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Hansen solubility parameter analysis on the dispersion of zirconia nanocrystals

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ABSTRACT

Nanoparticle dispersible in a broad range of solvents is desirable when preparing an organic/inorganic nanocomposite. In this report, the dispersion behavior of carboxylate-grafted zirconia nanoparticle in 25 solvents covering a wide range of polarity was analyzed based on their Hansen solubility parameters (HSP). Particles grafted with alkyl-chain longer than four carbons could only be dispersed in non-polar solvents, while that grafted with acetic acid was dispersible in polar ones. However, particle modified with methacrylic acid (MA) was compatible with both types of solvents, which was rather unexpected. Further NMR analysis showed that the carboxylate-grafted samples contained a trace amount of triethanolamine (TEA) due to the particular ZrO_2 synthesis process employed. The combination of the hydrophilic TEA ligand with the short hydrophobic tail of methacrylate broadened the range of compatible solvents from benzene to methanol. Such an extended solvent compatibility was observed previously only for nanoparticles covered with large polymer surfactants having both hydrophilic and hydrophobic groups. Achieving this with two small molecules having separate functional groups is crucial when one needs to maximize the inorganic content in a composite.

1. Introduction

The incorporation of inorganic nanoparticles into organic resins is known to improve the mechanical, thermal and optical properties of the latter. For example, SiO_2 nanoparticles have been routinely added to hard coat formulation for its scratch resistance [1]. Nano-ZnO can be employed in resins for UV shielding [2]. TiO_2 and ZrO_2 are used to increase the refractive index of LED encapsulants [3]. In all the above cases, a transparent nanocomposite is needed.

The surface of inorganic metal oxide is, in general, incompatible with organic polymers. It is difficult to disperse the nanoparticles in resin directly without causing agglomeration. When large aggregates formed, the transparency of the composite will be compromised. Therefore, nanoparticles are often grafted with organic ligand to increase its compatibility with polymers. In our previously work [4], we have modified ~5 nm ZrO_2 nanoparticles with various carboxylic acids and investigated their dispersion behavior. Depending on the modifier, transparent sol could be obtained in different solvents, despite the formation of secondary clusters around 20 nm in size.

For example, ZrO_2 particles modified with acetic acid were dispersible in water and ethanol. Those with acrylic or propionic acid were miscible with less polar THF and chloroform. Particles became compatible with non-polar solvents such as hexane, toluene and benzene when covered with long chain linoleic acid. There was, however, a puzzling fact we fail to rationalize in that report. Specifically, the particle modified with methacrylic acid (MA) was found to be dispersible in both the polar (ethanol) and the non-polar solvent (benzene, toluene). To confirm the unexpected behavior, we have expanded the number of testing solvents to 25, covering a wide range of polarity, and re-examined the solvent compatibility of the modified particles.

Solvents are frequently classified as polar/non-polar, protic/aprotic and hydrophilic/hydrophobic. However, these descriptions are qualitative, and are only in a relative sense. They are not precise enough to interpret the dispersion of nanoparticle having different surface moieties. A more specific account has been developed for the prediction of liquid miscibility based on the total cohesive energy density measured by evaporation experiments. The cohesion properties of a liquid can be described by the Hansen solubility parameters (HSP) established by Charles M. Hansen in

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1967 [5]. In his approach, the total cohesion energy of a liquid (δ^2_{total}) was split into the contributions from atomic dispersion interaction (δ^2_d), dipole–dipole interaction (δ^2_p), and the hydrogen bonding interaction (δ^2_h), i.e.

$$\delta^2_{total} = \delta^2_d + \delta^2_p + \delta^2_h$$

The closer the HSP values of a liquid pair are in the 3D HSP space the higher is their similarity, and thus the stronger is their affinity. This analysis is particularly useful when applied to the dissolution of polymers. Consequently, the HSP values of many solvents and polymers have been tabulated, as well as the interaction radius (R_o) of the latter. A good compatibility is expected, between the polymer and those solvents located within its interaction sphere. The concept has since been extended from the mixing of polymers with liquid hydrocarbons to a broad range of materials, including carbon nano-structures [6,7], Polyhedral silsesquioxanes (POSS) [8], as well as nanoparticles of CeO_2 [9] or TiO_2 [10,11] and hydroxyapatite [11].

In the study, the 3D HSP sphere will be used to describe the compatibility between solvents and the modified nano-ZrO_2. The HSP value and R_o of the latter were calculated by the HSPiP software. The results pointed out that there must be some hydrophilic functional groups on the methacrylic acid modified nanoparticle. Further analysis with both ^1H and ^{13}C NMR confirmed this conjecture and identified TEA as the source of the hydrophilicity.

2. Materials and methods

2.1. The synthesis and modification of ZrO_2 nanocrystals

The ZrO_2 nanocrystals were produced, as detailed in our previous researches [4,12], by the digestion of hydrous zirconium hydroxide with NaOH solution at 110 °C. The zirconium hydroxide, on the other hand, was prepared from the neutralization of zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) with NaOH. Chelating agents, such as MA and triethanolamine (TEA), were employed during the neutralization step, in addition to the ammonium bicarbonate (NH_4HCO_3) buffer. The digested product was centrifuged, rinsed with acetone, and vacuum-dried into nano-ZrO_2 powders. The powders could be re-dispersed in water, leading to a transparent sol with pH ~10.

The carboxylic acids employed for surface modification includes oleic acid (OA), decanoic acid (DA), butyric acid (BA), methacrylic acid (MA), propionic acid (PA) and acetic acid (Ac). They were chemicals from Acros Organic or Alfa Aesar. All solvents employed were reagent grades from Merck or Sigma–Aldrich. Reverse osmosis water (RO-water) was used throughout.

The modification with OA and DA was conducted in a *1 N* ethanol solution, while the others were done in a *4 N* aqueous system. The nano-ZrO_2 powder was added to the carboxylic acid solution and stirred at 60 °C for 2 h. The acid to zirconia ratio was 6 mmol/g in the first case and 12 mmol/g in the latter. The pH value of the mixture was about 6 for the ethanol mixture and 4.2 for the aqueous one. The precipitate produced after the modification was retrieved by centrifugation (6000 rpm) and washed twice with the corresponding solvent. The amount of solvent employed each time was triple that of the zirconia. The washed product was centrifuged and vacuum-dried at 80 °C into a powder. However, the one modified with Ac formed a stable dispersion in water that could not be separated even with high-speed centrifugation (20,000 rpm). Therefore, it was directly evaporated at 60 °C into a powder. The loading of the organic ligand calculated from TGA analysis (*Fig. S1 in the supplement*) was 0.38, 0.47, 0.49, 0.55, 0.63 and 0.92 g per g of zirconia for the Ac, PA, MA, BA, DA and OA cases, respectively.

2.2. Characterization

Thermo-gravimetric analysis was performed with Perkin Elmer TGA-1. The morphology of the nanoparticle was observed by both the standard transmission electron microscope (TEM, JEOL JEM-2000FXα) and a high resolution one (HR-TEM, JEOL JEM-2100). The SAXS experiments were performed at beam line BL23A of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. More details on the SAXS experimental conditions and the model fitting have been given in our previous research [4].

The chemical moieties on the particle surface were further studied by ^1H liquid phase NMR and ^{13}C CP/MAS solid state NMR. The ^1H NMR was collected with a Bruker Avance 300 spectrometer (300 MHz) using $CDCl_3$ or D_2O as the solvent. Samples containing 10 wt% of modified nanoparticle were used. The ^{13}C NMR measurement was conducted on an OXFORD AS500 spectrometer (500 MHz). 2200 scans were used with a spinning rate of 6 kHz. Contact time was set at 1.0 ms and the delay time was 2.0 s.

The dispersion of the modified zirconia was tested in 25 solvents. In all cases, 0.5 g of powder were placed in a 20 mL glass vial before adding 4.5 g of solvent. If the solvent was incompatible, the powder remained as sediment even after intense ultrasonic agitation. For dispersible solvents, manual shaking of the vial for a few minutes was enough to produce a transparent/translucent sol. This is demonstrated for the MA-ZrO_2/THF case in the electronic supplement information. All dispersions were stable for at least 6 months without noticeable change in its appearance. The size distribution of the nanoparticles in the dispersion was measured by Dynamic Light Scattering (DLS, Malvern ZetaSizer) at 25 °C. A 10 wt% stocked dispersion was used directly without filtration. The scattered intensity fell within the range between 150 and 350 kcp, as suggested by the equipment vendor. The size distribution was reported in terms of the particle volume density.

3. Result and discussion

3.1. Particle size distribution

After modified by carboxylic acid, the zirconia nanocrystals could be dispersed in a number of organic solvents. In all cases, a transparent (translucent in the Ac and PA cases) dispersion was achieved even at more than 10 wt% loading, despite the formation of clusters or aggregates as discussed in our previous report [4]. To understand the size of the clusters, the DLS analysis was performed with a 10 wt% dispersion where clustering is expected. A bimodal size distribution was observed in all cases as demonstrated in Fig. 1. The size distribution fell broadly into two categories. In the OA, DA, BA and MA (Fig. 1a–d) cases, the majority of the particles were primary particles ranging from 6 to 10 nm in size. The larger particles, in the size range from 20 to 40 nm, can be attributed to the secondary clusters. The particles in the Ac- and PA-ZrO_2 cases (Fig. 1e and f) were, on the other hand, much bigger. Most of them appeared as ~20 nm secondary clusters. Those larger aggregates, between 40 and 60 nm in size, must have been the tertiary ones.

The same general features were again demonstrated by the TEM pictures in Fig. 2. The secondary clusters observed for MA, BA and DA cases were all about 20 nm. This is in consistent with the above DLS analysis, as well as the SAXS results presented previously [4]. The HR-TEM image of OA-ZrO_2 (Fig. 2b) further revealed that these soft clusters were irregular in shape and consisted of 3–5 primary particles. The SAXS analysis of this particular dispersion gave a gyration radius $R_g{}^2$ of 8.0 nm. This is similar to that obtained previously for the other modifications.