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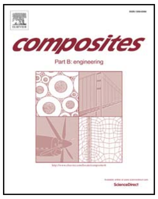

UV-curable photosensitive silicone resins based on a novel polymerizable photoinitiator and GO-modified TiO_2 nanoparticles

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ABSTRACT

A novel polymerizable benzophenone photoinitiator containing acryloxy (BPA) was synthesized. The photopolymerization of photosensitive methacrylic-silicone resins (MASR) initiated by BPA was studied. Results show that BPA is an efficient photoinitiator, which could generate radicals from the photolysis reaction and be consumed via copolymerizing with MASR. The designed UV-curing silicone resins system initiated by BPA showed a high carbon-carbon double bonds conversion above 80% after 20 s UV radiation. In addition, reduced graphene oxide (rGO)-TiO_2 composites were elaborated by hydrothermal reaction. The synergistic effects from graphene and TiO_2 further enhanced the carbon-carbon double bonds conversion of MASR to 86% with 15 s UV irradiation, demonstrating that the incorporated rGO-TiO_2 significantly improve the formulation UV-curing reactivity. Additionally, UV-cured MASR with rGO-TiO_2 showed an excellent thermal stability. This work proposes an efficient strategy to improve the polymerization degree of UV-curable photosensitive silicone resins.

1. Introduction

Silicone resins, as an interesting class of non-carbonic polymers, provide remarkable properties including excellent dielectric properties, good thermal stability, impressive antiweatherability and chemical resistance [1–3]. The crosslinking chemistries of silicone-based materials can be categorized into three main chemical reactions: (1) hydrosilylation between vinyls and hydride-terminated siloxanes in the presence of the metal catalyst such as platinum [4], (2) thiol-ene click chemistry between vinyl group and thiol group [5], (3) condensation reaction of alkoxysilane [6]. However, these crosslinking chemistries still present pitfalls that prevent their use for specific applications and have many drawbacks such as the harmful of heavy metal catalysts to the environment, high curing temperature and high energy consumption. Therefore, most researches focus on UV-curable silicone resins and most UV-curable system involves reactive acrylate, methacrylate, or allyl groups [7,8].

The light induced polymerization technique have been considered as ecofriendly due to its outstanding features such as high efficiency, low energy consumption, solvent-free formulation, and room temperature treatment [9]. These characteristics promote photopolymerization over thermally induced processes which require much time and high temperature to complete the reaction. Significantly, photopolymerization materials have wide application in elaboration of coatings, adhesives, and other products [10–12].

As a crucial component of a UV-curable system, photoinitiators could absorb light and generate active radicals to initiate the polymerization [13]. However, low-molecular-weight photoinitiators are generally treated as a problem in photopolymerization due to the disadvantages such as odor, yellowing, poor compatibility with the UV-curable resin and migration in the post-cured process [14]. Thus, polymerizable photoinitiators have been developed as a valuable alternative to overcome the disadvantages, which can not only generate free radicals to initiate photopolymerization, but also copolymerize with the polymer [15].

TiO_2 has also been testified to be free-radical photoinitiators for curing (meth)acrylic resins, due to its ability of generating electron-hole pairs under photoexcitation, which could react with resin monomers providing reactive radicals [7]. Due to the unique synergistic effect, incorporation of the graphene and TiO_2 is considered a promising nanocomposite [16]. Graphene, which is often prepared by reducing graphene oxide, have drawn interest from researchers owing to its large specific surface area, excellent electrical conductivity, high charge carriers mobility and high mechanical strength [17–19]. It turns out to be an electron acceptor/transporter for TiO_2 particles and anticipates to significantly enhancing the lifetime of electron-hole pairs [20]. Thus, it is a potential candidate to facilitate the adsorption capability and enhance the photoactivity of TiO_2 under UV light due to the unique

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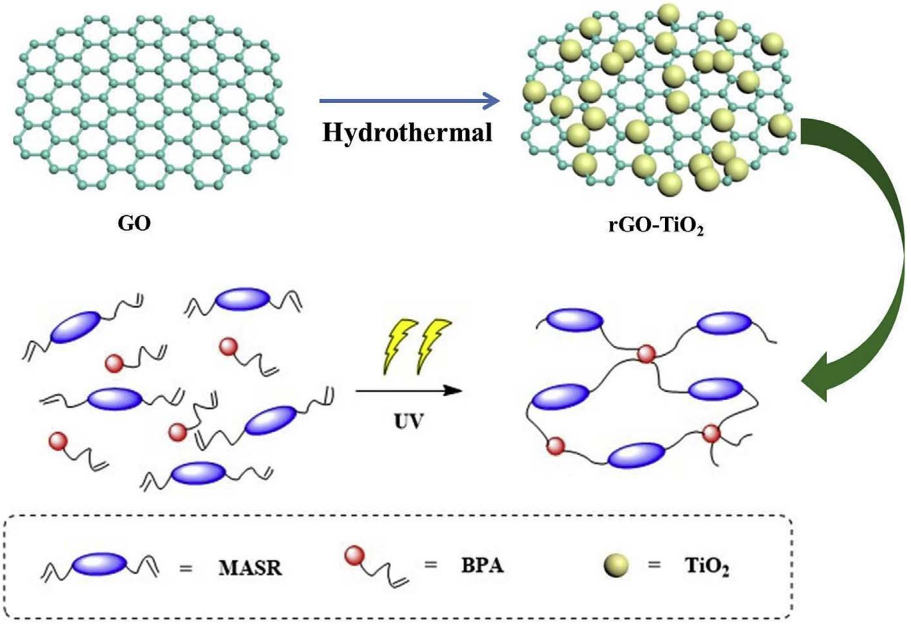

Fig. 1. Schematic of the preparation procedure of UV-cured MASR.

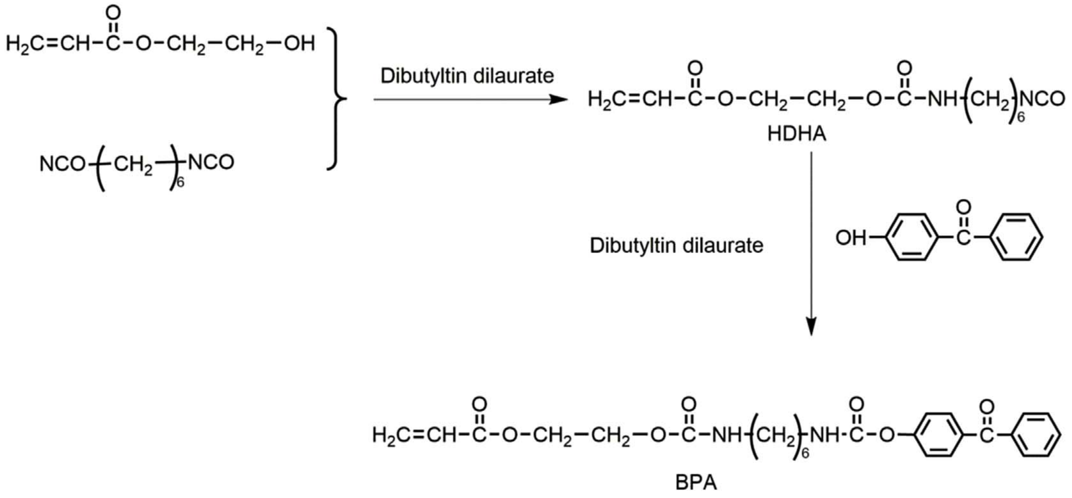

Fig. 2. The synthesis routes of BPA.

electron-transferring property. In addition, the incorporation of graphene could avoid TiO_2 particles suffering aggregation in an organic matrix, which consequently leads to good dispersity.

In this study, polymerizable photoinitiator was synthesized to initiate the polymerization of UV-curable photosensitive methacrylic-silicone resins. The effects of BPA and rGO-TiO_2 composites on the photopolymerization of MASR were investigated. The photoinitiation mechanism and the photopolymerization behavior were also presented. The schematic representation of UV-cured methacrylic-silicone resins based on a BPA and rGO-TiO_2 was shown in Fig. 1.

2. Experimental

2.1. Materials

Methyltriethoxysilane (MTES), dimethyldiethoxylsilane (DDS), 3-methacryloxypropyltrimethoxysilane (MPTS) were obtained from Qufu Chenguang Chemical Co., Ltd. (China). Hexamethylene diisocyanate (HDI), 4-hydroxybenzophenone, 2-hydroxyethyl acrylate (2-HEA), dibutyltin dilaurate, dibutylamine and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were supplied by Aladdin Reagent Shanghai Co., Ltd (China). Tetrabutyl titanate ($Ti(OC_4H_9)_4$), potassium permanganate, and concentrated sulfuric acid (98 wt%) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). All chemical reagents were used as received.

2.2. UV-Curing of MASR based on BPA and GO- TiO_2

MASR with initiator (0.5 μm film on glass) was irradiated by a light source of high-pressure mercury lamp (1000 W) with a distance of 10 cm from lamp to specimen at room temperature in air atmosphere. The composition of the samples investigated in the work was shown in Table S2. DMAEMA as the coinitiator, [BPA]/[DMAEMA] = 1:4 mol/mol [21].

2.2.1. Preparation of MASR

MTES, DDS and MPTS with different mole ratio 7:2:1 and 6:3:1 (supported in Table S1) were added into a flask connecting to mechanical stirrer and refluxing condenser. Then hydrochloric acid solution (10 wt%, diluted by ultrapure water) was slowly added dropwise through the constant-pressure funnel to adjust the pH value to 3–4. The blend was then refluxed at 60 °C for 4 h. The transparent viscous