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# DPD Simulations of PMMA-Oleic Acid Mixture Behaviour in Organic Capped Nanoparticle Based Polymer Nanocomposite

*E. Bianchino,*[1] *S. Piotto,*[*1,2] *F. Mavelli,*[3] *M. L. Curri,*[4] *M. Striccoli*[4]

**Summary:** Dissipative Particle Dynamics has been used to investigate the different morphology of polymer nanocomposites. Such a study was addressed to the definition of a suitable tool for understanding the distribution of oleic acid (OA) capped nanoparticles embedded into poly-methylmethacrylate (PMMA) matrix for the formation of nanocomposite materials. In particular, simulations of PMMA/OA mixtures at different composition have exhibited the self-assembly of amphiphiles to form separated nanosized domains with different morphologies going from spheres, to tubules up to the formation of continuous planar sheets as the OA composition increases. On the other hand, simulations carried out on nanocomposite systems have shown that NPs do not perturb the observed phase behaviour of PMMA/OA mixtures. In fact, at low OA compositions nanoparticles are confined in the spherical lipid domains to form NP clusters, while at high OA composition NPs appear homogeneously distributed in the continuous lipid domain.

**Keywords:** DPD simulations; PMMA-oleic acid mixture; polymer nanocomposite

## Introduction

The design of original functional materials able to combine tailored physical and chemical properties and versatile processing capabilities is currently one of the ultimate challenge of the material science. In particular, nanocomposites, formed of colloidal nanocrystals and nanoparticles embedded in polymer matrixes, combine the peculiar characteristics of both organic and inorganic moieties in a unique complex material. These hybrid materials join the structural flexibility and the convenient processing of the polymers with the original size and shape dependent properties of the inorganic nano-components, resulting in an effective assembly of their individual features. Such cooperative combination provides excellent opportunities to fabricate novel and original materials with interesting properties that have been explored in many application fields, including linear and nonlinear optical devices, waveguides, optical switches, sensors.[1]

One of the most crucial points for the fabrication of such class of nanocomposites relies on the ability to control the dispersion of the NPs in the host environment. In fact, nanoscale particles typically possess a strong tendency to aggregate, which might be disadvantageous for retaining their size dependent properties and for the processing steps of the resulting materials. As a consequence, for the preparation of polymer nanocomposites the fundamental requirement resides in optimizing the distribution of the NPs in the host environment. For this reason a critical challenge in the design of these inorganic-organic systems is to control the mixing between the two dissimilar phases and several chemical

[1] Department of Pharmaceutical Sciences, University of Salerno, Italy
E-mail: piotto@unisa.it
[2] Research Centre for Nanomaterials and nanotechnology NANOMATES, University of Salerno, Italy
[3] Department of Chemistry, University of Bari, Italy
[4] CNR-IPCF Bari Division, c/o Dip. di Chimica, University of Bari, Italy

approaches have been applied to overcome this problem.

Among the different approaches the methods based on mixing of synthesized inorganic NPs with pre-formed polymers has been reported to induce the formation of strongly connected aggregates, due to the high specific surface energy of NPs.[2] The occurrence of particle agglomeration tends to deteriorate optical, electrical, and mechanical and processing properties of the resulting composite materials. Nevertheless the process involving the blending of pre- made colloidal NPs into polymer matrix provides a remarkable advantage, as it allows for a careful control of both the inorganic and organic moieties. A driving factor, for ensuring the uniform dispersion of colloidal NPs in the polymer, deals with the control of the interaction between the polymer matrix and the NP surface.

The colloidal NPs represent a valuable candidate for such class of nanocomposite preparation, since they present a native layer of organic amphiphilic molecules, deriving from the synthesis, which coordinates the surface of NPs, (i.e. phosphines, phosphine oxide, carboxylic acid, etc) and make them soluble in a wide range of organic solvent. NP surface ligands, which can be also properly exchanged or modified [3] to improve the compatibility with the surrounding chemical environment, effectively represent a truly active chemical interface between the inorganic NP core and the external organic polymer component.

In this work the preparation of nanocomposite based on the incorporation of pre-synthesized oleic acid (OA) capped $TiO_2$ NPs into optically transparent, poly(methyl methacrylate) (PMMA) polymers has been considered in order to elucidate the role played by the native surfactant molecule, the oleic acid in the dispersion of NP in the polymer matrix.

In this perspective equilibrium miscibility, dispersion and spatial organization of particles, particle-induced modification of polymer conformation and packing, structure of the polymer-particle interface, and the calculation of new thermo-mechanical emerging properties are fundamental issues. Diverse theoretical and simulation approaches have begun to be employed to study fundamental aspects of model polymer-particle mixtures: Monte Carlo and Molecular Dynamics methods, both at atomistic and coarse grain levels, and mesoscopic methods such as like Dissipative Particle Dynamics[4] and Mean-Field Dynamics.[5]

In this contribution, $TiO_2$ NPs synthesised in surfactant solutions have been investigated.[6] As a consequence of the preparation method, NPs were coated by the oleic acid amphiphilic molecules, that, once NPs are embedded in a polymer host matrix, they can also play a role in defining the morphology of the blend.

In particular it has been observed that oleic acid capped titania NPs embedded in PMMA by exploiting a common solvent as dispersing medium, form loose aggregates in which the NPs, still preserving their individuality, are organized in larger assemblies in the PMMA matrix (Figure 1). These structures can be explained by the presence of a surfactant layers at the NPs surface which induces the formation of superstructures of self organised NPs. This work aims to evaluate the possibility to describe and foresee the characteristic features of the investigated polymer nonocomposites by using a commercially available software: Materials Studio® release 4.0 by Accelerys Inc..

In particular, Dissipative Particle Dynamics has been used to simulate the morphological features of PMMA/Oleic Acid and PMMA/Oleic Acid/Colloidal oxide NPs respectively. Indeed, this mesoscale method applies classical simulation techniques to coarse-grained systems. In this perspective polymer and surfactant molecules can be thought as decomposed in a collection of linked beads, representing homogeneous domains with approximately the same volume. Critical points in this approach stand on the description of NPs as rigid particles of different shapes and sizes and the calculation of the interaction parameters for the different type of beads

 

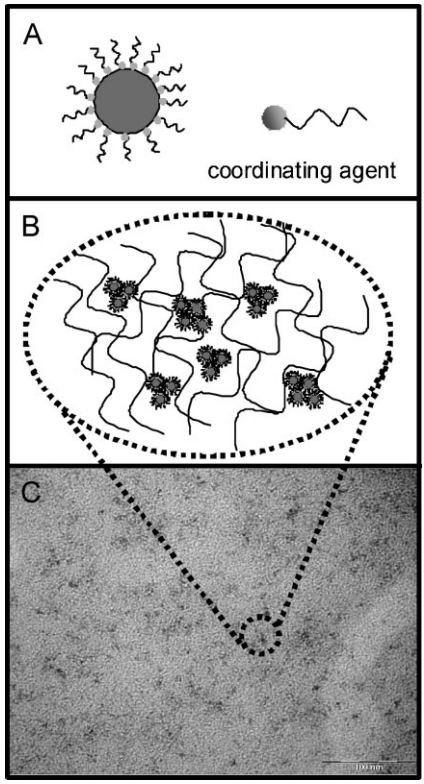


***Figure 1.***
A) picture of a nanoparticle coated with a layer of coordinating surfactant molecules; B) sketch of a possible formation of self assembled superstructures by crystallization of surface ligand alkyl chains in a host polymer matrix; C) TEM image of a film of PMMA embedding $TiO_2$ spherical nanoparticles coated with oleic acid.

in order to correctly simulate the dynamic behaviour of the studied system.

Some preliminary results will be presented and discussed. In particular, the formation of continuous surfactant domains in PMMA has been investigated as a function of the mixture composition.

## Theoretical Backgrounds

The simulation of the aggregation of polymer mixture at different composition has been carried out employing an efficient coarse grain algorithm, i.e. the dissipative particle dynamics (DPD). The DPD approach is a powerful, off-lattice, dynamical model. In a DPD simulation, the number of particles are significantly lower than a full atomistic representation and each particle represents the centre of mass of a cluster of atoms. An accurate description of the DPD approach can be found in the papers of Groot and Rabone.[4] In the present work we investigated the interaction of polymethylmetacrilate (PMMA) in the presence of a surfactant (oleic acid OA) for grafting nanocrystals of CdS. The molecule of PMMA and OA have been simplified in interacting particles as described below. For the simulation of PMMA and the OA as grafting agent, several types of particles were used and their mutual interactions were expressed in terms of repulsion parameters. The DPD parameters are related to the compressibility of fluid and to Flory-Huggins solubility parameters such that a reasonable description of the thermodynamics of the real system can be obtained. The simplest and best known theory of the thermodynamics of mixing and phase separation in binary systems is the Flory-Huggins model.[7] The general expression for the free energy of mixing of a binary system is:

$$\frac{\Delta G}{RT} = \frac{\phi_b}{n_b}\ln\phi_b + \frac{\phi_s}{n_s}\ln\phi_s + \chi\phi_b\phi_s$$

where $\Delta G$ is the free energy of mixing (per mole), $\phi_i$ is the volume fraction of component $i$, $n_i$ is the degree of polymerization of component $i$, $\chi$ is the interaction parameter, $T$ is the absolute temperature, and $R$ is the gas constant. The first two terms represent the combinatorial entropy. This contribution is always negative, hence favoring a mixed state over the pure components. The last term is the free energy due to interaction. If the interaction parameter, $\chi$, is positive, this term disfavors a mixed state. The interaction parameter, $\chi$, is defined as:

$$\chi = \frac{E_{mix}}{RT}$$

where $E_{mix}$ is the mixing energy; that is, the difference in free energy due to interaction between the mixed and the pure state. For

 

the calculation of $\chi$, rather than using traditional Flory-Huggins model, where each component occupies a lattice site, we employed a more sophisticated approach [8] that combines a modified Flory-Huggins model and molecular simulation techniques. In the present work, two important extensions to the Flory-Huggins model are used: first of all, the temperature dependence on the interaction parameter is considered explicitly.[9] This is accomplished by generating a large number of pair configurations and calculating the binding energies, followed by temperature averaging the results using the Boltzmann factor and calculating the temperature-dependent interaction parameter. Secondarily, the molecules are not arranged on a regular lattice as in the original Flory-Huggins theory, but the coordination number is calculated for each of the possible molecular pairs. A wide variety of force fields (including Dreiding, Universal, COMPASS, cvff, and pcff) have been extensively tested on our system. A force field refers to the functional form and parameter sets used to describe the potential energy of a system of particles.

## DPD Parameterization

In this section the assumed molecular topology and the calculated force constants will be presented and discussed.

The bead volume will be set equal to $0.16\,nm^3$, i.e. the volume of a - methylmethacrylate monomer. A single polymer chain will be described as composed by 50 beads to simulate polymeric blends with an average molecular weight about 5000 g/mol. By the macroscopic density of the pure oleic acid: $331.89\,cm^3$/mol was possible to estimate the volume of a single molecule $0.551\,nm^3$ and then the number of beads per amphiphile: $0.551/0.16 \approx 3$. In particular, one beads was used for the hydrophobic head (H) and other two for the hydrophilic tail (T) assuming a linear topology: H-T-T.

To simulate $TiO_2$ spherical NPs 700 beads have been used so that their total volume corresponds to a sphere of the a 3 nm radius. Also in this case a linear morphology was assumed but some initial *ad hoc* force constants have been adopted to obtain the formation of a nearly spherical folded structures.

Different force fields are designed for different purposes and in the present work the most adherent to experimental observation resulted to be the CVFF.[10] Groot and Warren[4] performed a series of DPD calculations on binary mixtures in which they found a linear relationship between Flory-Huggins parameter $\chi$ and repulsion parameters. This relationship can be used to obtain input parameters for a pair of species with a known $\chi$ value. The relationship between the Flory-Huggins parameter and the repulsion parameter is:

$$a_{ij} = 25 + 3.50\chi$$

According the previous formula, the DPD repulsion parameters among the PPMA and OA beads were calculated and the obtained values are listed in Table 1. The repulsion parameters relative to NPs, could not be obtained by Flory-Huggins parameters. In fact, the values choice respond to experimental observation that will follow in a future publication.

## Simulation Results

In this sections, the DPD simulations results of a PMMA/Oleic acid mixtures of different compositions will be presented and discussed as first. All the studied cases are reported in Table 2. In any simulation, a squared box of $19 \times 19 \times 19$ DPD reduced

***Table 1.***
Force Constants for the pair wise repulsive bead-bead interactions.

| DPD Repulsion Parameters | | | | | |
|---|---|---|---|---|---|
| Bead Type | | P | T | H | NP |
| *PMMA Monomer* | P | 25 | | | |
| *Oleic Acid tail* | T | 42 | 25 | | |
| *Oleic Acid head* | H | 30 | 33 | 25 | |
| *$TiO_2$ Nanoparticles* | NP | 45 | 76 | 10 | 3 |

 

***Table 2.***
PMMA Compositions of the PMMA/Oleic Acid mixtures investigated

| N | PMMA | | | Equilibrium morphology |
|---|---|---|---|---|
| | %Beads | Molecular Fraction $\chi_M^{PMMA}$ | Wheigth Fraction $\chi_W^{PMMA}$ | |
| 1) | 90 | 0.351 | 0.905 | spheres |
| 2) | 84 | 0.236 | 0.846 | |
| 3) | 81 | 0.204 | 0.819 | |
| 4) | 78 | 0.171 | 0.785 | tubules |
| 5) | 71 | 0.130 | 0.725 | |
| 6) | 69 | 0.118 | 0.703 | |
| 7) | 65 | 0.100 | 0.664 | layers |

length units was used and the total number of beads in the box was set about $2 \cdot 10^5$. This number of beads corresponds to a 3.0 density value, for which the repulsion parameter/Flory-Huggins parameter relationship has been established.

The system temperature was set to 1.0 corresponding to 298 K, that is the temperature at which the repulsive and dissipative interaction parameters were determined. All the simulations were run for $10^5$ steps, with a time step of 0.05, starting from a random distributions of beads in the box. Both the temperature and the hydrostatic pressure time courses were checked at the end to be sure that they fluctuate around an equilibrium value. Typical trends of temperature and pressure are plotted in Figure 2 for the system N.4 where tubules are formed. In each run, the pressure time trend shows that after an interval of time about $5.0 \cdot 10^2$ DPD units ($10^4$ steps) the system reach the equilibrium configuration and the rest of the time it oscillates around this equilibrium state. The morphology of the equilibrium configurations collected at the end of all the carried out simulations are reported in Table 2 as a function of the system composition. As shown in Figure, in all the studied cases, the system spontaneously organizes in two domains: the polymer (PD) and the lipid domain (LD) respectively. At low oleic acid composition the lipid molecules self-assembly in spherical discontinuous domains of growing radius that transform into continuous tubules that convert into continuous layers.

Having explored the behaviour of PMMA/OA mixtures, simulations were carried out in order to investigate if the observed domain morphology is affected by the presence of NPs. NPs were represented as spherical conglomerate of 700 beads linearly connected with a total volume approximately equal to a sphere of 3.0 nm radius. The formation of the NPs was

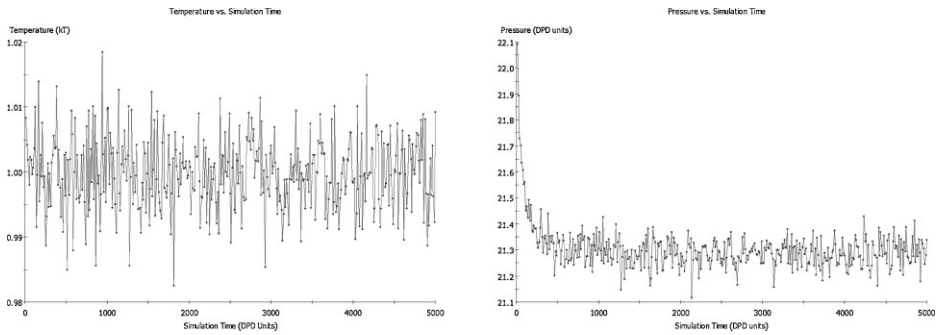


***Figure 2.***
Time course of temperature (on the left) and pressure (on the right) throughout the DPD simulation N.4 in Table 2.

 

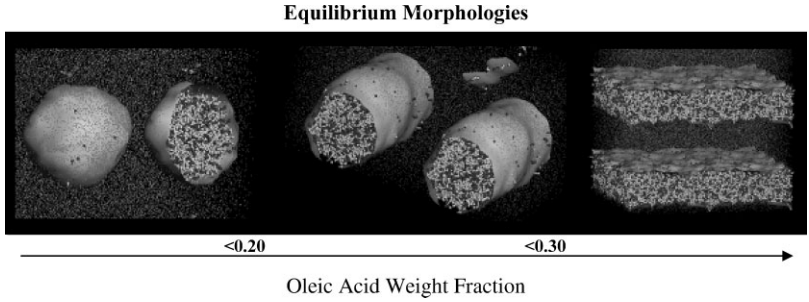


***Figure 3.***
Different morphologies observed in DPD simulations of PMMA/Oleic Acid mixtures with different compositions: surfactant molecules are represented by dark grey (hydrophilic head) and light grey (hydrophobic tail) spheres, while polymers are not explicitly reported. The gray surface is the interface between the two domains.

obtained at the beginning of each simulation by a suitable choice of the starting force constants.

As first we investigate the case of a singular NP embedded in a PMMA/OA mixture as reported in Figure. The results show that the embedded NP does not perturb the range of stability of spherical LD. In fact, it does not promote the formation of tubules at a lower surfactant composition of the PMMA/OA mixture as shown by the simulation done at $\chi_W^{OA} = 0.194$. Moreover, above 0.128 oleic acid weight fraction the NP is completely coated by a layer of amphiphilic molecules with hydrophobic tails located in the middle of the sheet and the hydrophilic heads orientated towards the NP and the polymeric domain. Therefore, the used set of force constants well reproduce the orientation of OA molecules around the NP. Since this preferential orientation was less evident in a pure PMMA/OA mixture we can conclude that the presence of NPs at low OA compositions contributes to better organize the lipid domain. At higher OA composition the NP appear located in the middle of LD domains both in the case of tubules and layers (data not shown).

In Figure is reported the case of two NPs embedded PMMA/OA mixture. These simulations were carried out in order to study the interactions and structural organization of coated NPs. Both NPs were made

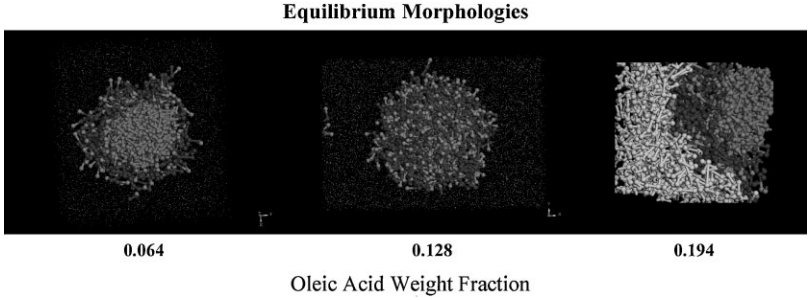


***Figure 4.***
Different morphologies observed in DPD simulations of PMMA/Oleic Acid mixtures with a single $TiO_2$ nanoparticle embedded. Surfactant molecules are represented by light grey (hydrophilic head) and dark grey (hydrophobic tail) beads, while the nanoparticle is in grey. Polymers are not explicitly reported. Different compositions in the range of stability of spherical LD domains ($\chi_W^{OA}$)*whereinvestigated* : $\chi_W^{OA} = 0.128$ is the minimal OA weight fraction to observe a completely coated NP. A section of the spherical structure obtained at $\chi_W^{OA} = 0.194$ is reported on the left where polymers are explicitly represented as white beads to better shows the structure of lipid domain.

 

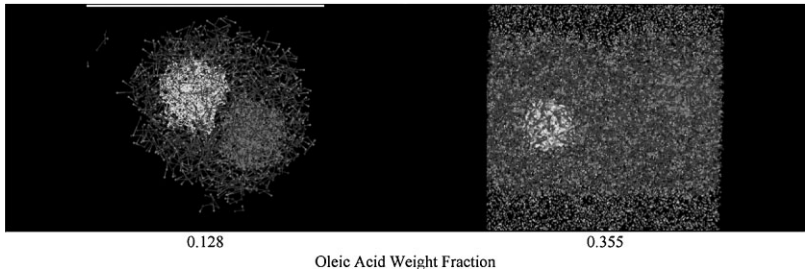


***Figure 5.***
Different morphologies observed in DPD simulations of PMMA/Oleic Acid mixtures with two $TiO_2$ nanoparticles embedded.

of 700 beads with the same matrix of force constants (see Table 1). In addition, a repulsive force constant for beads belonging to the two different NPs was set equal to 90 to mimic an electrostatic repulsion.

In spite of this high repulsive force constant, at low oleic acid composition the two NPs are confined in the same lipid domain rather than form two separated structures coated by amphiphilic molecules, see Figure on the left. It is worthwhile to remark that the box simulation was slightly resized to ensure the same number of OA per NP, for the PMMA/OA composition $\chi_W^{OA} = 0.128$. As $\chi_W^{OA}$ increases, see Figure on the right, the lipid domain growth in size and NPs tend to spontaneously separate. So we can conclude that at low PMMA/OA composition the NPs appear to be self-assembled to form clusters while at high composition they can be homogeneously distributed in the polymeric matrix. This behaviour is a consequence of the amphiphilic molecules capability to form continuous domains in the polymer blend.

## Conclusion

The design of original functional materials is currently one of the ultimate challenge of the material science. One of the most crucial points for the fabrication of nanomaterials with controlled properties relies on the ability to control the dispersion of the nanoparticles in the host matrix. The control of the dispersion process was the subject of the present work. We have shown that a mesoscale simulation tool as Dissipative Particle Dynamics (DPD) is a reliable method to study the morphology of polymer nanocomposites. In particular, the case of oleic acid capped $TiO_2$ nanoparticles embedded into poly-methylmethacrylate matrix has been addressed. In spite of the fact that this computational approach is mainly devoted to the study of soft-matter, we were able to reproduce the observed behaviour of $TiO_2$ nanoparticles that self-assemble to form clusters in the polymeric matrix when the oleic acid composition is low. DPD simulations account for this behaviour showing it is driven by surfactant molecules. In fact, when oleic acid molecules are mixed with PMMA polymers, they can spontaneously form OA rich domains of different morphology going from discontinuous spherical droplets, to continuous cylindrical tubules up to forming 2D continuous layers. When NPs are added to the blend, they appear to be embedded into these oleic acid rich regions. So, at low surfactant content they remain confined into the same spherical oleic acid domain rather than being dispersed as separated coated nanoparticles into the polymeric matrix. On the other hand, when the surfactant composition increases NPs appear to be homogeneously distributed into the oleic acid continuous domain. Our DPD simulations suggests that in order to obtain homogeneous

 

polymeric nanocomposite materials the compositions of surfactant molecule should be increased. This hypothesis needs further investigations.

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