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Supercritical CO2 Foaming of Polypropylene Nanocomposites: Surfactant and Reinforcing Effects of Silsesquioxane-based Hybrid Janus Molecules

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The development of high melt-strength (HMS) long-chain-branched polypropylene (PP) has enhanced foamability of PP by extrusion foaming process, even with supercritical CO_2 *(sc*CO_2*) as blowing agent. However, numerous issues still persist in sc*CO_2*-foaming of HMS PP that tend to limit such foams to having lower expansion ratio (ER), higher foam density, and poorer compression strength (CS). One of such issue is the high diffusion rate of* CO_2 *through PP. This causes high diffusive gas losses which results in reduced ER and higher foam density. Even if ER can be improved by optimizing process parameters or by introducing organic surfactants such as glycerol monostearate, the increased void fraction would generally produce foams with lower CS. Moreover, organic surfactants may also pose degradation concerns during application, especially when exposed to UV. Another issue encountered is the poor nucleation rate of* CO_2 *in PP, which results in low cell density and large cell size. This would cause poor homogeneity in the PP foam's cell structure, which also leads to CS reduction. Although nucleating agents such as Talc could be introduced to achieve high cell density, small cell size, and hence a higher compression strength, it is often associated with ER reduction due to increase diffusive gas losses via the talc-polymer interface. In this study, we have demonstrated a novel approach of incorporating HMS PP with a low-cost hybrid Janus molecule surfactant, heptaisobutyl open-cage silsesquioxane (HOS), and achieved PP foams with simultaneous enhancement in ER and CS. Since HOS' organic-side consists of isobutyl groups that are compatible with PP while the inorganic-side consists of a partially condensed silsesquioxane cage that has good affinity with* CO_2*, HOS could act as a surfactant that can diffuse to the PP-*CO_2 *interface during foaming to stabilise the cells during their growth stage while reinforcing the cell surface with its rigid silsesquioxane structure upon solidification. Our results show that with 1 wt% HOS, the PP/HOS nanocomposite foam could offer 38 % ER improvement, 23 % foam density reduction, and 20 % CS increase when compared to neat PP foam. Using X-ray Photoelectron Spectroscopy characterization, this surfactant effect of HOS has also been validated. In addition, HOS could also provide further energy savings during processing by acting as a lubricant to reduce PP's shear viscosity without deteriorating its extensional viscosity and melt strength. This hybrid surfactant approach hence opens a new avenue for simultaneously enhancing the ER and CS of polymer foams in a simple and economically viable way and has the potential to be applied or further developed for other polymer foams.*

NOMENCLATURE

ER = Expansion ratio, which describes the degree of expansion and the foamability achieved by a foam.
LVSEM = Low Vacuum Scanning Electron Microscope, an equipment that allows non-conductive samples to be analyzed without the sputtering of a conductive layer.

1. Introduction

Polymeric foams are lightweight cellular material that possess unique insulation and energy absorption properties. Ranging from Styrofoam cups to packaging foams, it is widely used in daily applications. These foams are often fabricated through foaming processes that typically involves the dissolution of gas in a polymer melt, nucleation of these dissolved gas in the polymer melt, and subsequent growth of these nuclei into cells by further effervescence of dissolved gas. [1] Of the many foaming processes available, Supercritical CO_2 ($scCO_2$) extrusion foaming stands out as it combines the sustainability benefits of $scCO_2$ with the high throughput continuous process advantage of an extruder. [2] When polypropylene (PP) foams are fabricated using this foaming process, foams possessing PP's excellent mechanical and thermal properties can be obtained in a quick and sustainable manner. These benefits of $scCO_2$ extrusion foamed PP would make it highly attractive for numerous applications, such as transportation and packaging industry.

However, the $scCO_2$ extrusion foaming of PP faces numerous hurdles. One of which is the high diffusion rate of CO_2 through the PP material. Consequently, this causes the effervescing CO_2 to rapidly escape from the PP foam, resulting in lower expansion and hence poorer foamability. [3] Although surfactants, such as glycerol monostearate (GMS), has been used to act as an additive to stabilize the gas cells against diffusive loss, the experimental studies are severely limited. [4] Furthermore, as PP is prone to free radical degradation, the presence of these organic surfactant may exacerbate PP degradation during fabrication and applications. Another hurdle faced by PP is its poor melt strength, which results in its cell wall to easily rupture during cell growth. This leads to cell coalescences and foam deflation which causes pronounced CO_2 losses that will adversely affect foamability. [5] Thus, in the experimental work, High Melt Strength (HMS) PP with long-chain branched (LCB) structure is used to overcome this problem. Aside from these hurdles imposed by the foaming process and the material, another challenge often encountered in foams is the tradeoffs between foamability and compression strength. With higher foamability, the higher void content would generally reduce the cross-sectional area for effective load bearing, resulting in reduced compression strength.

In this work, we proposed that heptaisobutyl open-cage silsesquioxane (HOS), as shown in Fig.1 with three polar inorganic silanol groups exhibiting good CO_2 affinity on one face [6] and seven functionalised PP-philic non-polar organic isobutyl corners with good PP compatibility on the other face, can act as Janus molecule surfactant that would diffuse to the PP-CO_2 interface to stabilize the growing cells. Furthermore, as HOS possess a rigid inorganic silica core, a large concentration of HOS at the interface will reinforce the cell surface, leading to compression strength improvement. Herein, we demonstrate the use of HOS in HMS PP as an organic-inorganic hybrid Janus molecule surfactant that not only enhances Expansion Ratio (ER) by 38 % at just 1 wt% loading, but also simultaneously improve the compressive strength by 20 %. These improvements are due to the surfactant effect of HOS, which has been verified using X-ray Photoelectron Spectroscopy (XPS). Additionally, HOS exhibit excellent dispersion in PP and could act as a melt lubricant that also improves PP's melt extensional properties.

2. Characterization of PP/HOS nanocomposite foam.

2.1 Dispersion of HOS in PP

The degree of additive dispersion in a polymer is important to ensure that the properties and performance observed is homogeneous throughout the material. From Fig. 2a-d, it can be observed that no HOS agglomerations or aggregates could be observed under Low Vacuum Scanning Electron Microscope (LVSEM). Furthermore, in Fig. 2e, the X-ray Diffraction (XRD) pattern of the nanocomposites and foams do not exhibit the crystalline peaks of neat HOS powder. Hence, these implies that HOS molecules have achieved excellent dispersion in PP where they are in the form of single molecules (size of ~ 1.2 nm) and/or extremely small, disordered clusters whose size is beyond the resolution limit of the LVSEI-mode SEM. Furthermore, as the decomposition temperature at 5 % weight loss is 255.1 ˚C, it is unlikely that the HOS has broken down in the nanocomposite during compounding or foaming. This excellent dispersion of HOS is likely due to the isobutyl function groups that bear structural similarity to the repeating units of the PP chain. This gives HOS a good interaction and compatibility with the PP chains, which allow it to be easily dispersed in the PP matrix.

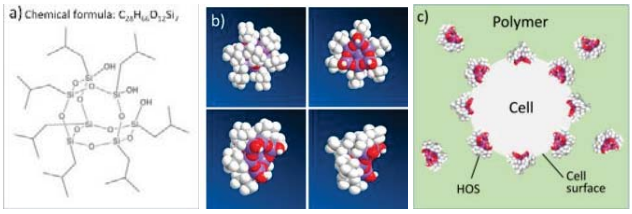

Fig. 1, a) Structural formula of HOS. b) Energy minimised HOS model produced using Merck Molecular Force Field 94, where the white side contains isobutyl groups while the coloured side contains silanol groups. c) Schematic showing the likely arrangement of HOS in the PP/HOS nanocomposite foams.

2.3 Surfactant effect of HOS

The improvements achieved in this study is attributed to HOS acting as a surfactant. To facilitate the characterization of HOS' surfactant effect, XPS analysis is used to quantify the Si content at a location to determine its local composition of HOS. Firstly, experimental work was done to determine if HOS can diffuse through the PP matrix to an interface. From Fig. 2f where a 5 wt% loading PP/HOS nanocomposite melt is exposed to CO_2, it shows that with increasing CO_2 exposure time, the composition of HOS at the CO_2-exposed surface increases rapidly. This implies that HOS, like a surfactant, can over time diffuse through the polymer melt to the interface and can respond quickly to the presence of an interface. Secondly, as shown in Table 1, XPS analysis was subsequently performed on a 5 wt% loading PP/HOS foam where the cell surface was found to have a significantly higher Si content than the cell wall cross-section bulk. Thus, during foaming, HOS has indeed diffused from the bulk and gathered at the PP-CO_2 interface. These results therefore support the surfactant behaviour of HOS during PP $scCO_2$ foaming and that it is likely the main reason for the improvements observed.

2.2 Foamability and foam morphology

Expansion ratio (ER) describes the degree of expansion and hence the foamability achieved by the foam. From Fig. 3a, it can be observed that an increase in HOS loading generally results in a higher ER. Furthermore, at a HOS loading of only 1 wt%, the ER of the nanocomposite foam is 38 % higher than the neat PP foam, which also corresponds to 23 % foam density reduction. This verifies that HOS indeed reduces the diffusive losses of CO_2 during foaming, which provide further foam expansion. This phenomenon can be described by the Laplace pressure difference between cells, $\Delta P = 2\sigma(\frac{1}{r1} - \frac{1}{r2})$ (where ΔP, σ, and r are Laplace pressure difference, surface tension, and cell radius, respectively). [7] As HOS act as a surfactant at PP-CO_2 interface, the surface tension at the interface is reduced which diminishes ΔP. As the diffusion rate of a gas is also driven by pressure differences, the lower ΔP leads to a lower gas diffusion rate between cells, hence slowing the diffusive loss of gas. Since lesser gas is loss from the foam prior to the cooling and solidification of the polymer foam structure, ER is improved.

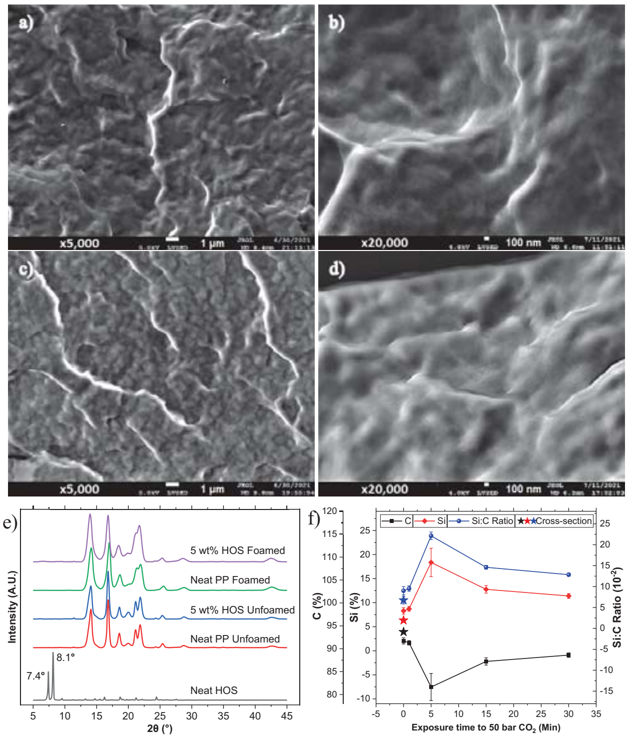

Fig. 2, SEM cross-section images of (a-b) non-foamed and (c-d) foamed PP with 5 wt% HOS. (e) XRD patterns of Neat HOS, Neat PP, and PP/HOS samples. (f) HOS content on the surface of the 5 wt% loading PP/HOS nanocomposite as a function of CO_2 exposure time at 50 bars. The star signs represent the HOS content in the bulk of the films before CO_2 exposure.

In typical polymer foams, the cell density can be easily improved by multiple orders of magnitude when nucleating agents, such as Talc, are added. This in turn would lead to cell sizes that are often in micron scales. [8] Hence, the changes in PP/HOS foams' cell densities and cells sizes, as shown in Fig. 3c-d, are relative insignificant. These results imply that HOS do not have nucleating effect, and this is likely due to the higher barrier against heterogeneous nucleation that is often experienced by smaller particles with nanoscale diameter.

Table 1. XPS results of PP/HOS nanocomposite with 5 wt% HOS.

Location	C content (wt%)	Si content (wt%)	Si:C weight ratio (10^{-2})
Theoretical value for homogeneous sample	83.55	1.24	1.49
Polymer bulk	98.42 ± 0.06	1.58 ± 0.06	1.60 ± 0.06
Cell surface	97.28 ± 0.4	2.72 ± 0.4	2.80 ± 0.4

2.3 Foam compression properties

As shown in Fig. 3b, with increasing loading of HOS, the compressive strength of PP/HOS foam is improved by 16 to 49 % over that of the neat PP foam. Furthermore, the specific compressive strength of PP/HOS, which is the compressive strength per foam density, increases monotonically from 24 to 77 %. It is important to note that the tensile strength of a foam's intrinsic material directly contributes to the compression strength of a foam. But prior to foaming, the tensile strengths of such PP/HOS nanocomposites with 0.25 to 1 wt% HOS are reported to only have 3.4 to 4.6 % improvements over neat PP. [10] Hence, the observed compressive strength enhancement of PP/HOS nanocomposite foams is unlikely to be solely attributed to the reinforcement of matrix by the dispersed HOS molecules in PP. Furthermore, the cell density, cell size, and cell size distribution of the PP/HOS foams are in the typical range of conventional macrocellular foams. Hence, unlike microcellular foams, the enhanced compressive strength could not be attributed to the improved foam structural factors. [3] Moreover, Differential Scanning Calorimetry (DSC) thermal analysis did not show significant changes in crystallinity % and melt temperature, which indicates negligible change in crystal size. Hence, the enhanced compressive strength of the PP/HOS foams is not caused by changes in PP crystallization. Therefore, the surfactant effect of HOS remains as the likely reason, which not only reduced diffusive gas loss and stabilize cells, but also reinforced the cell surface. Nevertheless, the compressive strengths of polymer foams remain highly complex. Thus, future simulation studies would still be required to investigate this unusually strong reinforcement effect in detail.

2.4 Rheological properties of HOS foams.

As shown in Fig. 4a, the addition of HOS causes the shear viscosity of the PP/HOS nanocomposites to decrease. Although Trouton's ratio describes states that a decrease in shear viscosity usually cause a proportionate decrease in extensional viscosity prior to melt strain hardening effect, the extensional viscosity of PP/HOS, as shown in Fig. 4b, has instead increased till an optimum is reached at 1 wt% loading. Furthermore, with the presence of HOS, the melt strength of the material is found to have also enhanced at low strain rates. These results show that HOS could act as lubricating agent that can reduce the energy usage during processing without deteriorating the melt extensional properties that are critical for foaming. A likely explanation could be that the high degree of HOS dispersion has caused HOS molecules to be present between PP chains to space and reduce their interchain interaction, thereby lowering its shear viscosity. Also, due to the rigid nature of HOS' inorganic silica core, HOS acts as rigid obstacles against the disentanglement of the HMS PP's LCB structure, resulting in a longer relaxation time that increases its extensional viscosity and promotes more melt strain hardening effect for higher melt strengths. [5]

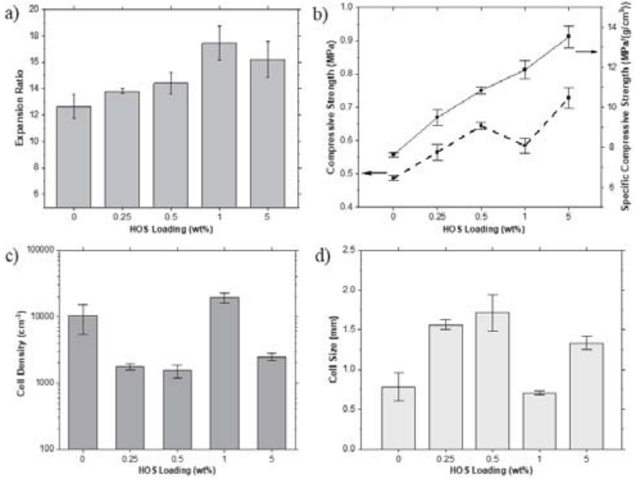

Fig. 3, a) Expansion ratio, b) compressive strength, specific compressive strength, c) cell density, and d) cell size of neat PP and PP/HOS foams at different HOS loadings.

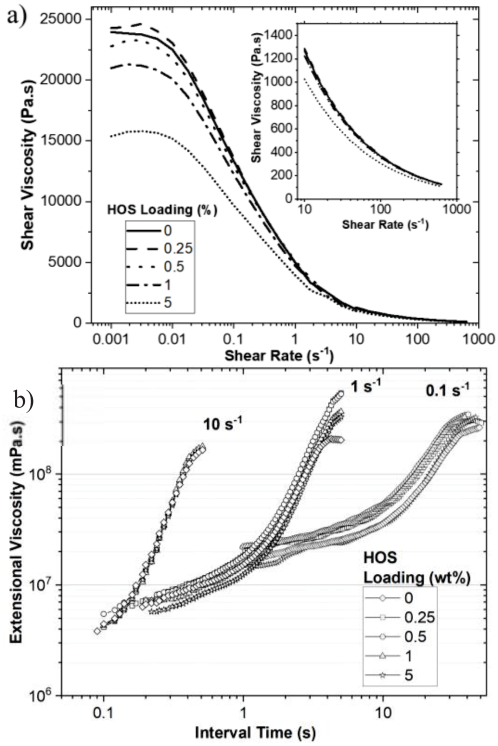

Fig. 4, a) Shear viscosities and b) extensional viscosities of PP/HOS nanocomposites.

3. Conclusions

In this work, HOS has been studied as a hybrid Janus molecule surfactant to simultaneously enhance the foamability and compression strength of $scCO_2$ extrusion foamed PP. Additionally, the study also demonstrates the multifunctional properties of HOS where it can also serve as a lubricating agent that provide energy savings without deteriorating the melt extensional properties. These findings would provide future foaming process with a new straightforward and economically viable method to alleviate the foamability-compressive strength tradeoff of macrocellular polymer foams while achieving reduced processing cost. Lastly, the surfactant effect of the hybrid material has been verified by XPS. This would inspire the development of new non-organic surfactants for future foaming systems to achieve enhanced foamability and multifunctional benefits while avoiding the degradation issues faced by organic surfactants.

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