for 3 h at 60 °C and 4 wt.% of the photo initiator with respect to the solid polymer was then added to the polymer solution. The resulting mixture was cast on a polyethylene film and partially dried before being cured under a UV lamp (365 nm, 8 W, Crosslink) positioned about 10 cm above the sample for 2 h in air.

2.4. Measurements

The progress of the HEA capping reaction was monitored by Fourier transform infrared (FT-IR) spectroscopy using the characteristic isocyanate peak. Resolved X-ray photoelectron spectroscopy (ESCALAB 250 spectrometer) and standard X-ray photoelectron spectroscopy measurements were performed using a monochromated Al K α X-ray source. The morphology of the film was examined using scanning electron microscopy (Zeiss FE-SEM SUPRA25 and Raith Quantum Elphy). The tensile properties of the cast film at room temperature were measured with a universal testing machine (Lloyd LRX) at a crosshead speed of 200 mm/min using specimens prepared according to ASTM D-1822. Thermal analyses were carried out by differential scanning calorimeter (TA instrument DSC Q100) at 10 °C/min.

The shape memory properties were characterized using the universal testing machine attached with a heating chamber. The sample was first heated to the glass transition temperature (T_g) + 20 °C and stretched uniaxially to a maximum strain (ϵ_m) of 100%, followed by cooling and unloading at $T_g - 20$ °C. Upon unloading, a small part of the strain ($\epsilon_m - \epsilon_u$) was recovered instantaneously, leaving an unload strain (ϵ_u). The sample was reheated to $T_g + 20$ °C to recover the strain, leaving a substantial amount of permanent strain (ϵ_p). These three steps completed one thermomechanical cycle. The shape fixity (R_f) and shape recovery (R_r) ratios for the cycle are defined as follows:

$$\text{Shape fixity ratio, } R_f = \frac{\epsilon_u}{\epsilon_m} \quad (1)$$

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