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CHEMICAL MODIFICATION AND CHARACTERIZATION OF BOEHMITE PARTICLES

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Abstract: Polymerizable organic silane molecules 3-(trimethoxysilyl)propylmethacrylate (3MPS) and vinyltri(2-methoxyethoxy)silane (VTMES) have been introduced onto surfaces of high purity Boehmite (a commercial alumina) via hydroxyl groups on the oxides in order to obtain organic-inorganic hybrid “macromonomers”. Changes of surface characteristics have been determined using thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). The influence of the type of silane used and modification conditions have been determined. Preheating was applied to some Boehmite samples; it leads to lower concentrations of –OH groups on the powder surface and the adsorption yields lower than in samples without preheating. Modification leads to surface hydrophobicity and thus reduces significantly water adsorption; in TGA we see desorption of water below 423 K only in un-modified Boehmite.

Keywords: Boehmite, macromonomer, silica coupling agent, surface modification, powder filler.

1. Introduction

We see increasing use of fillers – including those containing ceramic oxides – in the development of polymer composites [1]. One thus obtains composites with better mechanical, thermal, electrical or other properties. This is particularly important for the ongoing process of gradual replacement of metallic components by polymer-based ones. The latter are weak mechanically [2] while ways of lowering wear are under development [3]. The properties of polymer-based composites are strongly influenced by the nature of the filler and also by adhesion between the filler particles and the polymer [4-16]. In fact, interfacial tensions are decisive for properties of multiphase materials [17]. The main problem here is the incompatibility of hydrophilic ceramic oxide fillers and hydrophobic polymer matrix which yields composites with poor properties. Thus, control and/or manipulation of the surface properties of the particles are of importance. We know that during the preparation process formation of covalent bonding

between organic polymers and inorganic components contributes to enhancement of the compatibility in the composites. This can be achieved through the grafting of a polymerizable group onto the oxide surfaces via hydroxyl groups followed by its copolymerization with organic monomers [18-23]. Among others, silane coupling agents have been used to improve dispersion, adhesion and compatibility in such materials [24-28].

The purpose of the present work is modification and characterization of Boehmite, that is aluminum oxyhydroxide (AlOOH) powder through adsorption of polymerizable organic silane molecules 3-(trimethoxysilyl)propylmethacrylate (3MPS) and vinyltri(2-methoxyethoxy)silane (VTMES) onto surfaces of ceramic oxide powders via hydroxyl groups on the oxides. In order to obtain organic-inorganic hybrid “macromonomers”, effects of modification conditions have to be carefully determined to optimize the process.

Additional experiments were conducted on SCA modified Boehmite powders. These hybrid macromonomers were blended with low density polyethylene (LDPE). Investigation of powder loading and powder morphology effects on thermal, mechanical and tribological properties of the resulting materials is reported in another paper [29].

The present paper is one of a series dealing with polymer + ceramic oxide powder composites. There are other papers addressing the free radical copolymerization of the modified SiO₂ oxides with methylacrylic monomers and the characterization of resulting organic-inorganic hybrids [12, 29, 30].

2. Experimental

2.1. Materials

Silane coupling agents (SCA), namely VTMES – SCA 972 and 3MPS – SCA 989 and high purity Boehmite (under the HiQ alumina trade name) were received as a gift from Struktol Company of America and Engelhard Co., respectively. Toluene was from Sigma Chemicals Co. All reagents were of analytical grade and were used as received.

2.2. Characterization of Boehmite sample

Boehmite is a low cost material used in many areas; it is an important precursor because the heat treatment of Boehmite produces a series of transition aluminas from γ - Al_2O_3 and η - Al_2O_3 to δ - Al_2O_3 and θ - Al_2O_3 , which exhibit high surface areas (200–500 m^2/g) and thermal stability up to 1273 K.

Boehmite was thought to exist under two distinct forms, well-crystallized Boehmite and pseudoboehmite

(also called gelatinous Boehmite) [31], with significantly different morphologies, porosity and surface areas. However, more recent studies [32, 33] have clearly demonstrated that pseudoboehmite is simply micro- or rather nano-crystallized Boehmite; the difference observed between the two forms comes from a difference in crystallite sizes.

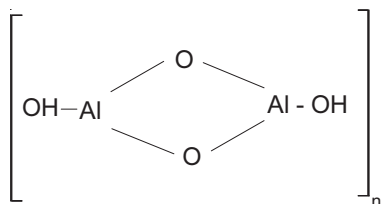
Table 1 lists the chemical composition and physical properties of the Boehmite commercial ceramic powders.

Table 1

The chemical composition and physical properties of commercial ceramic powders

Chemical composition		Physical properties	
Al_2O_3 , wt %	72	Pore volume, cm^3/g	0.4–0.5
Carbon, wt %	< 0.3	Surface area, m^2/g after 3 h 823 K	270
SiO_2 , ppm	< 150	Acid dispersibility, wt %	85
Fe_2O_3 , ppm	< 150	Loose bulk density, g/l	670–750
Na_2O , ppm	< 20	Particle size (d50), μm	55
		Crystallite size, nm	4.3

From Table 1 we see very small sizes of the crystallites. Generally, the structural elements in Boehmite crystals consist of double chains of AlO_6 octahedra resulting in double molecules [34]:



These chains are parallel, forming layers with the OH groups outside. The double chains are linked by hydrogen bonds between hydroxyl ions. Boehmite crystals exhibit perfect cleavage perpendicular to the general direction of the hydrogen bonding [35].

2.3. Grafting of SCA onto ceramic particles

Introduction of reactive groups onto the commercially obtained and preheated at 3 h 823 K ceramic surfaces was achieved by a reaction of SCA with the hydroxyl groups of alumina. Two different types of SCA were used and the temperature dependence of the process was characterized.

A typical example can be described as follows. Reaction mixture contained 25 ml SCA, 200 ml of toluene and 20 g of powder. After dispersing the powder in solvent SCA was added and the resulting mixture refluxed at the boiling temperature of the solution for 24 h. The process was also conducted with 24 h mixing at room temperature.

Afterwards the powder was centrifuged and washed with fresh toluene for 24 h to remove the excess SCA absorbed on the surfaces. Final products were dried at 363 K under vacuum for 24 h.

2.4. Characterization techniques

All the samples were analyzed by TGA in nitrogen atmosphere at the heating rate of 10 K/min. The technique has been described by Menard and his colleagues [36, 37].

Isothermal thermogravimetry (TG) was used to determine a temperature profile. A Perkin Elmer TGA-7 instrument was used. Several milligrams of each dried sample were placed on a balance located in the furnace which was heated over the temperature range from 323 to 973 K.

The FTIR spectra were recorded on a Nexus 470 FTIR ESP Series spectrometer at the resolution of 4 cm^{-1} wave number, in the midinfrared range from 4000 to 250 cm^{-1} . To enhance the signal to noise ratio, each of the reference and sample spectra presented constitutes an average of 40 scans recorded.

For infrared spectroscopy measurements, CsI pellets containing 1 wt % of material were used and the background noise was corrected with pure CsI data.

3. Results and Discussion

3.1. Characteristics of the surface modified Boehmite

The basic principles of the surface modification of ceramic powder are presented schematically in Figure 1:

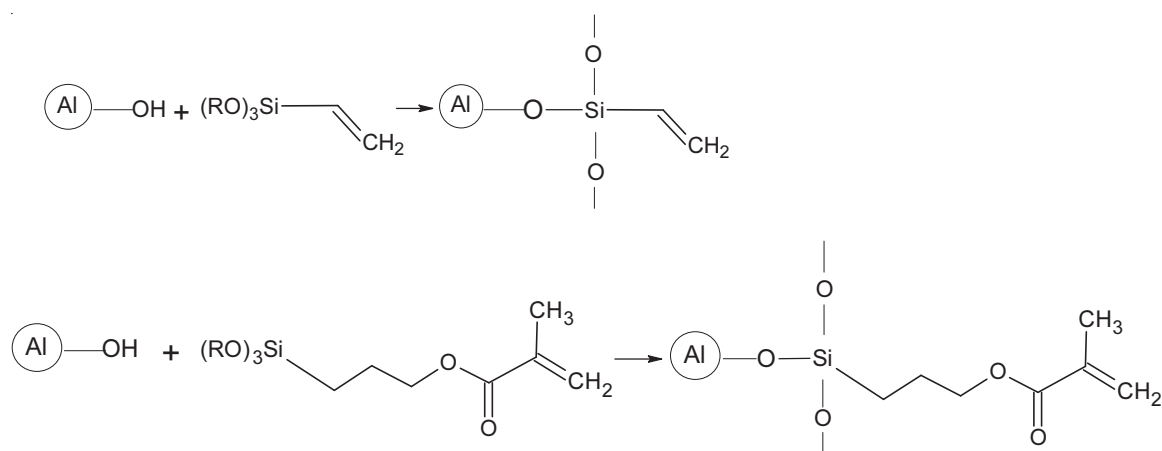


Fig. 1. The surface modification of ceramic powders

Formation of new groups on powder surfaces was investigated by Fourier-transform infrared (FTIR) spectroscopy which is sensitive to both inter- and intra-molecular interactions. Fig. 2 shows the FTIR spectra of Boehmite powder before and after modification with two polymerizable organic silane molecules, 3MPS and VTMES, onto surfaces of ceramic oxide powders via hydroxyl groups on the oxides.

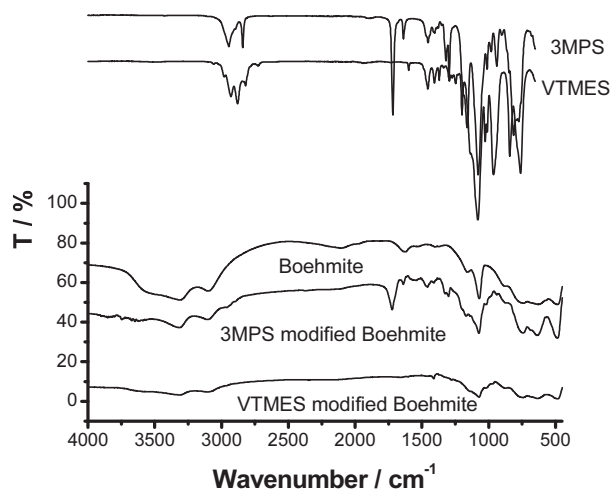
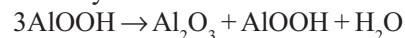


Fig. 2. FTIR of Boehmite powder before and after modification

We see that the samples exhibit stretching vibrations of $-OH$ groups in the $3000\text{--}3600\text{ cm}^{-1}$ range. The vibrations appear for unmodified Boehmite powder as strong peaks. These peaks are characteristic for the $-OH$ fragments of physisorbed water. A small fraction of these $-OH$ groups also appears in modified samples. They are evidence of the same physisorbed water. Furthermore, we can see a different picture in the case of preheated Boehmite powder (Fig. 4); namely, these samples do not exhibit stretching peaks in the $3000\text{--}3600\text{ cm}^{-1}$ range due to the desorption of physisorbed water after heating above 773 K . The TGA

diagram in Fig. 3 supports these results, as indicated by the main weight loss between 373 and 773 K .

The reaction that takes place can be simply represented by



The dehydration of the Boehmite appears to occur in three main steps. The first gives a sharp symmetrical endotherm and ends at 423 K . It accounts for $10\text{--}13\text{ wt } \%$ of the mass loss. The second step gives a broad unsymmetrical endotherm and ends before 773 K . It represents the major part of the mass loss, about $15\text{--}17\text{ wt } \%$. The last step does not correspond to a specific thermal event but appears as a continuous mass loss. It only corresponds to about $2\text{--}3\text{ wt } \%$ of the mass loss.

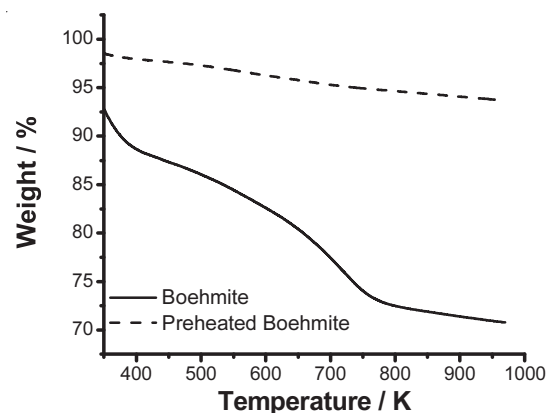


Fig. 3. TGA scans of Boehmite powder before and after heating

The first step has been attributed to the desorption of physically adsorbed water, the second step to the conversion of Boehmite into α -alumina, and the last step to elimination of residual hydroxyls. Several authors [34, 35, 38, 39] explain the asymmetrical profile of the second peak by removal of chemisorbed water before the conversion into alumina.

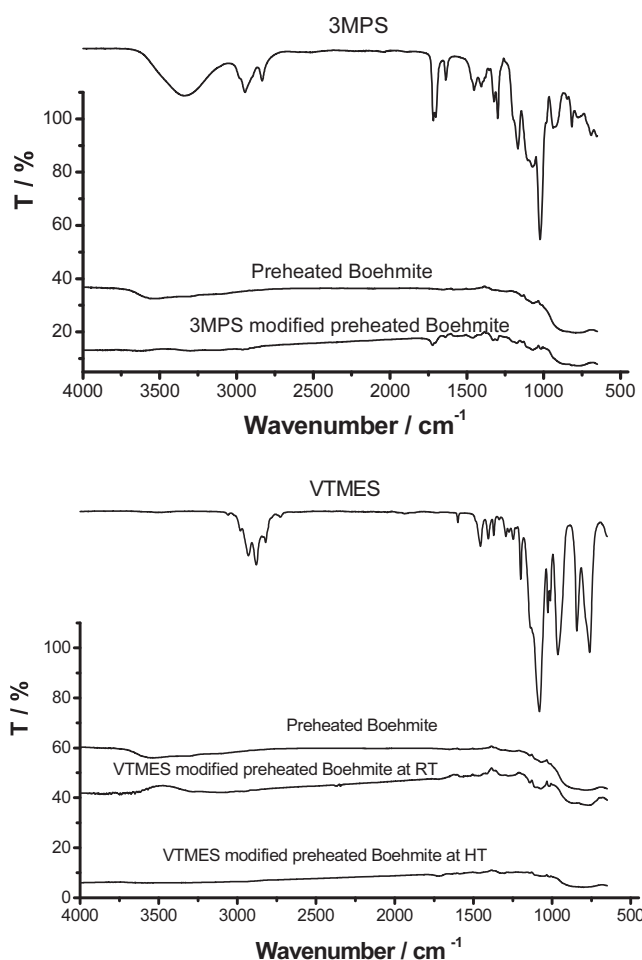


Fig. 4. FTIR of preheated Boehmite powder before and after modification

For modified Boehmite samples small trace peaks in the region $2800\text{--}3000\text{ cm}^{-1}$ are associated with the methylene ($-\text{CH}_2-$) and dimethylene ($-\text{CH}_2-\text{CH}_2-$) stretching which comes from polymerizable organic molecule contamination. We see the same stretching peaks in the $2800\text{--}3000\text{ cm}^{-1}$ range for polymerizable organic silane molecules.

Compared with unmodified powder, formation of peaks is observed in the $800\text{--}1700\text{ cm}^{-1}$ region. These signals are characteristic for the silane coupling agents.

The characteristic peaks for the modified powders have the absorption bands at the $1500\text{--}1750\text{ cm}^{-1}$ and $1000\text{--}1500\text{ cm}^{-1}$ range which correspond to unsaturated bands of the SCA. The strong signal at 1733 cm^{-1} is characteristic of the carbonyl ($\text{C}=\text{O}$) stretching of the SCA 989 (Fig. 2); the peaks decrease in size for SCA 989 grafted onto the surfaces of preheated Boehmite powders. This can be explained by decreasing amounts of $-\text{OH}$ groups on the powder surfaces after heating at 823 K for 3 h immediately before modification (Fig. 4). As expected, the mass loss for preheated Boehmite below 823 K is only

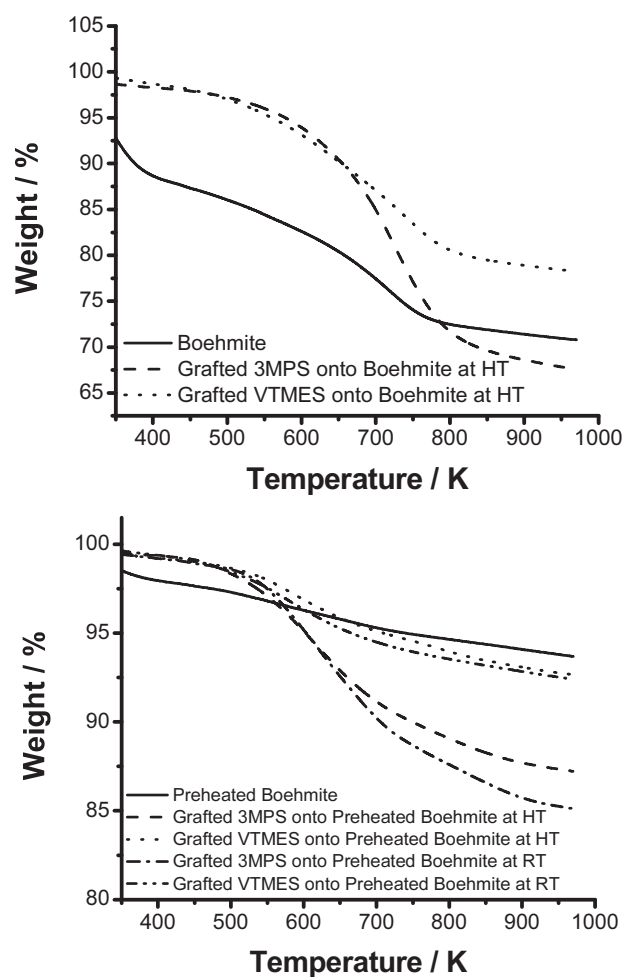


Fig 5. TGA scans of Boehmite and preheated Boehmite powders before and after modification

$5.0\text{--}7.0\text{ wt } \%$ while for the Boehmite powder a significant mass loss $25.0\text{--}27.0\text{ } \%$ occurs below 823 K (Fig. 3).

As noted above, to evaluate organic group reactivity in the modification process of Boehmite surfaces we have used SCA 972 and SCA 989 with vinyl and methacryl groups respectively. The experiments show clearly more chemical activity of the methacryl groups in SCA 989. Formation of larger amounts of organic-inorganic hybrid macromonomers takes place. At the same time SCA 972 provides lower activity and exhibits nearly the same grafting efficiency for both Boehmite powders. On the other hand, both SCAs provide higher yields of adsorption onto the Boehmite particles as compared to preheated samples.

As observed by other authors [26, 40] the main peak at 1699 cm^{-1} indicates that SCA 989 monomers are successfully adsorbed onto the Boehmite and preheated Boehmite powder surfaces (Figs. 2 and 4) through covalent bonding. The second system shows weaker interactions between functional groups of SCA 972 and

hydroxyl groups of the preheated powder and even weaker ones for unheated powder.

A significant difference in thermal behavior between the unmodified and modified Boehmite samples (Fig. 5) also indicates the role of the modification efficiency.

At the same time, TGA data reveal hydrophobic characteristics of the modified powder surfaces; the mass loss is significant only above 423 K while for unmodified powders such loss occurs below 423 K due to physisorbed water desorption. The thermograms of all the modified samples show two regions of characteristic weight loss at 423–623 K and 623–823 K. This can be explained by a decomposition of the organic constituent of the grafted SCA.

From TGA curves we also see that the modification process remains the same when reaction temperature ranges from room to boiling. The use of high temperature treatment did not cause marked improvement in percentage modification and adsorption efficiency – as we see in Fig. 5.

Apparently introduction of new groups onto microsize Boehmite surfaces takes place. A large excess of the SCA or an increase of the process temperature does not significantly affect the products since the amounts of group adsorbed onto the surfaces appears to be limited. Apparently, growing adsorbed chains of SCA on the powder surfaces have a blocking effect on the diffusion of monomers to the surfaces of Boehmite particles.

As already mentioned, mechanical properties of low density polyethylene (LDPE) reinforced with Boehmite grafted as described above are reported elsewhere [29]. Finally, we note a large variety of current and potential uses of Boehmite. To give just one more example, metal catalysts of hydrogenation reactions in oil refinery industry can be deposited on porous Boehmite [41].

Acknowledgments

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ХІМІЧНА МОДИФІКАЦІЯ І ХАРАКТЕРИСТИКА БЕМІТОВИХ ЧАСТИН

Анотація. Показано, що полімеризаційноздатні органічні силанові молекули 3-(триметоксисиліл)пропілметакрилату та вінілтри(2-метоксиетокси)силану для одержання органічно-неорганічного гібриду “макромо-

номерів” можуть бути введені на поверхню бемітів високої чистоти (промисловий глинозем) за допомогою гідроксильних груп на оксиди. Зміни у поверхневих характеристиках визначені термогравіметричним аналізом (ТГА) та інфрачервоною спектроскопією з перетворенням Фур'є. Визначено вплив типу силану та умови процесу модифікування. Встановлено, що у попередньо нагрітих зразках спостерігається зменшення концентрації –ОН груп на поверхні і зменшення адсорбційного виходу порівняно із зразками без нагрівання. Модифікація приводить до гідрофобності поверхні, внаслідок чого значно зменшується адсорбція води; за результатами ТГА десорбція води нижче 423 К має місце тільки в немодифікованих бемітах.

Ключові слова: беміт, макромономер, кремнеземний агент, модифікація поверхні, порошковий наповнювач.