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Blends of amorphous/crystalline nanoalumina and hydrophobic amorphous nanosilica

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ABSTRACT

Initial Al-100 and hydro-compacted amorphous/crystalline nanoalumina cAl-100 alone or in blends with hydrophobic amorphous nanosilica AM1 were characterized using low-temperature ¹H NMR and IR spectroscopies, adsorption, XRD, DSC, microscopy, and cryoporometry. Mechanical treatment of weakly hydrated (0.5 g/g) nanooxides results in their hydro-compaction changing many of the material characteristics. There is overlapping of confined space effects for water bound in voids between nanoparticles with effects caused by the colligative properties of aqueous solution of trifluoroacetic acid in a chloroform medium. The interfacial phenomena determine the temperature behavior of bound water/ice depending on dispersion media features. Contact area between unfrozen water and nanooxide surface is smaller than the specific surface area due to incomplete water filling of voids between hydrophilic/hydrophobic nanoparticles. In composites with cAl-100/AM1, there is a tendency of diminution of the contact area of water with hydrophobic nanosilica AM1 and hydrophobic chloroform immiscible with water. This effect changes the temperature behavior of water, which becomes more strongly bound to hydrophilic alumina. The observed effects can be of importance upon practical applications of nanooxide based composites.

1. Introduction

Unmodified fumed metal and metalloid nanooxides (FMO), which can be totally (*e.g.* silica) or partially (alumina, titania, *etc.*) amorphous, are hydrophilic due to surface hydroxyls [1–5]. However, this property, as well dust forming, of FMO could be rather negative for some applications, *e.g.* on preparation of hydrophobic polymer – FMO composites. Therefore, FMO modified by hydrophobic compounds are of interest for similar applications [6–8]. The hydrophobization of nanosilica (by various silanes, depolymerized polydimethylsiloxanes, *etc.*) is a relatively simple task, and the bonds Si-O-SiR₃ formed between a silica surface and hydrophobic functionalities are hydrolytically stable [1–8]. Various aspects of functionalization of FMO are of importance from a practical point of view upon creation of stable, environmentally resistant materials [9–33], as well to reduce the interactions with water [5,34,35] and to control the interfacial and mechanical behaviors of complex systems [36–38], especially FMO filled polymers [39–42]. In the case of hydrophobized FMO with M ≠ Si, *e.g.* M = Al, Ti, *etc.* [5,9,43], the formed bonds M-O-SiR₃ are hydrolytically less stable than Si-O-SiR₃ that can lead to relatively fast degradation of the composites.

There is another pathway (to change the hydrophilic/hydrophobic FMO characteristics) based on preparation of blends with hydrophilic unmodified FMO (UFMO) and hydrophobic modified FMO (MFMO) additionally treated [44–48]. Not very strong mechanical loading or mechanochemical activation of weakly hydrated UFMO/MFMO blends can result in reorganization of the secondary structures (*e.g.* formation of complex core-shell aggregates) with nonporous nanoparticles (NPNP) that depends on the dispersion medium (hydrophilic or hydrophobic) and other conditions with no changes in the nature of NPNP *per se* [45–50].

The blends of hydrophilic and hydrophobic nanosilicas previously studied [45,46] showed unusual changes (depending on preparation conditions) in the interactions with bound water at $T < 273$ K. Enhanced mechanical loading on weakly hydrated UFMO/MFMO blends resulted in increased interactions of water bound in the hydrophilic components of the composites due to certain effects of hydrophobic silica and hydrophobic dispersion medium. Note that the interfacial and temperature behaviors of various adsorbates depend on many factors including the chemical composition, morphology, and texture of FMO with respect to nanoparticles and their aggregates and agglomerates

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[1–5,51–56]. Therefore, one could expect that upon relatively weak mechanical treatment of the UFMO/MFMO blends they could demonstrate some unusual properties and characteristics with respect to bound liquid phases of various polarity.

Air bubbles bound to hydrophobic functionalities attached to a hydrophilic surface can prevent interactions of these functionalities not only with bulk water layers but also with water clusters/domains. If a separated phase of liquid water is absent in weakly hydrated UFMO/MFMO blends, e.g., because of strong clusterization of relatively small amounts of bound water, that the water clusters can be located between hydrophobic functionalities to contact with hydrophilic ones (e.g. residual hydroxyls) or bound to a hydrophilic UFMO component. Mechanical activation of weakly hydrated UFMO/MFMO blends can result in changes in the organization of both secondary structures with NPNP and water bound to them [45–55]. The aim of this study was to elucidate the influence of features of UFMO (nanoalumina Al-100) and MFMO (AM1 corresponding to completely hydrophobized nanosilica A-300), relatively weak mechanical loading (stirring at pressure < 20 atm), dispersion media (air, chloroform alone or with addition of trifluoroacetic acid, TFAA), and temperature on the behavior of water/ice bound in the systems.

2. Materials and methods

2.1. Materials

Fumed nanosilica A-300 unmodified and completely hydrophobized by hydrolyzed dimethyldichlorosilane, DMDCS (AM1) and fumed nanoalumina (Al-100) (Pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine) were used as the initial materials. After addition of water ($h = 0.5$ g per gram of dry solids) to fumed Al-100 and gentle mixing for 2–3 min, the bulk density slightly increases to $\rho_b = 0.07$ g/cm³ (corresponding to the empty volume $V_{em} \approx 1/\rho_b - 1/\rho_0 = 13.8$ cm³/g, where ρ_0 is the true density of the material, in the powder [5]). If this mixture was stirred under a certain mechanical loading (~20 atm in a ceramic mortar) for 15 min that the value of ρ_b increases to 0.69 g/cm³ ($V_{em} \approx 1.0$ cm³/g). The Al-100/AM1 (1:1) blend weakly hydrated ($h = 0.5$ g/g) and mixed without strong mechanical loading for 10 min has the value of $\rho_b = 0.06$ g/cm³ ($V_{em} = 16.2$ cm³/g). If this weakly hydrated blend was stirred under mechanical loading for 15 min that $\rho_b = 0.22$ g/cm³ ($V_{em} = 4.1$ cm³/g). Note that the used mechanical loading is too weak to change the inner structure of both alumina and silica nanoparticles [54–57].

2.2. Infrared spectroscopy

The infrared (IR) spectra were recorded for air-dry samples in the range of 4000–300 cm⁻¹ using a Specord M80 (Carl Zeiss). To record the IR spectra, samples with modified silica AM1, nanoalumina Al-100, and their mixtures were pressed into thin pellets (15–20 mg). The transmittance spectra were recorded with 4 cm⁻¹ steps.

2.3. Microscopy

The surface morphology of composites was analyzed using field emission scanning electron microscopy (SEM) employing a QuantaTM 3D FEG (FEI, USA) apparatus operating at the voltage of 30 kV. AFM images were recorded using a NanoScope III (Digital Instruments, USA) using a tapping mode. High-resolution transmission electron microscopy (HRTEM, JEM-2100F, Japan) was used to analyze the morphology and structure of FMO nanoparticles and their aggregates.

2.4. ¹H NMR spectroscopy

¹H NMR spectra of static samples of FMO (with bound water at $h = 0.5$ g) located in air or chloroform media (alone or with addition

of trifluoroacetic acid, TFAA) were recorded using a Varian 400 Mercury spectrometer (magnetic field 9.4 T) utilizing 90° pulses of 3 μs duration. Each spectrum was recorded by co-addition of eight scans with a 2 s delay between each scan. Relative mean errors were less than ± 10% for ¹H NMR signal intensity for overlapped signals, and ± 5% for single signals. Temperature control was accurate and precise to within ± 1 K. The accuracy of integral intensities was improved by compensating for phase distortion and zero line nonlinearity with the same intensity scale at different temperatures. To prevent supercooling, the spectra were recorded starting at $T = 200$ –210 K for samples precooled to this temperature for 10 min. The samples were heated to 280–285 K at a heating rate of 5 K/min with steps $\Delta T = 10$ K or 5 K and maintained at a fixed temperature for 8 min for data acquisition at each temperature. Applications of this method and NMR cryoporometry to nanooxides were described in detail elsewhere [5] (see additional information in Electronic Supplementary Material (ESM) file).

2.5. Textural characteristics

To analyze the textural characteristics of FMO degassed at 373 K for several hours, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2420 adsorption analyzer. The specific surface area (S_{BET}) was calculated according to the standard BET method [58]. The total pore volume V_p was evaluated from the nitrogen adsorption at $p/p_0 \approx 0.98$ –0.99, where p and p_0 denote the equilibrium and saturation pressure of nitrogen at 77.4 K, respectively [59]. Calculations of the pore size distributions (PSD) are described in detail in ESM file.

3. Results and discussion

Microscopic images (Figs. 1 and S1–S5 in ESM file) show that nanooxides, which are composed of NPNP with a certain primary particle size distribution (e.g. 5–60 nm in diameter for Al-100), form such secondary structures as aggregates of NPNP (< 1 μm in size) and agglomerates of aggregates (> 1 μm) (*vide infra*). Voids between NPNP in the secondary structures are responsible for the textural porosity of the FMO powders. The textural characteristics (Fig. 2 and Table S1) demonstrate that the void (pore) size distributions (PSD) have two main maxima corresponding to voids between neighboring particles in aggregates (first IPSP maximum, Fig. 2a) and voids between neighboring aggregates in agglomerates or NPNP from the same aggregates, but far located one from others (second maximum, Fig. 2a). Note that differential (dV/dR) PSD calculated using the NLDFT method (Fig. 2b) demonstrate many small maxima due to a small value of the

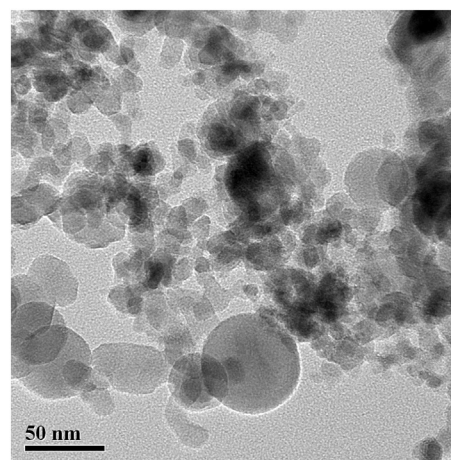


Fig. 1. TEM image of Al-100.

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