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Morphology and crystallization kinetics of polyethylene/long alkyl-chain substituted Polyhedral Oligomeric Silsesquioxanes (POSS) nanocomposite blends: A SAXS/WAXS study

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Abstract

The dispersal, quiescent crystallization kinetics and morphology of a series of unique polyethylene –polyhedral oligomeric silsesquioxanes (PE-POSS) nanocomposite blends is presented. POSS molecules with long linear alkyl-chain substituents were blended at one composition into a commercial low density polyethylene. Time-resolved Small- and Wide-Angle X-Ray scattering (SAXS/WAXS) and thermal techniques were used to elucidate the affect that POSS and its substituent groups have on the dispersal and crystallization kinetics of the host polymer. The miscibility and dispersal of the POSS molecules was seen to increase with the increasing alkyl-chain length substituents suggesting increased compatibility and interaction with the host polymer chains. The POSS molecules act as nucleating agents increasing the crystallinity, crystallization kinetics and influencing the final lamellar morphology. Thus, these unique POSS compounds show great potential as nanocomposite filler particles in polyolefins where the alkyl-chain substituent plays a vital role in its compatibility and subsequent improvement of physical properties in the host polymer.

Keywords: Polyhedral Oligomeric Silsesquioxanes (POSS); nanocomposite blends; quiescent crystallization kinetics; Small- and Wide-Angle X-Ray scattering (SAXS/WAXS).

1 Introduction

The addition of silicon-containing molecules to commodity polymers such as polyolefins and polyesters, have in recent years, been the focus of many investigations with several comprehensive reviews now available detailing the properties and applications of these materials [1-6]. In particular, polyhedral oligomeric silsesquioxanes (POSS) molecules [7-9] have been identified as potential nanocomposite fillers when physically blended or

chemically grafted into the host polymer. POSS molecules have a general nomenclature of $(\text{RSiO}_{3/2})_n$, where n can be 6, 8, 10 or 12. Cubic or cage POSS molecules, $(\text{RSiO}_{3/2})_8$, denoted as 'T₈', have eight substituent groups (R) each one attached to the silicon atoms at the corners of the cube. These are the most commonly studied POSS systems and therefore often utilized as nanoparticles. The substituent groups are often hydrocarbon chains or other similar organic derivatives [7-9] and can be functionalized to compatibilize them with host polymers or biomaterials [2,5,10].

The incorporation of POSS molecules as nanoparticles into polymers such as polyolefins, polyesters, and polyamides are seen to bring about advantageous changes in physical and chemical properties of the polymer itself, e.g. modulus, strength, glass transition temperature, mechanical performance and thermal stability [5,6,11-15]. Changes in the physical properties of the host polymer are usually attributed to the molecular aggregation of the POSS molecules themselves which then serve to reinforce the polymer network by acting as nucleating agents or plasticisers, which can influence the final crystalline morphology by either retarding or increasing the host polymer's crystallisation process. However, the addition of POSS molecules to polymers and the actual extent of the improvements to the physical and chemical properties is still quite speculative. Furthermore the influence of the POSS molecule's actual architecture on the crystallization process and morphology development in the host polymer, is less well defined.

In previous studies, the effect of POSS molecular structure, dispersion and blending methods of the polymer were found to affect the crystallization behaviour and hence mechanical and thermal properties [5,6]. Waddon *et al.* [16,17] reported on the crystallization and structure of polyethylene (PE) copolymer-POSS blends of different weight fractions. Aggregates of both PE and POSS were found when crystallized from the melt in the material. The presence of POSS disrupted the crystallization process and perfection of PE crystallites as the weight fraction of POSS was increased. X-ray scattering studies showed that both POSS and PE crystal structures were present at all weight fractions but the PE lattice was not distorted by POSS, implying that the POSS and PE form a self-assembled two-phase crystalline structure. Fu [11] studied the crystallization kinetics in quiescent and shear states of melt blended PP-octamethyl POSS blends. POSS was seen to act as a nucleating agent up to ~15% wt fraction under both isothermal and non-isothermal conditions, increasing the rate of crystallization of the polymer. Higher POSS fractions in the blend saw the crystallization rate reduced owing

to the dispersal of POSS molecules in the polymer matrix which retards the molecular motion of the chains and hence, decreases crystal growth. Fu [18] also investigated the physical gelation in ethylene-propylene (EP) copolymer-POSS melts. Blends of 10% wt fraction, gave POSS aggregates due to POSS-POSS interactions which dominated the rheological behaviour of the polymer. Two types of interactions contributed to the physical gelation of the blends in the melt: the strong POSS-POSS particle interactions of POSS crystals and the weak particle-to-matrix interactions between the POSS crystals and the EP matrix.

Chen [19,20] also studied isothermal crystallization and morphology development in melt blended polypropylene (PP)-octamethyl POSS nanocomposites. They found that the crystallization rate increased with increasing POSS content due to the aggregation of POSS nanocrystals. These effectively acted as nucleating agents where the interaction between POSS-POSS molecules was greater than between POSS-polymer molecules. However, they postulated that this interaction would depend on the chain length of functionalized substituents on the POSS cage. Joshi [21,22] investigated the isothermal crystallization kinetics, morphology and rheological behaviour of HDPE –octamethyl POSS melt blends with varying weight fraction (0-10%) of POSS. Here, POSS dispersed nanocrystals occur in the polymer matrix at 1% wt fraction and act as nucleating agents increasing crystallization kinetics. However, at higher loadings the POSS molecules aggregate and are less dispersed in the matrix reducing their effect on the crystallization process. Pracella [23] also reported on the morphology and crystallization behaviour of PP-POSS blends, having different alkyl substituents (methyl, isobutyl, isooctyl). The results showed that the length of alkyl substituent groups on the POSS molecule played a fundamental role in determining the dispersion degree and crystallization process of PP from the melt. The crystallization kinetics were seen to increase in the octamethyl POSS blend but were retarded in the isooctyl POSS blend. This behaviour again was attributed to the increased alkyl-chain length on POSS which leads to greater dispersal therefore of POSS in the polymer matrix. Finally, Fina [12,24] and Baldi [25] both investigated the morphology, thermal and mechanical properties of polypropylene-POSS blends bearing different alkyl groups (Methyl, isobutyl, vinyl, phenyl and isooctyl). Both saw that the alkyl group chain length can have significant effects on the dispersion, morphology and mechanical properties but could not be predicted simply by the compatibility of the POSS and polymer matrix.

From the former reports cited here, many investigations have focused on the crystallization processes and thermal properties of POSS-polymer blends with varying weight per cent

fraction of the POSS particles in the polymer matrix. Indeed, a few have detailed the effects of chain length of POSS substituent groups on these characteristics, but the POSS substituent groups have been relatively short, the longest being isooctyl [12,23,25]. The crystal structure and packing morphology of the POSS molecules themselves have not been comprehensively characterised and therefore any influence of these characteristics once blended in the host polymer, have not been taken into account. In this study we address this lack of information; specifically that of the influence of the molecular architecture on the crystallization kinetics and morphology of a series of polyethylene-POSS blends.

We have synthesised a unique set of T₈ POSS compounds with long linear alkyl-chain substituents where the chain length is C_nH_{2n+1}, and $n = 8, 12$ and 18 which have been blended at one composition into a well characterized commercial low density polyethylene (LDPE) [26,27]. Recently, we have reported on the thermal behaviour and crystalline packing morphology of these pure POSS cages, which have shown a distinctive self-assembled packing morphology [28-30]. The long alkyl-chain groups were seen to align in an axial disposition from the POSS core giving a ‘rod-like’ self assembled packing morphology, which has a length-scale correlating exactly to the overall length of the molecule. Interestingly, features in the thermal and crystal texture of these molecules were seen to be analogous with those of bulk n -alkanes; the building blocks of commodity polymers. Hence, these molecules are seen as ideal candidates for blending into polyethylene due to a more favourable interaction of the long alkyl groups with the polymer chains. We present thermal and time-resolved small- and wide-angle X-ray scattering (SAXS/WAXS) data which has allowed us to investigate the dispersion, kinetics and morphology development in the POSS-polymer blends during quiescent crystallization. The scattering techniques used have allowed us to elucidate the crystalline structure of the blends over a large length-scale; WAXS giving crystal structure or micromorphology and SAXS giving information on the long-range ordering or macromorphology. Both techniques are highly sensitive to the dispersal of the POSS in the polymer matrix. The data presented here gives an insight into how POSS and its substituents affect the dispersal and hence crystallization kinetics and morphology of the blends compared with the pure LDPE host polymer.

2 Experimental

2.1 Materials

$T_8(n\text{-alkyl})_8$ cage system synthesis

Reagents were obtained from the Aldrich Chemical Company (alkenes, trichlorosilane and solvents) and stored under nitrogen. Octa(hydrosilsesquioxane) T_8H_8 (starting material for $T_8(n\text{-alkyl})_8$ synthesis) was achieved following Agaskar's synthetic route [31]. Following this $T_8(n\text{-alkyl})_8$ cage systems were synthesised by a well established route involving the direct hydrosilylation [32-34] of T_8H_8 with the appropriate 1-alkene using a platinum (Speier's) catalyst which gave a highly pure product with excellent final yields [34]. Specific synthesis and characterisation of the $T_8(n\text{-alkyl})_8$ cage systems are detailed elsewhere[28-30]. $T_8(n\text{-alkyl})_8$ cage systems were synthesized where the length of the alkyl-chain group is C_nH_{2n+1} , and $n = 8, 12$ and 18 . Herein, these will be referred to as T_8C_n cages where C_n is: C_8 , C_{12} , and C_{18} . The structures of the three POSS cages with increasing alkyl-chain length are given in Figure 1.

Figure 1. Structure of T_8C_8 , T_8C_{12} and T_8C_{18} POSS cages.

2.2 POSS Blend materials

The T_8C_n POSS cages were blended with a low density commercial grade polyethylene, Lupolen 1840H (GPC $M_w = 250\,000$ g/mol, $M_w/M_n = 13.5$, T_m (DSC) ≈ 109 °C), provided by BASF. Lupolen 1840H has a significant amount of short-chain (30 $CH_3/1000$ C) and long-chain branching [26,27]. The LDPE-POSS composites were prepared using the solution

compounding method described by Huang [35] which has been effectively applied to LDPE and POSS systems previously. All blends were prepared with a 10% wt fraction of POSS. The POSS was dissolved in CHCl_3 and LDPE was dissolved in *para*-xylene at 95 °C. The POSS/ CHCl_3 solution was added to the solution of LDPE/*para*-xylene and the resulting mixture stirred at 95 °C for 2 hrs. The resulting composites were dried at 130 °C in a vacuum for 10 hrs. Each composite is denoted with respect to the 10% wt fraction of T_8C_n POSS it contained: PE-C₈, PE-C₁₂ and PE-C₁₈ and the pure Lupolen LDPE as PE.

2.3 Characterization techniques.

Differential Scanning Calorimetry (DSC) measurements for all samples were performed using a Mettler Toledo DSC822 instrument under a continuous flow of argon gas at 80 mL min⁻¹ and calibrated with an indium metal standard. Samples of between 5 mg – 20 mg were loaded into standard 40 µL aluminium pans and heat-cool cycles were run from 25 °C to 130 °C at a rate of 10 °C min⁻¹. The percent crystallinity of each sample was calculated using the following relationship:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0 (1 - \phi)} \quad (1)$$

where ΔH_f is the enthalpy of fusion from the integrated area under the melting transition from the DSC thermogram, ΔH_f^0 is the enthalpy of 100% crystalline material (298 J g⁻¹) for LDPE [36], and ϕ is the weight fraction of POSS blended with LDPE.

X-ray diffraction (XRD) patterns were collected using a PANalytical Empyrean diffractometer employing filtered CoK_α radiation ($\lambda = 1.79 \text{ \AA}$) operating at 40 kV and 40 mA. The samples were mounted in flat, circular holders and rotated during measurement (0.5 s⁻¹). Data were collected on a PIXcel detector system (1D mode) with a continuous scanning mode over a scattering angle range of $2\theta = 5^\circ - 40^\circ$.

Time-resolved small- and wide-angle X-ray scattering (SAXS/WAXS) measurements were performed at the I22 beamline (Diamond synchrotron X-ray source, Didcot, UK) operating with an X-ray energy of 12.4 keV. SAXS data was recorded using a 2D gas-filled multiwire detector located at a distance of 3.5 m from the sample position and calibrated using a sample of oriented rat-tail collagen. A vacuum chamber was positioned between the sample and SAXS detector reducing air scattering and absorption. WAXS data was recorded using a 1D

detector situated at the entrance of the vacuum chamber at the sample position and was calibrated with high density polyethylene.

The sample environment consisted of a Linkam DSC600 heating stage positioned vertically in the incident X-ray beam before the vacuum chamber [37-39]. Individual samples of LDPE and POSS blends were sealed in aluminium DSC pans fitted with mica windows (25 μm thickness, 7 mm diameter). Quiescent SAXS/WAXS crystallization experiments were performed on the samples as prepared. The samples were heated to 130 $^{\circ}\text{C}$, held for three minutes and then quenched at a rate of 50 $^{\circ}\text{C min}^{-1}$ to the quiescent crystallization temperature, T_i . Once the crystallization temperature was reached data collection was started at a rate of between 8 and 15 s per frame depending on T_i , with a 10 μs wait time, and continued throughout the crystallization process.

2.4 SAXS/WAXS data analysis.

Both SAXS and WAXS data were corrected for sample thickness and transmission, background scattering and corrected for any detector spatial distortion. All 2D SAXS data were reduced to 1D intensity plots, $I(q,t)$, by sector averaging symmetrically around the meridian by a fixed angle and radius, q . The peak positions of the 1D SAXS/WAXS data were obtained by fitting a Gaussian function to the peaks. The quiescent 1D SAXS crystallization data were reduced to integrated intensity I , as a function of scattering vector $q = (4\pi \sin \theta/\lambda)$, where θ is the scattering angle and λ is the X-ray wavelength, as described elsewhere [37]. The normalized invariant Q_s , derived from the 1D SAXS data was used to follow the development of the quiescent crystallization process with respect to time [38,39], where:

$$Q_s(t) = \int_0^{\infty} q^2 I(q,t) dq \approx \int_{q_1}^{q_2} q^2 I(q,t) dq \quad (2)$$

The normalized 1D SAXS invariant data, was used in further analysis to obtain Avrami plots[40,41] for the quiescent crystallizations. The Avrami model takes the general form

$$1 - X_s = e^{-kt^n} \quad (3)$$

where $X_s(t) = Q_s(t)/Q_s(\infty)$ is the crystallinity, k is the crystallization rate constant, and n is the Avrami exponent. To obtain values of n and k from the SAXS invariant data the double logarithmic form of the Avrami equation was applied:

$$\ln(-\ln[X_s(t)]) = n \ln t + \ln k \quad (4)$$

The Avrami exponent n , can be related to nucleation process and the dimensionality of the growth unit during quiescent crystallization.

3 Results and Discussion

3.1 Thermal properties

DSC thermograms during the heating and cooling cycles at $10\text{ }^{\circ}\text{C min}^{-1}$, were obtained for the pure PE and the PE-POSS blends and are shown in Figure 2A and 2B respectively. The melting temperature (T_m) and crystallization temperature (T_c), and corresponding percent crystallinity (obtained from the enthalpy of fusion and Equation 1), from the DSC results are summarised in Table 1.

Figure 2. DSC thermograms (off-set vertically for clarity) of pure PE and PE-POSS blends. A: Heating scans; B: cooling scans at $10\text{ }^{\circ}\text{C min}^{-1}$.

Table 1. DSC melting temperature and crystallinity of pure PE and PE-POSS blends.

Sample	$T_m/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$	% crystallinity
PE	109.6	92.2	37.1
PE-C ₈	109.5	92.5	38.0
PE-C ₁₂	108.0	93.6	38.7
PE-C ₁₈	108.7	92.3	41.5

The value of T_m for pure PE ($\sim 109^{\circ}\text{C}$) is seen to decrease only very slightly when the POSS is added. Likewise there is no significant change in crystallization temperature T_c , as POSS is added to the PE. Similar results were obtained for HDPE-octavinyl POSS blends by Huang [35], where the addition of POSS did not change the melt temperature or crystallinity by any significant amount. However, here we see that there is a small increase in the per cent crystallinity on the addition of POSS into the PE. Although, it should be noted that the overall crystallinity is low in the pure PE and blends due to the molecular nature of the PE having significant short and long chain branching. This prevents large crystallites forming and reduces the overall bulk crystallinity which is a common feature of low density polyethylene's [38,42,43].

However, the DSC thermograms do show a few interesting additional features during the heat-cool cycles. From Figure 2A, during the heating of the PE-C₈ blend a small but relatively sharp melting peak at $\sim 50^{\circ}\text{C}$ is observed. This corresponds directly to the melting temperature of the pure POSS T₈C₈ cage system [28]. Hence, from this separate melting peak for PE-C₈ POSS blend it would be reasonable to suggest that the POSS is actually aggregated in crystals rather than well dispersed in the PE matrix. In contrast, there is no evidence of the melting peaks of the other pure POSS cages (T₈C₁₂ at 74°C and T₈C₁₈ at 85°C) occurring in the heating thermogram for the blends, indicating that the POSS is dispersed in the PE matrix of these two blends. The melting points of the pure POSS cages [28] are all lower than pure PE, thus it can be assumed that the POSS components of the blends are therefore in their melt state and dispersed in the melted PE matrix above 109°C .

From the cooling thermograms in Figure 2B, a second broad crystallization peak is observed at $\sim 57^{\circ}\text{C}$ for pure PE and more pronounced in the PE-C₁₈ blend. Multiple crystallization curves are often seen in PE with low crystallinity and are attributed to the insertion of thin lamellae crystals forming at lower temperatures, whereas the thicker lamellae are formed at higher temperatures [44]. This is due to the branching effects and molecular weight distribution of the PE, where the linear regions tend to crystallize first at higher temperatures

into thick lamellae excluding the branches which form thinner less perfect lamellae at low temperatures, hence different fractions of crystallites can occur as the PE is re-crystallized from the melt. Interestingly, the PE-C₁₈ blend gives a more distinct second crystallization peak compared to pure PE indicating that this blend influences the crystallization of thinner lamellae to a greater extent in the PE matrix. The POSS could either be acting as a nucleating point for lamellae to grow in the amorphous regions and/or has the potential to be incorporated in the lamellae via the long unbranched alkyl-chain substituents on the POSS. Moreover, we have reported that these particular POSS systems, with long linear alkyl-chains, pack and crystallize in a lamellar fashion analogous to that of bulk *n*-alkanes [28-30]. The difference in dispersion and crystallization of the PE- POSS blends is further investigated using X-ray scattering.

3.2 X-ray scattering data.

Small-angle X-ray scattering (SAXS) and XRD data were obtained for the pure and blended samples at 25 °C given in Figure 3. Firstly, looking in detail at the SAXS data which gives information of the long-range ordering and molecular length-scale; Figures 3A and 3B show the 1D SAXS data for the pure POSS materials and the pure PE and PE-POSS blends respectively, where the *d*-spacings of the peaks are labelled in Angstroms. As previously reported [29,30], the SAXS data for the pure POSS material show very strong 1st order peaks which have been related directly to the length-scale of the POSS molecule, where the alkyl-chains point away from the POSS cage core, giving an overall rod-like structure. The POSS molecules pack in an efficient manner in a highly crystalline layered structure, where the alkyl-chains do not interdigitate with each other. In fact, the 2nd and 3rd order peaks can also be observed for the T₈C₁₈ POSS cage system (and 2nd order for T₈C₁₂); this regular repeat distance is characteristic of a lamellar or bilayer type of packing [30].

Figure 3. SAXS and XRD scans of pure POSS and PE-POSS blends at 25 °C. A: SAXS of pure POSS cages; B: SAXS of PE and PE-POSS blends. C: XRD of pure POSS cages; D: XRD of PE and PE-POSS blends where inset plot shows PE-C₁₂ and PE-C₁₈ XRD at low 2θ . Data in all plots is off-set on the vertical axis for clarity.

In Figure 3B SAXS data for pure PE and the blends is given. For pure PE a scattering maximum at ~ 200 Å, representing the long period (L_p) is observed, which relates to the overall average length-scale of crystalline and amorphous layer thicknesses [11,38,45]. From the SAXS data for the two blends PE-C₈ and PE-C₁₂, the 1st order peaks at 26 Å and 36 Å respectively are visible indicating that the pure POSS crystals coexist in the PE matrix. However, the peaks are quite weak and reduce in intensity with increasing alkyl-chain length. The 1st order peak for the T₈C₁₈ POSS system is not apparent in the SAXS data for this blend (PE-C₁₈). This would suggest that there is some aggregation of POSS crystals in the PE matrix but, as the alkyl-chain length increases the POSS disperse into the amorphous domains of the PE. Similar results have been reported for the dispersion of POSS with increasing alkyl-chain length in PP blends where longer alkyl-chains have better interaction with the host polymer chains increasing the POSS dispersal [23-25]. It should be noted as well that the

scattering maximum, L_p , shifts to shorter d -spacings for the blends with the smallest being that for the longest alkyl-chain length POSS blend, PE-C₁₈.

The decrease in L_p , indicates increased crystallinity and shorter average lamellar and amorphous stacking units, often from insertion and subsequent growth of other lamellae into the amorphous component [11,29,45]. This decrease is seen as a function of alkyl-chain length and may indicate that the alkyl-chain compatibility and subsequent crystallization in the PE matrix is permissible. Again, this is in agreement with the DSC crystallization thermograms (Figure 2B), where the second minor crystallization peak is attributed to the insertion of thinner less well defined lamellae into the PE matrix. This crystallization peak was most enhanced for the PE-C₁₈ blend which from the SAXS data at 25 °C, shows a marked decrease in L_p compared to pure PE and the other two blends, which confirms the potential of the long alkyl-chain on the POSS to be incorporated into the crystal structure of the PE lamellar morphology.

Figure 3C and 3D shows the XRD data for pure POSS and PE and PE-POSS blends respectively, which gives information about the crystal lattice structure. Pure POSS are all crystalline solids at 25 °C and the XRD (Figure 3C) shows a group of common peaks in the 2θ region of 22°- 27° for these materials. As the alkyl-chain length increases the peak broadening also increases and can be attributed to the alkyl-chains dominating the packing rather than POSS cages [28,46]. These peaks have previously been assigned to the distance between POSS cages and *intra* and *inter* chain packing distances [7,9,28,30]. The strong peaks in the 2θ range of 10° - 16° are assigned to the overall dimensions of the POSS molecules, and can be correlated to the repeat distances (2nd and 3rd orders) from the corresponding SAXS data for T₈C₁₂ and T₈C₈ [30]. In Figure 3D the XRD data for the pure PE and POSS-PE blends are shown. There are similarities with the main group of peaks in the 2θ region of 22°- 27° when compared to the pure POSS. The two main peaks for PE are labelled as the (110) and (200) which are associated with the orthorhombic structure of polyethylene. These peaks do not seem to change with the three PE-POSS blends, that is, they do not shift so we can assume that the PE crystal lattice is not distorted by the addition of the POSS particles. However, the XRD of PE-C₈ (inset plot) shows two prominent peaks at ~8.4° (12.4 Å) and 12.4° (8.3 Å) which correlate with the intense peaks at these angles in the pure POSS XRD (Figure 3C). The inset plot also shows that for the PE-C₁₂ blend, there is some evidence of a peak at ~8.6° (11.8 Å), which again links with the strong peak at this

angle in the XRD scan of this pure POSS sample. These results coupled with the SAXS data indicates that in these particular blends, the POSS crystals aggregate in the polymer matrix. In contrast, the PE-C₁₈ does not show any discrete scattering peaks in the XRD correlating with the pure T₈C₁₈ POSS suggesting that these molecules are well dispersed in the amorphous regions and fewer crystalline aggregates of POSS-POSS molecules exist in this blend.

The crystallization kinetics and structure evolution were investigated for pure PE and blends using time-resolved SAXS/WAXS data. Quiescent crystallization studies of pure PE and the blends were performed at several temperatures, which were below the melt temperature of PE (109 °C). During the crystallization SAXS/WAXS data were recorded to show the appearance of the scattering intensities. Figure 4 shows examples of X-ray surface plots for pure PE and PE-C₁₈ blend which were crystallized at 95 °C. The SAXS plots for pure PE and PE-C₁₈ blend (Figure 4A and 4C) both show the emergence and development of the scattering peak at $\sim 0.02 \text{ \AA}^{-1}$. However, it is clear that this peak appears in the blend first. Similarly, the WAXS data (Figures 4B and 4D) show the subsequent development of the (110) and (200) major peaks, again these peaks appear in the blend before the pure PE material. This indicates that at this temperature, the long-range lamellar ordering and crystalline structure develops faster in the blend compared to the pure PE homopolymer.

Figure 4. X-ray surface plots during the time-resolved quiescent crystallization at 95 °C of PE and PE-C₁₈ blend. (A) SAXS development of pure PE; (B) development of the (110) and (200) WAXS

peaks of pure PE; (B) SAXS development of PE-C₁₈ blend and (D) development of the (110) and (200) WAXS peaks of PE-C₁₈ blend.

To see the development and variation of long period, L_p , in the SAXS data from Figure 4, the peak position was fitted with respect to time, which is plotted in Figure 5. The data is plotted from the point during the crystallization when the peak position could be fitted with confidence. The L_p begins to decrease as the crystallization process proceeds and the final L_p for the blend is ~ 20 Å smaller than that for pure PE at 95 °C.

Figure 5. Variation of long-period, L_p , with respect to time during the quiescent crystallization of pure PE and PE-C₁₈ blend at 95 °C.

The development and position of the SAXS peak in pure PE and the blends at different quiescent crystallization temperatures was often difficult to fit reliably as the peak presented itself as a shoulder of intensity moving towards the back-stop. For example, Figure 6A and 6B, shows the final 1D SAXS data frames for pure PE and the PE-POSS blends having undergone quiescent crystallization at 95 °C and 100 °C, respectively. Here, at 95 °C, it is clear that pure PE and the blends PE-C₁₂ and PE-C₁₈ produce a well defined but broad scattering peak, where the peak position shifts to higher q in the blends, indicating a smaller d -spacing. This suggests again that some insertion of lamellae occurs in the blends compared with the pure PE. However, the scattering maximum in the PE-C₈ blend is very broad indicating a more random and less well defined lamellar morphology at this temperature. At 100 °C, the scattering maximum for all the blends shift to lower q values (larger d -spacing) where the lamellar morphology develops with small and imperfect lamellae and large amorphous regions giving low crystallinity. The pure PE sample at this temperature shows a

very weak scattering maximum ($\sim 0.015 \text{ \AA}^{-1}$) compared to the blends, suggesting this has the least crystalline morphology at this temperature.

Figure 6. Final 1D SAXS data for pure PE and PE-POSS blends. A: quiescent crystallization at 95 °C and B: quiescent crystallization at 100 °C.

From the X-ray scattering data it is clear that the addition of POSS in the PE matrix influences the PE's crystalline morphology when the PE and blends are crystallised under the same quiescent conditions. Thus, to gain further insight into the type of crystallization, that is, the dimensionality of the growth unit, nucleation process and crystallization kinetics it is necessary to extract additional information from the time-resolved SAXS data.

3.3 Crystallization kinetics and Avrami analysis

The crystallization curves with respect to time for the pure PE and PE-POSS blends were obtained from the SAXS invariant data (Equation 2). Figure 7 shows the normalised quiescent crystallization curves for pure PE and PE-POSS blends at several temperatures. As the crystallization temperature is increased (lesser undercooling from the melt) the crystallization process decreases, as to be expected. The plots are used to compare the temperature dependence of crystallization and therefore to evaluate the difference between the pure PE and PE-POSS blends. Thus, from this data the crystallization half-times ($t_{1/2}$) were obtained for comparison (values are given in Table 2). The half-time represents the time for the crystallization to reach 50% conversion to the final full crystallinity at a particular temperature.

Figure 7. Normalised quiescent crystallization curves for pure PE and PE-POSS blends at several temperatures from the SAXS invariant data. (A) pure PE; (B) PE-C₈ blend; (C) PE-C₁₂ blend; (D) PE-C₁₈ blend.

The values of $t_{1/2}$ are plotted in Figure 8A which shows that generally the values in the pure PE sample are larger (slower crystallization times) compared with all the PE-POSS blends at each equivalent temperature. Hence, the blends increase the rate of crystallization compared to the pure PE (at the same temperatures). There is some suggestion from this plot that at lower crystallization temperatures the PE-POSS blends decrease the $t_{1/2}$ values (increase the rate of crystallization) by similar amounts, that is, there is no obvious influence of the increasing POSS alkyl-chain length on the crystallization kinetics. However, at higher crystallization temperatures, the PE-C₈ appears to have less of an effect on crystallization rate compared with the PE-C₁₂ and PE-C₁₈ blends. Figure 8B shows $\ln(t_{1/2})$ plotted as a function of $1/T$. The linear form of the plots for PE and PE-POSS blends all lie on similar slopes, which confirms a consistent Arrhenius type of temperature dependence during crystallization [23,38].

Figure 8. (A): Crystallization half-times ($t_{1/2}$), with respect to temperature for pure PE and PE-POSS blends. (B): Crystallization half-times $\ln(t_{1/2})$ as a function of $1/T$.

The normalised quiescent crystallization curves in Figure 7, were used to obtain Avrami plots. The Avrami model allows the rate constant k , and Avrami exponent n , to be obtained which gives information on the dimensionality of the growth unit during the crystallization process and can be used to describe the quiescent crystallization kinetics for the pure PE and PE-POSS blends [22,23,38,47]. The double logarithmic form of the Avrami equation (Equation 4) is used to extract the values of k and n ; where n is the slope of the linear region of the plot which is associated with the primary nucleation and crystallization process [38,43,48,49], and k is the intercept at $t = 1$. Figure 9, shows example Avrami plots and fits to the linear region for the pure PE and PE-POS blends at a crystallization temperature of 95 °C. Table 2, gives all the Avrami parameters extracted from similar plots and values $t_{1/2}$, at each quiescent crystallization temperature for pure PE and PE-POSS blends.

Figure 9. Avrami plots from the crystallization curves for pure PE and PE-POSS blends during quiescent crystallization at 95 °C.

The Avrami exponents, n , for the quiescent crystallization process in pure PE range from 2 to 1.4, that is, decreasing as the temperature is increased. For PE, typical values of n are in the region of 2 to 4 [49] and similar values have been reported for isothermal and nonisothermal crystallization of pure and HDPE–octamethyl POSS blends [21,22,50]. These values are comparable with a low dimensional growth unit, where $n \leq 2$ indicates homogeneous nucleation of fibril or heterogeneous growth of fibrils or disc shaped crystalline units. However, the Avrami analysis cannot separate the nucleation process from the type of growth unit, but here homogeneous nucleation can be thought of as the spontaneous aggregation of polymer chains, whereas heterogeneous nucleation occurs by an externally nucleated process. The latter implies that impurities which are randomly distributed or localized as surface aggregates provide nucleation sites in the bulk polymer [43]. Also, often the Avrami analysis yields non-integer values of the Avrami exponents which can be attributed to the nucleation and simultaneous or consecutive growth of different crystalline units [43,49].

Looking at the Avrami exponents for the PE-POSS blends, we see that generally, the values are still about 2 (indicating a low dimensionality of growth unit; fibril or disc like) but have increased somewhat over the temperature range compared to those values for pure PE. However, there is no obvious difference between each blend, that is, there is no apparent affect of alkyl-chain length on type of dimensionality of crystal growth unit. Further to this, the rate constant k , is slightly higher in the PE-POSS blends compared to pure PE at lower crystallization temperatures. This indicates that the addition of POSS increases the rate of crystallization. As the temperature increases, the rate of crystallization also decreases,

supporting the idea that the nucleation and crystalline growth process slows down with increasing temperature. Interestingly though at the highest crystallization temperature (100 °C), the PE-C₁₈ blend has a slightly reduced rate of crystallization more so than the other blends, compared with pure PE at this temperature.

Table 2. Crystallization half-times ($t_{1/2}$) and Avrami parameters for pure PE and PE-POSS blends during quiescent crystallization at several temperatures.

Sample	$T_i/^\circ\text{C}$	$t_{1/2}/\text{s}$	Avrami exponent, n	$\ln(k/\text{s}^{-1})$
PE	95	81	2.0	-8.9
	98	225	1.6	-9.1
	100	403	1.4	-9.6
PE-C ₈	95	46	2.1	-8.5
	97	88	1.8	-8.2
	98	163	1.9	-9.8
	100	286	1.8	-10.3
PE-C ₁₂	95	39	2.2	-8.6
	97	72	1.9	-9.0
	98	186	1.8	-10.1
	100	224	1.8	-10.2
PE-C ₁₈	95	33	1.9	-7.1
	97	117	1.9	-9.3
	98	165	1.9	-10.2
	100	234	2.2	-12.6

From all the data presented we are in a position to be able to relate how the addition of POSS into pure PE affects morphology and crystallization kinetics. From the crystallization half-times and Avrami analysis the addition of POSS into PE evidently affects the crystallization process and kinetics and can be linked to the level of POSS dispersal in the PE matrix which, in turn, is related to the length of the alkyl-chain substituent on the POSS cage. In the data discussed (thermal and X-ray) there is clear evidence that the blends PE-C₈ and PE-C₁₂ show some aggregation of POSS crystals, indicating that the POSS molecules are not fully dispersed in the PE matrix; an obvious melt peak for the PE-C₈ blend was observed in the DSC thermogram and distinct scattering peaks from crystalline POSS in PE-C₈ and PE-C₁₂ were also seen in the SAXS/WAXS data. Whereas, in the PE-C₁₈ blend the POSS is dispersed into the PE matrix to a greater extent; no evidence of additional thermal peaks in the DSC or scattering peaks in the X-ray data were observed for this blend. From this data it is apparent that the alkyl-chain substituent on the POSS directs its miscibility and dispersal

into the PE matrix. The longer the alkyl-chain substituent on the POSS the greater the compatibility and hence dispersal of the POSS molecules in the PE matrix at the same weight fraction loading. The dispersal of POSS in the PE matrix was then seen to influence the morphology and crystallization kinetics. The time-resolved SAXS data during the quiescent crystallization process showed that the long-range ordering and crystalline structure developed in the blends before that in the pure PE. The PE-POSS blends developed a more defined crystalline lamellar structure compared to the pure PE, where the insertion of lamellae into the amorphous regions occurred which was marked by a reduction in the long-period repeat distance. This effect was more pronounced as the alkyl-chain length on the POSS increased, thus the greatest reduction of long-period was seen in the PE-C₁₈ blend.

From the quiescent crystallization data the crystallization half-times are decreased in the blends compared to pure PE, suggesting that the addition of POSS acts as a nucleating agent for the crystallization process of PE whether it be aggregated or dispersed to any extent in the polymer matrix. The type of growth unit from the Avrami exponent was found to be similar in the pure PE and PE-POSS blends, whereas the rate of crystallization from k , was higher for the PE-POSS blends than pure PE at lower temperatures. At higher quiescent crystallization temperatures the rate of crystallization was reduced as expected, but the PE-C₁₈ showed the largest reduction. This may well be due to the fact that as quiescent crystallization is a diffusion controlled process, the apparent improved dispersal of the POSS in the PE matrix of this particular blend may well hinder the slow crystal growth front at higher temperatures but allow the incorporation of the POSS molecule into the latter formed crystalline lamellae. This is supported by the significant reduction of the long-period obtained from SAXS data during quiescent crystallization at higher temperatures and at 25 °C, as well as in the DSC analysis where enhancement of the crystal fractions during crystallization is observed. The other two PE-POSS blends still showed significant increases in the overall rate of crystallization and again some reduction in long-period indicating that these blends also encourage lamellae growth and enhance the final crystallinity, but tend to be less well dispersed in the PE matrix. Certainly, it would be necessary to vary the loadings of the POSS molecules in the PE matrix to see if the compatibility, crystallization kinetics and morphology are affected in turn. Further investigations to this end, including mechanical testing and crystallization under shear flow conditions are underway and will be reported in a further publication later by the authors.

4. Conclusions

The dispersal, quiescent crystallization kinetics and morphology of a series of PE-POSS nanocomposite blends have been investigated. The principle aim was to reveal the effects of increasing the length of the alkyl-chain substituents attached to the POSS cages on the morphology and properties of the PE homopolymer. The POSS molecules were synthesized with long linear alkyl-chain substituents and from previous studies are characterized as highly crystalline materials which self-assemble into a regular lamellar or bilayer type of morphology. The POSS were blended at a relatively high weight fraction of 10% into a commercial sample of LDPE which in the pure state has low crystallinity due to significant short and long chain branching.

Thermal and X-ray scattering techniques were used to probe the compatibility of the POSS molecules and subsequently the effect on the crystalline morphology during quiescent crystallization of the PE. The miscibility and dispersal of the POSS molecules was seen to increase with the increasing alkyl-chain length substituent groups. The shorter alkyl-chain POSS molecules showed some aggregation as POSS crystals in the PE matrix but progressively become more dispersed as the alkyl-chain length increased, suggesting better compatibility and interaction of the substituent groups with the PE chains. The POSS molecules in all cases were seen to act as nucleating agents regardless of their dispersal in the PE matrix, increasing the crystallinity, crystallization kinetics and influencing the lamellar morphology when compared with pure PE. However, the addition of POSS at this particular weight fraction did not seem to have any significant effect on the melting and crystallization temperature of the bulk PE homopolymer.

This study has revealed that at relatively high weight fractions, linear long alkyl-chain substituted POSS molecules are very compatible with LDPE and as the alkyl-chain length increases so does the miscibility and molecular interaction of the molecules. The morphology development and crystallization kinetics are enhanced in all cases. Thus, these unique POSS compounds have shown great potential as nanocomposite filler particles in polyolefins where manipulation of the architecture of the alkyl-chain substituent plays a vital role in its compatibility and subsequent improvement of physical properties in the host polymer.

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