Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

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 $\gamma$ -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<sub>2</sub>) nanocrystals were functionalized with  $\gamma$ -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<sub>2</sub> (MPS-ZrO<sub>2</sub>) as well as its mechanical reinforcement for the PU/TPGDA matrixes was investigated. It was found that the dispersion of MPS-ZrO<sub>2</sub> nanoparticles in UV-curable formulation strongly depends on the ZrO<sub>2</sub> load, the grafting density of MPS, the composition of organic matrix and the type of monomer. A critical ZrO<sub>2</sub> load beyond which phase separation of MPS-ZrO<sub>2</sub> nanoparticles takes place exists for all cases. MPS-ZrO<sub>2</sub> 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<sub>2</sub> load of as high as 60 wt.% can be obtained, and has absolutely high refractive index of 1.78.

© 2009 Elsevier B.V. All rights reserved.

## 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.  $\gamma$ -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 tri-

\* Corresponding author. E-mail address: zhoushuxue@fudan.edu.cn (S. Zhou). acrylate (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<sub>2</sub>) nanoparticles into a UV-curable formulation which was consisted of two monomers and two oligomers. Scholz and Kaskel [7] also blended MPSfunctionalized ZrO<sub>2</sub> 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<sub>3</sub>) and silicon carbide (SiC) nanoparticles with HDDA while Schulz et al. [11] introduced MPSmodified Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> 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

<sup>0300-9440/\$ -</sup> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> nanoparticles were primarily illustrated. In this article, we focused on the dispersion behavior of MPS-functionalized ZiO<sub>2</sub> (MPS-ZrO<sub>2</sub>) 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<sub>2</sub> material has advantages of chemical inertness, excellent thermal stability, high refractive index and high hardness. The nano-sized ZrO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> nanocrystal with monodisperse particle size of 3.8 nm and 9.2 g/100 g ZrO<sub>2</sub> of organic component was inherently chemically adsorbed on the as-synthesized ZrO<sub>2</sub> nanoparticles [13].

## 2.3. Preparation of MPS-ZrO<sub>2</sub> nanoparticles dispersions

The as-synthesized ZrO<sub>2</sub> 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<sub>2</sub> nanoparticles according to the molar ratio of MPS to as-synthesized ZrO<sub>2</sub> (0.05-0.20:1) and 1.2 wt.% of ZrO2. 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<sub>2</sub> aggregates. The obtained transparent ZrO<sub>2</sub>/THF dispersions were concentrated to about 10 wt.% of ZrO<sub>2</sub> using a rotary evaporator and precipitated with fivefold volume of methanol, and then centrifuged to get the MPS-ZrO<sub>2</sub> nanoparticles. These MPS-ZrO<sub>2</sub> nanoparticles were further washed with methanol two times to remove free MPS molecules. The wet MPS-ZrO<sub>2</sub> nanoparticles were dispersed in THF again to form a MPS-ZrO<sub>2</sub>/THF dispersion with 15 wt.% of ZrO<sub>2</sub> concentration.

#### 2.4. Preparation of UV-curable nanocomposite coatings

MPS-ZrO<sub>2</sub>/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 vacuumdried overnight in an oven with temperature of 50 °C to remove all THF. The dispersion of MPS-ZrO<sub>2</sub> 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<sup>2</sup>, 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  $6^{\circ}$  to  $3^{\circ}$  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 ( $\Delta T$ ) was calculated by equation:

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

The lower value of  $\Delta T$  means a better scratch resistance of the coatings. Nano-scratch test was conducted using a Nano Indenter XP system (MTS Systems Co., Ltd., USA). A Berkovich diamond tip with a diameter of 2  $\mu$ m was used. An initial surface profile of the samples was detected by a pre-scan procedure with a minimum load of 0.1 mN. After that, the tip was pushed with increasing load from 0 to 40 mN into the sample, and moved with a constant velocity of 10 mm/s. The surface profile was recorded by a depth sensor. A post-scan was performed to determine the deformation recovery and the residual depth of the scratch after the diamond tip was removed. Five parallel scratches were carried out for each sample and average values were adopted.

The refractive index of the coatings was measured by a variable angle ellipsometer (UVISEL, Horiba Jobin Yvon Co., Ltd., France) and with a fixed wavelength of 633 nm.

# 3. Results and discussion

# 3.1. Dispersion behavior of MPS-ZrO<sub>2</sub> nanoparticles

Because of the high refractive index of ZrO<sub>2</sub> nanoparticles, its dispersion behavior in UV-curable coatings could be easily revealed from the optical transmission change of the nanocomposites. Our previous works [15,16] indicated that completely transparent UV-cured polymer/ZrO<sub>2</sub> nanocomposite coatings generally mean the homogeneous dispersion of ZrO<sub>2</sub> nanoparticles at primary particle size level. Whereas, transparency reduction of the nanocomposite coatings corresponds to the occurrence of ZrO<sub>2</sub> aggregation. The lower the transparency of the nanocomposite coatings is, the more serious the ZrO<sub>2</sub> aggregation is. Since MPS-ZrO<sub>2</sub> nanoparticles can participate in photopolymerization, its dispersion state does not change after photopolymerization. Thus, the optical transmission of the UV-cured nanocomposites was mainly adopted to illustrate the dispersion behavior of MPS-ZrO<sub>2</sub> nanoparticles in the corresponding UV-curable precursors herein.

#### 3.1.1. Effect of the amount of MPS grafted

Our previous researches on the dispersions of MPS-ZrO<sub>2</sub> nanoparticles in pure PU oligomer [15] or PU/isobornyl acrylate/HDDA [16] have demonstrated that the amount of MPS used is critical for the phase separation of ZrO<sub>2</sub> nanoparticles in the coatings and hence the transparency of the nanocomposite coatings. Herein, MPS-ZrO<sub>2</sub> nanoparticles prepared at different molar ratios of MPS/ZrO2 were introduced into a new UV-curable formulation, that is, PU/TPGDA mixture with weight ratio of 40:60 (PU/TPGDA46). Fig. 1 displays the transparency of the nanocomposite coatings. At low ZrO<sub>2</sub> content (<25 wt.%), the nanocomposite coatings have comparable transparency as that of pure polymer coating, regardless of the molar ratio of MPS/ZrO<sub>2</sub> and the ZrO<sub>2</sub> load. However, when the ZrO<sub>2</sub> load is beyond a certain value, the transparency of the nanocomposites quickly reduces with increasing ZrO<sub>2</sub> load. The dispersion of MPS-ZrO<sub>2</sub> nanoparticles in the nanocomposite prepared at 0.2:1 of MPS-to-ZrO<sub>2</sub> molar ratio was typically observed by TEM, as shown in Fig. 2. It can be seen that the nanoparticles are homogeneously dispersed at primary particle size level in the films at 10, 20 and 30 wt.% of ZrO<sub>2</sub> content. As ZrO<sub>2</sub> content was increased up to 35 wt.%, the ZrO<sub>2</sub> agglomerates were germinated (see Fig. 2d). Comparing Fig. 1 with 2, it is found that utilization of the optical transmission of nanocomposite to indicate the dispersion state of ZrO<sub>2</sub> nanoparticles would be indeed reasonable. The ZrO<sub>2</sub> load beyond which the optical transparency of the nanocomposites begins to decline could be regarded as the critical ZrO<sub>2</sub> load for the phase separation of MPS-ZrO<sub>2</sub> nanoparticles.

Fig. 1 shows that the critical  $ZrO_2$  loads in PU/TPGDA46 precursor are about 25, 25, 30, and 35 wt.% at MPS-to- $ZrO_2$  molar ratios



**Fig. 1.** Effect of molar ratio of MPS/ZrO<sub>2</sub> on the transparency of PU/TPGDA46-based nanocomposite coatings.

of 0.20:1, 0.15:1, 0.10:1 and 0.05:1, respectively. Namely, the critical ZrO<sub>2</sub> load increases as the molar ratio of MPS/ZrO<sub>2</sub> decreases, which is similar to our findings in other two UV-curable precursors [15,16]. The critical ZrO<sub>2</sub> load in nanoparticle dispersion is analogous to the critical volume fraction to produce phase separation in polymer blend or polymer solution, and thus could be expected by Flory–Huggins theory [24]. Unfortunately, the Flory–Huggins interaction parameters of PU/MPS-ZrO<sub>2</sub>, TPGDA/MPS-ZrO<sub>2</sub>, and PU/TPGDA systems are unknown, so prediction of the absolute critical ZrO<sub>2</sub> load is rather difficult.

Fig. 1 also indicates that when the ZrO<sub>2</sub> load exceeds the critical load the phase separation of MPS-ZrO<sub>2</sub> nanoparticles depends on the molar ratio of MPS/ZrO<sub>2</sub>. The higher the molar ratio of MPS/ZrO<sub>2</sub> is, the lower the transparency of the nanocomposite coatings is, that is, the more seriously the phase separation of MPS-ZrO<sub>2</sub> nanoparticles occurs. In other words, relatively better dispersion of MPS-ZrO<sub>2</sub> nanoparticles in PU/TPGDA46 precursor is achieved at lower grafting density of MPS. It is converse to the conventional viewpoint that high amount of MPS attached is benefit for the dispersion of nanoparticles in organic matrix. The reason lies in the higher molecular weight of PU/TPGDA46 precursor relative to the attached MPS segments (molecular weight: 127 g/mol if it is attached based on  $T^3$  mode). As wet brush theory points out, dense polymer brushes are wetted by polymer matrix only when the molecular weight of the polymer brush equals (and is greater than) that of the polymer matrix. That theory has been successfully adopted to theoretically explain the dispersion of polymer-grafted nanoparticles in polymer matrix, such as polystyrene (PS)-grafted gold nanoparticles in PS or poly(ethylene oxide)-grafted gold nanoparticles in poly(ethylene oxide) [25], PS-grafted silica nanoparticles in PS homopolymer [26], and PMMA-grafted magnetic nanoparticles in PMMA homopolymer and poly(styrene-b-methyl methacrylate) copolymer [27]. In our cases, MPS-ZrO<sub>2</sub> nanoparticles can still be well dispersed in PU/TPGDA46 precursor at low ZrO<sub>2</sub> content although the molecular weight of matrix is higher than the MPS brush. It suggests that MPS-ZrO<sub>2</sub> nanoparticles can be wetted to some extent by PU/TPGDA46 precursor, which should be due to the voids in the MPS brush. At lower grafting density of MPS, the MPS brush has relatively larger voids that are more easily penetrated by the organic precursor molecules, which provides better compatibility between nanoparticles and organic matrix and thus better dispersion of nanoparticles. Similar phenomenon was also observed by Corbierre et al. [25] for the dispersion of PS-grafted gold nanoparticles in PS. Therefore, the disper-



Fig. 2. TEM images of PU/TPGDA46-based nanocomposite films with ZrO2 content of (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, and (d) 35 wt.%. (Molar ratio of MPS/ZrO2: 0.2:1.)

sion behavior of nanoparticles with MPS brush in UV-curable formulations could be qualitatively expected by the wet brush theory.

#### 3.1.2. Effect of the weight ratio of PU/TPGDA

Fig. 3 shows the effect of PU-to-TPGDA weight ratio on the transparency of nanocomposite coatings as function of ZrO<sub>2</sub> load. The critical ZrO<sub>2</sub> load remarkably decreases as the molar ratio of PU/TPGDA increases. Only 18 wt.% of critical load was reached for PU/TPGDA82 precursor while 60 wt.% of critical load was attained for pure TPGDA. It is obvious that TPGDA has better compatibility with MPS-ZrO<sub>2</sub> nanoparticles than PU oligomer. This phenomenon could still be explained by the wet brush theory. That is, the molecular weight of UV-curable precursor is mainly responsible for the different dispersion behaviors of MPS-ZrO<sub>2</sub> nanoparticles. The organic precursor containing higher amount of PU oligomer possesses higher average molecular weight and thus is more difficult to wet the MPS-ZrO<sub>2</sub> nanoparticles. Poorer wettability means poorer compatibility between MPS-ZrO<sub>2</sub> nanoparticles and organic matrix, leading to easier phase separation of MPS-ZrO<sub>2</sub> nanoparticles. Hence, the molecular weight of UV-curable precursor also greatly impacts the dispersion of MPS-functionalized nanoparticles, just like it works on the dispersion of polymer-bonded nanoparticles in polymer matrix.

On the other aspect, Fig. 3 demonstrates that transparent UVcurable nanocomposite coatings in wide range of  $ZrO_2$  content can be achieved via addition of monomer. It means that the optical properties, for example, refractive index, of the nanocomposite can be adjusted in a wide range and meanwhile the transparency of the coatings is not influenced.

# 3.1.3. Effect of the type of monomer

Besides TPGDA, dispersions of MPS-ZrO<sub>2</sub> nanoparticles in other two monomers, TMPTA and HDDA, were studied. Fig. 4 compares the optical transmission of nanocomposite coatings prepared from different monomers. It is clearly seen that the transparency of nanocomposite coatings does not deteriorate at relatively low ZrO<sub>2</sub> load and quickly declines at high ZrO<sub>2</sub> load as the ZrO<sub>2</sub> load increases for all three monomers. The critical ZrO<sub>2</sub> loads are about 40, 50, and 60 wt.% for TMPTA, HDDA, and TPGDA, respectively, which are much higher than those in PU/TPGDA46 and PU/TPGDA82 precursors. This phenomenon further confirms that the dispersion of MPS-ZrO<sub>2</sub> nanoparticles in monomers is better than that in PU oligomer, regardless of the chemical structure



Fig. 3. The transparencies of different organic matrix-based nanocomposite coatings as a function of  $ZrO_2$  content. (Molar ratio of MPS/ $ZrO_2$ : 0.2:1.)

of monomer. Nevertheless, the existence of the critical load suggests that the MPS-ZrO<sub>2</sub> nanoparticles is also not intermiscible with monomers, which could be still attributed to the higher molecular weight of the monomers (TMPTA, 296 g/mol, HDDA, 226.3 g/mol and TPGDA, 300 g/mol) relative to the attached MPS species (127 g/mol). However, Fig. 4 shows that bigger molecule of monomer does not always correspond to lower critical ZrO<sub>2</sub> load. For example, the biggest molecule, TPGDA, possesses the highest critical ZrO<sub>2</sub> load. Therefore, the chemical structure should be the crucial factor influencing on the dispersion behavior of MPS-ZrO<sub>2</sub> nanoparticles when organic monomer is used as the dispersing medium.

# 3.2. Mechanical properties of nanocomposite coatings

Enhanced mechanical properties of UV-curable coatings via addition of MPS-ZrO<sub>2</sub> nanocrystals have been demonstrated in our previous reports [15,16]. However, how the mechanical reinforcement depends on the type of organic matrix is not clear. In this article, the pendulum hardness and scratch resistance of the ZrO<sub>2</sub>-based nanocomposite coatings with different weight ratios of PU/TPGDA was determined so as to reveal the efficiency of mechanical improvement by ZrO<sub>2</sub> nanoparticles for different organic matrixes. To eliminate the influence of nanoparticle aggregates, only transparent nanocomposites were adopted.



**Fig. 4.** The transparencies of different monomer-based nanocomposite coatings as a function of ZrO<sub>2</sub> content. (MPS-to-ZrO<sub>2</sub> molar ratio: 0.20:1.)



**Fig. 5.** The pendulum hardness of the samples with different ZrO<sub>2</sub> contents. (Symbol: the determined value; Solid line: linear fitting curve.)

#### 3.2.1. Pendulum hardness

Fig. 5 shows the pendulum hardness (Koenig hardness) of the nanocomposites as a function of ZrO<sub>2</sub> content. It is clearly seen that the pendulum hardness linearly increases with increasing ZrO<sub>2</sub> content for all nanocomposites. However, for TPGDA-based nanocomposite coatings, the change of hardness has two linear stages, one at low ZrO<sub>2</sub> content level and another at high ZrO<sub>2</sub> content level. Table 1 summarizes their linear fitting equations. The slope falls as the amount of PU oligomer in the formulation increases, suggesting that MPS-ZrO2 nanoparticles are less efficient to enhance the hardness of coatings containing higher content of PU oligomer. This should be due to the low compatibility of PU oligomer with MPS-ZrO<sub>2</sub> nanoparticles. Since MPS-ZrO<sub>2</sub> nanoparticles act not only as the reinforced component for the organic matrix but also as the highly efficient crosslinker due to the multifunctional character, the cross-linking density of the transparent nanocomposite coatings increases as MPS-ZrO<sub>2</sub> nanoparticles were added [16]. Contribution of cross-linking by MPS-ZrO<sub>2</sub> nanoparticles to the enhanced hardness of the nanocomposite was ever observed in poly(methyl methacrylate)/ZrO<sub>2</sub> nanocomposites [20]. Because of the poor compatibility, the copolymerization between MPS-ZrO<sub>2</sub> nanoparticles and PU oligomer is limited, which results in low increment of cross-linking density and thus alleviates the increasing rate of hardness. Fig. 5 also shows that TPGDA-based nanocomposites have smaller slope of pendulum hardness ~ZrO2 load curve at high ZrO<sub>2</sub> load level relative to at low ZrO<sub>2</sub> load level. It should be due to the decreased contribution from the cross-linking density because the influence the cross-linking density on the hardness is alleviated when the cross-linking of the organic matrix is sufficiently high.

Due to the serious oxygen inhibition, pure TPGDA cured in air has lower hardness in comparison with PU/TPGDA46 and PU/TPGDA82. To eliminate the influence of oxygen, TPGDA-based nanocomposite coatings were also photopolymerized in the nitrogen. The hardness of the coatings markedly increases and is even much higher than the hardness of PU/TPGDA46 series. Moreover, the increasing rate of hardness is higher than PU/TPGDA46 and PU/TPGDA82 series. A second linear stage with low slope was also observed. Therefore, the efficiency for enhancing the hardness of the coating is independent on the inherent hardness of organic matrix but strongly related to the compatibility of MPS-functionalized nanoparticles with UV-curable precursor. In addition, slopes of 0.54 and 0.50 were obtained for PU/TPGDA82 series and the linear stage of the TPGDA series cured in  $N_2$  at high ZrO<sub>2</sub> load. These slopes would be close to the inherently improving efficiency of ZrO2 nanoparticles for the pendulum hard-

Table 1	
The linear equation between pendulum hardness (H) and $ZrO_2$ content ( $C_{ZrO_2}$ ) for various nanocomposite coatings.	

Organic matrix	Curing atmosphere	Linear fitting equation <sup>a</sup>
TPGDA	Air	$H = 18.2 + 1.15C_{ZrO_2}, \ 0 \le C_{ZrO_2} \le 20; \ H = 28.4 + 0.73C_{ZrO_2}, \ 0 \le C_{ZrO_2} \le 60$
PU/TPGDA46	Air	$H = 40.7 + 0.83C_{ZrO_2}, \ 0 \le C_{ZrO_2} \le 30$
PU/TPGDA82	Air	$H = 30.0 + 0.54C_{ZrO_2}, \ 0 \le C_{ZrO_2} \le 18$
TPGDA	N <sub>2</sub>	$H = 59.0 + 1.5C_{ZrO_2}, \ 0 \le C_{ZrO_2} \le 30; \ H = 95.3 + 0.50C_{ZrO_2}, \ 40 \le C_{ZrO_2} \le 60$

Note: aunit: H, second; C<sub>ZrO2</sub>, %.

ness because the increment of the cross-linking density of organic matrix was maximally restrained due to the poorest compatibility for PU/TPGDA82 precursor and the reduced influence of cross-linking density for TPGDA at high ZrO<sub>2</sub> load.

#### 3.2.2. Scratch resistance

Abrasion tests were used to simulate the anti-scratch performance of nanocomposite in real world in term of transparency reduction. The results are shown in Fig. 6. The reduction of transparency gradually decreases as the  $ZrO_2$  content increases for all nanocomposites. At 30 wt.% of  $ZrO_2$  content, TPGDA-based nanocomposite coating has only 1.1% of transparency reduction after abrasion test, indicating the excellent anti-scratch performance of the coatings. In addition, the figure illustrates that the transparency of coatings reduces more quickly for the organic matrix containing higher amount of TPGDA. This result accords with the change of pendulum hardness. Therefore, the efficiency of scratch resistant improvement by embedding  $ZrO_2$  nanoparticles could be enhanced by blending with small molecule monomer.

Nano-scratch tests were also done to evaluate the scratch resistance of the UV-cured nanocomposites. Fig. 7 displays the penetration depth profiles as well as the residual depth profiles for the samples. The serious fluctuation of the residual depth profile for PU/TPGDA46-based nanocomposite coating (Fig. 7b) is caused by the high surface roughness. Being similar to the common loaddepth profile in scratch tests, all the samples show an increase in penetration depth and residual depth as the load increased. The residual depth is much less than the penetration depth, indicating the high reflowability of the coatings. The nanocomposite coatings have lower penetration depth and lower residual depth than their corresponding organic coatings at the same applied load, in spite of the type of organic matrix. Fig. 8 displays the photographs of the sample after scratch tests. It can be clearly seen that the samples reinforced with ZrO<sub>2</sub> nanoparticles exhibit shallower troughs relative to pure polymer coatings. TPGDA-based nanocomposite



**Fig. 6.** The abrasion-induced transparency reduction of PUA/ZrO<sub>2</sub> nanocomposite films as a function of ZrO<sub>2</sub> content.

coating exhibits illegible trough (Fig. 8b), suggesting a deformation recovery close to 100%. Therefore,  $ZrO_2$  nanoparticles can improve the scratch resistance of UV-curable coatings, agreeing with the abrasion tests very well.



**Fig. 7.** Profiles of nano-scratch tests of (a) TPGDA and TPGDA-based nanocomposite coatings cured in N<sub>2</sub>, (b) PU/TPGDA46 and PU/TPGDA46-based nanocomposite coatings cured in air, and (c) PU/TPGDA82 and PU/TPGDA82-based nanocomposite coatings cured in air. (The ZrO<sub>2</sub> content in the nanocomposite coatings is 10 wt.%.)

# Author's personal copy

K. Xu et al. / Progress in Organic Coatings 67 (2010) 302-310



(e) PU/TPGDA28 coating

(f) PU/TPGDA28/ZrO2 coating

Fig. 8. Photographs of the surface of the samples after nano-scratch tests. (The ZrO<sub>2</sub> content in the nanocomposite coatings and the curing condition are the same as Fig. 7.)

The efficiency (*E*) of scratch resistant improvement via addition of  $ZrO_2$  nanoparticles was evaluated by the reflow capability of nanocomposite coatings ( $R_N$ ) dividing the reflow capability of pure organic coatings ( $R_P$ ). It can be calculated as follows:

$$R_{\rm N} = \frac{d_{\rm Np} - d_{\rm Nr}}{d_{\rm Np}} \tag{3}$$

$$R_{\rm P} = \frac{d_{\rm Pp} - d_{\rm Pr}}{d_{\rm Pp}} \tag{4}$$

$$E = \frac{R_{\rm N}}{R_{\rm P}} \tag{2}$$

where  $d_{\text{Np}}$ ,  $d_{\text{Nr}}$ ,  $d_{\text{Pp}}$  and  $d_{\text{Pr}}$  denote the penetration depth and the residual depth for pure organic coating and nanocomposite coat-



**Fig. 9.** Effect of the type of organic matrix on the efficiency of scratch resistant improvement for UV-cured coatings. (The ZrO<sub>2</sub> content in the nanocomposite coatings and the curing condition are the same as Fig. 7.)

ing, respectively. The calculated efficiency as a function of the applied load and their smoothed curves are plotted in Fig. 9. Most of efficiency is higher than one for all three organic matrixes-based coatings during the applied load range. Efficiency less than one is only observed for PU/TPGDA46-based coating at applied load lower than 10 mN and PU/TPGDA82-based coating at applied load lower than 1 mN. It means that the nanocomposite coatings have better reflowability than their corresponding organic coatings, which further demonstrates the improvement of scratch resistance by ZrO<sub>2</sub> nanoparticles. The figure also shows that the efficiency of TPGDA-based coating is higher than that of PU/TPGDA82-based coating. This result illustrates that higher amount of TPGDA in the UV-curable coatings leads to higher efficiency of scratch resistant improvement, being consistent with the pendulum hardness tests and abrasion tests. But abnormal trend was found for PU/TPGDA46based coating. It may presumably be resulted from the higher roughness of the sample, as seen in Fig. 8d.

#### 3.3. Refractive index of nanocomposite coatings

TPGDA-based nanocomposite coatings with the highest critical  $ZrO_2$  load were typically employed to examine the influence of  $ZrO_2$  content on the refractive index of the coating. Fig. 10 shows the refractive index of TPGDA/ZrO<sub>2</sub> nanocomposite coatings as a function of  $ZrO_2$  content. As expected, the refractive index of the



Fig. 10. Refractive indices of TPGDA/ZrO<sub>2</sub> nanocomposite coatings as a function of  $ZrO_2$  content.

nanocomposite coating increases with increasing ZrO<sub>2</sub> content. Refractive index of 1.78 was attained for the nanocomposite containing 60 wt.% of ZrO<sub>2</sub>. To our knowledge, it is the highest refractive index ever reported for ZrO<sub>2</sub>-based organic–inorganic nanocomposite coating. Moreover, an approximately linear relationship was found between the refractive index and the ZrO<sub>2</sub> content. Thus, the refractive index of UV-curable coatings can be easily adjusted by ZrO<sub>2</sub> content in a wide range using appropriate organic matrix.

# 4. Conclusions

Nonaqueous synthesized ZrO<sub>2</sub> nanoparticles functionalized with MPS can be dispersed at primary particle level in the UVcurable nanocomposite coatings with low ZrO<sub>2</sub> content. However, phase separation of MPS-ZrO<sub>2</sub> nanoparticles, depending on the ZrO<sub>2</sub> load, the grafting density of MPS, the composition of organic matrix and the type of monomer, takes place beyond a certain critical ZrO<sub>2</sub> load. Lower grafting density of MPS and higher amount of monomer in the UV-curable formulation are benefit for the compatibility between MPS-ZrO<sub>2</sub> and organic matrix, and thus, leading to higher critical ZrO<sub>2</sub> load. Among the monomers (HDDA, TMPTA, TPGDA), TPGDA has the best compatibility with MPS-ZrO<sub>2</sub> nanoparticles. A critical ZrO<sub>2</sub> load of 60 wt.% could be obtained in pure TPGDA coatings. All dispersion behavior of MPS-ZrO<sub>2</sub> nanoparticles in UV-curable coatings could be qualitatively expected by Flory–Huggins theory and wet brush theory.

Pendulum hardness tests, abrasion tests and nano-scratch tests demonstrate the mechanical reinforcement of MPS-ZrO<sub>2</sub> nanoparticles for all UV-curable coatings involved. Moreover, the efficiency of mechanical improvement is not related to the inherent mechanical properties of the organic matrix but strongly depends on the amount of TPGDA in the organic matrix (PU/TPGDA mixture). That is, the higher the amount of TPGDA is, the more efficient the improvement of mechanical properties (pendulum hardness and scratch resistance) via addition of MPS-ZrO<sub>2</sub> nanoparticles is, despite the fact that the MPS-ZrO<sub>2</sub> nanoparticles are dispersed at primary particle size level in all organic matrixes. The quicker increase of cross-linking density, resulting from the better compatibility of MPS-ZrO<sub>2</sub> nanoparticles with organic matrix, may contribute to the higher efficiency of mechanical reinforcement. In addition, transparent nanocomposite coating with refractive index of as high as 1.78 was obtained using pure TPGDA as the organic matrix. It is convinced that the above dispersion law of MPS-functionalized nanoparticles and the efficiency of mechanical reinforcement should also work on the nanocomposites using nanopowder as the filler.

# Acknowledgements

We are grateful for the financial support from the New Century Excellent Talent Foundation of the Ministry of Education of China (NCET-07-0210), National Nature Science Foundation (No. 50703005) of China and Shanghai Leading Academic Discipline Project (No. B113).

## References

- F. Bauer, H.-J. Gläsel, U. Decker, H. Ernst, A. Freyer, E. Hartmann, V. Sauerland, R. Mehnert, Prog. Org. Coat. 47 (2003) 147.
- [2] F. Bauer, R. Flyunt, K. Czihal, M.R. Buchmeiser, H. Langguth, R. Mehnert, Macromol. Mater. Eng. 291 (2006) 493.
- [3] F.S. Li, S.X. Zhou, G.X. Gu, B. You, L.M. Wu, J. Appl. Polym. Sci. 96 (2005) 912.
- [4] F.S. Li, S.X. Zhou, B. You, L.M. Wu, J. Appl. Polym. Sci. 99 (2006) 1429.
- [5] F.S. Li, S.X. Zhou, L.M. Wu, J. Appl. Polym. Sci. 98 (2005) 2274.
- [6] V. Landry, B. Riedl, P. Blanchet, Prog. Org. Coat. 61 (2008) 76.
- [7] S. Scholz, S. Kaskel, J. Colloid Interface Sci. 323 (2008) 84.
- [8] N. Lu, X.D. Lu, X. Jin, C.L. Lu, Polym. Int. 56 (2007) 138.

# Author's personal copy

K. Xu et al. / Progress in Organic Coatings 67 (2010) 302-310

- [9] W. Posthumus, J. Laven, G. de With, R. van der Linde, J. Colloid Interface Sci. 304 (2006) 394.
- [10] B. Mcmorrow, R. Chartoff, P. Lucas, W. Richardson, P. Anderson, Compos. Interfaces 13 (2006) 801.
- [11] H. Schulz, B. Schimmoeller, S.E. Pratsinis, U. Salz, T. Bock, J. Dent. 36 (2008) 579.
- [12] S.X. Zhou, G. Garnweitner, M. Niederberger, M. Antonietti, Langmuir 23 (2007) 9178.
- [13] K.Q. Luo, S.X. Zhou, L.M. Wu, G.X. Gu, Langmuir 24 (2008) 11497. [14] G. Garnweitner, L.M. Goldenberg, O.V. Sakhno, M. Antonietti, M. Niederberger,
- J. Stumpe, Small 3 (2007) 1626. [15] S.X. Zhou, L.M. Wu, Macromol. Chem. Phys. 209 (2008) 1170.
- [16] K. Xu, S.X. Zhou, L.M. Wu, J. Mater. Sci. 44 (2009) 1613.
- [17] A. Rosidian, Y.J. Liu, R.O. Claus, Adv. Mater. 10 (1998) 1087.
- [18] M. Sangermano, B. Voit, F. Sordo, K.J. Eichhorn, G. Rizza, Polymer 49 (2008) 2018.

- [19] S. Lee, H.J. Shin, S.M. Yoon, D.K. Yi, J.Y. Choi, U. Paik, J. Mater. Chem. 18 (2008) 1751.
- [20] Y.O. Hu, S.X. Zhou, L.M. Wu, Polymer 50 (2009) 3609.
  [21] K.Q. Luo, S.X. Zhou, L.M. Wu, Thin Solid Films 517 (2009) 5974.
  [22] H.W. Zhou, J. Ma, Z.C. Li, C.H. Chen, Chem. J. Chin. Univ. 26 (2005) 1582 (in Chinere).
- Chinese).
- [23] A. Dey, S.K. De, J. Appl. Polym. Sci. 105 (2007) 2225.
   [24] M.J. He, W.X. Chen, X.X. Dong, Polymer Physics, Fudan University Press, Shang-
- hai, 1990, pp. 139-141, 191-194 (in Chinese). [25] M.K. Corbierre, N.S. Cameron, M. Sutton, K. Laaziri, R.B. Lennox, Langmuir 21
- (2005) 6063. [26] Q. Lan, L.F. Francis, F.S. BATES, J. Polym. Sci. Part B: Polym. Phys. 45 (2007)
- 2284. [27] C. Xu, K. Ohno, V. Ladmiral, R.J. Composto, Polymer 49 (2008) 3568.

310