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Self-photoinitiated oligomers of water-diluted polyurethane acrylate grafted with zinc oxide of low concentrations

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ABSTRACT

In order to eliminate some problems of organic photoinitiators, self-photoinitiated oligomers of water-diluted polyurethane acrylate grafted with 0.1–0.3 wt.% zinc oxide (ZnO) were prepared. ZnO was first facilely treated by vacuum dehydration and sonication, and then reacted into the oligomers by —NCO and —OH groups. The oligomers were synthesized using toluene diisocyanate, polyether diols, 2, 2-dimethylol propionic acid, hydroxyl propyl acrylate, pentaerythritol triacrylate, ZnO, and triethylamine. The prepared oligomers were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, particle size analyzer, and UV–vis spectroscopy. The kinetics of the UV-curing process was investigated. We observed a maximum kinetic rate constant with ZnO content of 0.2%, and the best film performance with ZnO content around 0.25%. The photoinitiation efficiency of the oligomers was similar to the value of 2-hydroxyl-2-methyl-1-phenyl-1-propanone. In general, the physical properties of the films with physically mixed ZnO were worse than those of the films with chemically grafted ZnO. This investigation demonstrated novel oligomers grafted with a few ZnO can be self-photoinitiated and facilely prepared.

1. Introduction

Zinc Oxide (ZnO) can be used as an inorganic photoinitiator [1]. In recent years, there are many researches about ZnO to be used in polymers, in which ZnO is utilized as either a photoinitiator [2,3] or an inorganic functional material [4,5].

Joseph C. Kuriacose and M. Clare Markham [1,6] investigated the photopolymerization of methyl methacrylate in suspensions of ZnO in different solvents with UV irradiation. Their work shows that the dissolved oxygen and water in the suspension is a key factor in the photopolymerization reaction, which is related to the formation of active free radicals. Oxygen in the solution increases the production of chain radicals; but it reduces the average molecular weights of the polymers. Masahide Yamamoto and Gerald Oster [7] found that, when there is water in the system, ZnO under UV irradiation reacts with water to form hydrogen peroxide and then the active free radicals are generated to initiate the photopolymerization of vinyl monomers. A. J. Hoffman et al. [8] used quantum grade ZnO as a photoinitiator to initiate polymerization of methyl methacrylate, which brings an increase in the concentration of ZnO that can improve the conversion rate of monomer in a certain range [8]. A. L. Stroyuk et al. [9] synthesized nano ZnO, nano Fe_2O_3 and nano CdS of different sizes that were used as efficient inorganic photoinitiators for the photopolymerization of butyl methacrylate. Michael Schmitt [10] used real-time UV and Raman spectroscopy to detect the free radical photopolymerization of nano ZnO, the polymerization rates, and efficiency. Sajjad Dadashi-Silab et al. [11] prepared nano-ZnO and nano Fe/ZnO for the free radical photopolymerization and studied the initiation and photopolymerization of these two kinds of nano materials in aqueous phase and organic phase. Xiangning Zheng et al. [3] prepared a magnetic nanocomposite hydrogel by ZnO-initiated the photopolymerization of N, N-dimethylacrylamide, which exhibits good adsorption capacity and separation selectivity to La (III) ions [3]. Sajjad Dadashi-Silab et al. [12] used nano ZnO and nano Fe/ZnO as photoinitiators to investigate photo-induced atom transfer radical polymerization of methyl methacrylate in the presence of Cu (I), which can be controlled by the switch of the UV light. Guo-Xiang Wang et al. [13] studied the photo-induced single-electron transfer living radical polymerization of methyl methacrylate with ZnO as an inorganic photoinitiator, and investigated the effects of initiator, catalyst, ZnO, and light intensity on the photopolymerization of methyl methacrylate. Michael Schmitt [2] studied ZnO nanoparticle-based initiators with the effects of particle type, structure, particle size, and surface modification on the catalytic performance, which demonstrated that the nanoparticle ZnO is an efficient inorganic photoinitiator [2].

The migration of organic photoinitiators and harmful photolysis

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species [14] prompt the investigation of inorganic photoinitiators [12,15], macrophotoinitiators [16,17], hybrid organic-inorganic photoinitiators [18,19], and self-photoinitiated UV-curable oligomers [20,21]. Many scientific researches have been done to investigate the self-photoinitiated photopolymerization [21–27]. Maleimides and vinyl ethers have been efficiently used as the self-photoinitiated UV-curable oligomers [20,28,29]. Then, the maleimide substituted acrylate oligomers are found to be self-photoinitiated [20,22,30,31]. Some thiol-ene oligomers possess the ability of the self-photoinitiated photopolymerization [21,23].

UV irradiation of some inorganic pigments [27], such as titanium dioxide [32], ZnO, magnetite nanoparticles [33], and other semiconductor nanoparticles [11,34], leads to the photopolymerization without organic photoinitiators [27]. These inorganic pigments are simply physically mixed in the UV-curable formulations [27]. This investigation grafted ZnO into the macromolecular oligomers of water-diluted polyurethane acrylate (PUA). It turns out that only a few grafted ZnO had a novel and self-photoinitiated feature.

Among these self-photoinitiated UV-curable oligomers, a novel method is to graft an inorganic photoinitiator into the UV-curable oligomers. Especially, only a few grafted ZnO can lead to the photoinitiator-free UV-curable function, which compares to traditional 3–5 wt.% organic photoinitiator in a UV-curable coating formulation. Thus, a novel kind of self-photoinitiated UV-curable oligomers was prepared. This ZnO grated water-diluted PUA oligomers eliminates the problems of residual odor, emission of photolysis species, both migration and transport of photoinitiators etc.

There are three more advantages of this grafting process. Firstly, it overcomes the size limitation of ZnO as a photoinitiator, with a reported ZnO size in a range of 1–100 nm in several published journal articles [8]. Secondly, it simplifies the treatment process of ZnO as a photoinitiator, in which the ZnO is dried in a vacuum oven and dispersed by an ultrasonic equipment. Thirdly, it helps stabilize the ZnO grafted PUA oligomers. There are no obvious changes of the grafted samples when they were stored at 50 °C for two weeks. In contrast, the ZnO, which was physically mixed in PUA oligomers, settled down to the bottom after 1–2 days.

In this paper, we grafted ZnO into the WPUA oligomers. To obtain a detailed understanding of the role of ZnO in the curing process, we studied the effect of grafted amount of ZnO on the curing process by real-time UV. The effect of ZnO contents on the film performance was also studied. We compared the ZnO grafting results with those results of the physical mixing of ZnO and Darocur 1173.

2. Materials and methods

2.1. Materials

The industrial grade toluene diisocyanate (TDI) was purchased from Bayer material science (China) Co., Ltd. The industrial grade polyether diols (N210) was provided from Nanjing Zhongshan chemical Co., Ltd, with an average molar weight of 1000. The industrial grade 2, 2-dimethylol propionic acid (DMPA) was supplied from the Swedish company, Perstorp. The industrial grade pentaerythritol triacrylate (PETA) and hydroxypropyl acrylate (HPA) were bought from Sartomer (Guangzhou) chemical Co., Ltd. The chemically pure 4-Methoxyphenol (MEHQ), ZnO, acetonitrile, and triethylamine (TEA) was obtained from Tianjin Institute of Chemical Reagents, with the average size of ZnO about 100 nm. The chemical reagent dibutyltin dilaurate (DBTDL) was purchased from Shanghai Reagent Factory. The spectrally pure KBr was supplied from Guangzhou Reagent Factory. The industrial grade acetone was purchased from Guangzhou Donghong chemical plant. The industrial grade 2-hydroxyl-2-methyl-1-phenyl-1-propanone (Darocur 1173) was bought from BASF Corporation.

2.2. Synthesis of water-diluted polyurethane acrylate grated with ZnO

ZnO was dried in a vacuum drying oven at 60 °C for three hours under a pressure about 0.095 MPa. ZnO was mixed with HPA, PETA, catalyst (DBTDL), and MEHQ. Then, the mixture was dispersed by ultrasonic for 20 min at room temperature.

The oligomers of water-diluted polyurethane acrylate prepared by the acetone process [35,36] were synthesized using toluene diisocyanate as the hard segment, polyether polyol as the soft segments, dimethylol propionic acid as the hydrophilic reactant, hydroxyl propyl acrylate and pentaerythritol triacrylate as the end-capping reagent, ZnO, and triethylamine as the neutralizer. Certain amounts of N210 (25.51 g), TDI (26.65 g), and three drops of DBTDL were added into a four-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then the mixture was heated to 80–85 °C and kept at this temperature for 1.5–2 h. Once the temperature cooled down to 60 °C, a certain amount of DMPA (8.654 g) with acetone (15–20 g) were added into the four-necked flask and reacted for 2–3 h. When the temperature cooled down to 50 °C, the dispersed ZnO (0.1–0.3 g) in a mixture of PETA (25.30 g), HPA (7.36 g) and MEHQ (0.06 wt.% of PETA and HPA) was added and reacted for 3–4 h. Finally, when the temperature cooled down to 40 °C, TEA (6.53 g) were added into the flask dropwise and reacted at 40 °C for 10–30 min. The water-diluted polyurethane acrylate grafted with ZnO (ZnO-PUA) was obtained. This oligomeric synthesis process is shown in Fig. 1.

2.3. Preparation of UV-curable coatings and UV-cured films

ZnO-PUAs were diluted with deioned water of 50–200% to be UV-curable coatings. Then, these coatings were brushed and applied onto the surfaces of woody test boards, test pieces of glass, and iron test plates, respectively. After these coatings were evaporated at room temperature for 30 min, these coatings were put in an electric oven at 60 °C for another evaporation of 30 min. Then, the UV-curing of these UV-curable coatings were carried out under UV irradiation of an intensity of 80 mW/cm^2 with a polyspectral UV-curing machine made by a Dongguan Co., which was equipped with 1 kW UV lamp.

2.4. Characterization

The average particle size of the ZnO and ZnO-PUA oligomer particles was determined by a ZS Nano S Malvern particle size analyzer (Malvern Instruments Ltd.). The samples were suspended in ultrapure deionized water produced from a Milli-Q Academic A10 of Millipore Company and diluted to a certain concentration. The samples were treated by the ultrasonic dispersion for half an hour before the particle size determination.

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin-Elmer Spectrum 2000 FTIR instrument and the wave number range was set from 400 to 4000 cm^{-1} for evaluation of the chemical structure of raw materials and the products. Both the chemicals and oligomers were coated with almost the same weights on the KBr pallets and dried in a vacuum oven at 60 °C for one hour.

Scanning electron microscope (SEM) was used to study the distribution of ZnO in the oligomers. In order to prepare the films with sufficiently required quality, the UV-curable coatings were sprayed on the conductive adhesive. After the UV-curing, the UV-cured films were snapped (the section is placed on the top). Then, gold was sprayed on the surface of the samples before the morphology observe. The cross-sectional morphology of the films was observed by a field emission scanning electron microscopy of Merlin (Germany, Zeiss).

UV–vis spectra were used to study the maximum absorption wavelength of the raw materials and the products. Ultraviolet spectra were measured using a L5 UV–vis spectrophotometer bought from Shanghai instrument electric analysis instrument Co., Ltd. The deionized water was directly used as the solvent for the measurement of UV-spectra of