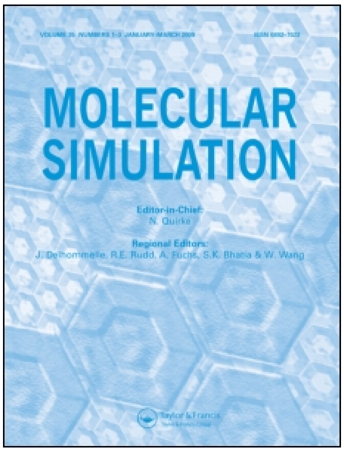

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Effect of Water Concentration on Sol Formation in Synthesis of Organic/Inorganic Hybrid Materials

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Effect of Water Concentration on Sol Formation in Synthesis of Organic/Inorganic Hybrid Materials

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Molecular dynamics simulations have been performed for precursor molecules used for organic/inorganic polymer hybrid preparation. The initial stage of the sol–gel process was simulated with the components at various water concentrations. Analyses of structural properties of the equilibrium configurations were performed via radial distribution functions. It was concluded that water concentration plays an important role in the agglomeration of the clusters due to the hydrophobic effect. Low water concentration leads to less pronounced hydrophobic interactions between the components resulting in structural instability.

Keywords: Molecular dynamics; Organic/inorganic polymer hybrids; Sol–gel process; Hydrophobic effect

INTRODUCTION

This study followed our initial investigation of molecular mechanisms of sol formation from commonly used precursors [1]. This preliminary communication reports the results from molecular modelling studies of the effect of water concentration on the sol formation from the precursor molecules, during the initial stages of the sol–gel process in OIPH synthesis. The molecular interactions of the components at this initial stage were studied using the molecular dynamics (MD) method, which has been previously used for theoretical studies of polymer aqueous solutions [2–6].

COMPOSITION OF MOLECULAR MODELS

The solution modelled in this work consisted of the following precursors: Glycidyloxypropyltrimethoxysilane (ES), Tetraethoxysilane (TEOS), and the polymer constituent Polyvinyl-alcohol (PVA), which is often used in polymer hydrogels due to its hydrophilic character [7]. Three model systems were constructed with varying water concentrations. Each system contained the same number of non-aqueous constituents: 4 ES molecules, 9 TEOS molecules, and PVA of a polymerisation degree 20. System 1 comprised 600 water molecules, system 2 comprised 300 and system 3 contained 150 water molecules representing 75, 60 and 43% of water by weight, respectively. The density of the systems was obtained as described in Ref. [1].

SIMULATION PROCEDURE

For each composition, 10 initial model configurations were constructed at the specified density by packing the molecular components of the system into a 3D periodic unit cell using the Theodorou–Suter algorithm [8] to allow realistic chain statistics for the polymer constituent. Subsequent relaxation of the initial system configurations was performed by MD method, using the periodic boundary conditions [9].

Interatomic interactions in the systems were described by the COMPASS forcefield that is specially designed for organic/inorganic interactions [10]. MD simulation (NVT ensemble) was initially performed on the systems for 500 ps (500,000 time-steps of 1 fs) at temperature of 298 K to ensure equilibrium has been reached. After that a production run of 500 ps was performed with data recorded to disk every 1000 time-steps (1 ps) for

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analysis, producing 500 equilibrium configurations. Additional details of the simulation procedures are described elsewhere [1].

RESULTS AND DISCUSSION

A typical equilibrium configuration for each system is graphically presented in Fig. 1. It can be seen from Fig. 1 that globular clustering of the non-aqueous components is apparent in all three systems with the polymeric component attaching itself around the cluster. However, Fig. 1a and b shows that systems 1 and 2 exhibit stronger association of the hydrophobic groups in ES and TEOS compared to that of system 3. It was observed in system 3 (Fig. 1c) that the agglomeration of the precursors was the weakest, resulting in more sparse clusters. Since agglomeration of the non-aqueous components is driven by the hydrophobic effect, i.e. the tendency to minimise surface area of contact between water and hydrophobic residues on the precursors, it can be suggested that water concentration affects the compactness, and thus stability, of the globular clusters.

The equilibrium configurations were analysed in terms of radial distribution function to estimate the extent of hydrophobic association of components and to confirm the visual observations made (Fig. 2). As can be seen from Fig. 2a, the two distinct peaks

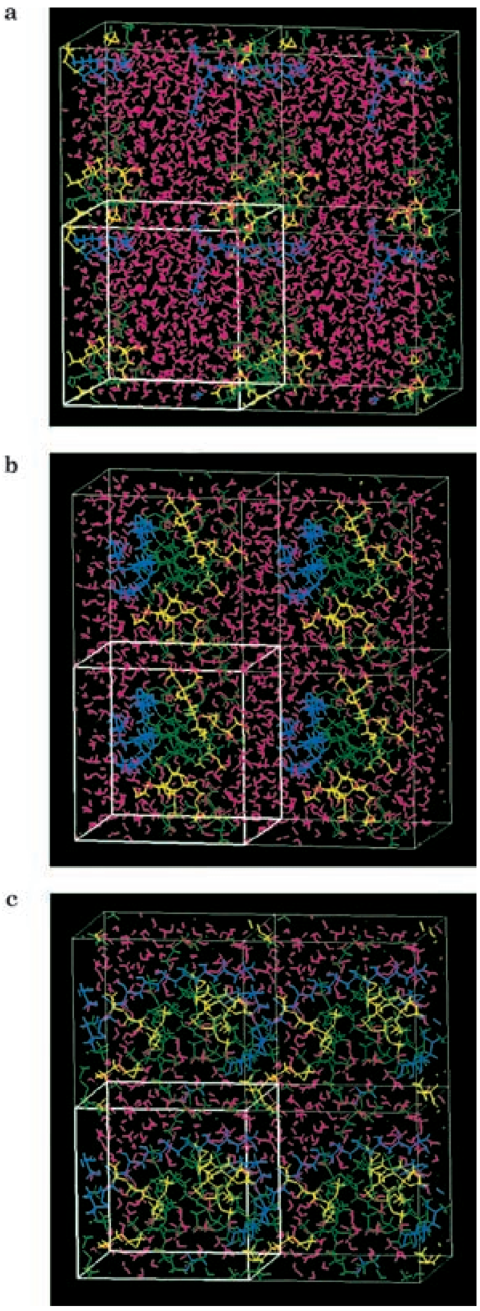

FIGURE 1 System structure after molecular dynamics: (a) system 1, (b) system 2, (c) system 3. (Pink-Water, Blue-PVA, Green-TEOS, Yellow-ES).

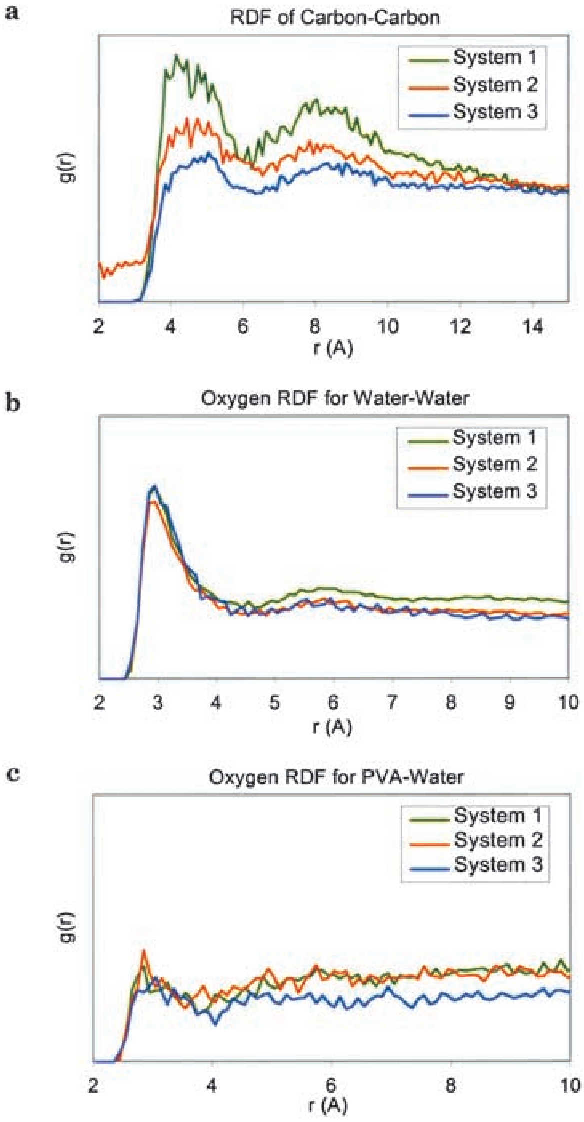

FIGURE 2 Radial distribution functions (RDF) of different atoms within the system.

suggests a high probability of locating a carbon atom at approximately 4.1 Å from another carbon atom which agrees with previous computational studies [7]. The consistent peak distance suggests the atoms are separated by van der Waals radii, with the first peak representing the first coordination shell and the second peak — the second coordination shell. The peaks are higher for system 1, and systematically diminish towards system 3 thus confirming the visual observation of more pronounced clustering in higher water concentration.

Figure 2b confirms the hydrogen bonds formed by water with itself, with the first peak at approximately 2.9 Å and the second at 5.8 Å, demonstrating structuring of water up to two hydration shells. The considerable peak in Fig. 2c suggest that PVA also hydrogen bonds with water molecules via its hydroxyl groups. This explains the PVA attaching itself to the cluster since it interacts with both water and hydrophobic residues of ES and TEOS molecules.

CONCLUSION

It was found that with higher water concentration, clustering of the precursors in the aqueous solution at the initial stages of OIPH preparation was more significant. This was attributed to the hydrophobic effect. At low water concentration, the hydrophobic effect was less pronounced. Since previous computational experiments performed suggested clustering of the components being the first step of the sol–gel process [1], it is vital the water concentration of the system be adequate.

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