

## Structure of alumina-silica nanoparticles grafted with alkylphosphonic acids in poly(ethylacrylate) nanocomposites



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### ABSTRACT

Alumina-coated silica nanoparticles (NPs) grafted with phosphonic acids of different hydrophobicity were used as filler in poly(ethylacrylate) nanocomposites. Phosphonic acids bearing short alkyl chains or a diethylene glycol group have been grafted at densities up to 3.2 P/nm<sup>2</sup> on NPs (20 nm) dispersed in water. Nanocomposites at particle fractions up to 10 vol% have been formulated by casting from the colloidal mixtures of modified NPs and nanolatex in water. The dispersion of the NPs in the polymer matrix has been studied by TEM combined with small-angle scattering, evidencing aggregation of NPs. TEM shows micrometer-scale inhomogeneities depending on the surface/polymer matrix compatibility. For the local interparticle correlations, a quantitative analysis of the intensity based on the mapping onto the effective structure factor of polydisperse hard spheres is developed. This mapping allows the model-free determination of the internal volume fraction of aggregates, termed compacity  $\kappa$ , to between 10% and 30%, compatible with the TEM analysis.  $\kappa$  is found to increase for the higher particle volume fractions, to decrease with grafting density, and to be mostly independent of the nature and mass of the graft. Preliminary evidence for an improved compatibility of grafted with respect to bare NPs is found, as opposed to their aqueous precursor suspensions where some pre-aggregation is induced by grafting.

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## 1. Introduction

A polymer nanocomposite (PNC) is a multicomponent system, in which at least one phase has a typical dimension in the nanometer range, in our case hard nanoparticles (NPs) of typical size 20 nm [1–3]. The macroscopic properties of such a material, including optical, rheological and mechanical ones, determine their suitability for applications, like, e.g., in the car tire industry [4,5]. These properties depend crucially on the filler structure [1,3], i.e., on the state of dispersion of NPs within the nanocomposite [6–8]. It is therefore important to be able to control and to tune the state of dispersion (referred to as “structure”) of the NPs in the polymer matrix. In previous approaches, this has been obtained using surface modification of the NPs with polymer molecules by grafting-to

[5,9–15] or grafting-from approaches [16], by tuning electrostatic interactions between NPs in suspension before casting [17], or by annealing and modifying the dynamics of the polymer chains [18–20]. In many of these approaches, small-angle scattering is used to characterize the resulting filler dispersion, or sometimes also the chain conformation [21–27], whereas advanced tomographic methods based on electron microscopy have also been used to describe the filler structure, and in particular aggregation of filler NPs [28].

Grafting small organic molecules on inorganic NPs is a convenient way to modify their interactions and their state of aggregation in suspension and ultimately in a polymer matrix [29–31]. Here we are interested in the formation of covalent bonds, deliberately excluding physisorption of, e.g., surfactant molecules [32] (in particular via ion exchange of clays [33]), from this discussion. Meth et al. have studied the structure of charge-stabilized silica NPs in DMF, and formulated nanocomposites with bare NPs in polymethylmethacrylate (PMMA), and with phenyltrimethoxysilane-

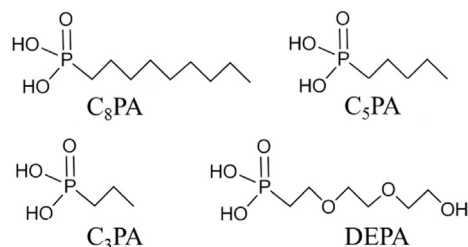
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modified NPs in polystyrene [34]. Grafted silica NPs have been used by Park et al. for the fabrication of ultrafine polyurethane reinforced fibers [35]. In this work, the grafting was performed by reaction of silica NPs with dodecyl trichlorosilane in dehydrated toluene followed by drying and redispersion illustrating the fact that silanization is not easily performed in water due to polycondensation. Nusser et al. have dispersed hydrophobic surface-modified silica NPs from Nissan in poly(ethylene co-propylene) (PEP), reaching very high volume fractions due to this compatibilization [26]. Some control by silanization of silica NPs clustering at high volume fractions in polymethacrylates has also been reported [36], and one should note that highest compatibility usually obtained by hydrophobization does not always imply best mechanical properties [37]. In addition, the initial aggregation state of the nanofiller, either well-dispersed colloids or aggregates, is of major importance. For instance, Aranguren et al. have studied the incorporation in polydimethylsiloxane (PDMS) of fumed silica modified by two different molecules, hexamethyldisilazane and dimethyldichlorosilane [38]. They focused on the determination of the adsorbed polymer layer, but provided evidence for aggregate size being determined by pre-existing bonds between particles in the fumed silica powders, independent of surface treatment. Zhang and Archer have studied dispersions in polyethylene oxide (PEO) of silica NPs modified with organosilanes bearing alkyl or PEO-like groups [39]. Rheology and atomic force microscopy (AFM) showed that silica aggregates may form stress-carrying networks only for bare silica having strong interactions both with the matrix and between NPs, whereas grafting makes the NPs more compatible with the matrix, leading to a better dispersion but a lower reinforcement. Le Strat et al. have investigated crosslinked PDMS-silica nanocomposites obtained by casting from different solvents, using bare, hydrophobic, or COOH-functionalized (enabling covalent bonding with PDMS) nanoparticles [40]. Their small-angle X-ray scattering (SAXS)/Transmission Electron Microscopy (TEM) and mechanical studies showed that strong reinforcement can be obtained at high volume fractions only in case of bare NPs due to strong interparticle interactions produced by H-bonding between surface silanol groups.

Phosphonic acids (PAs) are particularly interesting for the surface modification of oxide particles in aqueous medium [41]. We have used alkylphosphonic acids to simultaneously graft and transfer titanium oxide NPs from an aqueous to an organic phase [42]. Recently, we were able to vary the state of dispersion of alumina-coated silica NPs in aqueous sols by grafting small phosphonic acids bearing organic groups of various hydrophobicities [43] (Scheme 1). The aggregate size in water increased with the hydrophobicity and grafting density of the grafted molecules ( $C_8PA > C_5PA > C_3PA > DEPA$ ). In the case of the hydrophilic DEPA, aggregation occurred only at high grafting density ( $>3 P/nm^2$ ), due to the decrease of electrostatic repulsions between NPs [43].

In the present work, the same PA-modified nanoparticles [43] have been incorporated in a poly(ethylacrylate) (PEA) matrix following an aqueous route [6,17]. This method of NP incorporation



**Scheme 1.** Series of phosphonic acids with decreasing hydrophobicity.

in a polymer matrix presents various advantages. First, it avoids the use of NPs in the dried state, which is controversial, especially in terms of safety. Secondly, the aqueous NP colloidal dispersions are used directly as obtained after the grafting procedure: there is no need of additional drying, washing, or solvent exchange steps in the synthesis protocol. Moreover, the use of organic solvent is not necessary. The aim of this article is to find out if and how the aggregation state in the aqueous sols is transferred to the nanocomposites. Indeed, bare alumina-coated silica NPs are hydrophilic due to the presence of surface OH-groups. With increasing grafting density and depending on the nature of the grafted PA, the hydrophilicity of the NPs changes. This may affect differently dispersions in suspension and in nanocomposite. The first step is therefore to generalize the approach published previously [43], providing further evidence for aggregation in suspension with increasing grafting density. Knowledge of this initial state allows us to investigate if the dispersion in suspension is conserved in the nanocomposite, or if grafting of hydrophobic PAs can lead to a better compatibility with the polymer matrix. To check this, we have pushed the system towards increasing interactions between NPs by increasing the NP volume fraction, which is likely to induce collisions and aggregation.

The filler microstructure in PEA based nanocomposites is studied using small-angle neutron scattering (SANS), see Ref. [44] for a recent review of small-angle scattering techniques applied to PNCs. The resulting intensity curves are interpreted based on the signature of repulsive correlations between nanoparticles. For highly diluted suspensions, a reverse Monte Carlo approach gives access to direct space images. We investigate the impact of NP concentration, as well as different parameters linked to the surface chemistry of the NPs: the hydrophobicity of the grafted groups, and the grafting density.

## 2. Materials and methods

### 2.1. $SiO_2$ sols

The commercial colloidal suspension Levasil 200S/30 (L200S) was a gift from Akzo Nobel. This product contains silica NPs covered with an aluminium oxo-hydroxide layer, at pH 3.8, with 30 wt% solid content. The NP form factor has been measured by SAXS in dilute suspensions and described by a log-normal size distribution of NP radii with  $R_0 = 7.4$  nm,  $\sigma = 0.38$  [43]. The corresponding average radius is given by  $R_0 \exp(\sigma^2/2) \approx 8$  nm. Such results were found in good agreement with dynamic light scattering (DLS) measurements and TEM, see Ref. [43] for details.

### 2.2. Phosphonic acids and grafting

The PAs used for surface modification were n-propyl, n-pentyl, n-octyl, and (2-(2-(2-hydroxy-ethoxy)-ethoxy)-ethyl)phosphonic acid, named  $C_3PA$ ,  $C_5PA$ ,  $C_8PA$ , and DEPA, respectively (see Scheme 1).  $C_8PA$  and DEPA were purchased from SiKÉMIA.  $C_3PA$  and  $C_5PA$  were prepared in the laboratory. The grafting was done as follows. 5 g of commercial colloidal solution was diluted by adding 10 mL of ultra-pure water and then the pH was increased up to 5 by dropwise addition of 0.1 M NaOH. PA grafts were separately dissolved in 15 mL of water, and the pH of the resulting solution also adjusted to 5. Both solutions were then mixed yielding a final concentration of NPs in the solution of 5 wt%, and stirred at 200 rpm at room temperature for 24 h. Note that previously, the dispersion in suspension has been studied for samples initially prepared at the same concentration [43]. These samples are immediately used as precursor for nanocomposites following the route described below. The grafting density  $\rho$  is given by the number of grafted molecules – or

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