Progress in Organic Coatings 67 (2010) 302–310

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Dispersion of γ-methacryloxypropyltrimethoxysilane-functionalized zirconia nanoparticles in UV-curable formulations and properties of their cured coatings

Kun Xu, Shuxue Zhou*, Limin Wu

Department of Materials Science and Advanced Coatings Research Center of China Educational Ministry, Fudan University, Handan Road 220, Shanghai 200433, PR China

ARTICLE INFO

Article history:
Received 8 August 2009
Received in revised form 22 October 2009
Accepted 28 October 2009

Keywords:
Dispersion
Refractive index
Scratch resistance
UV-curable coatings
Zirconia nanoparticles

ABSTRACT

Highly dispersible zirconia (ZrO_2) nanocrystals were functionalized with γ-methacryloxypropyltrimethoxysilane (MPS) and dispersed in trimethylolpropane triacrylate (TMPTA), 1,6-hexandiol diacrylate (HDDA), tripropyleneglycol diacrylate (TPGDA) and aliphatic polyurethane oligomer (PU)/TPGDA mixtures, respectively. The dispersion behavior of MPS-functionalized ZrO_2 (MPS-ZrO_2) as well as its mechanical reinforcement for the PU/TPGDA matrixes was investigated. It was found that the dispersion of MPS-ZrO_2 nanoparticles in UV-curable formulation strongly depends on the ZrO_2 load, the grafting density of MPS, the composition of organic matrix and the type of monomer. A critical ZrO_2 load beyond which phase separation of MPS-ZrO_2 nanoparticles takes place exists for all cases. MPS-ZrO_2 nanoparticles are more efficient to improve the pendulum hardness and scratch resistance of PU/TPGDA-based coatings that contains higher amount of TPGDA, being presumably due to quicker increase of the cross-linking density of the coatings. Additionally, a completely transparent TPGDA-based nanocomposite coating with ZrO_2 load of as high as 60 wt.% can be obtained, and has absolutely high refractive index of 1.78.

1. Introduction

As we know, surface property of nanoparticles strongly influences their dispersion behavior in organic matrix and thus the properties of the resulted nanocomposites. Attaching of organic species (carboxylic acid, silane coupling agent, polymer dispersants, etc.) to the surfaces of inorganic nanoparticles is generally employed to improve the compatibility and even to render the reactivity of nanoparticles with organic matrix. γ-Methacryloxypropyltrimethoxysilane (MPS) is one of the commonest surface modifiers for organophilation of nanoparticles, since its trimethoxysilyl group can bind to the free –OH groups at the surface of the nanoparticles while its methacrylate group makes the nanoparticles polymerizable in radical polymerization. The MPS-functionalized nanoparticles have been widely used in the fabrication of UV-curable nanocomposites. For examples, Bauer et al. [1,2] incorporated MPS-functionalized silica or alumina nanoparticles into a radiation curable formulation, comprising with aliphatic urethane hexaacrylate and 1,6-hexandiol diacrylate (HDDA), for preparation of abrasion and scratch resistant nanocomposite coatings. Li et al. introduced MPS-modified silica nanoparticles into the mixture of trimethylolpropane triacrylate (TMPTA) and epoxy acrylate [3,4] or into MPS itself [5] to realize mechanical enhancement. Landry et al. [6] embedded MPS-functionalized alumina or zirconia (ZrO_2) nanoparticles into a UV-curable formulation which was consisted of two monomers and two oligomers. Scholz and Kaskel [7] also blended MPS-functionalized ZrO_2 nanoparticles with butanediol monoacrylate and TMPTA. Lu et al. [8] mixed MPS-functionalized ZnO nanoparticles with polyurethane acrylate oligomer and 2-hydroxyethyl methacrylate to fabricate luminescent nanocomposite films. Posthumus et al. [9] embedded MPS-treated antimony doped tin oxide nanoparticles into Ebecryl 745 (commercial acrylate mixture), polyethyleneglycol diacrylate, or TMPTA to get electrically conductive nanocomposites. Mcmorrow et al. [10] blended MPS-treated barium titanate ($BaTiO_3$) and silicon carbide (SiC) nanoparticles with HDDA while Schulz et al. [11] introduced MPS-modified Ta_2O_5/SiO_2 nanoparticles into a typical dental adhesive monomer. Among these studies, addition effect of MPS-modified nanoparticles on photopolymerization kinetics or on the properties of the resulted nanocomposites has been well presented. Although dispersion of MPS-modified nanoparticles in UV-cured nanocomposites was ever quantitatively or qualitatively described, these results cannot disclose the true thermodynamic relationship between the dispersion and the surface property of nanoparticles because of the difficult deagglomeration for nanopowders [1,2,6,7,9–11]. Dispersion of colloidal particles is not influenced by deagglomeration force, but so far, only the effect of MPS-modified

---

* Corresponding author.
E-mail address: zhoushuxue@fudan.edu.cn (S. Zhou).

0300-9440/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2009.10.029

nanoparticle load on dispersion was involved [3–5,8]. Investigation on the dispersion behavior of MPS-modified nanoparticle in different UV-curable formulations is insufficient to precisely reveal the true thermodynamics of MPS-modified nanoparticle in the nanocomposites.

Recently, ZrO_2 nanocrystals, synthesized from zirconium isopropoxide isopropanol complex in anhydrous benzyl alcohol (99%), are found to be highly dispersible in organic solvents with the help of surface modifiers [12,13]. Unlike the nanopowder, the dispersion of the nonaqueous synthesized ZrO_2 nanocrystals is not influenced by the deagglomeration force, and thus the dispersion behavior could be regarded as the unique results of the thermodynamics of the system. In previous reports, these ZrO_2 nanocrystals have been introduced into SR349/isooctylacrylate mixture (20:80 in weight ratio) [14], pure aliphatic polyurethane oligomer (PU) [15], and PU/isobornyl acrylate/HDDA (52.5:17.5:30 in weight ratio) [16], to fabricate UV-curable nanocomposites. Effects of the surface property of nanoparticles and the composition of UV-curable formulation on the dispersion behavior of ZrO_2 nanoparticles were primarily illustrated. In this article, we focused on the dispersion behavior of MPS-functionalized ZiO_2 (MPS-ZrO_2) nanoparticles in tripropyleneglycol diacrylate (TPGDA), TMPTA, or HDDA, or PU/TPGDA mixtures with different weight ratios, and thoroughly examined the influence of the attached MPS species on the dispersion of nanoparticles in different UV-curable formulations.

On the other aspect, ZrO_2 material has advantages of chemical inertness, excellent thermal stability, high refractive index and high hardness. The nano-sized ZrO_2 has been demonstrated useful to fabricate nanocomposites with better mechanical properties and high refractive index [14–21], to reduce the thermal expansion coefficient of poly(ether-sulfone) [22], to increase the dielectric permittivity of conductive polymer [23], and so on. Therefore, influence of MPS-ZrO_2 nanoparticles on the mechanical and optical properties of UV-cured coatings was also investigated in this article. Especially, the efficiency of mechanical reinforcement by ZrO_2 nanoparticles for different coatings was compared.

2. Experimental

2.1. Materials

Zirconium isopropoxide isopropanol complex (purity 99.9%) and anhydrous benzyl alcohol (purity 99%) were purchased from Aldrich and MPS from Sigma. Aliphatic urethane diacrylate (UVU6219, comprising 80 wt.% PU and 20 wt.% TPGDA) was kindly offered by Shanxi Xilaiwu Industrial Co., Ltd. (China). TPGDA, TMPTA, HDDA and 1-hydroxy-cyclohexyl-phenyl-ketone (Iragure 184) were got from Shanghai Baorun Chemical Co., Ltd. (China). Tetrahydrofuran (THF, purity $\geq 99.5\%$), absolute ethanol (purity > 99.7) and methanol (purity $\geq 99.9\%$) were obtained from Sinopharm Chemical Reagent Co. All chemicals were used as received.

2.2. Synthesis of ZrO_2 nanoparticles

ZrO_2 nanocrystals were synthesized according to the procedure described elsewhere [13]. That is, 3.33 g of zirconium(IV) isopropoxide isopropanol complex and 50 mL of benzyl alcohol were charged into a 100 mL Teflon liner. Subsequently, the Teflon liner was slide into a stainless steel autoclave and carefully sealed. The autoclave was put into an oven with temperature of 240 °C to carry out the reaction. After 4 days the reaction mixture was allowed to cool down, and a white turbid suspension was obtained. The product was cubic ZrO_2 nanocrystal with monodisperse particle size of 3.8 nm and 9.2 g/100 g ZrO_2 of organic component was inherently chemically adsorbed on the as-synthesized ZrO_2 nanoparticles [13].

2.3. Preparation of MPS-ZrO_2 nanoparticles dispersions

The as-synthesized ZrO_2 nanoparticles suspension in benzyl alcohol (solid content: 33 mg/g) was centrifuged to remove the benzyl alcohol and then washed with absolute ethanol three times. MPS and THF were then mixed with the wet ZrO_2 nanoparticles according to the molar ratio of MPS to as-synthesized ZrO_2 (0.05–0.20:1) and 1.2 wt.% of ZrO_2. The mixture was sonicated at room temperature for 30 min and then heated at 60 °C for 24 h, followed by centrifugation at 8000 rpm for 10 min to remove the possible ZrO_2 aggregates. The obtained transparent ZrO_2/THF dispersions were concentrated to about 10 wt.% of ZrO_2 using a rotary evaporator and precipitated with fivefold volume of methanol, and then centrifuged to get the MPS-ZrO_2 nanoparticles. These MPS-ZrO_2 nanoparticles were further washed with methanol two times to remove free MPS molecules. The wet MPS-ZrO_2 nanoparticles were dispersed in THF again to form a MPS-ZrO_2/THF dispersion with 15 wt.% of ZrO_2 concentration.

2.4. Preparation of UV-curable nanocomposite coatings

MPS-ZrO_2/THF dispersion was mixed with UV-curable formulations: TPGDA, TMPTA, HDDA, UVU6219 (named as PU/TPGDA82 below) or UVU6219/TPGDA mixture with weight ratio of 1:1 (named as PU/TPGDA46 below). Then, the mixture was vacuum-dried overnight in an oven with temperature of 50 °C to remove all THF. The dispersion of MPS-ZrO_2 nanoparticles in the UV-curable formulation was believed to reach thermodynamic equilibrium. Afterwards, 5 wt.% of Iragure 184 (based on the weight of monomer or monomer/oligomer mixture) was added to get a UV-curable coating. The coating was spin-coated on silicon wafer at a spinning speed of 3000 rpm for 1 min or cast on glass slides using a wire-wounded applicator (100#), and then exposed to a UV crosslinking apparatus (Shanghai SCREENET Co., Ltd., Model: 2 kW/11, maximal peak: 365 nm) for curing in air, or to a UV Crosslinker (Spectroline Company, USA, powder: 2.8 mW/cm^2, exposure time: 10 min) for curing in nitrogen.

2.5. Characterization

The optical transparency of the cured nanocomposite coatings at wavelength of 550 nm was determined by a UV–vis spectrophotometer (UV-1800, Shanghai Mapada Instrument Co., Ltd., China). The morphology of nanocomposites was observed by a transmission electron microscope (Hitachi H-600, Hitachi Co., Japan). Samples were prepared by ultramicrotomy at room temperature, giving nearly 100 nm thick sections. No further staining was used to improve the contrast.

The pendulum hardness of the nanocomposites was measured with 707KP pendulum hardness rocker (Sheen Instrument Co., Ltd., UK). The times of the König-pendulum swing from 6° to 3° were automatically recorded at 25 °C. The average value from three measurements on different points of the same sample was adopted.

The scratch resistance was evaluated by two methods: abrasion tests and nano-scratch tests. The former was conducted on a 5131 abrader (Taber, USA) at 25 °C using a CS-10 abrasion wheel, 1000 g load and 40 cycles. The optical transmissions before (T_0) and after (T_1) abrasion were measured with a UV-1800PC spectrophotometer. The reduction of transparency (ΔT) was calculated by equation:

$$\Delta T = \frac{T_0 - T_1}{T_0} \times 100\% \qquad (1)$$