



Synthesis and characterization of UV-cured epoxy acrylate/POSS nanocomposites

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ABSTRACT

In this study, epoxy acrylate (EA)/vinyl-polyhedral oligomeric silsesquioxane (POSS) nanocomposites were prepared through in situ polymerization and by UV-curing technique. The vinyl-POSS monomers were added to EA matrix by physically blending at loadings between 0 wt.% and 15 wt.%. The microstructure of the EA/vinyl-POSS composites was studied by X-ray diffraction (XRD) measurements, and the result indicated that the separate POSS domains were present in EA/POSS composites. Aggregates were observed in the nanocomposites by SEM and the EDS results indicated that there were vinyl-POSS molecules existing in the EA matrix. TEM images further proved there were both POSS aggregates and monomers dispersed in the EA matrix. The kinetics of the photopolymerization was investigated by real time FTIR spectroscopy. The DSC analysis showed that the increasing POSS content caused a decrease on the composite's glass transition temperature. TGA measures confirmed that the degradation mechanism of EA was not affected by POSS and the nanocomposites thermal stability was slightly improved with the increasing of POSS loadings. It can be seen that the degradation rate slowed down with the increasing of POSS content and the 50% mass loss temperature of EA/POSS hybrids all increased conspicuously relative to plain EA.

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1. Introduction

Hybrid materials with both inorganic and organic components draw more and more attention because of its improved properties. To reinforce the polymers with nano-sized inorganic particles (defined herein as having at least one dimension less than 100 nm) is an effective way to improve the properties. The nanofillers may have spherical (metal or semi-conductive nanoparticles (NPs)), layered (clay) or fibrous (nanofibers and carbon nanotubes) shapes [1]. Such polymer nanocomposites are applied in systems ranging from electronic devices to biosensors and catalysts, and display outstanding properties. Thus, the field of polymer nanocomposite materials has attracted great attention of both polymer scientists and engineers in recent years.

Polyhedral oligomeric silsesquioxanes (POSS) is a class of organic–inorganic hybrid nanomaterial constituted by an inorganic silica $R_n(\text{SiO}_{1.5})_n$ core cage structure, where n ($n=8, 10, 12$) is the number of silicon atoms of the cage and the R is a hydrogen atom or an organic functional group such as alkyl, alkylene, acrylate, hydroxyl, or epoxide unit. These functional groups attached on POSS make it easier to incorporate with thermoplastics or thermosets, and finally lead to the improvement of properties. Usually, the good compatibility between POSS and polymer matrix

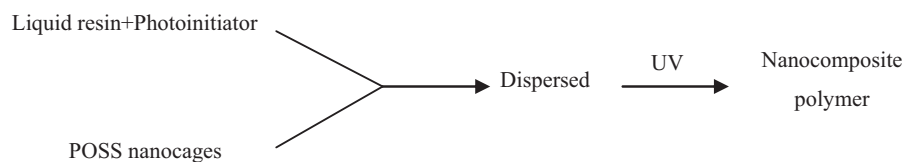
contributes to positive reinforcement. The compatibility and reactivity are determined by the functional groups, which can be either reactive or non-reactive. If the organic groups contain reactive functionalities, they can link with the polymer through covalent bonding. In terms of non-reactive groups, compatibility can be achieved by either similarities in the chemical structure or by specific polar interactions between the polymer and functional groups [2].

Traditionally, copolymerization is the most common approach used to obtain polymer/POSS nanocomposites. The incorporation of POSS monomer into polymers by this way can lead to the improvement of the miscibility, flammability, thermal or polymer mechanical properties [3–6]. In recent years, melt blending and solution blending processes draw more and more attentions due to their advantage of being inexpensive and simple to scale up at industrial level, although poor miscibility may exists generally [5,7,8–11].

This work tried to apply the UV-curing technology to the synthesis of nanocomposites containing POSS monomers. UV-curing technology owns a number of advantages, including environment-friendly such as no emission of volatile organic compounds and low energy consumption, ultrafast curing and ambient temperature operation. The principle of in situ curing process can be schematically represented in Scheme 1.

In recent years, varies of nanoparticles including silica nanoparticles, alumina particles, organoclay bismuth nanoparticles, montmorillonites, boehmites, layered silicate, ZnO, layered

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Scheme 1. Sketch of preparation and curing process of nanocomposite.

double hydroxide and so on, have been introduced into the UV-curing system and display improved properties [12–23]. This study first reports the synthesis of polymer/POSS nanocomposites by UV-radiation curing of epoxy acrylate containing vinyl-POSS. The morphology, UV-curing process and thermal properties of EA/vinyl-POSS nanocomposites were investigated using XRD, SEM, TEM, FTIR, DRS, DSC, and TGA techniques.

2. Experimental

2.1. Materials

Epoxy acrylate (EA, Product No.: CN120), as photosensitive oligomer, was provided by Sartomer USA, LLC, used as received. The nanofiller, vinyl-POSS (Product No.: MX-YXJP, Mw: 633.05 g/mol, CAS No.: 69655-76-1) was obtained from Liaoning Am Union Composite Materials Co., Ltd., China. The schematic representation of both vinyl-POSS and EA are shown in Fig. 1. Benzophenone (BP, Mw: 182.22 g/mol, CAS No.: 119-61-9) and triethanolamine (TEA, Mw: 149.19 g/mol, CAS No.: 102-71-6), as photoinitiators, were purchased from Sinopharm Chemical Reagent Shengyang Co., Ltd., China. Tetrahydrofuran (THF, Mw: 72.11 g/mol, CAS No.: 109-99-9) was used as solvent to dissolve vinyl-POSS nanoparticles, and was purchased from Sinopharm Chemical Reagent Shengyang Co., Ltd., China. Tripropylene glycol diacrylate (TPGDA, Mw: 300.35, CAS No.: 256-032-2), as reactive diluents, was provided by Tianjin Chemical Reagent Research Institute, China.

2.2. Sample preparation

A series of UV-cured EA/vinyl-POSS nanocomposite films with different vinyl-POSS contents (0 wt.%, 1 wt.%, 3 wt.%, 5 wt.%, 10 wt.%, 15 wt.%) were prepared. Firstly, the pre-weighed vinyl-POSS monomers were dissolved in THF, and then mixed with the reactive diluents (TPGDA) solutions. The mixture was dispersed in a high speed dispersing machine for 30 min and in ultrasonic cleaner for 30 min, and then mixed with EA (the mass ratio of EA and TPGDA is 4:5), 3 wt.% of BP and 1 wt.% of TEA. The mixture obtained was high-speed dispersed and ultrasonic dispersed for 60 min, respectively, and degassed under vacuum at 30 °C for 12 h to remove the residual solvent. After that, the liquid mixtures were coated onto a glass substrate using a wire-wound applicator. At last, the wet films were exposed to UV radiation with a high-pressure mercury lamp (5.0 kW) in air for 15 s, with radiation intensity of 260 mW/cm² on the surface of samples.

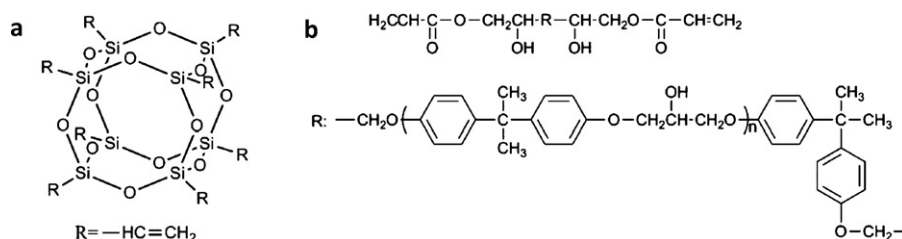


Fig. 1. Chemical structure of (a) vinyl-POSS and (b) epoxy acrylate.

2.3. Characterizations

2.3.1. X-ray diffraction (XRD)

The UV-cured films (25 μm, cured for 15 s with radiation intensity of 260 mW/cm²) were scanned at a speed of 4 °C/min at ambient temperature using an X-ray diffractometer (DX-2600) at a generator voltage of 35 kV and a current of 25 mA. The data were collected from 5° to 40° intervals.

2.3.2. Scanning electron microscopy (SEM)

The morphology of EA/POSS composites was observed by Hitachi S-3400N scanning electron microscopy with 20 kV accelerating voltage. The samples were coated with thin layers of gold to make the surface conductive. The thickness of films used in SEM was 25 μm, and the wet films were cured for 15 s with radiation intensity of 260 mW/cm².

2.3.3. Transmission electron microscopy (TEM)

TEM was carried out on a JEM-1200EX microscope at 60 kV. The EA/POSS nanocomposite samples were embedded in resin (Epon812) at 70 °C for 24 h, and then were cut to 70 nm with a Weiyong ultramicrotome.

2.3.4. Fourier transform infrared spectroscopy (FTIR)

The kinetics of the photopolymerization was determined by real time FTIR spectroscopy, employing a Nicolet380 Fourier Transform interferometer. The scan range was from 4000 to 400 cm⁻¹. The liquid mixtures were coated onto the KBr wafer with the thickness of 10 μm, and immediately exposed to ultraviolet beam with a light intensity of 40 mW/cm². Because the IR absorbance is proportional to the monomer concentration, carbon-carbon double bonds (1635 cm⁻¹) conversion versus irradiation time profiles can be obtained.

2.3.5. Diffuse reflectance spectra (DRS)

The UV diffuse reflectance spectra (DRS) of vinyl-POSS was tested by UV-2550 ultraviolet and visible spectrophotometer, using BaSO₄ as the reference.

2.3.6. Gel content

The pre-weighed UV-cured films (25 μm, cured for 15 s with radiation intensity of 260 mW/cm²) were extracted in acetone for 48 h at room temperature. Then, the residue was dried to constant weight and weighted. The gel content refers to the weight ratio of UV-cured films before and after extraction.

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