

## Atomistic Simulations of Interfaces in Polymer Composites based on Silica Nanoparticles

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### Abstract

*Fully atomistic molecular dynamics (MD) simulations have been carried out on a series of amorphous bulk melt PMMA oligomers and MMA monomers-silica systems. A realistic model of silica nanoparticle, in which  $\alpha$ -quartz crystal structure is retained for the core, was used. Significant changes were found to occur in the immediate vicinity of the interface with PMMA polymer melt and MMA monomer bulk. A higher density shell was found for PMMA/silica interface compared with MMA/silica one, as shown by number density profile. The range of influence of the nanoparticle was evident for structural properties in a shell between 10-15 Å.*

### 1 Introduction

Composite of inorganic particles embedded in a polymer matrix, also named hybrids or nanocomposites, have attracted scientific and technological attention for several reasons. These materials offer a wide range of unique properties that depend strongly on nanoparticle size and shape, and consequently on the interfacial region. For example, silica nanoparticles are currently used in the rubber industries as fillers to improve the mechanical properties of composites<sup>1</sup>. In the last years the usage of nanoparticles as additives, to modify polymer properties, has been increasing constantly<sup>2-5</sup>. For example the PMMA/silica hybrids copolymers maintain high transparency, and their storage elastic modulus and surface hardness, grows with increasing silica content<sup>6</sup>.

Experimental studies<sup>7</sup> of dispersed nanoparticles in polymer matrix have showed that many polymer properties such as diffusion coefficient, relaxation time  $T_2$  in NMR, viscosity, change dramatically in the interfacial region. These differences are attributed to the mobility restrictions of polymer chains close to nanoparticle surface. Recently, experimental evidence have shown different distribution of the molecular weight for in situ polymerization of methylmethacrylate (MMA) in presence or absence of silica nanoparticles<sup>8</sup>.

The knowledge of structural and dynamic properties of the interface region, at a molecular level, offers an important tool to understand and correlate the microscopic mechanisms to the macroscopic properties. Experimental structural information at the atomic level for nanoparticles dispersed in polymer matrices nowadays is extremely difficult especially for characterization of the interfaces between the nanoparticle and the polymer phase.

Within the last 10 years, computer simulations have become a predictive tool for addressing structural investigations of complex materials based on polymers. However, in the case of nanostructured materials, the computational prediction of detailed molecular structures is still

difficult. This is particularly true for polymer-based materials because of the very broad range of length and time scales governing the chain molecular motions<sup>9</sup>.

Several simulation studies to investigate the structuration of solid nanoparticles embedded in a polymer matrix have been reported<sup>7,10-11</sup>. In particular Brown<sup>12-13</sup> and co-workers reported an atomistic model of silica nanoparticle embedded in an amorphous phase of polyethylene oxide (PEO). Müller-Plathe<sup>14</sup> and co-worker reported, recently, an atomistic model of grafted and ungrafted silica nanoparticle embedded in atactic polystyrene melt, whereas Milano<sup>15</sup> and co-worker have recently reported a study of gold nanoparticles, naked and coated, in a polystyrene melt with all atom model.

The main purpose of this work is a computational study, with the molecular dynamic (MD) technique; of the interfacial region between spherical silica nanoparticle embedded respectively in MMA and poly methylmethacrylate (PMMA).

We know that experimentally<sup>8</sup> a variation of molecular weight distribution of atactic PMMA is observed when an *in situ* synthesis, through a free radical mechanism, is performed in absence or not of silica nanoparticles. We decided to investigate also a system in a pre-polymerized situation, in which silica nanoparticle is surrounded by MMA monomer liquid.

The details of simulations are given in section 2, while the results are analyzed and discussed in section 3.

## 2 Model and Simulation Details

To understand better the structural properties of a chemically polymeric matrix of PMMA close to spherical silica nanoparticles, we have used MD simulations. The systems studied are summarized in the Table 1.

Nr. Nanoparticle Diameter = 3 nm	Nr. of MMA monomer	Nr. of PMMA chains/MW	Box length nm	Simulation time/ns	Temperature K	Pressure Pa
1	3981	-	10.36 ± 0.01	40	500	1013.25
1	-	757 (500)	8.68 ± 0.01	40	500	1013.25

**Table 1.** Studied Nanocomposite Systems.

For the model of MMA monomer we used in a first time the standard OPLSAA force-field<sup>16</sup>. The initial parameters taken from the OPLSAA have been refined to obtain a better reproduction of density and Enthalpy of vaporization of MMA bulk (Table 2).

Property	Calculated	Experimental <sup>17</sup>
Density (293 K)	0.955 (g/cm <sup>3</sup> )	0.946 (g/cm <sup>3</sup> )
$\Delta H_{\text{vap.}}$ (300 K)	38.854 (kJ/mol)	38.866 (kJ/mol)

**Table 2.** Comparison of density and Enthalpy of vaporization between refined model of MMA and experimental data. 300 MMA molecules form the system used for the calculation of properties. The simulations have been performed in NPT ensemble for 300 ns.

The silica core was constructed from a lattice of crystalline silica with a procedure described by Brown<sup>12</sup> and Müller-Plathe<sup>14</sup>. Basically to construct a nanoparticle of radius  $r$ , a point into lattice crystal of silica, that has enough extension in the 3D space, it chose. A sphere of chosen radius is cutted from the selected point. Then, all the oxygen atoms into the sphere but not connected to retained silicon atoms are removed. Finally all silicon atoms that had bonds with three surface oxygen atoms are removed.

The procedure just reported allows to reproduce a spherical nanoparticle with the crystal structure of  $\alpha$ -quartz, as reported by Brown<sup>12</sup> and Müller-Plathe<sup>14</sup>. We constructed a

nanoparticle of silica with a diameter of 3 nm and we used the same model described in work of Müller-Plathe<sup>14</sup>.

For the PMMA polymer we used an all atoms model reported by Maranas<sup>18</sup>. Differently from that model, we used atactic sequences of polymer chains. We setup three system with different molecular weight (MW), respectively 502; 1003 and 2004, that correspond at 5, 10, 20 monomers per chain.

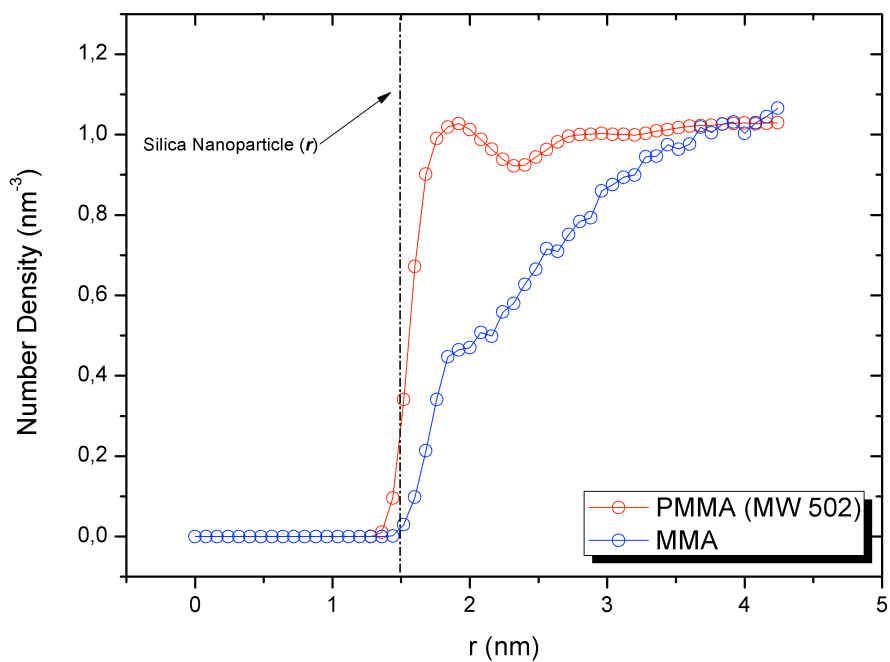
The MD simulations code, GROMACS<sup>19</sup> 4.5.4, was used at constant temperature  $T$  and pressure  $P$ , employing Berendsen's thermostat weak coupling to a temperature bath of 500 K and pressure bath of 1013.25 Pa. The coupling times were 0.1 ( $T$ ) and 0.2 ps ( $P$ ), whereas a time step of 1 fs was employed. A cutoff radius of 0.8 nm was employed for nonbonded interactions and a reaction-field correction for the Columbic interactions. The effective dielectric constant  $\epsilon_{RF}$  of 6.23 corresponding to the amorphous PMMA at room temperature<sup>17</sup> was set.

### 3 Results and Discussion

The radial number density  $\rho_N(r)$  as function of the distance  $r$  from the nanoparticle center of the mass (c.o.m.) are shown in Figure 1.

The red line, corresponding to the radial number density of system composed by PMMA (MW 502) and silica nanoparticle (Table 1), shows a single peak about 1.7 nm. This peak indicates a structuration of chains in the vicinity of the nanoparticle. Beyond 3.0 nm the value of density becomes equal to the polymer melt density. The blu line, which corresponds to the system of MMA surrounding the silica nanoparticle, shows a weak ordering of MMA respect to PMMA. At 1.7 nm the maximum value of number density of MMA is less than half of value reached by PMMA.

Using MD simulations we have characterized, at atomic level, the interface between silica nanoparticle and PMMA melt, with MW of 502. Moreover, we compare the structuration of silica nanoparticle interface between MMA and PMMA (MW 502). The radial density profiles reveal that a low density layer of MMA, situation that mimic pre-polymerization system, is present on the surface of silica nanoparticle.



**Figure 1.** Radial density profiles of the center of mass of MMA/PMMA chains, for systems containing silica nanoparticle. The MW of PMMA polymer melt is 502.

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