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Morphology and properties of UV-curing epoxy acrylate coatings modified with methacryl-POSS

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ABSTRACT

In this work, the morphology and properties of UV-curing epoxy acrylate (EA) coatings modified with methacryl polyhedral oligomeric silsesquioxanes (M-POSS) were studied. The M-POSS nanocages were introduced into EA UV-curing system via copolymerization at loadings between 0% and 10 wt%. The XRD and FTIR analysis indicated that M-POSS chemically incorporated into the hybrid materials and formed a cross-linked network between M-POSS and EA. The morphological analysis showed that the discrete spherical POSS-rich particles were dispersed in the EA matrix uniformly, and both of the number and mean diameter of POSS-rich particles increased with the increasing M-POSS loadings. The influence of M-POSS on the kinetics of the photopolymerization was determined by real time FTIR spectroscopy and the result showed that the addition of POSS enhanced both of the UV-curing rates and final double bond conversion. The DMA analysis showed that increasing the amount of M-POSS nanocages caused an increase on the nanocomposite's T_g. TGA curves showed that at the later period of degradation process, the thermal stability of nanocomposites was enhanced by M-POSS. With respect to the mechanical properties, the most remarkable trend was an improvement on the impact resistance of nanocomposites with the increasing POSS contents. Because both of the craze and plasticity deformation caused by POSS nanocages would absorb impact energy, hinder the growth of craze.

1. Introduction

The UV-curing technology has been widely used in industrial coatings owing to many advantages, including no emission of volatile organic compounds, low energy consumption, low process costs, high chemical stability, ultrafast curing rate and ambient temperature operation [1,2]. The epoxy acrylate (EA) is one of the most important and extensively used acrylate monomer in UV-curing systems due to its excellent properties, such as superior chemical and solvent resistance, good adhesion properties and high mechanical strength [3,4]. In the last few years, the improvement of thermal stability and mechanical properties of EA networks by the incorporation of nanofillers has drawn many attentions [5–8].

In the last two decades, polyhedral oligomeric silsesquioxanes (POSS) have been used as a novel class of nanofillers with unique properties [9]. Polyhedral oligomeric silsesquioxanes (POSS) is a class of organic–inorganic hybrid nanomaterial constituted by an inorganic silica $R_n(SiO_{1.5})_n$ core cage structure, where n (n = 8, 10 or 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, such as thermal stability, thermomechanical and electrical properties, flame retardant as well as mechanical strength [10–13]. POSS cages can be introduced into polymer systems via copolymerization or physical blending [14]. 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 and other properties [15,16]. Nanocomposites obtained by physical blending, including melt blending and solution blending, own the advantages of being inexpensive and simple to scale up at industrial level, however, poor miscibility may exist generally [17–21].

In previous studies, few investigations have reported the synthesis of polymer/POSS nanocomposites employing UV-curing technology. Wang et al. [3] studied the preparation and thermal stability of UV-cured epoxy-based coatings modified with octamercaptopropyl POSS. The octamercaptopropyl-POSS was incorporated into epoxy acrylate networks by thiol-ene photopolymerization. La et al. [22] investigated novel anti-fouling coatings prepared with a UV-curable-molecular reinforcing material,

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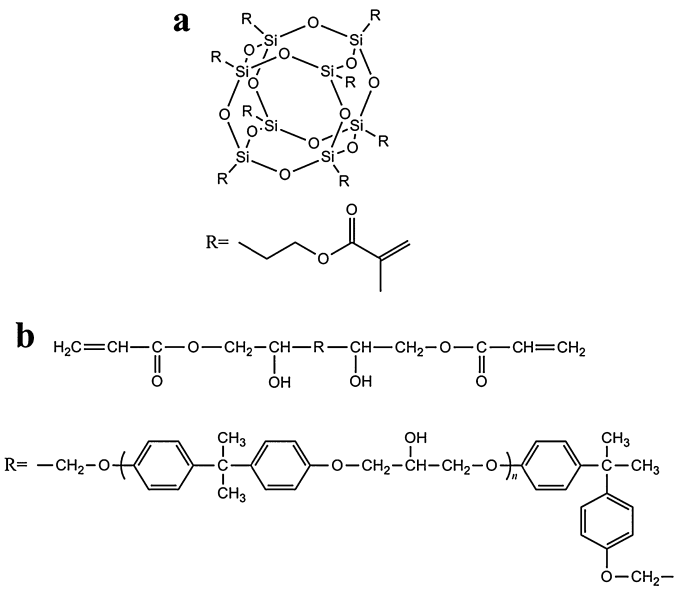
methacryl-POSS, and a hydrophilic comonomer, polyethylene glycol methacrylate (PEGM). Water uptake of the UV-cured POSS–PEGM films was varied from 8% to 90% depending on the relative ratio between POSS and PEGM. Gao et al. [23] prepared the waterborne UV-curable EA coatings modified with methylacryloylpropyl-POSS and investigated the cure kinetics of the coating by differential scanning calorimetry (DSC). Few works have studied the influence of POSS on the kinetics of the photopolymerization and the mechanical properties of nanocomposites.

In our previous study, we have synthesized UV-curing EA/vinyl-POSS nanocomposites via physical blending [24]. The microstructure and thermal properties of the EA/vinyl-POSS composites was studied. In this work, in order to improve the dispersion of POSS molecules in EA matrix, methacryl-POSS (M-POSS) were introduced into UV-curing systems. Methacryl-POSS is a hybrid molecule with an inorganic silsequioxane as the cage-like core, and organic methacrylate groups attached at the corners of the cage. It is a kind of colourless and transparent liquid with low viscosity. It is soluble in most of polar organic solvents, acrylate and methacrylate monomers, and aromatic and aliphatic resins. The molecular structures of methacryl-POSS and epoxy acrylate are shown in Scheme 1. Methacryl-POSS was utilized because the methacrylate groups can copolymerize with epoxy acrylate (Scheme 2). The microstructure and morphology of EA/methacryl-POSS nanocomposites were investigated by FTIR, XRD, SEM and TEM. The influence of M-POSS on the kinetics of the photopolymerization was determined by real time FTIR spectroscopy. The glass transition temperature and thermal stability were tested by DMA and TGA, respectively. The mechanical properties of the EA/POSS nanocomposite films were investigated employing pencil hardness, impact resistance and flexibility tests.



Scheme 1. Chemical structure of (a) methacryl-POSS and (b) epoxy acrylate.

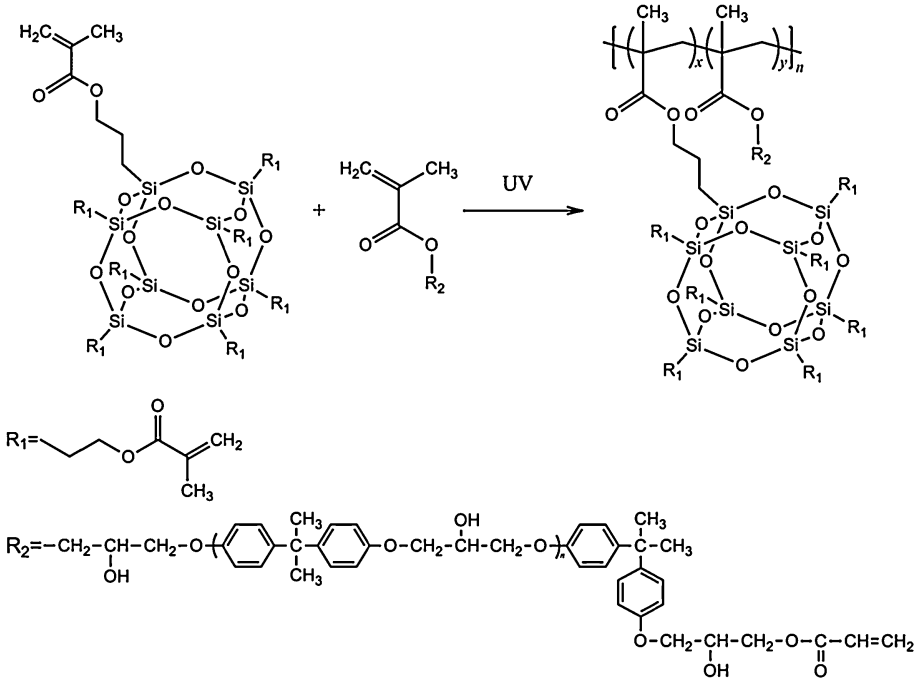
2. Experimental

2.1. Materials

Epoxy acrylate (EA, Product No.: CN120), as photosensitive oligomer, was provided by Sartomer USA, LLC, used as received. Methacryl-POSS (M-POSS, Product No.: MA0735, $(C_7H_{11}O_2)_n(SiO_{1.5})_n$; $n = 8, 10, 12$, F_w: 1433.97) was obtained from Hybrid Plastics, Inc. Benzophenone (BP, M_w: 182.22 g/mol, CAS No.: 119-61-9) and triethanolamine (TEA, M_w: 149.19 g/mol, CAS No.: 102-71-6), as photoinitiators, were purchased from Sinopharm Chemical Reagent Shengyang Co., Ltd., China. Tripropylene glycol diacrylate (TPGDA, M_w: 300.35 g/mol, 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/M-POSS nanocomposite films with different M-POSS contents (0 wt%, 1 wt%, 3 wt%, 5 wt%, 10 wt%) were prepared. The formulations of coatings are shown in Table 1. Firstly,



Scheme 2. Chemical incorporation of M-POSS cages into epoxy acrylate chains.

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