

A MOLECULAR DYNAMICS STUDY OF A MODEL NANOPARTICLE EMBEDDED IN A POLYMER MATRIX

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INTRODUCTION

At the molecular level, the influence of interactions at the polymer/filler interface on the molecular mobility and structure of neighbouring chains is amplified in the case of objects of small dimensions in a more or less complex way, because the relative amount of material in the vicinity of the interface is inversely proportional to the size of the inclusions. Thus, although experimental work [1, 2] points to a reduction in molecular mobility in the region of the interface little is known about the origin of this immobilisation, the possible accompanying changes in structure or the spatial extent of these two effects.

For the above reasons it is interesting to undertake a study of such a system using a molecular modelling approach. To our knowledge, the structure and dynamics of the nanoparticle/polymer matrix interface has received very little attention to date using such simulation techniques. In many other areas of chemical physics molecular dynamics (MD) simulations have provided detailed atomic-level insight into phenomena not readily observable by conventional experiment [3]. In this paper, results are presented of a pilot study of a model polymer matrix reinforced by a mineral nanoparticle. This preliminary project is designed to probe the feasibility and the possible insights that can be gained before attempting a subsequent more detailed study using more realistic systems.

DETAILS OF THE SIMULATIONS

All simulations performed in this study used the *gmq* suite of molecular dynamics and associated programs [4]. Simulations were either carried out on SGI O2 workstations or on the Cray T3E multiprocessor at the IDRIS computing centre in Orsay, France. These latter calculations used the parallel (domain decomposition) version of the code, *ddgmq* [5, 6].

This initial study has used a model silica nanoparticle made up of just Si and O atoms. For the purpose of testing the general approach a simple model can be used and so the model of Tsuneyuki [7] has been chosen. This model is relatively straightforward consisting of just pair-wise additive interactions; a Buckingham (exponential-6) potential represents the Van der Waals interactions and partial charges are placed on each atom ($q_{\text{Si}}=2.4e$, $q_{\text{O}}=-1.2e$) to describe the Coulombic interactions. To create a roughly spherical nanoparticle an α -quartz supercell crystal structure was first created and then all Si and O atoms outside a radius of ~ 20 Å from the centre were discarded. The resulting cluster contained 914 Si atoms and 1828 O atoms and was thus electrically neutral. For this feasibility study the use of a starting crystalline configuration rather than an amorphous phase of silica is of no consequence. The subsequent problem of embedding this nanoparticle in a polymer matrix and relaxing the system is the same.

The model polymer matrix used in this study is based on a one which has been often employed to study model amorphous polymer systems [8-11]. In this model, linear chains of n united-atom "CH₂" sites are held together by rigid bonds and a valence angle and torsion angle potentials give internal structure and rotational barriers. Non-bonded interactions are represented by a purely repulsive potential. In the original model this latter potential took the form of a Lennard-Jones (LJ) 12-6 potential truncated at the minimum and raised up by the well depth to give a repulsive potential smoothly decaying to zero; often referred to as a Weeks-Chandler-Andersen, or WCA, potential. In this case the WCA potential is replaced by the Buckingham form so as to facilitate the interactions with the Si and O atoms. As only a repulsive interaction is required the potential took the following form

$$\Phi(|\mathbf{r}_{ij}|) = A \exp(-|\mathbf{r}_{ij}|/B) \quad (1)$$

The two adjustable constants, A and B , were obtained from non-linear least squares regression fits to the original WCA form in the range from 3.9 to 4.8 Å which corresponds to the important region of nearest neighbour interactions. The resulting parameters ($A=4208$ keV and $B=0.20829$ Å) were found to lead to a good correspondence with the WCA model.

For the purpose of this study one long chain of $n=30000$ sites was constructed using a generation technique [10] known to produce representative configurations from the dense amorphous phase [11]. The model polymer matrix formed is thus one in which one single chain gives a dense system through the replicative properties of the periodic boundary conditions. This system was subsequently relaxed using standard molecular dynamics techniques for 1000 ps at a temperature 300 K under constant pressure conditions. To compensate for the lack of attractions an over pressure of 5000 bars was

applied; this results in relaxed densities which correspond closely to those found if attractions are included and atmospheric pressure is applied.

To introduce the silica nanoparticle into the relaxed polymer matrix a cavity was first created using a soft repulsive potential [4]. By gradually increasing the size of this cavity from zero to a value large enough to accept the silica particle over a period of time, disruption of the carefully prepared polymer matrix was minimized. The combined nanoparticle/matrix system was then relaxed for a further 2500 ps. Cross interactions between the polymer and the silica were described using standard combining rules and were thus completely repulsive in nature.

RESULTS AND DISCUSSION

Figs. 1 to 4 show some of the principle results obtained from averages over the last 500 ps of the MD simulations. Fig. 1 gives the density of polymer as a function of R , the distance from the centre-of-mass of the silica nanoparticle. It shows a distinct first and second shell of polymer is formed around the nanoparticle. At larger distances the density tends to that expected of the polymer matrix. Despite this clear interfacial structure, the mean square amplitudes of vibration of the polymer atoms, shown in Fig. 2 as a function of R , only show a slight tendency for immobilisation of the chains in the range 22-30 Å. Indeed, comparisons (not shown) of the mean square displacements of polymer atoms in the composite and those in the pure matrix are statistically indistinguishable. Analysis of the percentage of backbone -C-C-C-C- *trans* conformers as a function of R (Fig. 3), however, confirms that statically the structure is affected. The characteristic dynamic relaxation behaviour of the *trans* state, as given by the $C_{TT}(t)$ function [12], does not show any significant variation with R . Fig. 4 shows that the normalized $C_{TT}(t)$ functions for -C-C-C-C- torsions in different ranges of R are very similar to that found in the pure polymer matrix.

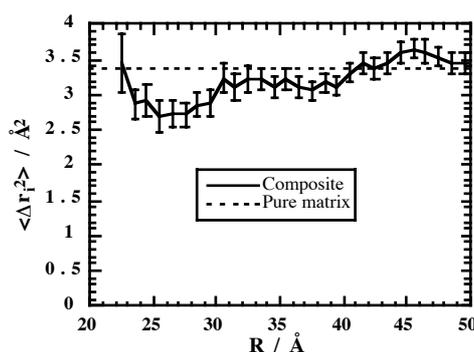
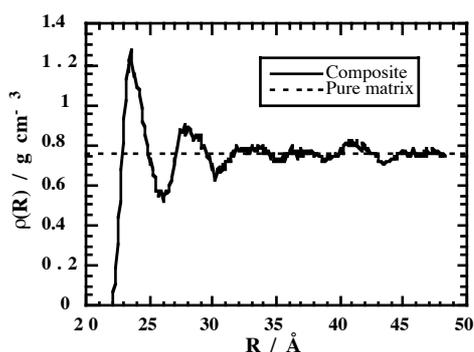


Fig. 1 The density of the polymer atoms as a function of R , the distance from the centre of mass of the silica particle. The dotted line gives the density of the pure polymer matrix.

Fig. 2 The mean square amplitudes of vibration of polymer atoms plotted as a function of R . The dotted line gives the value found in the pure polymer matrix.

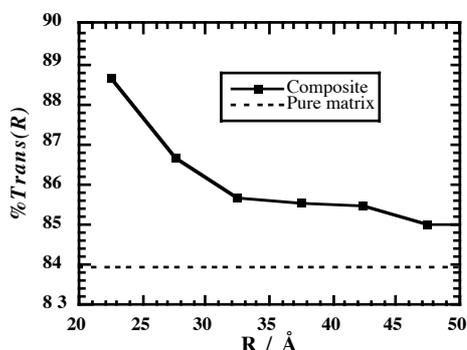


Fig. 3 The mean percentage of *trans* conformers plotted as a function of R. The dotted line gives the $\langle \%trans \rangle$ of the pure polymer matrix.

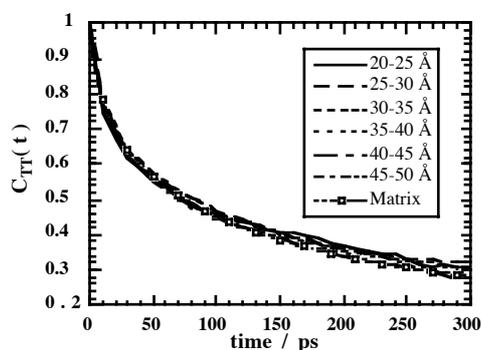


Fig. 4 The normalized $C_{TT}(t)$ relaxation functions found in the regimes of R given compared to that in the pure polymer matrix.

CONCLUSION

The feasibility of performing atomistic level simulations of nanoparticles embedded in polymer matrices has been demonstrated. Sufficient statistics can be gathered to enable properties to be determined as a function of the distance from the interface. This is encouraging for the next stage where more realistic potentials will be used. In this pilot study the nanoparticle/matrix interface is found to be well-defined statically although dynamically the effects are less evident. This latter lack of immobilisation may to some extent be due to the use of a purely repulsive polymer-silica potential.

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