

Re-dispersible ZrO₂ nanopowders for transparent high RI nanocomposite

S.H. Wang, Y.S. Sun, A.S.T. Chiang*

* Dept. Chem. Mater. Eng., National Central University
300 Junda Rd., ChungLi, 32054 Taiwan ROC. stchiang@cc.ncu.edu.tw

ABSTRACT

Previous products of nano-ZrO₂ usually come in the form of transparent sol. The solvent accompanied may not be compatible with the target polymer system, when they are to be used in organic/inorganic composite. We have developed a low temperature hydrothermal crystallization process to produce nano-ZrO₂ clusters. The product could be made as re-dispersible fine powders after carboxylic acid modification. By “re-dispersible”, we are referring to the situation that a slightly bluish but transparent sol containing more than 10 wt % of ZrO₂ could be prepared by adding the powder into a solvent or monomer followed by a few minutes of ultrasonic agitation. The most interesting surface modifiers are methacrylic acid (MA). A dispersion of MA modified ZrO₂ could be directly coated on substrate and UV cured into transparent film with refractive index as high as 1.76. It could also be blended with PUA for the preparation of a hard film on PMMA.

Keywords: ZrO₂, high refractive index, dispersion, nanocomposite

1 INTRODUCTION

Zirconia (ZrO₂), with its chemical inertness, thermal stability, high hardness and refractive index (RI~2.2) is an ideal inorganic for the fabrication of high RI organic-inorganic nanocomposite. ZrO₂ nanoparticles smaller than 10 nm have been produced by Sumitomo Osaka Cement Co. [1,2] with the hydrothermal route, or by Niederberger's group [3,4] with the benzyl alcohol route. However, they were usually supplied as dispersion or have to be processed immediately after synthesis. For practical applications, it is more desirable to have nano-ZrO₂ as re-dispersible powders.

We [5,6] have recently developed a low temperature hydrothermal crystallization process to produce nano-ZrO₂, from which re-dispersible powders could be prepared after carboxylic acid modification. By “re-dispersible”, we are referring to the situation that a slightly bluish but transparent sol containing more than 10 wt % of ZrO₂ could be prepared by simply adding the powder into a solvent followed by a few minutes of ultrasonic agitation. SAXS, SANS and DLS analysis showed that the primary particle size of the dispersed ZrO₂ was about 5 nm. A small fraction of the particles appeared as 10 to 15 nm size clusters depending on the ligand-solvent pair.

The most promising surface modifiers are methacrylic acid (MA) and butyric acid (BA). With ~ 30 wt% organics on the surface, the powder became dispersible in toluene, benzene, etc., as well as in MMA and Alkyl Glycidyl ether. Transparent nanocomposite with PU-acrylate have been prepared. With increasing ZrO₂ loading from zero to 52 wt%, the thermal degradation temperature increased from 251 to 365°C, the indent hardness from 173 to 478 MPa, the reduced modulus from 1.36 to 6.70 GPa. Most importantly, the refractive index increased from 1.51 to 1.63, while the transmittance at 450 nm only dropped by 2.5 % for a 25 μm thick film. A transparent composite can also be produced from the MA modified ZrO₂ without adding monomer. At low particle concentration, only intra-cluster reaction occurred in a dispersed sol. Inter-cluster polymerization became dominating and multi-aggregate clusters were formed with increasing particle concentration. The partially cross linked clusters could be used to produce transparent films. A transparent film could also be prepared by depositing ZrO₂@Ma nanoparticles directly on a substrate with UV curing. With no extra monomer added, a nanocomposite film with refractive index as high as 1.76 could be achieved. This is the highest value reported on polymer-ZrO₂ nanocomposite.

2 EXPERIMENTALS

The ZrO₂ employed in this study was prepared from the low temperature hydrothermal reaction of zirconium hydroxide according to our previous research [6]. Briefly, 64.4 g of ZrOCl₂·8H₂O was dissolved in 58 g of DI water, to which 2.1 g of MA was added. The mixture was stirred for 30 minutes at RT to dissolve the ZrOCl₂ until a pale green transparent solution resulted. It was then aged at 110°C for 24 h before neutralized in a buffer solution with 4 M NaOH. The buffer solution consists of 10 g NH₄HCO₃, 11 g of TEA in 800g of DI water. The neutralization was done at a fixed pH value of 10 by controlling the addition rates of the acid and base. The buffered mixture remained clear during the whole neutralization process if the neutralization step last for more than 3 hrs. The neutralization product was collected by flocculating with acid (HCl) and washing away the excess electrolytes. The washed product was adjusted to 6 wt% and a pH value of 11.5, and subjected to hydrothermal reaction at 110 °C for 15 hrs. The reaction product was centrifuged and washed with acetone, then vacuum-dried into aqueous dispersible ZrO₂ nanocrystal powders. Carboxylic acid modification

was conducted by adding these powders into aqueous acid solution and stirred at 60 °C for 30 minutes. A series of carboxylic acids, acetic (HAc), propionic (PA), butyric (BA), acrylic (AA), methacrylic (MA), Benzoic (BZ), oleic (OA), and linoleic acid (LOA) was tested. The precipitates were centrifuged and repeatedly washed, then vacuum-dried at 80 °C to obtain solvent re-dispersible powders.

The MA modified ZrO₂ (MA/ZrO₂) formed a transparent dispersion in THF, to which the PUA resin composition was added and ultrasonic agitated for 5 minutes. The resin composition was acrylic acid (ECOH Chemical company), dipentaerythritol pentaacrylate (sartomer SR-399), aliphatic urethane diacrylate (cognis PHOTOMER[®]6210) and 2-hydroxy-2-methyl-propio-phenone (Ciba, Darocur[®]1173) at 4/3/1/1 ratio by weight. The composite was coated on a PMMA substrate with doctor blade and cured with 365 nm UV for 3~5 seconds. The cured films were 12~34 μm thick depend on the composition. For comparison, the photo-initiator was also added to the THF dispersion of MA modified ZrO₂ and directly spin coated on Si wafer. It took six coating/UV cycles to reach a film thickness of 105 nm.

3 RESULTS AND DISCUSSIONS

The dispersion of the above carboxylic acid modified ZrO₂ in various solvent and monomers was tested, and the results were tabulated in Table 1. In here, BAc is Butyl acetate. MMA is methyl methacrylate. IOA stands for isooctyl acrylate. IBA stands for isobornyl acrylate. From this table, we can observe that only the acetic acid modified powder was hydrophilic thus can be dispersed in water and low alcohols. Propionic and butyric modification made the powder less hydrophilic. They were then dispersible in aprotic solvent such as THF and BAc. Chloroform seems to be the best solvent for all modifications except acetic acid. For the dispersion in monomers such as MMA, IBA and IOA, either oleic acid or butyric acid modification worked.

	H ₂ O	MEOH	EtOH	BAc	THF	CHCl ₃	MMA	IBA	IOA
HAc	O	O	O	X	X	X	X	X	X
PA	X	X	X	X	O	O	X	X	X
BA	X	X	X	O	O	O	O	O	X
AA	X	X	X	X	O	O	X	X	X
MA	X	X	X	X	O	O	O	X	X
BZ	X	X	X	X	X	O	X	-	-
OA	X	X	X	O	X	O	X	O	O
LOA	X	X	X	-	X	O	X	-	-

Table 1: The dispersion of modified ZrO₂ in various solvents. X means non-dispersible. O stands for transparent bluish dispersion at 10 wt%.

Figure 1 demonstrate the MA modified ZrO₂ powder and the transparent dispersion of this powder in selected

solvents not listed in Table 1. For nonpolar solvents such as benzene and toluene, only those modified by MA, OA and LOA formed a transparent dispersion. The transparency of the dispersion was further characterized by the spectroscopy as demonstrated in Figure 2. In here, we find that the transmittance at 600 nm of a chloroform dispersion did not reduce drastically with increasing loading of the solid. The MA modification produced transparent sol in benzene, toluene as well as hexane.



Figure 1: The MA modified ZrO₂ nanoparticles in dried powder form and its 10 wt% dispersion in selected solvents.

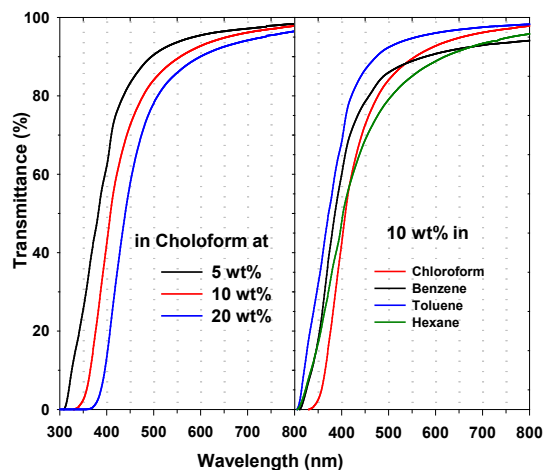


Figure 2: The spectral transmittance of the dispersion in 10 mm liquid cell

The TEM picture of the MA modified nanoparticles can be observed in Figure 3. From the picture, we can count the particle size distribution is centered at ~ 10 nm. This is in consistent with the DLS analysis results. However, the particles observed in this TEM are not the primary particles. Rather, according to the SAXS and SANS analysis[7], they formed cluster aggregates with a fractal dimension of 2.2-

2.5. Only in the case of LOA modification and in chloroform was the ZrO_2 dispersed as primary core-shell particles. The size of the core-shell primary particles was about 5 nm.

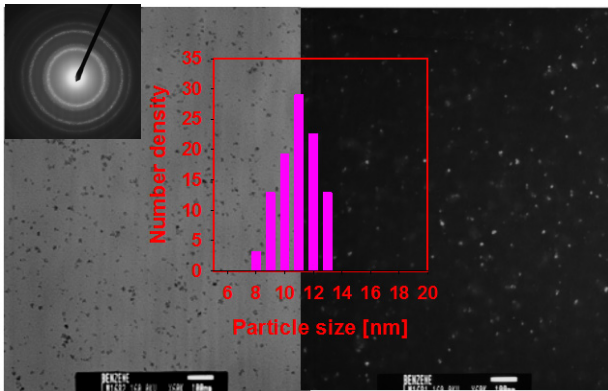


Figure 3: Bright and dark field TEM image of MA modified ZrO_2 nanoparticles dispersed in benzene. The insert is the SAED image and the counted size distribution.

The clustering of the modified ZrO_2 nanoparticles can be more clearly observed in the HRTEM picture showed in Figure 4. Here we found a large cluster of MA/ ZrO_2 composite, possibly formed during the drying of the TEM sample. Interestingly, the lattice fringe of the ZrO_2 crystals seemed to align across two domains in a cluster. Therefore, the clustering might not have formed after the surface modification. Rather, they could have formed in the hydrothermal process. If this was the case, the MA chelating would occur only on the accessible surface of the cluster, and formed an organic overlay on the cluster.

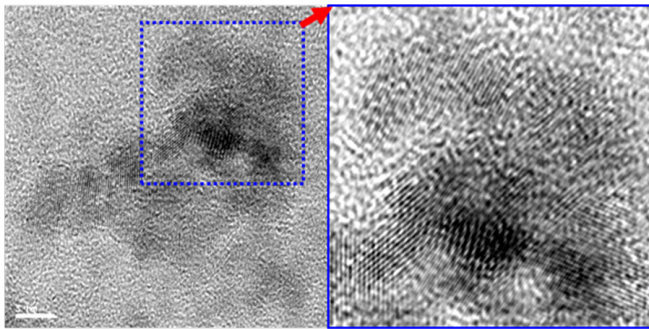


Figure 4: HRTEM picture showing the clustering of modified ZrO_2 nanoparticles. The bar in the left is 5 nm.

The fact that our ZrO_2 was not distinct nanoparticle does not preclude its applications in transparent nanocomposite. As we have seen, the dispersion of these clusters was highly transparent in the correct solvent. The reasons for the transparency are two-fold. First, the primary ZrO_2 particles, or the scattering center, was indeed smaller

than 5 nm. Second, the cluster was not a dense spherical particle, but a loosely linked fractal structure. The organic/inorganic weight ratio in this dispersible nano-cluster was about 30/70. According to the effective medium theory, the average refractive index would be about 1.75. The scattering from a fractal structure with $RI \sim 1.75$ would not be excessive.

The MA/ ZrO_2 composite clusters have an additional benefit for it is possible to induce the chain reaction between the vinyl groups. Since it was found compatible with several important acrylate monomers, the reaction of these vinyl groups with the acrylate monomer is also expected. One can easily blend these clusters with acrylate or other polymers to prepare a transparent composite. Therefore, the MA/ ZrO_2 powder might be considered as the master batch for the formulation of organic/inorganic composite. Only in this case, the inorganic fraction in the mater batch is very high, and is in the form of fine powder.

We have tested the blending of these clusters with high molecular weight PMMA, and found that transparent pieces thicker than mm could be produced after hot press even with 10 wt% of ZrO_2 . Transparent hard coat film on PMMA was also made by blending the MA/ ZrO_2 clusters into a PU/acrylate recipe. The addition of ZrO_2 into the film increased the RI of the hard coat, as can be predicted by the effective medium theory. As demonstrated in Figure 5, a loading of 53 wt% ZrO_2 could be achieved, leading to a RI of 1.63. This figure also showed that the MA/ ZrO_2 composite clusters, when directly coated on substrate and UV cured with an appropriate photoinitiator, resulted in a transparent film with RI of 1.76.

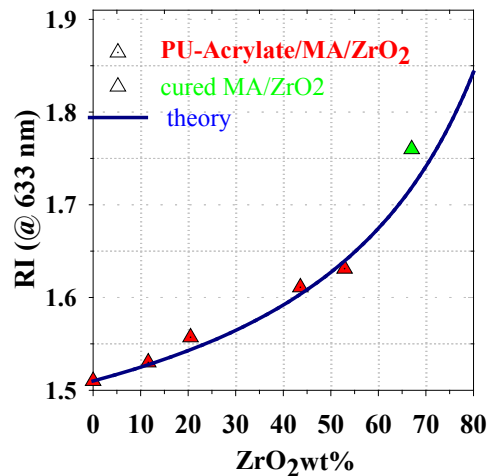


Figure 5: Measured refractive index of PUA/ ZrO_2 hard film and that of the film made directly with MA/ ZrO_2 clusters.

The increase of RI might be predictable, but the increase of mechanical property of the PUA composite as measured by nano-indentation (Hysitron TI 950 TriboIndenter™ with a diamond Berkovich probe) was better than expected.

Given in Figure 6 is the hardness and the elastic modulus of the composite films. The increase of hardness and modulus was linear up to 20 wt% ZrO₂, and at a smaller slope up to 45 wt%. The good mechanical strength suggested that there was no phase separation nor the formation of large clusters. The fact that the vinyl group on MA could react with the acrylate could have provided a strong bonding between the MA/ZrO₂ cluster with the matrix. Nevertheless, if the MA/ZrO₂ clusters aggregated during the polymerization, the mechanical strength would still be hampered. It is anticipated that the diffusion of the MA/ZrO₂ clusters in the monomer would be slower than individual nanoparticle. Consequently, it will be more difficult for the clusters to form a dense aggregate than the individual nanoparticles. However, we could not rule out the possibility that the cluster might grow larger and eventually become a span cluster when the solvent is evaporated. If this did happen, this span cluster would become an inorganic network that, when fill by the organic matrix, provides a better strength to the film. Unfortunately, we are yet to conduct SAXS on the PUA composite to determine the cluster size in the cured film to prove this conjecture.

REFERENCES

- [1] Lee S, Shin HJ, Yoon SM, Yi DK, Choi JY, Paik U., *J Mater Chem*;18(15):1751-5, 2008
- [2] Otsuka T, Chujo Y., *Polymer*;50(14):3174-81, 2009.
- [3] Garnweitner G, Goldenberg LM, Sakhno OV, Antonietti M, Niederberger M, Stumpe J., *Small*;3(9):1626-32, 2007.
- [4] Zhou SX, Garnweitner G, Niederberger M, Antonietti M., *Langmuir*;23(18):9178-87, 2007.
- [5] Chen CW, Yang XS, Chiang AST, *J. Taiwan Inst. Chem. Eng.*;40(3):296-301, 2009.
- [6] Chiang AST, Yang X, Chen C; US patent 7,393,518. 2008.
- [7] Wang SH, Sun YS, Chiang AST, Hung HF, Chen MC, Wood K., Submitted to. *J Phys Chem C*, 2011.

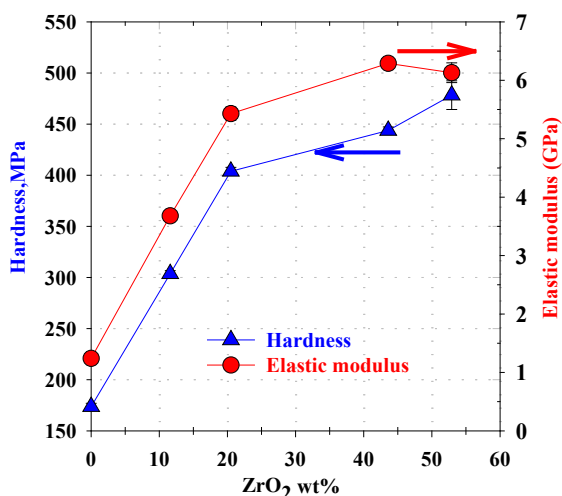


Figure 6: Hardness and elastic modulus of the PUA/ZrO₂ nanocomposite films.

4 CONCLUSIONS

Organic/ZrO₂ composite clusters less than 15 nm have been prepared as powders that can be re-dispersible in various solvents and monomers. The fact that they were not distinct core/shell nanoparticles did not hamper their application as fillers for transparent high refractive index nanocomposite. In the contrary, the fractal structure of the cluster might have reduced the diffusion and aggregation of the inorganic domains thus prevent the micro phase separation. Consequently, a marked increase of the elastic modulus and hardness of the resulted PUA composite was observed.