

# CLICK COUPLED SEBS-POSS COMPOSITES FOR DIELECTRIC ELASTOMER ACTUATORS

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## 1 Introduction

Electroactive polymers have been a developing technology in the past decades. They are soft, flexible materials that could convert electrical energy to mechanical energy. Dielectric elastomer actuators are one kind of promising types of electroactive polymer and are considered as the next-generation polymeric actuators. Soft dielectric elastomer actuators have attracted much attention due to their remarkably large actuation strain and energy density [1].

Very recently, the carbon nanotube/polymer composites with high dielectric constant and good mechanical properties have been paid more attention due to their potential applications as dielectric elastomer [2]. They can generate strain higher than the rigid piezoelectric ceramic. Organic-inorganic hybrid materials have attracted immense interest, with regard to the possibility of developing novel materials with high potential for many new applications including dielectric elastomer. These hybrid materials can be broadly depicted as a multi-component system where both organic and inorganic materials are unified to form a new nanomaterial holding attractive unique properties.

A crucial category of hybrid material holds silica or silsesquioxane as the inorganic components. Polyhedral oligomeric silsesquioxane (POSS) is a type of model inorganic three-dimensional Si-O case nanostructured (formula  $[\text{RSiO}_{1.5}]_n$ , where  $n = 8, 10, 12$ ) and an overall diameter of 1-3 nm [3]. It has been touted for its potentials; its presence has shown property enhancement, such as low flammability, oxidation resistance, low density, and increased mechanical and thermal of the composites. On the other hand, the click chemistry has received much attention from researchers in the fields of organic synthesis and materials chemistry, following a report by Sharpless et al. [4,5] The Cu(I)-catalyzed [3+2]

Huisgen cycloaddition reaction is the most successful variant between azide and alkyne moieties, forming a high yielding 1,4-substituted 1,2,3-triazole with an enormously high tolerance of functional groups and solvents under highly moderate reaction conditions [6].

In this study, we investigated the covalent functionalized poly(styrene-*b*-ethylene-co-butylene-*b*-styrene) (SEBS) / polyhedral oligomeric silsesquioxane (POSS) composites via click coupling with high mechanical and dielectric properties for dielectric elastomer actuators.

## 2 Experimental Sections

### 2.1 Materials and characterization

SEBS block copolymer with 30 wt% polystyrene was provided by Kraton Polymers. Its polydispersity index was 1.2, and the number average molecular weight of SEBS was 68000 g/mol as measured using gel permeation chromatography. EP0402-epoxycyclohexylsobutyl POSS (Hybrid Plastic Co.), propargyl bromide, p-nitrophenol, tetrabutyl ammonium bromide, 3-methyl butyl nitrite, copper iodide, and 1,8-diazabicyclo[5.4.0]undecene-7-ene were used.

Fourier transform infra-red (FT-IR) spectroscopic measurements were performed using a Jasco FT-IR 300E device to confirm the synthesis of nanohybrids. <sup>1</sup>H-NMR spectra were recorded in a Bruker 600 MHz NMR spectrometer using tetramethylsilane (TMS) as the internal standard and CDCl<sub>3</sub> as a solvent. X-ray photoelectron spectroscopy (XPS, ESCA 2000) was used to analyze the surface composition of nanohybrid. The fractured surface morphology of nanohybrids was observed by using a field emission scanning electron microscope (FE-SEM, S-4300SE, Hitachi).

The mechanical properties of the nanocomposites were measured at an elongation rate of 10 mm/min at room temperature using a tensile tester machine (Instron 4468) with a dumbbell type specimen. The dimension of the test specimen was  $60 \times 3 \times T \text{ mm}^3$ , where T indicates the thickness. Thermogravimetric analysis (TGA) was carried out in a TA Q 50 system TGA. The samples were scanned at a heating rate of  $10^\circ\text{C}/\text{min}$  under flow of nitrogen.

## 2.2 Synthesis of azide-modified SEBS (SEBS- $\text{N}_3$ )

SEBS- $\text{N}_3$  was prepared by chloromethylation of SEBS and subsequent azidation of chloromethylated SEBS (SEBS- $\text{CH}_2\text{Cl}$ ), as reported elsewhere [7]. For the chloromethylation of SEBS, 2.5 g of SEBS and 2.7 g of trioxane were dissolved in 150 mL of distilled chloroform, yielding a clear solution. Then, 11.4 mL of chlorotrimethylsilane (TMCS) and 1.5 mL of  $\text{SnCl}_4$  were added dropwise to the above solution in an ice-water bath under vigorous agitation. The mixture was stirred at  $0^\circ\text{C}$  for 0.5 h and further at room temperature for 6 h. After completion of the reaction, 50 mL of methanol-water solution (50% v/v) was added to stop the reaction.

Finally, the reaction mixture was precipitated in methanol, purified by three cycles of dissolving-precipitation in chloroform-methanol, and dried overnight in a vacuum oven at room temperature, producing SEBS- $\text{CH}_2\text{Cl}$ . For the azidation of SEBS- $\text{CH}_2\text{Cl}$ , 2.5 g of SEBS- $\text{CH}_2\text{Cl}$  and 218 mg of  $\text{NaN}_3$  were dissolved in 50 mL of dimethylformamide (DMF). The reaction mixture was stirred at room temperature for 24 h and the polymer was precipitated in water to remove unreacted  $\text{NaN}_3$ .

## 2.3 Preparation of alkyne-functionalized POSS

In a typical reaction 1g of POSS- $\text{NH}_2$  (1.14 mmol) and 91.1 mg of propionic acid (1.30 mmole) were dissolved in 10 mL of dichloro methane (DCM) in two neck flask, subsequently 270 mg DCC (1.30 mmole) were added. The reaction mixture stirred at room temperature for 24 h than filtered and solvent was evaporated in vacuo.

## 2.4 Preparation of SEBS-POSS composites

Coupling of the azide moiety containing SEBS block copolymer (SEBS- $\text{CH}_2\text{N}_3$ ) and alkyne functionalized POSS was carried out via Cu(I)-catalyzed click chemistry. The POSS solution was added to a two-necked flask containing SEBS- $\text{CH}_2\text{N}_3$  solution in dimethylformamide with a reflux condenser and magnetic stirrer, and thereafter a homogenous solution was obtained. After an addition of copper iodide and 1,8-diazabicyclo[5,4,0]undecene-7-ene, the solution was heated to  $60^\circ\text{C}$  with continuous stirring for 24 h under a nitrogen atmosphere. After completing the reaction, the product was precipitated in methanol and further purified. The product was dried overnight under vacuum at room temperature.

## 3 Results and Discussion

The click chemistry reaction between alkyne-functionalized POSS and azide-functionalized SEBS block copolymer was carried out, which is shown in Fig. 1. SEBS was modified by attaching the azide group for click coupling with POSS. FT-IR spectra confirmed a successful synthesis of SEBS-POSS composites. It was finally confirmed that the successful functionalization of POSS with SEBS was achieved via click coupling by the IR peak around the  $1670 \text{ cm}^{-1}$  due to the triazole ring.



Fig. 1. Scheme of click chemistry reaction .

The XPS spectra of SEBS-POSS nanohybrid material were measured. Three characteristic peaks at 285, 532, and 400 eV were observed for C 1s, O 1s, and N 1s, respectively. Two relatively weak signals were also observed at 102 and 152 eV, which are characteristic peaks of Si 2s and Si 2p from the POSS cage. The N (1s) high resolution peak for the SEBS-POSS nanocomposite suggests the presence of only one kind nitrogen atom due to the formation POSS- $\text{N}_3$  molecule reacted with alkyne-functionalized SEBS (Fig. 2) [8].

The fractured surface (broken under liquid nitrogen) of SEBS-POSS hybrids was investigate via FE-SEM. It is found that the fractured surface of the all SEBS-POSS composites demonstrated

homogeneous dispersion without any discernible phase separation, and it is difficult to detect POSS molecules in the fracture surface since POSS is totally embedded in the SEBS matrix. The stress-strain curves and modulus of various SEBS-functionalized POSS were measured. All the POSS composites showed a higher modulus and breaking strength than those of SEBS, which is due to the dramatic reinforcement effect of the covalent functionalized POSS with SEBS matrix. This strengthening effect increased as the amount of POSS increased. The high stretchability of composites could be explored for high performance dielectric elastomer actuators.

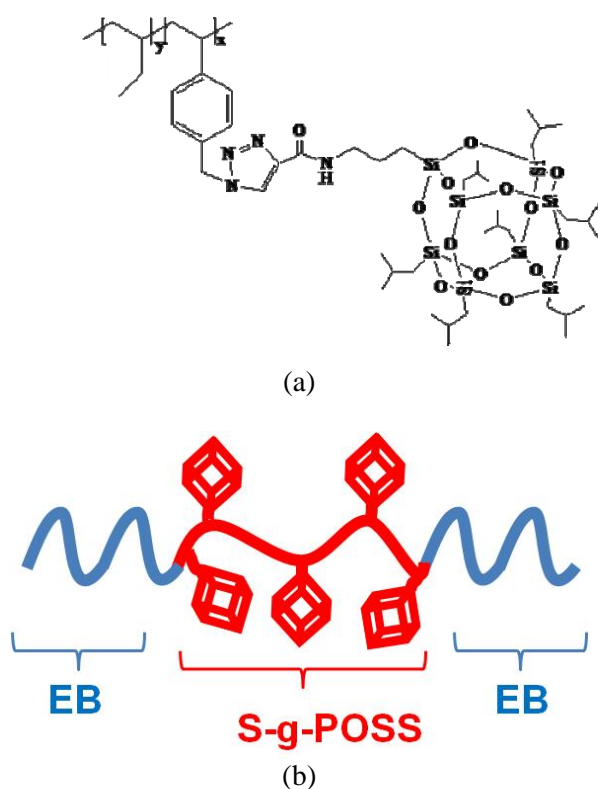


Fig. 2. Scheme of chemical structure of SEBS-POSS composites synthesized in this study (a) and schematic molecular structure for SEBS-POSS composites (b).

The thermal degradation of composites was measured using a thermogravimetric analysis (TGA). The initial degradation temperature decreased proportionally with POSS content. The carbon atoms of the POSS attached to the SEBS are  $sp^3$  hybridized,

with high inherent strain, rendering them more susceptible to thermal degradation of the linkage between POSS and SEBS in the initial stage of degradation. However, at higher temperatures, the thermal stability of the composites increased, compared to that of SEBS. This is attributed to the barrier properties of the nanotubes, which is responsible for enhancing the thermal stabilization of the composites. TGA of POSS shows near about complete mass loss at temperatures over 450 °C due to its sublimation.

#### 4 Conclusions

SEBS-functionalized POSS composites have been synthesized successfully using click chemistry. The POSS composites showed a higher modulus and breaking strength than those of SEBS, which is due to the dramatic reinforcement effect of the covalent functionalized POSS with SEBS matrix. This strengthening effect increased as the amount of POSS increased. The high stretchability of composites suggests a potential application for high performance dielectric elastomer actuators.

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