

Inner Voids of Octavinyl Polyhedral Oligomeric Silsesquioxane Acting as Cell Embryos for Polymer Foaming

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(Received: 14 January 2011;

Accepted: 3 October 2011)

AJC-10470

A new strategy was developed by using octavinyl polyhedral oligomeric silsesquioxane containing inner voids acting as cell embryos to enhance cell structure for polymer foaming through low-cost injection foaming process by using chemical foaming agent. The effect of octavinyl polyhedral oligomeric silsesquioxane on the cell structure was evaluated solely on the basis of cell nucleation. The pre-existing microvoids can lower the activation energy for cell nucleation or even act as cell embryos for polymer foaming. The favourable size and stiff structure of the inner voids are believed to play a crucial role, leading to markedly enhanced cell structure at exceedingly low level, despite the fact that it is not sufficient to obtain fine microcellular structure solely by nucleation effect because of the limited rheological properties.

Key Words: Microcellular foaming, Cell embryo, Octavinyl polyhedral oligomeric silsesquioxane, Inner void.

INTRODUCTION

Microcellular polymer foams (MCFs) have shown strong potential for the applications in thermal, acoustic or electrical insulation and as structural materials due to their benefits of lowered weight, reduced material usage and maintaining the essential mechanical properties¹⁻⁴. However, special equipments or the reorganization of existing equipments are required for a continuous microcellular foaming process assisted by supercritical fluid⁵⁻⁸. This increases considerably manufacturing cost which is crucial to the industrial implementation. Another alternative could be relatively inexpensive foaming process by employing chemical foaming agents (CFAs) and utilizing prevalent processing machinery, but fine microcellular structure is difficult to obtain. It could be of great interest if the microcellular foams of common plastics can be obtained through low-cost foaming process by using chemical foaming agents. Some efforts have been made to enhance cell structure during the chemical foaming process by facilitating cell nucleation, but the quality of cell structure appear to be not comparable to its counterpart with physical foaming agents (PFAs)⁹⁻¹⁵. It is worthwhile to note that pre-existing microvoids in thermo-plastic polymer matrix facilitate significantly cell nucleation^{16,17}, though the size and dispersion of the microvoids could not be readily controlled. During the cell nucleation, an energy barrier must be overcome to form a new phase (embryo). When the

embryo of the new phase is greater than a critical size, it will grow spontaneously, otherwise it can collapse. The pre-existing microvoids with favorable size can lower the activation energy for cell nucleation or even help to leap over the cell nucleation process when the void size is larger than the critical size. If the microvoids can be well dispersed and exist stably in polymer matrix, cell structure could be enhanced essentially even if using conventional foaming processes. Polyhedral oligomeric silsesquioxanes (POSSs) with inner voids^{18,19} offers a good chance of achieving the above target.

In the work reported here, octavinyl polyhedral oligomeric silsesquioxane (OVS)/polystyrene (PS) composites were foamed through continuous injection foaming process by using chemical foaming agents and the effect of octavinyl polyhedral oligomeric silsesquioxane on the cell structure was evaluated solely on the basis of cell nucleation process. The size of the microvoid inside octavinyl polyhedral oligomeric silsesquioxane cage is comparable to the radius of critical nucleus predicted by the classical nucleation theory. The octavinyl polyhedral oligomeric silsesquioxane is expected to act as the embryos for polymer foaming and will not collapse against the large surface elastic energy forces due to its stiff structure. Moreover, octavinyl polyhedral oligomeric silsesquioxane could be dispersed homogeneously *via* copolymerisation or grafting and mixing. We demonstrate the inner voids of octavinyl polyhedral oligomeric silsesquioxane can act as embryos for polymer

foaming and enhanced markedly cell structure. Octavinyl polyhedral oligomeric silsesquioxane provides a new avenue to achieve simple and low-cost fabrication of microcellular foamings.

EXPERIMENTAL

Octavinyl polyhedral oligomeric silsesquioxane was purchased from Hybrid Plastics, Hattiesburg, MS. Sodium dodecyl sulfate (SDS), potassium persulfate (KPS), hydrogen chloride (HCl) and azodicarbonamide (AC) used as the chemical blowing agent were commercially available and used as received. Azodicarbonamide decomposes at 175–185 °C in the plastic and produces nitrogen and carbon dioxide as the principal gases. The gas yield is roughly 200–220 mL/g.

General procedure

Preparation of octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposites: In order to achieve optimum dispersion of octavinyl polyhedral oligomeric silsesquioxane in host polymer, octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles were prepared firstly. The synthesis was carried out in 250 mL glass reactors equipped with a reflux condenser, an inlet for inert gas supply, and two more inlets for feeding the reactants. 10 mL styrene was mixed with a given amount of octavinyl polyhedral oligomeric silsesquioxane and added to 150 mL distilled water including sodium dodecyl sulfate. After purging with N₂ for 20 min and stirring for 10 min, the mixture was warmed to 80 °C and the initiator potassium persulfate was added to start the polymerization. After the reaction completed, the emulsion was destabilized by adding dense HCl. The precipitate was washed repeatedly with ethanol and distilled water, then dried in air at ambient temperature for 24 h. Fig. 1 illustrates the molecular structures of octavinyl polyhedral oligomeric silsesquioxane and synthetic procedures of octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles.

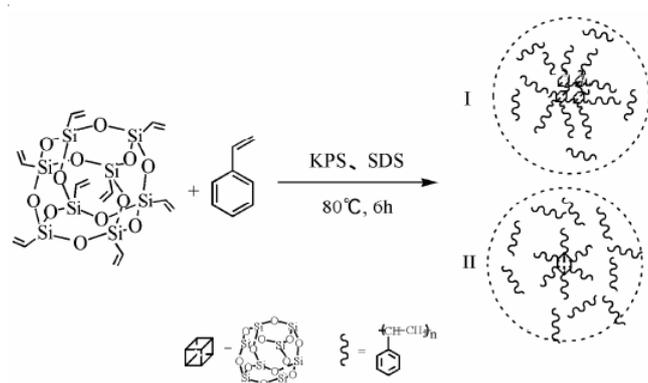


Fig. 1. Synthesis procedure of OVS/PS nanocomposite particles by emulsion polymerization.

Preparation of foams: The foams were prepared to check the effect of octavinyl polyhedral oligomeric silsesquioxane on the cell nucleation. Some disturbing effects, such as changes in rheological behavior of the system, must be taken into account to ensure that the addition of octavinyl polyhedral oligomeric silsesquioxane and foaming temperature would not lead to any significant difference in rheological behaviour

between two contrast systems to evaluate solely the effect of octavinyl polyhedral oligomeric silsesquioxane on cell nucleation. Hence, a relative low octavinyl polyhedral oligomeric silsesquioxane content and a relatively high foaming temperature were chosen to avoid the above disturbing effects. Polystyrene was firstly melt blended with azodicarbonamide (0.5 wt % based on the total amount of the mixture) and octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles according to a given proportion to ensure the octavinyl polyhedral oligomeric silsesquioxane content of 0.15 wt %. The prepared blend was injected into the mold cavity at a melting temperature of 180 °C and an injection pressure of 35 MPa by an injection molding machine. The foamed standard tensile test bars (200 mm × 10 mm × 4.4 mm) according to ISO3167: 2002 were molded through a two-step molding process. The two-step molding process is designed to involve two sequential steps: (i) mold cavity is partially opened yet kept under certain pressure (the mold cavity is still closed) after injection to allow cells to nucleate and grow within certain limit; (ii) mold cavity is completely opened when the sample is cooled to room temperature.

Detection method: Transmission electron microscopy measurements were performed with a high-resolution transmission electron microscope (H-7000-F) at an accelerating voltage of 80 kV. The suspension of octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles was dropped onto copper grids and evaporating them prior to observation.

Fourier transform infrared spectra were obtained on octavinyl polyhedral oligomeric silsesquioxane, polystyrene and octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles using a Nexus FTIR (Mattson Instruments, Inc.). Optical grade potassium bromide (KBr, International Crystal Laboratories, Garfield, NJ) was used as the supporting medium. The resolution was ± 2 cm⁻¹.

The X-ray measurements were carried out on a Rigaku D/Max-III A X-ray generator with Cu-K α radiation at a wavelength of 1.54 Å. Specimens were scanned from 5° to 40° with a scan speed of 0.5°/min.

The viscosity measurement of the samples was performed using a Reologica ViscoTech oscillatory rheometer with a heating rate of 3 °C min⁻¹ and angular frequency of 1 rad/s in the temperature range of 155–185 °C. The elastic modulus (G') was measured at 150 °C as a function of the angular frequency (ω) from 0.1 to 60 rad/s.

A TA Instruments Q1000 dynamic mechanical analyzer (ARES, TA Instruments) was used to acquire storage modulus, loss modulus, and tan delta for specimens in tensile mode. The testing temperature ranged from 40 to 140 °C with a 2 °C/min heating rate at frequencies of 1 Hz. The same tests were repeated three times using three different specimens.

The cellular morphologies of the foamed samples were investigated by a Toshiba S-4800 field emission scanning electron microscopy (FESEM). The foamed samples were fractured and sputter-coated with platinum.

The number-average cell diameter (D_n) and cell size distribution (D_w/D_n) of foamed samples were determined by a survey of a minimum of 150 cells picked up from the SEM images. The SEM images of foamed samples were analyzed

with Image-Pro plus software (Media Cybernetic) to quantitatively assess cell size. D_n and D_w are defined as follows:

$$D_n = \sum n_i D_i / \sum n_i \quad (1)$$

$$D_w = \sum n_i D_i^2 / \sum n_i D_i \quad (2)$$

where, D_i ($i = 1, 2, \dots, q$) and n_i are cell size and mole fraction, respectively.

The number of cells per unit volume (cm^3) of foamed sample is determined from²⁰

$$N_0 = \left[\frac{nM^2}{A} \right]^{3/2} \left[\frac{1}{1-V_f} \right] \quad (3)$$

where, n is the number of cells in the micrograph, M the magnification of the micrograph, A the area of the micrograph, and V_f the void fraction of the foamed sample. The void fraction is defined as:

$$V_f = 1 - \frac{\rho_f}{\rho} \quad (4)$$

where ρ_f and ρ are, respectively, the densities of the foamed and unfoamed samples.

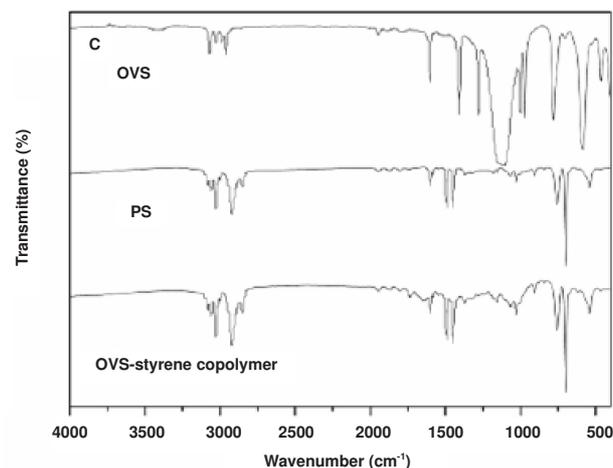
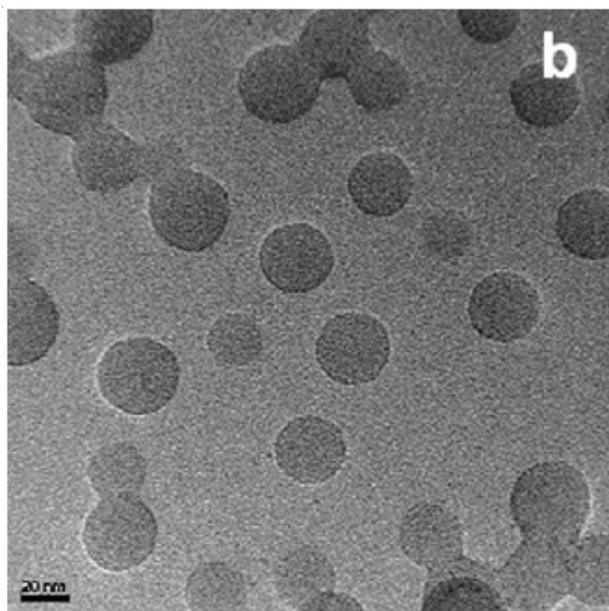
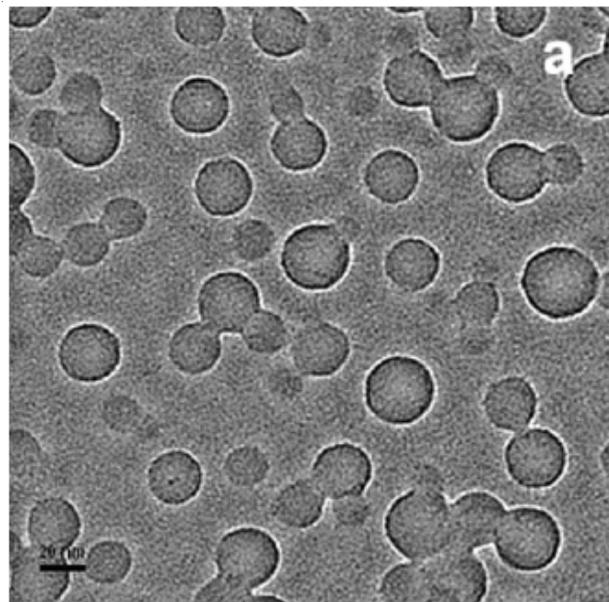
RESULTS AND DISCUSSION

Morphology and composition of octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles: As illustrated in Fig. 2a and b, TEM images of the as-prepared octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles show distinct spherical nanoparticles with an average size of around 25 nm. The spherical particles with relatively homogeneous structure and dispersion are clearly visible, implying the octavinyl polyhedral oligomeric silsesquioxane was wrapped by polystyrene.

To verify the composition of octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles, the as prepared particles were characterized by FTIR. Fig. 2c shows the FTIR spectra for octavinyl polyhedral oligomeric silsesquioxane, neat polystyrene and octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles. For the pure polystyrene, the strong absorption bands at 1600, 1492 and 1452 cm^{-1} assigned to C=C stretching vibration of phenyl ring, while the intensities of absorption bands at 696 and 756 cm^{-1} attributed to monosubstituted benzene. The characteristic absorbance at 1117 cm^{-1} corresponded to Si-O-Si stretching vibrations are observed for the octavinyl polyhedral oligomeric silsesquioxane and octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles as well as the absorbance at 1117 cm^{-1} is absent in the neat polystyrene spectrum, indicating the covalent bonding between octavinyl polyhedral oligomeric silsesquioxane and polystyrene backbone.

Fig. 2d shows the X-ray diffraction patterns of the octavinyl polyhedral oligomeric silsesquioxane, polystyrene, and octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles with various octavinyl polyhedral oligomeric silsesquioxane content. The octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles show broad peaks at 18°, which is quite similar to the amorphous polystyrene, while the sharp characteristic peaks of octavinyl polyhedral oligomeric silsesquioxane at 9.7°, 13°,

22.7° and 23.6° disappeared, which suggests that octavinyl polyhedral oligomeric silsesquioxane existed in the nanocomposite particles at the molecular level.



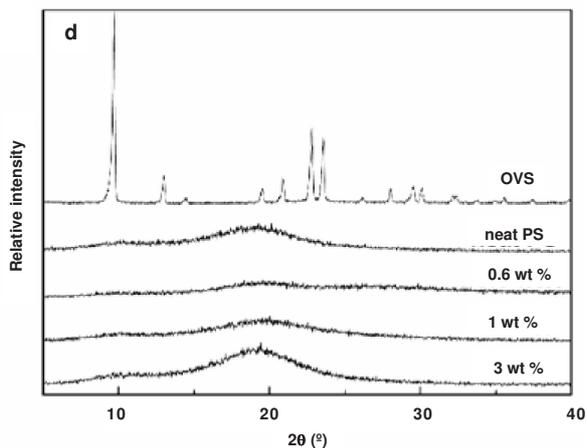


Fig. 2. (a) and (b) TEM images of OVS/PS nanocomposite particles with various OVS loading. Scale bar: 20 nm. FTIR spectra (c) and X-ray diffraction patterns (d) of OVS, neat PS and OVS/PS nanocomposite particles

Rheological properties of octavinyl polyhedral oligomeric silsesquioxane/polystyrene composite blend: The experimentally determined apparent melt viscosity data as a function of melt temperature and elastic modulus at 150 °C with variable frequencies for neat polystyrene and octavinyl polyhedral oligomeric silsesquioxane/polystyrene composite at a given concentration of octavinyl polyhedral oligomeric silsesquioxane are presented in Fig. 3. Over a temperature range from 155 to 185 °C, the melt viscosities appear to fall, whereas the data give no obvious deviation between neat polystyrene and the octavinyl polyhedral oligomeric silsesquioxane/polystyrene composite. In the shear rate range between 0.0025 and 0.0375 S^{-1} , the two curves superpose very well (Fig. 3a). At equivalent octavinyl polyhedral oligomeric silsesquioxane loading, similar elastic modulus with variable frequencies has been observed for the neat polystyrene and the octavinyl polyhedral oligomeric silsesquioxane/polystyrene composite as shown in Fig. 3b. The octavinyl polyhedral oligomeric silsesquioxane/polystyrene composite at the relatively low octavinyl polyhedral oligomeric silsesquioxane level failed to reveal any significant effect on the rheological behaviour of the system within the experimental range. Octavinyl polyhedral oligomeric silsesquioxane has not strongly impacted the rheological behaviour due to the exceedingly low level of octavinyl polyhedral oligomeric silsesquioxane.

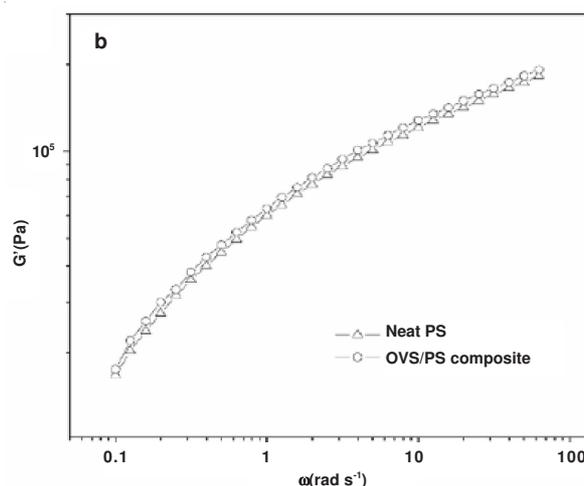
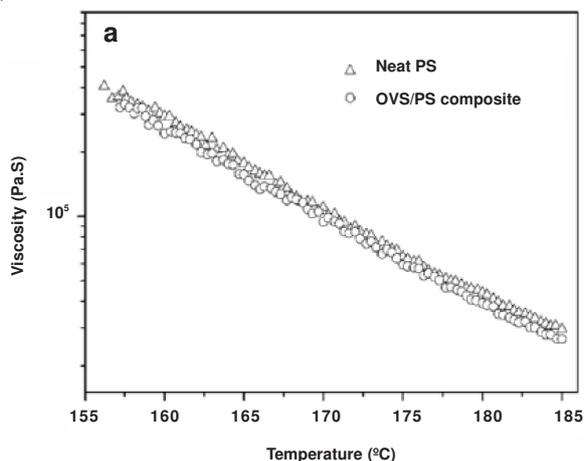


Fig. 3. Apparent melt viscosity presented as a function of temperature (a) and elastic modulus at 150 °C with variable frequencies (b) for neat PS and OVS/PS composite at an OVS content of 0.15 wt %.

The plots of tensile storage modulus (E') and loss tangents ($\tan \delta$) are shown in Fig. 4. No large difference is observed between the two samples from Fig. 4a. The slight increase in storage modulus as octavinyl polyhedral oligomeric silsesquioxane was added into the polystyrene matrix appears to be associated with the local chain entanglement. Slight differences in loss tangents $\tan \delta$ of the melts can be seen in Fig. 4b. The slight variation of the T_g of the composite by the addition of octavinyl polyhedral oligomeric silsesquioxane, which was observed by DMA measurement, supported the invariability of the viscosity at a certain temperature by the addition of octavinyl polyhedral oligomeric silsesquioxane. The appreciably lower T_g of the composite relative to that of neat polystyrene provides an indication that free volume in the polystyrene matrix increases slightly upon addition of the octavinyl polyhedral oligomeric silsesquioxane/polystyrene nanocomposite particles.

It is concluded based on the above analysis that the octavinyl polyhedral oligomeric silsesquioxane at the exceedingly low level had no obvious effect on the rheological properties of the composite, so for the foams of the corresponding composites the degree of cell coalescence and coarsening should be similar to that of neat polystyrene. We can evaluate the effect of octavinyl polyhedral oligomeric silsesquioxane on cell nucleation solely on the basis of the cell structure.

Effect of octavinyl polyhedral oligomeric silsesquioxane on cell nucleation: Fig. 5 shows the SEM images and the cell size distributions of the typical resulting foams of neat polystyrene and the octavinyl polyhedral oligomeric silsesquioxane/polystyrene composites. As expected, the addition of octavinyl polyhedral oligomeric silsesquioxane to polystyrene significantly improves the cell density. The cell densities of 10^7 - 10^8 cells/ cm^3 for the composite foams are almost two orders of magnitude higher than that of neat polystyrene. The cell density did not increase proportional to the amount of octavinyl polyhedral oligomeric silsesquioxane present in the melt, which could be attributed to cell coalescence or coarsening. Actually, the foaming conditions in this work are less appropriate for optimal foam structure because we intended to avoid the effect of the octavinyl polyhedral oligomeric

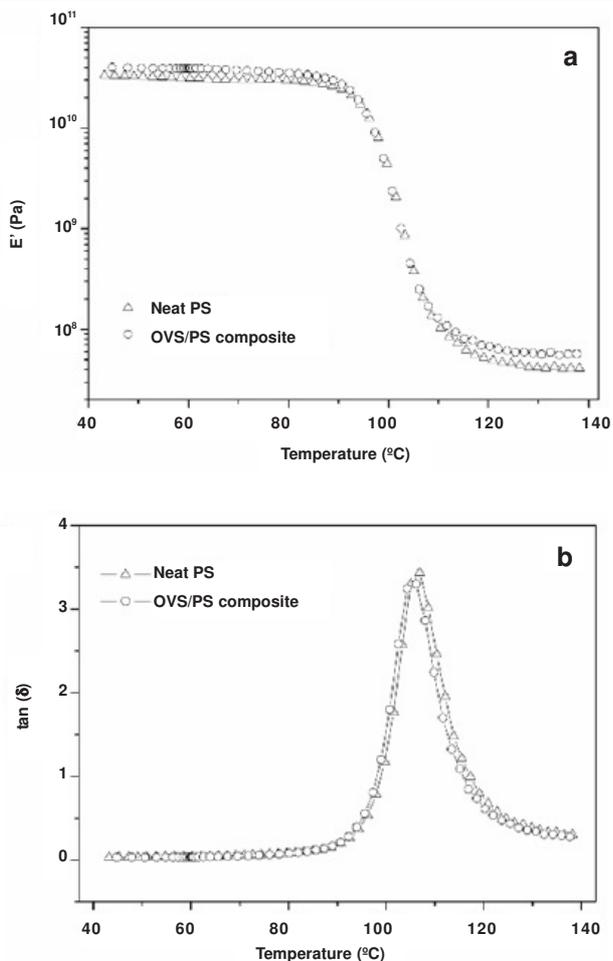


Fig. 4. Tensile storage moduli E' (a) and loss tangents $\tan \delta$ (b) versus temperature curves at 1 Hz for neat PS and OVS/PS composite containing 0.15 wt % OVS

silsesquioxane on the rheological behaviour by reducing the content of octavinyl polyhedral oligomeric silsesquioxane and increasing the processing temperature. Moreover, the composite foams exhibited much narrower cell size distribution relative to the foam generated from neat polystyrene, reflecting the increase in nucleation rate due to the presence of octavinyl polyhedral oligomeric silsesquioxane²⁰. The large decrease in average cell size of the composite foams also implied the enhancement for cell nucleation.

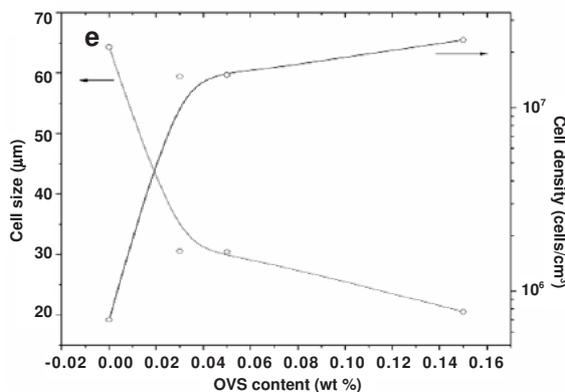
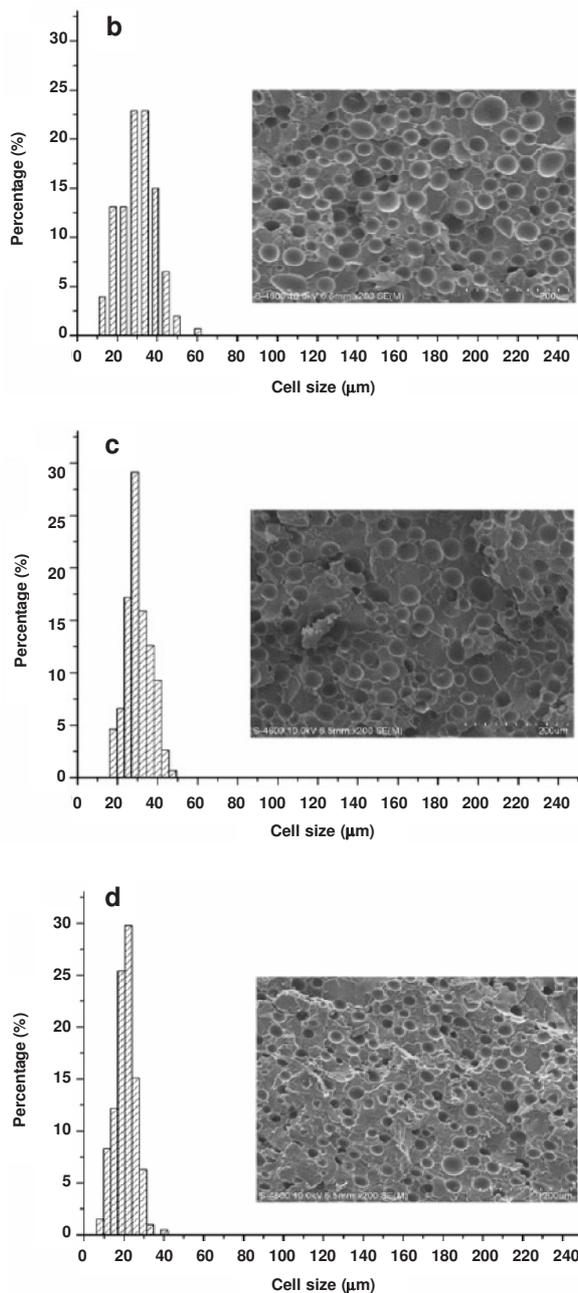
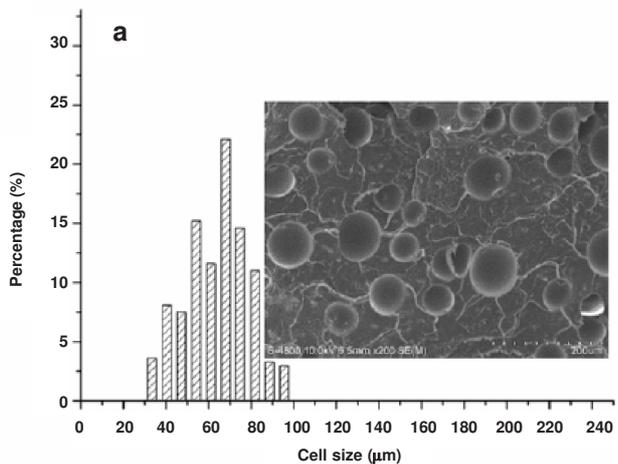


Fig. 5. Cell size distributions of the foams prepared from neat PS (a) and OVS/PS composites containing 0.03 (b), 0.05 (c) and 0.15 (d) wt% OVS, the inset presents the SEM images of fracture surfaces of the corresponding foams at a magnification of 200. (e) Plot of the cell size and cell density of the foams versus OVS content



In view of the slight differences in T_g for the composite and neat polystyrene, we cannot attribute this improvement to the variation in the tacticity of the composite caused by the presence of the octavinyl polyhedral oligomeric silsesquioxane. The rheological results also suggest that the degree of cell coalescence or coarsening for octavinyl polyhedral oligomeric silsesquioxane/polystyrene system is equivalent to that of polystyrene owing to the similar melt viscosity. In addition, no appreciable evidence was found for a strong thermodynamic affinity of octavinyl polyhedral oligomeric silsesquioxane for nitrogen which could serve to thwart N_2 diffusion. Consequently, the improvement should be attributed solely to the effect of octavinyl polyhedral oligomeric silsesquioxane on the nucleation. However the effect of interfacial free energy seems to be negligible, because octavinyl polyhedral oligomeric silsesquioxane covalently bonded to polystyrene has good compatibility with polystyrene matrix as discussed previously, the interfacial free energy is expected to be very low. The information suggests that we could attribute solely this to the microvoid structure inside octavinyl polyhedral oligomeric silsesquioxane, which is stable in the experimental range. Ramesh *et al.*^{16,17} reported that the survival of microvoids inside polymer can provide nucleation sites and facilitate the cell nucleation. The size of voids inside the octavinyl polyhedral oligomeric silsesquioxane (5.4–10 Å for a single octavinyl polyhedral oligomeric silsesquioxane cage or several nanometers for the aggregate of multiple octavinyl polyhedral oligomeric silsesquioxane cages calculated based on the Si-Si diameter of 5.4 Å) is comparable to the radius of critical nucleus predicted by the classical nucleation theory, which is typically on the order of 5 to 20 Å¹⁶. The microvoids act as bubble embryos and would not collapse against the large surface elastic energy forces due to the stiff structure of octavinyl polyhedral oligomeric silsesquioxane. These pre-existing voids present a lower energy of activation for nucleation than that for homogeneous nucleation and thus provide accessible sites to induce nucleation or cell growth. When the void size of a single octavinyl polyhedral oligomeric silsesquioxane cage or an aggregate of multiple octavinyl polyhedral oligomeric silsesquioxane cages is larger than the critical size, it helps to leap over the cell nucleation process and the void would spontaneously grow to macroscopic size.

Conclusion

The inner voids of octavinyl polyhedral oligomeric silsesquioxane lower the activation energy for cell nucleation or even help to leap over the cell nucleation process by acting as cell embryos for polymer foaming, leading to obviously enhanced cell structure at exceedingly low level. This study

provides a simple and low-cost strategy toward the enhancement of foam quality by employing octavinyl polyhedral oligomeric silsesquioxane containing inner voids acting as cell embryos. It is possible that the microcellular foaming of common plastics is realized through continuous injection foaming by chemical foaming agents requiring no special equipments or reorganization of existing equipments. However, it is not sufficient to obtain fine microcellular structure solely by nucleation effect because of the limited rheological properties. More favorable cell structure is foreseeable if the rheological behaviour is modified by using more appropriate processing conditions or higher level of octavinyl polyhedral oligomeric silsesquioxane. Moreover, higher mechanical and thermal properties for octavinyl polyhedral oligomeric silsesquioxane-containing foams than the neat polymers also deserve attention in future research.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 50802068).

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