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A molecular dynamics study of siloxane diffusion in a polyester–melamine solution

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Abstract

This study examines the diffusion of small methylated and hydroxylated siloxanes through solutions of polymer and crosslinker molecules. The diffusivity of the siloxanes was calculated for bulk diffusion and for surface segregation. Our simulations demonstrate that there is significant interaction between 3,3-dimethylhexahydroxytrisiloxane (hexa-OH-TS) and the polar solvent components of the paint matrix at 298 K. The nature of these associations is largely due to hydrogen bonding between the siloxane and the polar solvent molecules. At 573 K the diffusivity of solvent molecules is sufficiently high to disrupt interactions. The smaller number of hydroxyl groups in 1,5-dihydroxyhexamethyltrisiloxane (hexa-Me-TS) results in a weaker interaction with the polar solvent. Surface segregation studies indicate that there is a slight increase in the concentration of hexa-OH-TS in the surface layer of the system as a result of curing and relaxation processes. However, for hexa-Me-TS there is in fact a decrease in the surface concentration of the siloxane relative to the bulk concentration.

Keywords: Molecular dynamics; Polyester; Siloxanes

1. Introduction

Topcoats used in the automotive industry need to be able to withstand both physical (scratch resistant) and harsh environmental (heat, UV, precipitation) conditions. The topcoats used in these applications usually consist of a two layer system of basecoat and clearcoat applied over a primer layer. It is the clearcoat that is the first line of defence in these coating systems and it usually consists of acrylic copolymers crosslinked with melamine or isocyanates [1–3]. Investigations have shown that the performance of this layer can be improved by the inclusion of additives such as light stabilizers and surface levelling agents in very low concentrations [4].

Siloxanes have been found to be important additives for powder coatings where they act as levelling agents or surface tension modifiers. This is due to the extremely low surface energy of siloxanes which favours migration of these components to the polymer–air interface. It is therefore possible to prepare systems with quite different surface properties without causing significant changes to the bulk properties. Grundke et al. [5] have investigated the effect of various polysiloxanes additives on the surface tension of acrylic resin based powder coatings. Results for three standard additive formulations indicated that a reduction of up to 50% in the surface tension, compared to the pure acrylic resin, could be achieved with some polysiloxane additives, even at very low concentrations (<1 wt%). Further to this, the temperature coefficient of the binder melt was lowered which is important with respect to film formation.

Darque-Ceretti and co-workers have carried out several studies [6–8] of the migration of siloxane additives in automotive coatings and the subsequent changes in surface composition of the coating. They noted that there is significant migration of additives to the paint surface from the topcoat during curing. However, they also noted that about 25% of siloxane additives in the underlying basecoat migrate towards the topcoat surface during curing.

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The compatibility of the components also has a significant effect on the surface segregation of siloxanes and the appearance of the coating [9]. For example, Gorelova et al. [10] investigated surface/bulk compositional relationships for blends of polydimethylsiloxane (PDMS) in polyvinylchloride (PVC). They found that for 0.015 wt% of PDMS the corresponding surface concentration was 25 at%, while at 6 wt%, the surface concentration increased to 80 at%. However, in the latter case there is significant inhomogeneity of the surface suggesting phase separation. Likewise, in 1 wt% blends of PDMS with poly(bisphenol A carbonate) or poly(bisphenol A sulfone), it was found that the surface concentration of siloxane could reach as high as 95 wt% [11]. However, the situation can be quite different for polymer surfaces prepared under non-equilibrium conditions. Gorelova et al. [12] reported that the surface segregation of a dilute blend of PDMS with polychloroprene (PCP) decreased substantially with increasing molecular weight of the siloxane. Reijme et al. [13] also noted that traces of silicon-based impurities in organic materials can also segregate to the surface and may seriously modify the surface composition, sometimes adversely.

In the present study we attempt to model diffusion and surface segregation of small model siloxanes in realistic polymer resin matrices during the initial stages of the curing process. Typical silanol additives are long chain polydimethylsiloxanes. Direct modelling of the diffusion of these large molecules would lead to prohibitively large atomistic systems and simulation times. We have therefore approximated these molecules using small model siloxanes which differ by the degree of hydroxylation.

2. Theoretical procedures

2.1. Composition of models

Formulations of coating mixtures for this modelling study included 3,3-dimethylhexahydroxytrisiloxane ($(HO)_3SiOSi(CH_3)_2OSi(OH)_3$, hexa-OH-TS), 1,5-dihydroxyhexamethyltrisiloxane ($HO(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2OH$, hexa-Me-TS), polyester (MW ~ 3500), crosslinker (tributoxymethyl melamine), polar solvent (butanol, 1-methoxy-2-propanol, 4-hydroxy-4-methyl-pentan-2-one) and aromatic solvent (toluene and xylene). The Amorphous Cell procedure, which incorporates some features of the original Theodorou–Suter approach [14] and the Meirovitch scanning method [15], has been used to generate 10 atomistic 3D periodic unit cells of a physical mixture of the resin, crosslinker, solvent and siloxane additives with molar ratio as shown in Table 1. The molar ratio of the components was calculated from the weight ratio used during the synthesis of real coatings [16]. Ten starting configurations were generated for each system at a density of $\sim 0.86\ \mathrm{g\,cm^{-3}}$. The COMPASS forcefield [17–19] has been employed to model the interatomic potentials within the studied systems. Due to the computational demands of systems of this size (>14 000 atoms for bulk and >22 000 atoms for layer diffusion), it was found necessary to use the atom-based procedure to evaluate non-bond interactions. The atom-based parameters used were a 15.50 Å cutoff, a spline width of 5.00 Å, a buffer of 2.00 Å and a long-range tail correction. The buffer defines the distance beyond the cutoff region at which non-bond interactions are zero. It is used to build the neighbour list for non-bond energy calculations and affects only the efficiency of the calculations and not the accuracy. The large non-bond cutoff was chosen for these systems to ensure that electrostatic effects are sufficiently accounted for in these processes. The initial relaxation of the systems was achieved by potential energy minimisation followed by NVT molecular dynamics (0.5 ns, 298 K) with the periodic boundary conditions.

Table 1
Composition of model systems

Component	Wt%	Mol%
Polyester	39.4	2.1
Crosslinker	9.8	2.1
Trisiloxane	1.5	0.2
Butanol	6.2	15.8
1-Methoxy-2-propanol	6.2	13.0
4-OH-4-Me-pentan-2-one	6.2	10.1
Xylene	24.6	44.1
Toluene	6.2	12.7

2.2. Modelling bulk diffusion

To simulate the curing regime, the systems were equilibrated at 573 K using the constant pressure/constant temperature (NPT) ensemble for 0.5–2 ns using the Berendsen barostat [20] and the Andersen thermostat [21]. After achieving equilibrium, the systems were subjected to MD simulations at 573 K for 1.0 ns for data acquisition. An additional series of runs were performed at 298 K for comparison. For each system, the linear region of mean-square displacement versus time plots was used to determine bulk diffusion coefficients (D), via the Einstein equation [22].

2.3. Modelling layer diffusion

A paint matrix layer (~40 Å in thickness) was prepared by energy minimisation of the 3D periodic atomistic models of resin, crosslinker and solvent (described above) under a restraining potential in the z-direction. An additional layer comprising polymer and crosslinker was constructed and energy minimized, also under a restraining potential in the z-direction, to give a compact layer representing the undercoat (~15.5 Å in thickness). The resin film was then combined with the undercoat layer under periodic boundary conditions in such a way that the majority of siloxane additives were initially closer to the basecoat interface than the "air" interface. In this way we maximise the z-direction path length, increasing the number of data points before evaporation of these low molecular weight siloxanes. The cell was extended to 150 Å in the z-direction to eliminate interactions across cells and to simulate quasi-2D periodic boundary conditions in which the paint film resides between a rigid undercoat and the atmosphere. The undercoat layer remained fixed during all

Table 2
Bulk diffusion coefficients (D) for Systems 1 and 2 ($\times 10^{-5}$ cm^2 s^{-1}) at 573 K

Component	System 1 (hexa-OH-TS)		System 2 (hexa-Me-TS)	
	D	Std	*D*	Std
Trisiloxane	1.64	0.28	1.59	0.47
*n*BuOH	4.03	0.39	4.39	0.54
1-Methoxy-2-propanol	3.54	0.33	3.79	0.50
4-OH-4-Me-pentan-2-one	2.40	0.33	2.68	0.57
Xylene	3.03	0.24	3.06	0.35
Toluene	3.04	0.48	3.40	0.39
Ethylbenzene	2.84	0.49	2.76	0.09
Crosslinker	0.44	0.11	0.50	0.14

subsequent calculations. The paint layer was then energy minimized without restraining potential. Molecular dynamics was carried out for 1.0 ns using the NVT at 573 K to simulate curing conditions of the topcoat. The process involves the evaporation of the solvent into the atmosphere (vacuum space) and therefore is a non-equilibrium process. Temperature was controlled by the Andersen thermostat. An additional series of runs were performed at 298 K for comparison. Diffusion constants were once again calculated from the mean-square displacements of the constituent molecules.

2.4. Surface concentration of siloxane

At the completion of the layer diffusion simulations described above, all solvent molecules were removed from the cell. Molecular dynamics was then carried out on the remaining polymer, crosslinker and siloxane mixture at 298 K for 0.5 ns to produce a relaxed surface. From these surfaces it was then possible to determine the atomic composition of the top 15 Å of the layers for comparison with experimental results on similar systems.

3. Results and discussion

3.1. Bulk diffusion

Table 2 presents bulk diffusion coefficients for all components of hexa-OH-TS (System 1) and hexa-Me-TS (System 2) systems at 573 K. The diffusion coefficients at 573 K range from 4.39×10^{-5} cm^2 s^{-1} for butanol down to 0.44×10^{-5} cm^2 s^{-1} for the crosslinker. As expected, for both systems, the low molecular weight solvent components exhibit the highest diffusivity. Generally the diffusion coefficients obtained for each component in System 1 are within the calculated standard deviation of the values obtained for System 2.

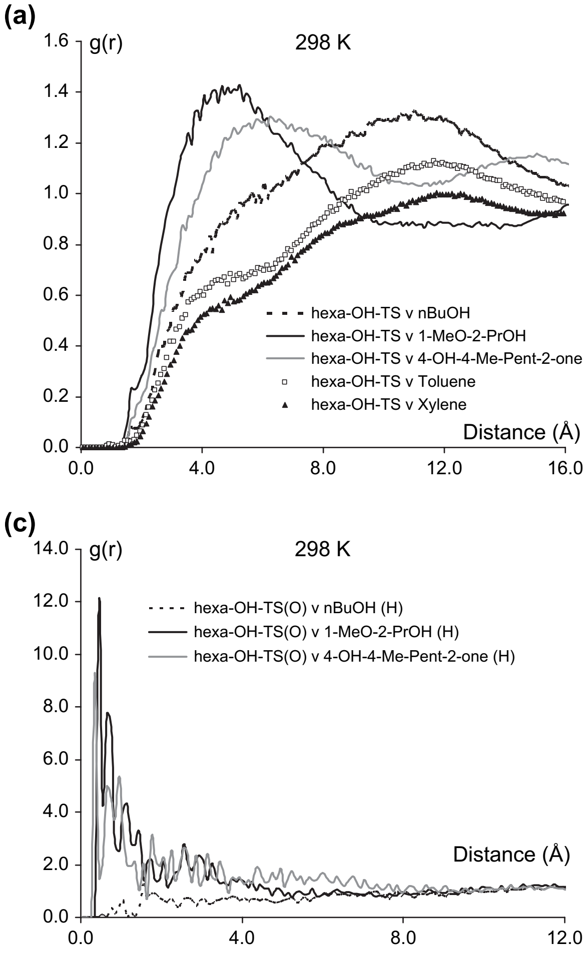

Fig. 1. Hexa-OH-TS radial distribution functions in the bulk system.

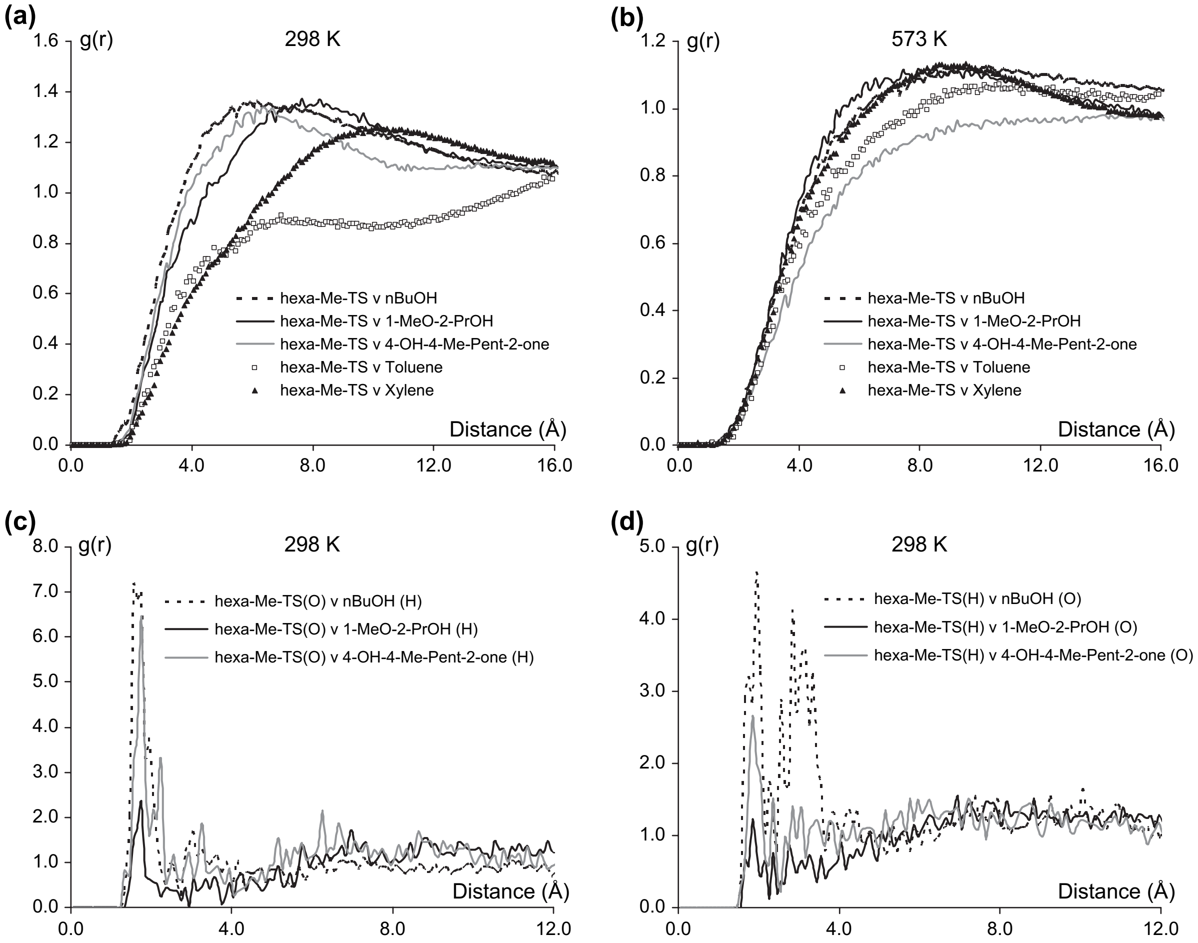

Fig. 2. Hexa-Me-TS radial distribution functions in the bulk system.

Diffusion constants calculated at 298 K for both systems are extremely small ranging between 0.02×10^{-5} cm^2 s^{-1} and 0.07×10^{-5} cm^2 s^{-1} for all components and cannot therefore be reliably estimated over the simulation time frame.

In conjunction with the slow diffusion at 298 K, there is some association between the polar solvent components and hexa-OH-TS in the order, 1-methoxy-2-propanol > 4-hydroxy-4-methylpentan-2-one > butanol, as shown by the radial distribution functions (Fig. 1a). This association can be attributed to H-bonding between the terminal OH groups of the siloxane and the OH groups of the polar solvents. In particular, there is a strong H-bonding interaction between the oxygen atoms of hexa-OH-TS and the hydroxyl hydrogen atoms of both 1-methoxy-2-propanol and 4-hydroxy-4-methylpentan-2-one, while the interaction with the butanol is much weaker (Fig. 1c). In comparison, the interactions between the hydroxyl hydrogens of hexa-OH-TS and each of the polar solvent components are much less pronounced (Fig. 1d). There is little association with the aromatic solvent components (toluene and xylene). At 573 K there is a "normalisation" of the association between hexa-Me-TS and each of the solvent components regardless of polarity (Fig. 1b).

Fig. 2a indicates that for System 2 at 298 K there is also an association between hexa-Me-TS and the polar solvent components although the variation is much smaller than that observed for System 1. This reflects the lower level of hydroxylation of hexa-Me-TS compared to hexa-OH-TS. There is quite a strong H-bonding interaction between the hydroxyl oxygen atoms of hexa-Me-TS and the hydroxyl hydrogens of both butanol and 1-methoxy-2-propanol, and a weaker interaction with 4-hydroxy-4-methylpentan-2-one (Fig. 2c). There is also a strong interaction between the hydroxyl hydrogens of hexa-Me-TS and the oxygen atoms of butanol (Fig. 2d). Interestingly, there is a stronger interaction of the hydroxyl hydrogens of hexa-Me-TS with the oxygen atoms of 4-hydroxy-4-methylpentan-2-one than the oxygen atoms of 1-methoxy-2-propanol, the reverse of the hexa-Me-TS(O) solvent(H) interactions. At 573 K there is again a "normalisation" of the association between hexa-Me-TS and each of the solvent components (Fig. 2b).

3.2. Layer diffusion

Table 3 presents layer diffusion constants for all components of Systems 1 and 2 at 573 K. The diffusion coefficients range from 11.48×10^{-5} cm^2 s^{-1} for butanol down to 0.48×10^{-5} cm^2 s^{-1} for the crosslinker and are generally higher than the corresponding bulk diffusion values. Diffusion

Table 3
Layer diffusion coefficients (D) for Systems 1 and 2 (x 10^{-5} cm^2 s^{-1}) at 573 K

Component	System 1 (hexa-OH-TS)		System 2 (hexa-Me-TS)	
	D	Std	D	Std
Trisiloxane	1.71	0.52	1.08	0.31
*n*BuOH	8.89	1.20	11.48	1.49
1-Methoxy-2-propanol	8.80	1.26	4.22	2.18
4-OH-4-Me-pentan-2-one	3.02	0.65	3.89	1.34
Xylene	4.95	0.74	5.44	0.68
Toluene	5.46	0.68	7.08	2.61
Ethylbenzene	3.51	1.30	5.07	1.25
Crosslinker	0.51	0.17	0.48	0.13

constants calculated at 298 K for both systems are again extremely small ranging between 0.07×10^{-5} cm^2 s^{-1} and 0.19×10^{-5} cm^2 s^{-1} for all components.

For System 1 at 298 K there is a strong association between hexa-OH-TS and the polar solvent components in the order: butanol > 4-hydroxy-4-methylpentan-2-one > 1-methoxy-2-propanol as demonstrated by the radial distribution function (Fig. 3a). It is clear from Fig. 3c that there are significant H-bonding interactions between the hydroxyl oxygen atoms of hexa-OH-TS and the hydroxyl hydrogen atoms of 1-methoxy-2-propanol and butanol. Similarly, there are strong interactions between the hydroxyl hydrogens of hexa-OH-TS and the hydroxyl oxygen atoms of 1-methoxy-2-propanol and butanol (Fig. 3d). At 573 K the association between hexa-OH-TS and each of the components tends to normalise due to the significantly increased mobility (Fig. 3b). However, the association of hexa-OH-TS with 4-hydroxy-4-methylpentan-2-one remains slightly higher than with the other solvent components.

The methylated trisiloxane, hexa-Me-TS, also exhibits a strong association with butanol at 298 K (Fig. 4a). However, there is a significantly reduced association with 4-hydroxy-4-methylpentan-2-one and 1-methoxy-2-propanol and increased association with toluene compared with hexa-OH-TS, reflecting the reduced number of polar OH groups in the trisiloxane. The strong association between hexa-Me-TS and butanol is demonstrated by large peaks in the RDF between hydroxyl oxygen and hydrogen atoms of the respective species (Fig. 4c and d) Again, at 573 K the association between the siloxanes and each of the components tends to normalise due to the significantly increased mobility (Fig. 4b). However, the interaction between hexa-Me-TS and 4-hydroxy-4-methylpentan-2-one is significantly weaker than the other solvent components.

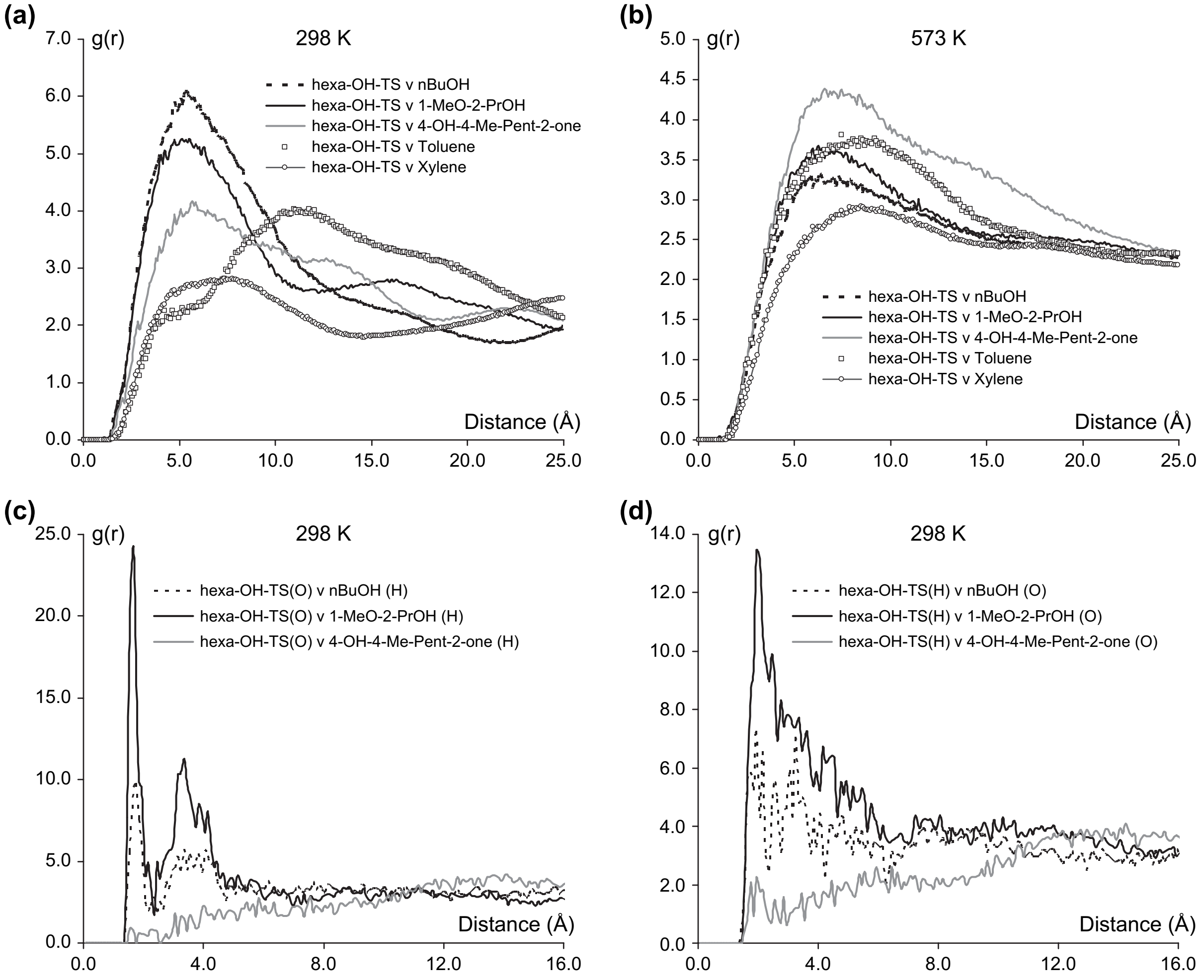

Fig. 3. Hexa-OH-TS radial distribution functions in the layer system.

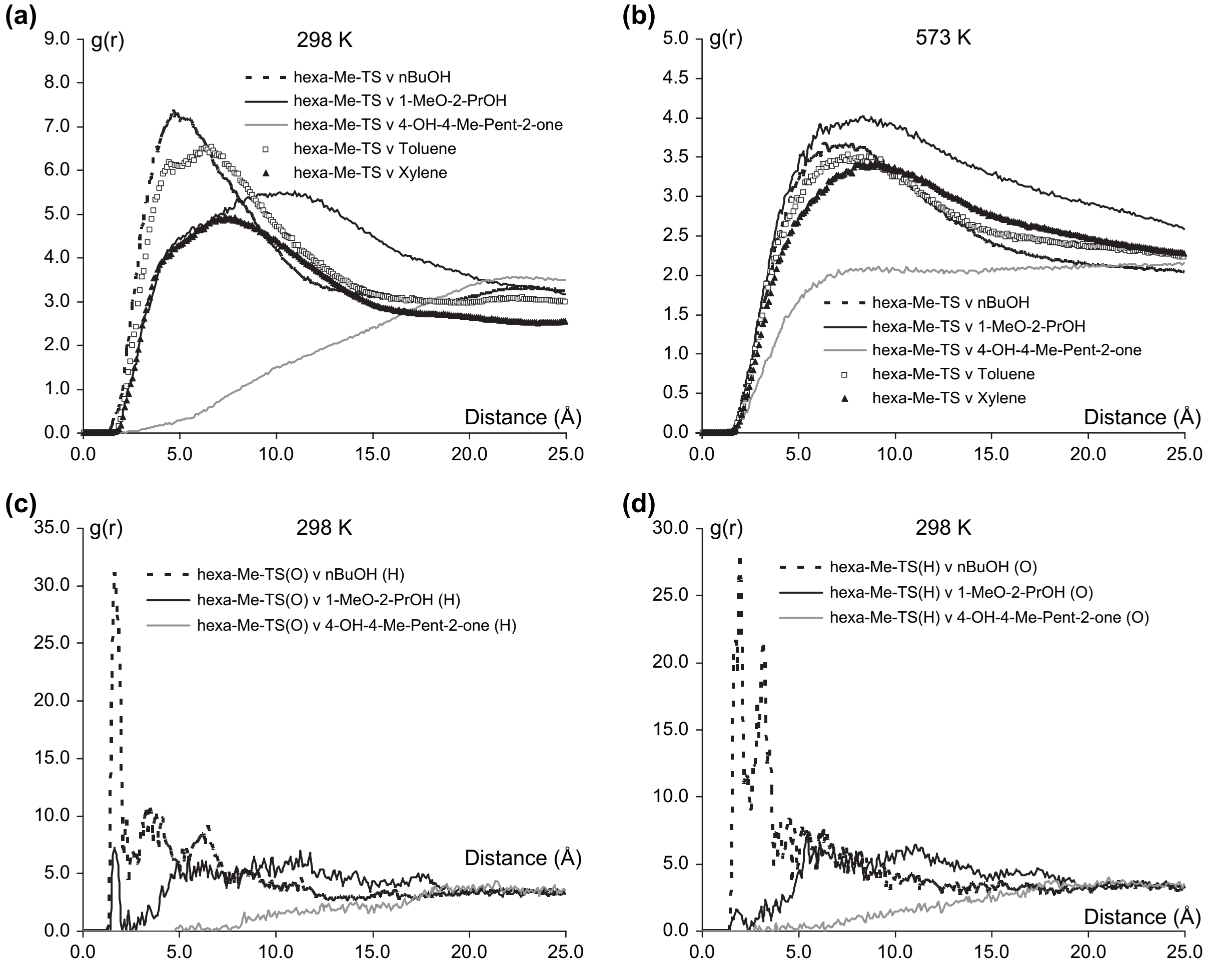

Fig. 4. Hexa-Me-TS radial distribution functions in the layer system.

3.3. Surface segregation

Following solvent removal and subsequent relaxation, the average atom percent of siloxane was determined in the top 15 Å of the layers. For hexa-OH-TS the average concentration of siloxane in the surface layer was found to be 2.53% compared with a total concentration in the system of 1.82%, indicating that there is increased segregation of hexa-OH-TS to the surface. The corresponding surface concentration of silicon atoms is 0.5% (excluding hydrogen).

For hexa-Me-TS the average concentration of siloxane in the surface layer was found to be 1.30% compared with a total concentration in the system of 2.66%. This indicates that there is in fact a decreased concentration of hexa-Me-TS at the surface. The corresponding surface concentration of silicon atoms is only 0.2% (excluding hydrogen).

Horgnies et al. [6] found significant migration of siloxane additives during curing of a polyester–melamine automotive clearcoat. In several formulations composed of less than 0.6% siloxane flow additive, the silicon concentration in the surface layer varied from 2.0% to 4.0%. They also estimated that ~25% of the basecoat siloxane additives migrate through the 50 m thickness of the clearcoat during 17 min of curing at 140 °C. We find that 36% of the hexa-OH-TS and 24% of the hexa-Me-TS migrate from the basecoat region to the surface of our polyester–melamine layers.

Horgnies and Darque-Ceretti [8] also found that following ethanol cleaning of the surface silicon was no longer detected. From this result they concluded that ethanol cleaning can remove the majority of siloxane additives from the outermost surface of clearcoats. While we have not attempted to simulate this cleaning process, it is clear from the RDFs that our model siloxanes have quite a strong affinity with butanol.

Thorstenson et al. [23] noted that more hydrophobic polysiloxanes, modified with poly(propylene oxide), exhibited greater compatibility with the acrylic–melamine coating system and the low polarity of the substrate than the poly(ethylene oxide) modified polysiloxane and therefore has a lower surface concentration. Likewise, our slightly less hydrophilic hexa-Me-TS appears to exhibit slightly greater compatibility with the coating system and also a lower surface concentration.

The surface concentration of silicon in our systems is significantly less than those observed experimentally by Pertsin and co-workers [10–12] and may indicate that the small siloxane molecules are more compatible with the polymer/crosslinker/solvent matrix used in this study than the

PDMS/polymer systems that they investigated. It is also possible that our models are too small to accurately represent polysiloxanes in these systems. However, larger siloxane models would require a significant increase in the system size (total number of atoms) and in the simulation times making this approach computationally, prohibitively expensive.

4. Conclusions

In this study we have used small siloxane molecules to investigate intermolecular interactions and the diffusivity of polysiloxanes in a typical polyester paint matrix during the curing process. Our simulations demonstrate that there is significant interaction between 3,3-dimethylhexahydroxytrisiloxane (hexa-OH-TS) and the polar solvent components of the paint matrix at 298 K. The nature of these associations is largely due to hydrogen bonding between the hydroxyl groups of the siloxane and the hydroxyl groups of the polar solvent molecules. However, at 573 K the diffusivity of solvent molecules is sufficiently high to disrupt the interactions. A similar situation is observed for 1,5-dihydroxyhexamethyltrisiloxane (hexa-Me-TS), however, the smaller number of hydroxyl groups on the siloxane results in a weaker interaction with the polar solvent, in particular with 4-hydroxy-4-methylpentan-2-one.

Surface segregation studies indicate that there is a slight increase in the concentration of hexa-OH-TS in the surface layer of the system as a result of the curing and relaxation processes. However, for hexa-Me-TS there is in fact a decrease in the surface concentration of the siloxane relative to the bulk concentration.

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