Polystyrene foams with inter-connected carbon particulate network

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Abstract

New polystyrene (PS)/carbon nanofiber (CNF) and PS/graphite foams with an inter-connected honeycomb-like carbon particulate network of CNF or graphite were prepared by first coating the surface of polymer pellets with either CNF or graphite and then conducting batch foaming using carbon dioxide (CO_2) as a blowing agent. It was found that the inter-connected honeycomb-like carbon particulate network could significantly reduce the compression yielding of conventional PS foams. With 1 wt% of CNFs or graphite, the PS foams with inter-connected honeycomb-like carbon particulate network were 5–9 times more electrically conductive than foams made of compounded PS nanocomposite with the same carbon particle loading. In addition, the PS foams with inter-connected honeycomb-like carbon particulate network were more thermally conductive and revealed significantly improved thermal stability comparing to foams made of compounded polymer nanocomposites.

Keywords

Polystyrene foams, inter-connected honeycomb-like carbon particulate network, carbon nanofibers (CNFs), graphite, composite

Introduction

Polymer foams have been widely used in many fields such as insulation, cushions, absorbents, and scaffolds for cell attachment and growth.[1,2] Recently, polymer nanocomposite foams, a new class of polymer foams containing a small quantity

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(usually <5%) of nanoparticles, have attracted a great deal of interest in the industry because they possess advantages of both polymeric foams and nanoparticles.[3] The gaseous voids within the polymer nanocomposite foams can reduce the weight of the products, while the presence of nanoparticles is able to compensate the reduction of mechanical strength and thermal stability caused by foaming.[4] Furthermore, nanoparticles may serve as the nucleation agent to control the foaming process and foam morphology.[3,5–9]

Nanoparticles usually refer to particles with at least one dimension on the order of 100 nm or less, which can be broadly divided into three types including platelet-like nanoparticles with a thickness in the nanometer range and lateral dimensions in the range from several hundred nanometers to a few micrometers (e.g. nanoclay, graphene), fiber/tube-like nanoparticles having an elongated structure with two dimensions at the nanometer scale (e.g. carbon nanofiber (CNF) and carbon nanotube (CNT)), and spherical nanoparticles with all three dimensions in the nanometer scale (e.g. buckyballs and silica particles).[3,5] In general, the morphology control and property enhancement for the polymer nanocomposite foams depend on the dispersion of nanoparticles in the polymer matrix.[1,3,5,6–11] For most polymer nanocomposite foams, the nanoparticles are pre-compounded into the polymer matrix to form a dispersed phase and then extrusion or batch foamed into the foam products by employing blowing agents such as hydrogen-containing chlorofluorocarbons (HCFCs), fluorocarbons (HFCs), and carbon dioxide (CO_2).[5,12–17] Consequently, the properties of polymer nanocomposite foams are still dominated by the continuous polymer matrix because it is difficult to let the nanoparticles form a continuous structure unless the particle concentration is very high. It would be highly desirable to develop new materials and new methods such that nanoparticles, even at a very low concentration, may form an inter-connected structure in the polymer nanocomposite foams. Such an inter-connected structure may provide superior mechanical, thermal, and electrical properties, not achievable by the conventional foams prepared from compounded polymer nanocomposites.

In the present study, nanoparticles were mechanically attached onto the surface of polystyrene (PS) pellets. The particles-coated PS pellets were then molded at elevated temperatures and pressures to form PS nanocomposites with an inter-connected structure. Finally, batch foaming was conducted with CO_2 as a blowing agent to prepare the PS nanocomposite foams with inter-connected honeycomb-like carbon particulate network. The foam morphology, compressive strength, and electrical and thermal conductivity of PS foams with the inter-connected nanoparticles were measured and compared with those of conventional nanocomposite foams.

Experimental

Materials

Polystyrene (PS, Ineos Nova 1600, softening temperature = 106°C) pellets were purchased from INEOS NOVA (USA). Carbon nanofibers (CNF, PR-24XT-HHT) and

expandable graphite flake (GRAFGUARD®) were purchased from Purograf and GRAFTech (USA), respectively. The grinding agent (10 mm steatite balls with band around the center) was from the Norstone, Inc. (USA).

Sample preparation

The schematic illustration of the sample preparation is shown in Figure 1. For a typical sample, PS pellets (30 g), CNF or graphite (0.75 g), and grinding media (150 g) were placed in a glass container (1000 ml) at 135°C under mechanical mixing (300 r/min). After 30 min, the mixture was sorted by different sizes of sieves to remove the unattached CNF or graphite and the CNF or graphite coated PS pellets were obtained. To obtain the coating percentage, the PS pellets were weighted before and after coating. In this case, the weight of PS pellets increased from 30.0 g to ~30.3 g after coating and sieving, which means that ~0.30 g of CNF or graphite was coated onto PS pellets for ~1 wt% coating content. At this stage, each PS pellet was coated with a layer of CNF or graphite.

An amount of 6.5 g of CNF or graphite coated PS pellets were placed between two aluminum plates with two Teflon mold release papers and a spacer (5 cm in diameter and 3 mm in thickness). This setup was placed in a press pre-heated to 210°C under 11.72 MPa (1700 lbf/in^2). After 10 min, the press was cooled to room temperature and a PS/CNF (or graphite) nanocomposite disc with inter-connected honeycomb-like carbon particulate network was obtained. The PS nanocomposite was then placed in a steel chamber that was pre-heated to 60°C. After temperature
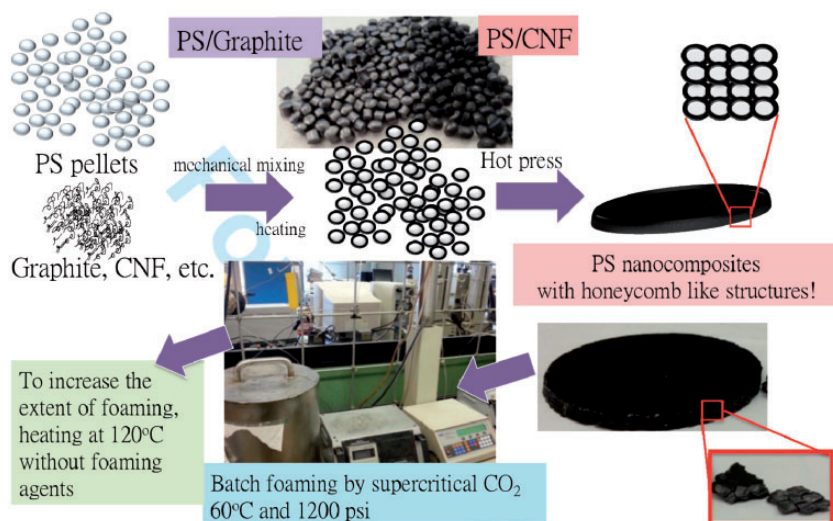
Figure 1. Schematic illustration of preparing PS composite foams with the honeycomb-like structure. CNF: carbon nanofiber; PS: polystyrene.

reached equilibrium, carbon dioxide (CO_2) gas was delivered to the steel chamber via a syringe pump under 8.27 MPa (1200 lbf/in^2) for 18 h.[3,6,7] The pressure was then released in 2–3 s for cell nucleation and foaming. To test the thermal stability, the 60°C foamed samples were further heated to 120°C after being stored at ambient conditions for 3 days. The densities of 60°C foamed samples and those after 120°C treatment are listed in Table 1.

For comparison, PS foams and conventional PS nanocomposites foams were also prepared according to the aforementioned foaming procedure. For the conventional PS nanocomposites foams, PS pellets were compounded with 1% CNF or graphite through twin screw extrusion to prepare PS/CNF or PS/graphite pellets.[7–9]

Morphology and property measurements

The microstructure of the PS foams and composite foams was observed by a scanning electron microscope (SEM, PhilipsXL30). The compressive properties of PS and PS nanocomposite foams were measured on a dynamic mechanical analyzer (RSA III, TA Instruments) in the controlled compressive rate mode. The electrical conductivity was measured by the Van Der Pauw method with a Keithley 6514 electrometer. To measure the heat transfer via the thickness direction, the composite foam disc was placed on a pre-heated hot plate (65°C) and the temperature increase on the opposite surface of the disc was measured. The solubility and swelling ratio were measured by using a microbalance and a laser detector, respectively. The solubility was calculated by the Sanchez-Lacombe equation of state.[18] Samples (6 mm diameter with 1 mm thickness) were prepared under the similar process as that of preparing samples for batch foaming.

Results and discussion

Figure 2 shows the cross-sectional views of the PS, PS/CNF, and PS/graphite honeycomb-like composite foams prepared at 120°C. The macroscopic view in

Table 1. Densities of PS and PS composite foams.

Samples	Density (g/cm^3) (foaming at 60°C)	Density (g/cm^3) (after 120°C treatment)
PS	0.82	0.38
1% PS/CNF_honeycomb	0.70	0.62
1% PS/CNF_compounding	0.70	0.42
1% PS/graphite_honeycomb	0.75	0.73
1% PS/graphite_compounding	0.75	0.57

CNF: carbon nanofiber; PS: polystyrene.
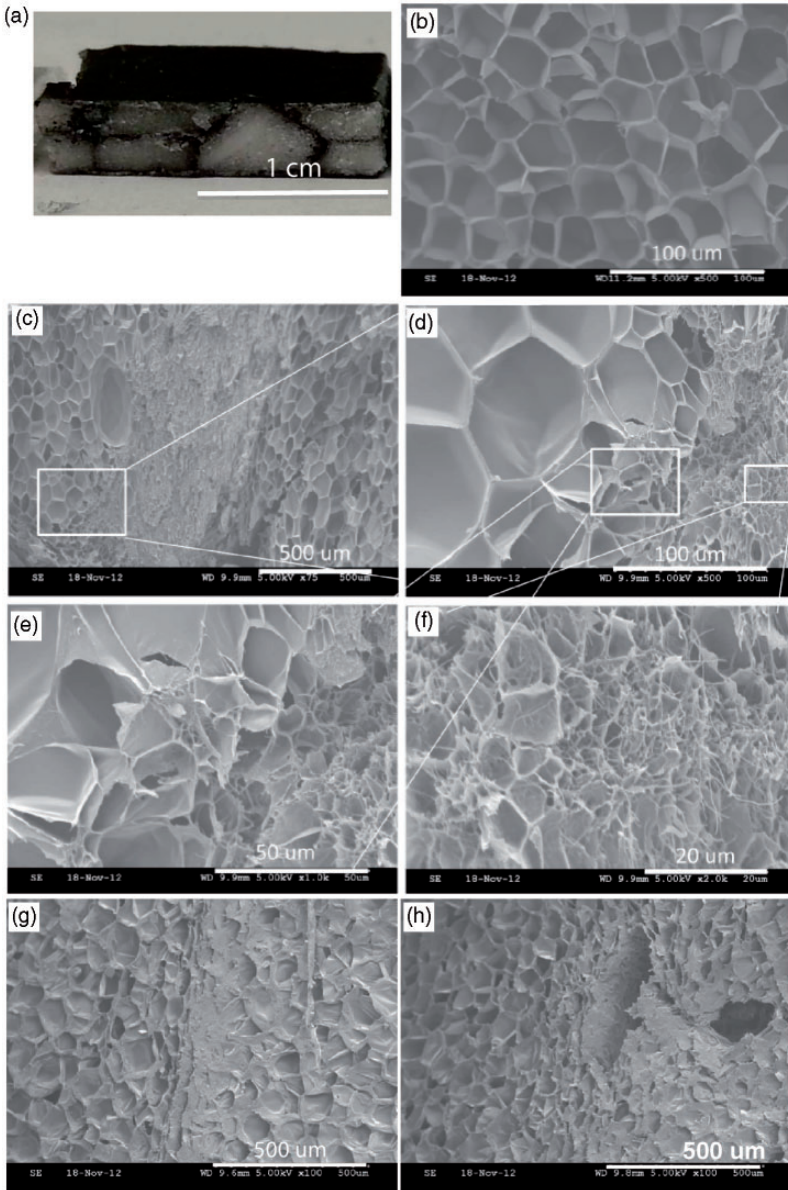
Figure 2. PS, PS/CNF, and PS/graphite composite foams prepared at 120°C. (a) An optical microscopic view of the cross-section of a PS/CNF foam with the honeycomb-like structure, (b) a SEM micrograph of pure PS foam, (c)–(f) SEM micrographs at different magnifications to show three different cell sizes in a PS/CNF foam with the honeycomb-like structure, (g) and (h) SEM micrographs showing two different cell sizes in a PS/graphite foam with the honeycomb-like structure. CNF: carbon nanofiber; PS: polystyrene; SEM: scanning electron microscope.

Figure 2(a) reveals the presence of inter-connected honeycomb-like carbon particulate network within the PS/CNF composite foam. For pure PS foam, the SEM micrograph in Figure 2(b) shows a fairly uniform foam morphology with an average cell size of ca. 40 μm. On the other hand, the PS/CNF honeycomb-like composite foam shown in Figure 2(c)–(f) reveals three different cell sizes, large cells in the PS core, smaller cells near the interface of the PS core and the PS/CNF shell, and very small cells within the PS/CNF shell. The PS/graphite foam with inter-connected honeycomb-like carbon particulate network (Figure 2(g)–(h)) reveals two cell sizes, very large cells in the PS core and small cells near the interface of the PS core and the graphite shell. Unlike the porous CNF shell, graphite is a layer-like particulate structure so there was little polymer within the graphite shell. Consequently, we could not observe any cells there. Cell size comparison of PS foam and PS/graphite and PS/CNF foams with the honeycomb-like structure is given in Figure 3. The very large cells observed in the polymer core of the foams with the honeycomb-like structure were a result of better containment of carbon dioxide there during foaming caused by the diffusion barrier of graphite or CNF shell. The very small cells observed within the PS/CNF shell were due to the strong nucleation effect of CNF nanoparticles, while the smaller cells near the interface of the PS core and the graphite or PS/CNF shell were a result of interface-induced heterogeneous foaming.

Figure 4 compares compressive stress and normalized compressive stress (i.e. stress/density) versus strain curves of PS foam and PS composite foams prepared at 60°C. The PS and conventional compounded PS composite foams showed a similar compressive curve, i.e. an initial linear elastic region follows with a yielding region. Adding graphite and CNF increased the compressive stress, but did not change the compressive behavior. The PS composite foams with the inter-connected honeycomb-like carbon particulate network, on the other hand, showed a substantially different compressive behavior. The initial elastic stress and modulus tended to be lower than those of the PS foams and conventional PS composites foams. However, the yielding region became unclear or occurred at a much higher strain. Consequently, the PS foams with the inter-connected honeycomb-like carbon particulate network could provide a much higher strength at the same strain, or could provide much less deformation at the same stress in the compressive mode. The compressive behavior may be explained by the aforementioned differences in foam morphology. Comparing to PS foams and the conventional PS/graphite and PS/CNF composite foams, the very large cells in the polymer core tended to reduce the initial compressive stress of the PS composite foams with the inter-connected honeycomb-like carbon particulate network. However, the inter-connected honeycomb-like structure consisting of inorganic particulates could substantially enhance the polymer composite foams at higher strains to prevent yielding. In polymer foams or conventional polymer composite foams where the polymer matrix is the continuous phase, yielding would occur at relatively low stresses.

Table 2 illustrates the electrical conductivity comparison of PS composite foams prepared at 60°C. Upon adding CNF and graphite to PS, the resulting composite
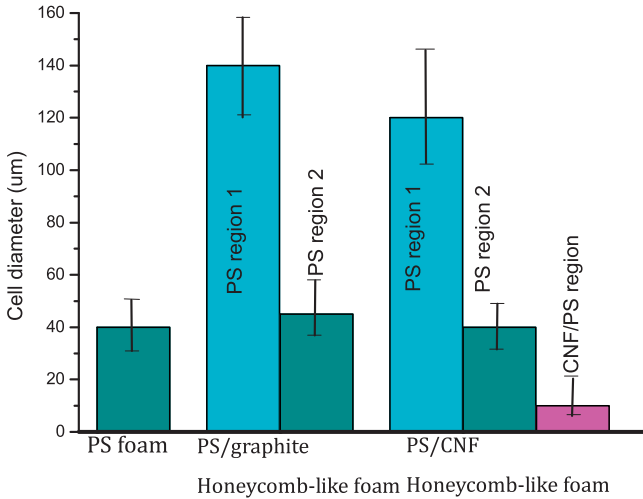
Figure 3. Cell diameter comparison between PS and PS composite foams with honeycomb-like structure. PS: polystyrene.
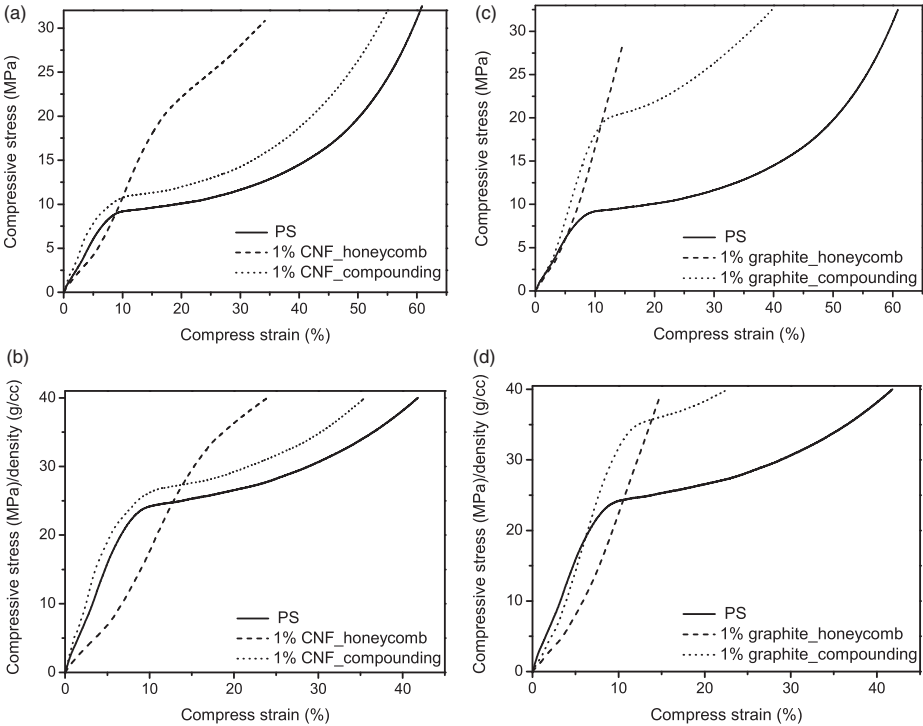

Figure 4. Compressive behavior of PS/graphite and PS/CNF composite foams. CNF: carbon nanofiber; PS: polystyrene.

Table 2. Electrical conductivity of PS and PS composite foams prepared at 60°C.

| Samples	Conductivity (S/m)
PS	N/A[a]
1% PS/CNF_honeycomb	0.0060
1% PS/CNF_compounding	0.0013
1% PS/graphite_honeycomb	0.0220
1% PS/graphite_compounding	0.0025

CNF: carbon nanofiber; PS: polystyrene.
[a]Too low to be measured.

foams became conductive. However, the composite foams showing an inter-connected honeycomb-like structure were able to achieve a substantially higher electrical conductivity compared with the compounded ones at the same particle loading and bulk density, i.e. ∼5 and ∼9 times increase for the PS/CNF and PS/graphite composite foams, respectively.

Table 1 shows the densities of these samples foamed at 60°C and after further expansion at 120°C three days later, and Figure 5(a) and (b) shows the CO_2 solubility and swelling ratio of the PS and 1 wt% CNF coated PS pellets. According to Figure 5(a) and (b), the pure PS possessed a slightly higher CO_2 solubility and swelling ratio compared to that with 1 wt% CNF coating. However, the pure PS foam has higher density than the coated ones after batch foaming at 60°C as listed in Table 1. The less expansion of the pure PS foam was probably due to the loss of more CO_2 during heating. As reported in our previous studies,[7,19] the homogenous nucleation and bubble growth of the pure PS were slow at temperatures below 100°C. This allowed the escape of a great deal of dissolved CO_2 before foaming. On the other hand, the presence of carbon particulates on the surface of the coated PS pellets allowed much efficient heterogeneous nucleation there, leading to faster foaming. This, together with the gas confinement effect from the CNF/graphite coating resulted in a lower density, i.e. higher foaming in the coated honeycomb foams even though the initial CO_2 solubility and swelling were slightly lower in those samples than in pure PS pellets.

Table 1 also indicates that the inter-connected honeycomb-like carbon particulate network can improve the thermal stability of polymer composite foams. For example, when the PS foam prepared at 60°C was subjected to further expansion at 120°C, its volume increased 115%, and the foam density decreased from 0.82 to 0.38 g/cm³. For the conventional PS/CNF foam subjected to the same thermal treatment, its volume increased 67%, and the foam density decreased from 0.70 to 0.42 g/cm³. The PS/CNF and PS/graphite foams with the inter-connected honeycomb-like carbon particulate network, on the other hand, only increased the
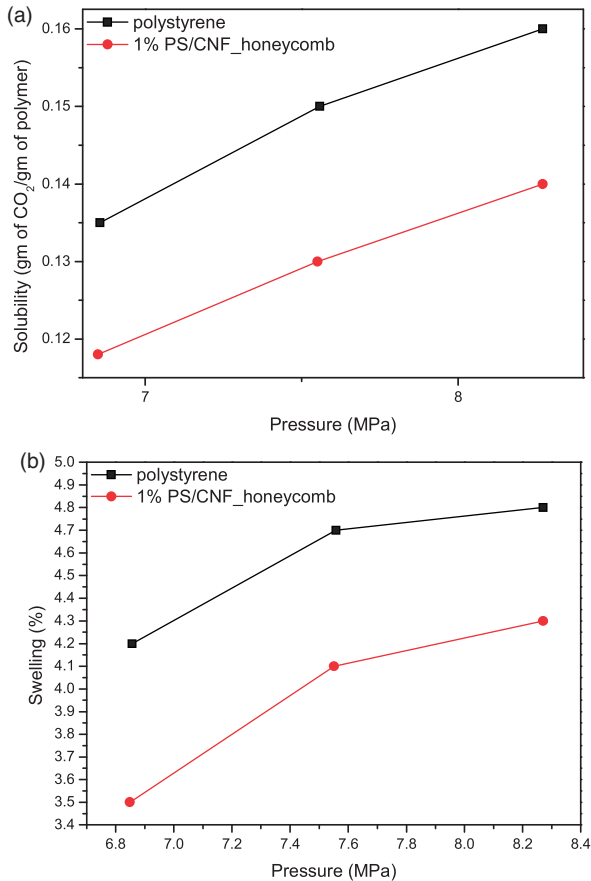
Figure 5. The (a) CO_2 solubility and (b) swelling ratio of polystyrene and 1% PS/CNF honeycomb. CNF: carbon nanofiber; PS: polystyrene.

volume by 11.5% and 2.7% and decreased the foam density from 0.70 to 0.62 g/cm³ and 0.75 to 0.73 g/cm³, respectively, at the same thermal treatment.

Figure 6(a) and (b) shows the temperature increase with respect to time via the thickness direction of PS/graphite and PS/CNF composite foams prepared at 60°C, respectively. With the addition of thermally conductive CNF and graphite to PS, the resulting PS composite foams possessed better heat transfer behavior even the densities of the composite foams were lower than that of the pristine PS foam. In comparison, the honeycomb-like PS/CNF and PS/graphite composite foams revealed a higher temperature increase comparing to composite foams made of the conventional PS/CNF and PS/graphite composite foams at the same CNF and graphite loading and the pristine PS.
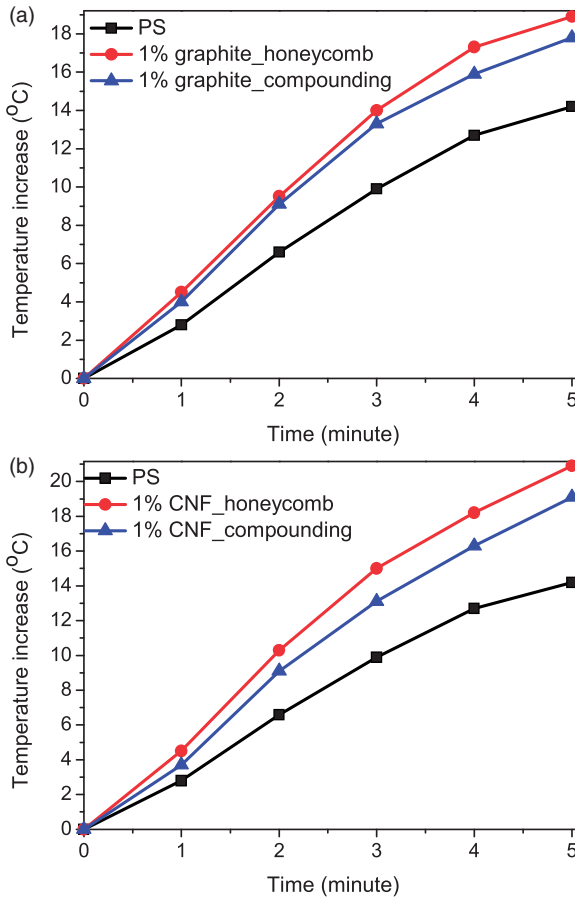
Figure 6. Heat transfer comparison of the PS composite foams with the honeycomb-like structure and the conventional PS composite foams made from compounding prepared at 60°C, (a) PS/graphite composite foams and (b) PS/CNF composite foams. CNF: carbon nanofiber; PS: polystyrene.

Conclusions

In this study, we coated CNF and graphite onto the surface of PS pellets, and then hot pressed and batch foamed the coated PS pellets into new PS composite foams with the honeycomb-like structure consisting of inter-connected particles. The PS composite foams with the inter-connected honeycomb-like carbon particulate network were able to provide substantially improved compressive strength at high strains, much better electrical conductivity, and significantly improved thermal stability. In addition, the inter-connected honeycomb-like carbon particulate network can increase the heat conduction of PS foams.

Acknowledgements

Conflict of interest

None declared.

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