Supercritical Fluids-Assisted Processing Using CO₂ Foaming to Enhance the Dispersion of Nanofillers In Poly(Butylene Succinate)-Based Nanocomposites and the Conductivity

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Supercritical fluids-assisted processing using CO₂ foaming to enhance the dispersion of nanofillers in poly(butylene succinate)-based nanocomposites and the conductivity

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Abstract:

With the rapid development of electronic information technology, traditional metal conductive materials can no longer satisfy the needs of a wider industry. Poly(butylene succinate)/multiwalled carbon nanotubes (PBS/CNT) conductive polymer nanocomposites with varied CNT content were prepared by a HAAKE torque rheometer. The addition of CNT significantly improved the crystallization, viscoelasticity, and mechanical properties as well as thermal and electrical conductivity. Conductivity of the PBS/CNT nanocomposite with 5 wt.% CNT increased from $8.23 \times 10^{-15} \text{ S} \cdot \text{m}^{-1}$ of pure PBS to $33.3 \text{ S} \cdot \text{m}^{-1}$, an increase of 16 orders of magnitude. Moreover, the electrical percolation threshold φ_c of the PBS/CNT nanocomposites was 2.8 wt.% and the critical index was 1.56, showing that the conductive network structure was between 2D and 3D and 2D network structure dominated. To further improve the conductivity, microcellular foams were successfully fabricated by batch foaming with supercritical fluids (scCO₂). The electrical conductivity of the PBS/CNT foam with 5 wt.% CNT reached $67.8 \text{ S} \cdot \text{m}^{-1}$ and it was 104% higher than the corresponding solid nanocomposite.

Keywords: Poly(butylene succinate), carbon nanotubes, nanocomposites, conductivity, supercritical fluid foaming

1. Introduction

With the rapid development of electronic information technology, the demand for high-performance conductive materials in the fields of automobile manufacturing, aerospace, microelectronics, and electrical engineering is increasing [1]. Traditional metal conductive material has excellent electrical conductivity, but high density, easy corrosion, poor flexibility and other disadvantages affect its industrial applications [2]. Recently, due to the excellent processing performance, low cost, low density, good mechanical properties, and corrosion resistance, conductive polymer composites (CPCs) materials have been widely used in the industrial field such as thermistors [3-6], strain sensors [7-9], electromagnetic shielding materials [10-12], etc.

A large number of studies have reported the preparation of CPCs, mainly including in-situ polymerization [13-14], solution mixing [15-17], and melt blending [18-21]. Although the first two methods can achieve better dispersion of nanofillers in the matrix and obtain more excellent comprehensive performance. However, there are still many disadvantages. Firstly, a large amount of chemical solvents are used which seriously pollutes the environment. Secondly, the preparation cycle is long and cannot be applied on a large scale. As a comparison, a simpler, greener, and more efficient method of melt blending is an alternative choice to prepare CPCs. As a kind of one-dimensional (1D) conductive filler, carbon nanotubes have the advantages of long aspect ratio and high conductivity, resulting in a preferred one in CPCs. However, CNT tend to agglomerate, resulting in high conductive percolation threshold. Therefore, many researchers are developing improved methods to increase the conductivity of CPCs and lower the percolation threshold by constructing better conductive network structures with low conductive-filler loading [22-24].

Some researchers have improved the electrical conductivity of CPCs by adding

third-phase substances in recent years [25-27], which has been proven to effectively increase CPC conductivity by changing its viscoelastic properties, leading to changes in the original morphology or structures [28-30]. However, such methods have been of limited benefit in terms of improving the conductivity of the composite.

However, in order to further enhance the electrical conductivity, introducing bubble holes into the polymer matrix using supercritical fluid (SCF) foaming technology was proved to be effective. The foaming process can effectively separate the aggregated conductive fillers by causing the polymer matrix to swell, resulting in a more uniform and expanded conductive path and higher electrical conductivity [31-32]. CNT were homogeneously dispersed in polymer matrix, thereby reducing the contact resistance between adjacent CNT, and then building a perfect conductive path. Fig. 1 shows the mechanism of increased filler (such as CNTs) exfoliation and dispersion during foaming process.

Fig. 1 Mechanism of increased CNTs dispersion during scCO₂ foaming process. Due to gas expansion when foaming, additional agglomerate break up. Equibiaxial flow occurs on the surface of bubbles and in struts between them as bubbles expand, which is extensional in nature and entails a greater viscosity than shear flow leading to imparting a greater force on agglomerates.

However, due to the current increasing environmental pollution problems, the application of degradable plastics has become increasingly widespread. Polybutylene succinate (PBS), one of the most important biodegradable plastics, is a kind of fatty acid polyester formed by polycondensation of succinic acid and butylene glycol and is stable in a dry environment and can be stored for a long time [33]. It can be completely degraded in fertilizers, soil and water, and the degradation products are non-toxic, which can well solve the environmental pollution problems caused by traditional plastics. Due to excellent biodegradability, biocompatibility, heat resistance, film formation and spinnability, it have a very wide range of applications in packaging materials [34], agricultural and forestry products [35], composite films [36], textiles industry [37], medicine [38] and electronic technology [39]. Using PBS as the polymer matrix of CPCs can have broad applications in the preparation of eco-friendly functionalized materials.

Therefore, in this study, a conventional HAAKE mixer (two rotors) combined with supercritical carbon dioxide (scCO₂) foaming technology were used to produce PBS/CNT CPCs and its foams with different CNT loadings. Few studies have reported on the improvement of the conductivity of PBS-based CPCs by SCF foaming technology. The effects of different CNT content and the introduction of a large number of pores on the crystallization behavior, rheological and mechanical properties, thermal conductivity, foaming behavior, and electrical conductivity were investigated. More importantly, this paper offers a simple, green, efficient, and cost-saving method for the large-scale production of high-performance CPCs without complicated processing steps such as polymerization or chemical treatments.

2. Experimental section

2.1 Materials

PBS (GS PLA FZ71PD) powder was purchased from Mitsubishi Chemical Corporation (Japan), with a density of $1.26\text{g}\cdot\text{cm}^{-3}$ and a melting point of 114.6°C . CNT (unmodified, 30-50 nm) was provided by Shandong Dazhan Nanomaterials Co., Ltd. (China), with a specific area of $230\sim 270\text{m}^2\cdot\text{g}^{-1}$ and a carbon purity of 97.57%. Commercial CO_2 (99.9 %) was supplied by Fuzhou Xinhang Gas Co., Ltd. (Fuzhou, China).

2.2 Preparation of PBS/CNT Composites and foams

PBS pellets and CNT were dried in a vacuum oven at 80°C for 2 hours before melt mixing. PBS/CNT composites with different CNT ratio (0 wt%, 0.5 wt%, 1.0 wt%, 3.0 wt%, 5.0 wt%) were prepared using a torque rheometer (HAAKE, HAAKE Polyab OS, Germany) with rotors speed 80 rpm at 175°C for 10 min. (e.g., nanocomposite with 0.5 wt% CNT content are marked as PBS-0.5CNT). The obtained nanocomposites were compression molded (rectangular sheet with a thickness of 1 mm) at 145°C 30 MPa for 5 min.

PBS/CNT nanocomposite foams were fabricated via a solid-state supercritical CO_2 foaming. Firstly, the nanocomposites were saturated with scCO_2 in a high-pressure autoclave at different temperature (below the melting point of PBS) and pressure for certain time to ensure equilibrium adsorption. And then the autoclave was rapidly depressurized and then cooled down. The schematic of batch foaming is shown in Fig. 2.

Fig.2 Schematic diagram of PBS/CNT foam prepared by supercritical CO₂ foaming method

2.3 Characterization

A field emission scanning electron microscope (FESEM, NovaNanoSEM450, FEI Company, USA) was used to observe the microscopic morphology of the nanocomposite sample and the foams with a voltage of 5 kV. The X-ray diffraction pattern of the nanocomposites was obtained with an X-ray diffractometer (XRD, Bruker D8, Bruker Company, Germany) with Cuka radiation (40 kV and 20 mA) in the range of 10-50°, and the step interval was 4°·min⁻¹. A differential scanning calorimeter (DSC, 200F3, Netzsch, Germany) was used to study the melting and crystallization behavior of the sample. The test is carried out in a nitrogen atmosphere.

The crystallinity of the sample is calculated by the equation [45]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{(1-\varphi)\Delta H_m^0} \quad (6)$$

Where ΔH_m is the measured enthalpy of melting, ΔH_{cc} is the enthalpy of crystallization, φ is the filler ratio, ΔH_m^0 is the standard theoretical enthalpy of PBS,

and X_c is the crystallinity.

A thermogravimetric analyzer (TGA, 209F1, Netzsch, Germany) was used to study the thermal degradation process of the sample in a nitrogen atmosphere, with $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and the temperature range of $25\sim 600^{\circ}\text{C}$. The rotating rheometer (ARES G2, TA Company, USA) was used to study the dynamic rheological properties of the sample at a temperature of 145°C and a strain of 1% and the frequency range was $100\text{ Hz}\sim 0.1\text{ Hz}$. The tensile properties of dumbbell specimens cut out from the compression template were performed on a universal tensile testing machine (AGS-x, Shimadzu Corporation, Japan) with a tensile speed of $5.0\text{ mm}\cdot\text{min}^{-1}$. The reported average is derived from at least 5 samples. A dynamic thermomechanical analyzer (DMA242E, Netzsch, Germany) was used to study the dynamic thermomechanical properties of the samples with a single cantilever clamp. The thermal conductivity (λ) was obtained by a laser flasher (LFA467, Netzsch, Germany) and the sample was made into a disc with a diameter of 12.5mm and a thickness of 0.9mm. The λ value is calculated by the following formula [40] :

$$\lambda = \alpha \cdot \rho \cdot C_p \quad (1)$$

Among them, α 、 ρ 、 C_p represent the thermal diffusivity, density and specific heat of the sample, respectively.

The electrical resistivity was measured by a digital four-probe detector (SX1934, China), and then converted into electrical conductivity by units.

$$\sigma = \frac{1}{\rho} \quad (2)$$

Pore sizes (D) of the foamed samples were obtained by the Image-Pro Plus 6.0 software from the SEM images. Pore density (N_f) was calculated by the equation [23],

$$N_f = \left[\frac{N}{A} \right]^{\frac{3}{2}} \quad (2)$$

where N is the number of pores and A is the area of the image (cm²).

The porosities of the foamed samples (cut into rectangles) were obtained by weighing the samples and measuring their volume using the equation [41] :

$$Porosity = \frac{V_f \rho_0 - W_f}{V_f \rho_0} \times 100\% \quad (3)$$

Among them, V_f is the volume of the foamed sample, W_f is the measured weight of the foamed sample, and ρ_0 is the mass density of PBS.

The volume expansion rate (Φ) of the foamed samples was defined as the ratio of ρ_s to ρ_f (g/cm³) [42] :

$$\phi = \frac{\rho_s}{\rho_f} \quad (4)$$

Where ρ_s and ρ_f are measured by water displacement method (ASTM D792) and represent the mass densities of the sample before and after foaming, respectively.

3. Results and discussion

3.1 Morphologies of PBS/CNT nanocomposites

Fig. 3a shows the morphology of CNT. In Fig. 3b, pure PBS presents a smooth and flat fracture surface. Since CNT tend to form larger agglomerated areas in polymer matrix during melt processing. After adding CNT (Fig. 3c), it can be seen some small aggregated CNT (As indicated by the arrow). With the increase of CNT content, the agglomeration phenomenon becomes more obvious. Fig. 3e shows that PBS-3CNT initially forms a relatively complete conductive path. In Fig. 3f, PBS-5CNT forms a denser conductive path, which indicates that the number of connections between adjacent CNT has further increased, and the surface morphology of PBS-5CNT has changed significantly. The change of CNT dispersion in polymer matrix is one of the most important reasons that can affect the conductivity of the final CPCs.

Fig.3 (a) FESEM image of CNT surface, FESEM images of the fractured surface of (b) PBS, (c) PBS-0.5CNT, (d) PBS-1CNT, (e) PBS-3CNT and (f) PBS-5CNT

3.2 Crystallization and thermal properties

Fig. 4a shows the XRD spectra of PBS/CNT nanocomposites. The main characteristic peak of CNT is shown at a 2θ of 25.8° , which corresponds to the (002) crystal plane. The characteristic peak of PBS is at 19.7° and 22.7° , corresponding to (020) and (110) crystal planes, respectively. With the increase of CNT content, the positions of PBS/CNT nanocomposite characteristic peaks move to the right relative to pure PBS, indicating a change in the crystalline structure.

Fig.4 (a) XRD patterns of PBS and CPCs; DSC curves of (b) the second heating and (c)

cooling samples; Results of thermogravimetric analysis: (d) TGA curve, (e) DTG curve.

The average grain size (D) is calculated by Scherrer formula [43]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (5)$$

Where θ is the Bragg angle, λ is the wavelength of the x-ray, k is the Scherrer constant, and β is the half-height width of the diffraction peak. Table 1 shows the calculated crystal face sizes of the samples. The (002) crystal plane is unique to CNT and the grain size of CNT is 15.7 nm, and the average thickness of the grains increases with the increase of its content. In addition, among the three crystal planes corresponding to PBS, the change of the grain size of (021) and (110) are not obvious, while the change in the direction perpendicular to the 020 crystal plane is relatively obvious. Additionally, the diffraction peak intensity becomes stronger with increased CNT concentration, indicating the formation of more perfect crystals and higher crystallinity due to the heterogeneous nucleation of CNT, which is consistent with the DSC results.

Table 1 D of different crystal planes (average thickness of grains perpendicular to the crystal plane).

$D(nm)$	$D020$	$D021$	$D110$	$D002$
PBS	14.2	10.7	10.0	--
CNT	--	--	--	15.7
PBS-0.5CNT	16.6	11.3	10.4	16.2
PBS-1CNT	17.3	11.5	10.7	16.3
PBS-3CNT	17.8	11.6	10.9	18.2
PBS-5CNT	20.1	11.8	11.2	20.0

Fig. 4(b and c) show DSC curves and Table 2 presents the corresponding statistical data. As shown in Fig. 4b, pure PBS has obvious cold crystallization peaks. With the addition of CNT, the cold crystallization peak of PBS/CNT nanocomposites shift to the right, indicating the enhancement of crystallization ability resulting from the heterogeneous nucleation of CNT. It can be seen from Fig. 4c, the melting temperature (T_m) of the nanocomposite gradually increase with adding CNT, but the change is not obvious. The increase of the melting point and cold crystallization temperature is mainly attributed to the heterogeneous nucleation of CNT, which increases the crystallization rate and crystallinity [44]. The crystallinity of the sample is calculated by the equation [45]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{(1-\varphi)\Delta H_m^0} \quad (6)$$

Where ΔH_m is the measured enthalpy of melting, ΔH_{cc} is the enthalpy of crystallization, φ is the filler ratio, ΔH_m^0 is the standard theoretical enthalpy of PBS, and X_c is the crystallinity.

Table 2 Statistical data of thermal properties for PBS and PBS/CNT CPC.

Sample	$T_m(^{\circ}\text{C})$	$\Delta H_m (\text{J/g})$	$T_{cc} (^{\circ}\text{C})$	$X_c(\%)$	$T_{5\%} (^{\circ}\text{C})$	$T_{95\%} (^{\circ}\text{C})$	$T_{\max} (^{\circ}\text{C})$
PBS	115.5	49.9	78.3	45.2	342.3	411.6	388.0
PBS-0.5CNT	115.6	53.2	92.2	48.2	340.3	414.0	389.0
PBS-1CNT	116.0	58.0	93.2	53.0	339.8	415.5	390.0
PBS-3CNT	116.5	64.6	96.2	60.3	336.4	427.5	395.3
PBS-5CNT	116.6	75.1	97.3	71.5	335.3	461.7	398.3

The thermal degradation curve is shown in Fig. 4(d and e) and Table 3 shows the specific TGA data. The initial degradation temperature T_{onset} (at 5% weight loss)

decreases with the increase of CNT content. In other words, CNT enables the thermal degradation of PBS/CNT nanocomposite in advance, which is because that high thermal conductivity of CNT itself makes heat transfer faster. However, the $T_{\max}$ (at 50% weight loss) increases with the increase of CNT, which may be due to the existence of CNT hindering the movement of PBS molecular chain. In addition, high thermal conductivity of CNT makes the heat dissipation faster and prevents local overheating [46]. This can be verified in the DTGA curve of Fig. 4e.

3.3. Rheological properties

The rheological properties can not only provide microstructure information of the composites but also the viscoelastic properties are crucial for the following scCO₂ foaming performance. Fig. 5 (a and b) show the curves of complex viscosity and storage modulus vs. frequency. In Fig. 5a, PBS is typical thermoplastic and exhibits pseudoplastic fluid behavior. After adding CNT, all PBS/CNT composites shows shear thinning behavior in the whole scanning frequency range. With the increase of CNT content, the shear thinning behavior becomes more pronounced and the complex viscosity increases by 1 to 2 orders of magnitude at high frequencies area and 1 to 3 orders of magnitude at low frequency area, resulting from the disentanglement of PBS molecular chains and lubrication of CNTs. The storage modulus of the nanocomposites also increase with the addition of CNTs and a plateau can be clearly observed in the low frequency region, indicating that the rheological behavior changed from liquid-like to solid-like, especially for PBS-3CNT and PBS-5CNT nanocomposites. Fig. 5(c and d) show the curves of complex viscosity and storage modulus vs. temperature. In Fig. 5c, the complex viscosity of all the samples decrease as temperature increases, and the complex viscosity increases with the increase of CNT content at the whole test temperature range which is because CNT restricts the

movement of PBS molecular chain. The storage modulus shows the same trend as that of complex viscosity as shown in Fig. 5d.

Fig. 5 (a) Complex viscosity vs. frequency, (b) storage modulus vs. frequency, (c) complex viscosity vs. temperature, (d) storage modulus vs. temperature for neat PBS and PBS/CNT nanocomposites.

3.4 Mechanical properties

Fig. 6(a and b) show the stress-strain curve and statistic histogram of PBS and PBS/CNT nanocomposites. It is obvious that all the samples present a typical brittle fracture (recall Fig. 3), which is due to the introduction of high-stiffness CNTs [47]. With the increase of CNT content, the tensile strength and young's modulus increase, and the elongation at break decrease. Specifically, under the loading of 5.0wt% CNT, the tensile strength increased from 31.7 MPa of pure PBS to 35.9 MPa and the Young's modulus increased from 689.9 MPa of pure PBS to 1134.7 MPa. Fig. 6(c and d) show the dynamic mechanical curves of PBS and PBS/CNT nanocomposites. In

Fig. 6c, the storage modulus of all samples decreases with increasing temperature. Pure PBS has high storage modulus and the addition of CNT reduces the storage modulus. However, the storage modulus suddenly rises again when CNT content reaches 5.0 wt%. This may be because the high content of CNTs constructs a very strong entanglement structure in the polymer matrix, which limits the deformation of PBS-5CNT, storing more deformation energy. Fig. 6d displays the $\tan\delta$ curves of PBS and PBS/CNT nanocomposites. Pure PBS has a higher $\tan\delta$ value compared to CPCs, which means that CPCs have lower energy damping behavior. The glass transition temperature (T_g) of the material is determined by the position of the highest peak of the curve and the peak shifts to a higher temperature with the increasing CNT; namely, the introduction of CNT increases T_g of the material, indicating that CNT effectively limits the movement of the PBS molecular chains.

Fig. 6 (a) stress-strain curve, (b) histogram of tensile strength, young's modulus and

elongation at break of PBS and PBS/CNT CPC; DMA curves: (c) storage modulus vs. temperature (d) $\tan\delta$ vs. temperature.

3.5 Thermal and electrical conductivity

Fig. 7(a and b) show the thermal conductivity of PBS and PBS/CNT CPC under variable temperature and the histogram of thermal conductivity at room temperature. CNT is one of the commonly used carbon-based fillers, which has excellent thermal and electrical conductivity. Usually, polymer (PBS) is poor conductor of heat. Thermal conductivity of PBS at room temperature is extremely low, only $0.22 \text{ W(m}\cdot\text{k)}^{-1}$ as shown in Fig. 7a. With increasing CNTs, the contact between adjacent CNTs increases, the path of heat conduction is gradually formed, and the thermal conductivity of PBS/CNT CPC increases. The increase of thermal conductivity under 0.5wt% and 1.0wt% CNT loading is not obvious, resulting from weak phonon heat conduction. However, PBS/CNT nanocomposite initially forms a stable conductive path when CNT loading reaches 3.0wt% (recall Fig. 3). The introduction of CNT can play a good role in promoting PBS-based CPCs in the application of thermoelectric materials.

Fig.7 (a) thermal conductivity vs. temperature (b) histogram of thermal conductivity at room temperature (c) electrical conductivity curves (d) histogram of conductivity of PBS and PBS/CNT CPC.

Electrical conductivity is one of the most important performance indicators of CPCs, which most intuitively reflects the pros and cons of CPCs. Conductivity can be divided into surface conductivity and volume conductivity, and the conductivity measured by the four probes is the volume conductivity, specifically for the value measured by the electrical signal feedback obtained by the probe going deep into the CPCs. Fig7.(c) shows the conductivity curves and the best percolation threshold fitting curves of PBS and PBS/CNT CPCs. With the increase of CNT content, the conductivity of CPCs rises sharply, showing a typical percolation behavior. Using the classical percolation theory, the percolation threshold under the conductive system can be further estimated from the measured conductivity curve, as shown in equation (7) [48]:

$$\sigma = \sigma_0(\varphi - \varphi_c)^t \quad (7)$$

Where φ_c is the percolation threshold, σ is the actual measured conductivity of CPCs, φ is the filler content, and t is the critical exponent. Calculated by equation (7), the φ_c of the melt-processed PBS/CNT composite material is 2.8wt%, which is relatively high, mainly due to the poor conductive path space caused by poor CNT dispersion in the polymer matrix. The t value of PBS/CNT CPC is 1.56. Theoretically, the critical exponent t in equation (7) follows a power law relationship of 1.1 to 1.3 in a 2D conductive network system, and a power law relationship of 1.6 to 2.0 in a 3D conductive network system [49]. CPCs prepared by a simple melting process do not have a 3D conductive network. The main conductive path lies in the direct contact or tunneling mechanism between adjacent CNT, or the internal conductive network is not strong or stable. Moreover, the low melt viscosity of PBS brings about the CNTs being easily wrapped by the polymer matrix, which leads to higher contact resistance, and it is difficult to construct a stable conductive network. The calculated t value is also easy to deviate from the assumptions of the classical percolation theory.

From Fig. 7d, it can be seen that pure PBS is an electrically insulating material, and its conductivity is extremely low, about $8.23 \times 10^{-15} \text{S} \cdot \text{m}^{-1}$. When 0.5wt% CNT is added, the conductivity of CPCs is nearly 10 orders of magnitude higher than that of pure PBS. This improvement effect is very significant, resulting from the excellent conductivity of CNT. The conductivity of PBS-3CNT is $1.28 \text{S} \cdot \text{m}^{-1}$, which exceeds the commercial standard conductivity of $1 \text{S} \cdot \text{m}^{-1}$. What is exciting, the conductivity of PBS-5CNT reaches $33.3 \text{S} \cdot \text{m}^{-1}$, which corresponds exactly to the previous morphology characterization (recall Fig. 3).

3.6 Foaming of pure PBS

To explore the best foaming conditions for the following PBS/CNT CPC foams. Fig. (8-10) show the morphologies of different foaming temperature, foaming

pressure and saturation time for neat PBS, respectively. In Fig. 8, the cell size of the PBS foam prepared at foaming temperature of 80°C is small and scattered, showing very poor foamability due to a low foaming temperature. In Fig. 8c₁, the PBS foam has a large cell size and extremely poor overall morphology, which is due to the high foaming temperature resulting in low melt viscosity of the polymer matrix and it is difficult to support the cell structure. In contrast, Fig8.(b₁) shows that the PBS foam prepared at 90°C has a moderate and evenly cell morphology. The average cell size is 16.2 μm and the cell density is $1.20 \times 10^7 \text{ cells} \cdot \text{cm}^{-3}$. Thus, choose 90°C as the following foaming temperature of PBS/CNT CPC.

Fig.8 SEM images of PBS foams at 20 MPa and 4h with different foaming temperature (a) 80°C, (b) 90°C, (c) 100°C.

Fig. 9 shows the cell morphologies at different saturation time. In Fig. 9a₁, many imperfect cells can be clearly observed and the cell distribution is very nonuniform. The main reason is that the polymer matrix is insufficient absorption of supercritical CO₂ and reaches saturation and eventually forms an imperfect cell structure. However, the cell size is uniform and densely distributed in Fig. 9b₁ the main difference is that the polymer matrix absorbs supercritical CO₂ to a saturated state (4 h). The cell uniformity of the foam shown in Fig. 9c₁ is slightly worse than Fig. 9b₁, indicating that the

foamability did not change much when increasing the saturation time from 4h to 6h. This further proves that after 4h of soaking, the polymer matrix is sufficient absorption of supercritical CO₂ and has reached saturation.

Fig.9 SEM images of PBS foams at 20 MPa and 90 °C with different saturation times (a) 2h, (b) 4h, (c) 6h.

Fig. 10 shows the cell morphologies at 90°C and 4h with different foaming pressure. It can be clearly seen that the cell morphologies in Fig. 10a₁ and Fig. 10b₁ are imperfect compared to Fig. 10c₁, and both show low cell density. The average cell size is 12.2μm and the cell density is $3.30 \times 10^6 \text{ cells} \cdot \text{cm}^{-3}$ at 16MPa, and the average cell size is 13.4μm and the cell density is $7.16 \times 10^6 \text{ cells} \cdot \text{cm}^{-3}$ at 18MPa. That is to say, as the foaming pressure is increased, the cell size decrease and cell density increase, and cell morphology becomes more uniform. Summarily, choose 18MPa, 90°C and 4h as the following foaming parameters of PBS/CNT CPC foams.

Fig.10 SEM images of PBS foams at 90 °C and 4h with different foaming pressures (a) 16MPa, (b) 18Mpa, (c) 20MPa.

3.7 PBS/CNT nanocomposites foams

The cell morphologies and cell distribution of PBS/CNT composite foams are shown in Fig. 11. Pure PBS shows uneven cell size distribution and ruptured cell wall, resulting from the low viscosity of the PBS melt. Fig.11(c₁-f₁) show changing cell morphology as the CNT content increases, that is, the cell diameter gradually becomes smaller and the cell density gradually increases due to the heterogeneous nucleation of CNT. Specifically, the cell size of the PBS-5CNT composite foam is 15.6 μm, and the cell density is $1.03 \times 10^7 \text{ cells} \cdot \text{cm}^{-3}$, which is 61% lower and 317% higher than pure PBS, respectively. The cell walls become thicker which is due to the high rigidity of CNTs that greatly increases the elastic modulus of the PBS matrix, thereby forming more stable cells structure. By observing the local enlarged images of Fig.11(c₃-f₃), it is found that the CNTs are selectively distributed on the cell walls, which makes CNT construct a conductive network structure, reducing the agglomeration of CNTs after foaming. Fig.12(a-e) show the dispersion mechanism of CNTs during the foaming process.

Fig.11 SEM images of the foams (a₁) PBS, (c₁) PBS-0.5CNT, (d₁) PBS-1.0CNT, (e₁) PBS-3.0CNT, (f₁) PBS-5.0CNT at low magnification; (a₂), (c₂), (d₂), (e₂) and (f₂) are the cell size distributions of (a₁), (c₁), (d₁), (e₁) and (f₁), respectively; (c₃), (d₃), (e₃) and (f₃) are the magnified region of (c₁), (d₁), (e₁) and (f₁), respectively; (b) the curves of average cell size and cell density.

As a contrast, the electrical conductivity of the foamed samples is also measured. Fig.12f compares the electrical conductivity of the samples before and after foaming. The results show that foaming greatly increases the electrical conductivity. The electrical conductivity of PBS-5CNT foam reaches $67.8 \text{ S} \cdot \text{m}^{-1}$ at 5 wt%, a 104% increase compared to the solid counterpart. In addition, the percolation threshold value of the foams has also been reduced from about 2.8 wt% to about 1 wt%. The

supercritical CO₂ foaming process has a more obvious effect on improving the conductivity of materials with low CNT content. For example, the electrical conductivity improvement effect at 1 wt% CNT loading is 291 times.

Fig.12 (a) dispersion mechanism of CNT during foaming process, (b) solid PBS-3.0CNT CPC, (c) foamed PBS-3.0CNT; (f) conductivity curve and (g) conductivity histogram of PBS and CPCs before and after foaming

4. Conclusions

The solid and foamed PBS/CNT nanocomposites with excellent properties were prepared by melt blending and supercritical CO₂ foaming technology. The results showed that adding CNT significantly improved the crystallization, viscoelasticity, and mechanical properties as well as thermal and electrical conductivity. Especially, foaming can significantly enhance the electrical conductivity of the nanocomposite. The electrical conductivity of PBS-5CNT foam reaches $67.8 \text{ S} \cdot \text{m}^{-1}$ at 5 wt%, a 104% increase compared to the solid counterpart. The cell size of the PBS-5CNT composite

foam is 15.6 μm , and the cell density is $1.03 \times 10^7 \text{ cells} \cdot \text{cm}^{-3}$. This study provided a simple, low-cost, environmentally friendly, and suitable for large-scale industrial production method. It can prepare high conductivity and excellent comprehensive performance foamed CPC, which can endow it many great potential applications, such as sensor, electromagnetic wave absorption, electronic packaging and so on.

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