Research Article

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Electrically conductive and light-weight branched polylactic acid-based carbon nanotube foams

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Abstract: In spite of the high electrical conductivity of carbon nanotube (CNT), its tendency to aggregate and expensive cost in fabricating aerogel, foams, and porous materials remains a problem. Therefore, we described a simple and feasible way to design light-weight, high electrically conductive, and cost-efficient polylactic acid (PLA)/CNT foams. The branched PLA (BPLA) resin with excellent melt elasticity and foamability was induced by nucleophilic ring-opening reaction of epoxy-based acrylic/styrene copolymer and PLA. After that, BPLA/CNT composites and foams were prepared by melt-mixing and supercritical carbon dioxide foaming technology, respectively. The thermal, electrical, and foaming properties were studied. The resultant BPLA/CNT foam possessed a low density of 0.174 g/cm^3 and high crystallinity of 3.03%. An improvement of the oriented structure of CNT induced by cell growth in BPLA matrix increased the conductivity of the foam up to $3.51 \times 10^4 \Omega/\text{m}$. The proposed foaming materials provided a way for designing and preparing high performance CNT products.

Keywords: foams, biopolymers, branched, nanofibers, conducting polymers

1 Introduction

Because of its desirable electrical conductivity, carbon nanotube (CNT) has been used in electrical materials for many purposes, which includes conducting materials (1,2),

electromagnetic shielding (3), piezoelectronic sensing (4), and optoelectronic sensing (5,6). Despite the growing interest in this material, the development of light-weight 100 wt% CNT materials remains a major challenge because it is difficult to produce uniformly individualized and even oriented CNT networks in the bulk materials, especially in porous structures such as CNT aerogels and foams (7–10). The oriented structure of CNT is expected to improve electrical conductivity by orienting and connecting individual CNT (11). Moreover, the cost of CNT is expensive, which further limits its wide applications. Therefore, it is important to develop oriented structure CNT materials and balance its cost and electrical, mechanical, density performance. Recently, works have been performed to design highly electrically conductive CNT materials that focus on improving the dispersion or the orientation of CNT in a different matrix, such as electrospinning method (12), coating method (13), and lamella Shish-Kebab inducing method (14). Besides these strategies, polymeric foaming method is also an efficient way to produce oriented CNT materials because of its advantages of cost-efficient and light-weight qualities. In the cell growth period, a rapid and strong biaxial stretching field produced in polymer matrix will induce the orientation of CNT. Romeo et al. fabricated nanowire/poly(vinyl alcohol) (PVA)-ordered scaffolds and they found that the nanowires were also highly oriented in the foamed PVA scaffolds (15). The electrical conductivity for polyester containing hybrid fillers of CNT showed 400 times that for single CNT loaded one at the 2 wt% filler loading (16), and the CNT/epoxy hybrids also exhibited higher electrical conductivity (17).

Among the various polymeric matrixes, bio-based and bio-degradable polylactic acid (PLA) have attracted many interests for structural and functional applications as an alternative to conventional petroleum-based plastics (18–21). The development of high performance foamed PLA has significant advantages (22,23). The abundant carboxyl and hydroxyl groups on the end of the molecular chain are convenient for reaction compatibilization with

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Figure 1: (a) Reaction between epoxy-based acrylic/styrene copolymer and LPLA chain, (b) reaction between carboxylated CNT, LPLA, and BPLA chains.

modified CNT. The electrical, mechanical, and thermal properties of foamed PLA materials can be designed by manipulating the structure (24–26). The processability and feasibility of developing novel foamed PLA are more practicable (27). The cost for developing PLA foam is gradually reduced by advanced processing technologies (28). The properties of foamed polymer/CNT are closely related to the morphology of the cells. An oriented CNT structure in foams has shown great potential applications in tissue engineering, separation, and environmental protection owing to their tunable foaming structure and enhanced mechanical properties along the oriented direction (29–31). However, because of the poor rheological properties of linear PLA (LPLA), it is still a challenge to fabricate foams with light-weight, which could not further give rise to oriented and even electrically connecting individual CNT on cellular walls. To settle the shortcoming of LPLA mentioned above, the branching reaction is considered as one of the efficient methods. The branching reaction could change the molecular structure and increase the molecular weight by producing branching and cross-linking structures, which improved its viscoelasticity performance (32).

In this study, we focused on developing a simple strategy for fabricating PLA/CNT foams. An epoxy-based acrylic/styrene copolymer, which has advantages such as efficiency, easy-control, and non-toxicity, was used to produce branched PLA (BPLA). The obtained BPLA was then melting mixed with varying concentrations of carboxylate CNT to produce BPLA/CNT nanocomposites. The branching structure was able to ensure cell stability in

the foaming process. Within the cell growth period, the CNT embedded in the cell wall both withstood intensively biaxial stretching force. The CNT aggregations will further be aligning. The BPLA/CNT nanocomposites would provide a feasible strategy to produce light-weight, cost-efficient, bio-degradable, and conductive nanocomposite foams.

2 Materials and methods

2.1 Materials

PLA resin (4032D) with M_w of 1,20,000 g/mol was purchased from Nature Works. Carboxylation CNT (XFQ034) with an average length of $\sim 30 \mu\text{m}$ and a diameter of 20 nm was obtained from Nanjing XFnano Materials Tech Co. Ltd. Its carboxyl content is 3 wt%. Epoxy-based acrylic/styrene copolymer (Joncryl 4032) was supplied by BASF Company, Germany.

2.2 Fabrication of BPLA/CNT nanocomposite and its foams

2.2.1 BPLA/CNT nanocomposites

The preparation of BPLA was carried out by an internal mixer (PolyLab, ThermoFisher, USA). The weight fraction

of epoxy-based acrylic/styrene copolymer was 0.3%. The branching reaction mechanism is shown in Figure 1a. After that, the resultant BPLA was melting mix with various CNT to produce BPLA/CNT composites. The sample was named BPLA/CNT x (x is the weight fraction of CNT). The LPLA and BPLA would graft onto CNT, and the mechanism of grafting reaction is esterification as shown in Figure 1b. As the mixing time was the reactive time, it could control the reaction degree flexibly by extending the mixing time. On the contrary, the internal mixer as a mainly reactive zone, its mixing temperature, known as reactive temperature, could be independently controlled to optimize the reaction kinetics. The reactive temperature was at 190°C. The mixing time and mixing speed were 6 min and 60 rpm, respectively. Afterward, the samples were compression molded into sheets of 2 mm in thickness for the subsequent characterizations and the foaming process.

2.2.2 BPLA/CNT foams

The BPLA/CNT foams were prepared using supercritical CO₂ foaming technology. First, samples were placed in a customized autoclave at a temperature of 140°C and high pressure of 16 MPa for 5 h. The supercritical CO₂ injection was achieved by a syringe pump. A pressure transducer was used to measure the pressure with an accuracy of ± 0.01 MPa and a needle valve to release the pressure. A computer equipped with a data acquisition system was connected to the pressure transducer to record and control the pressure-drop rate. A back buffer with a changeable volume was connected to the high-pressure autoclave to control the pressure-drop degree. When CO₂ was completely diffused and dissolved into the resin, a sudden pressure drop (3 MPa/s) by the release of CO₂ from 16 to 0.1 MPa provided the driving force for cell nucleation and growth. Then, the foams were obtained.

2.3 Analysis

2.3.1 CNT dispersion characterizations

The morphologies of CNT in foams were observed via a transmission electron microscope (TEM) (JEM-3010, JEOL, Japan) at 120 kV. The membrane of cell wall of BPLA/CNT foams was cryotomed into 100 nm thick slices.

2.3.2 Thermal analysis

The thermal behaviors of BPLA/CNT foams were studied on a differential scanning calorimetry (DSC) (Q100, TA, USA) system purged with nitrogen. The samples were heated to 200°C at a rate of 10°C/min to study the effect of CNT on the non-isothermal crystallization of PLAs. The degree of crystallinity of PLA, χ_c , was calculated using Eq. 1 (33):

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_c^0(1 - w_f)} \times 100\%, \quad (1)$$

where ΔH_m and ΔH_{cc} are the melting enthalpy and the cold crystallization enthalpy, respectively. The w_f is the weight fraction of CNT in nanocomposites. The enthalpy of 100% crystalline PLA (ΔH_c^0) is 93.6 J/g (34).

The spherulite morphologies of BPLA/CNTs were observed under a polarized optical microscope (POM) (BX-51, Olympus, Japan) equipped with a CCD camera. The samples were heated at 20°C/min from room temperature to 200°C, held there for 5 min, and then cooled at 20°C/min to 120°C and held for 20 min. The magnification ratio was 200.

2.3.3 Shear rheological measurements

The rheological property of BPLA/CNT was observed using a strain-controlled rheometer (MARS Rheometer, Thermo-Fisher, USA) at 190°C equipped with parallel plates (20 mm in diameter with a gap of 1.0 mm). The frequency range was from 0.1 to 100 rad/s, and the maximum strain was fixed at 5% to confirm that these conditions were within the linear viscoelastic region.

2.3.4 Foaming property characterizations

The densities of unfoamed, ρ , and foamed, ρ_f , samples in g/cm³ were measured using a density balance (BSA623S, Sartorius, Germany). The expansion ratio of foamed BPLA is equal to ρ divided by ρ_f .

The cellular structures of BPLA/CNT foams were observed by scanning electron microscope (SEM) (Nova Nano 450, FEI, USA) at an acceleration voltage of 1 kV. The magnification ratio was 500. The mean cell density N_c was calculated according to Eq. 2 (35):

$$N_c = \left(\frac{N^{\frac{3}{2}}}{A} \right) \times \text{Expansion ratio}, \quad (2)$$

where N and A are the number of cells obtained in the SEM image and the area of SEM image, respectively. The mean cell size value, R , can be calculated using Eq. 3 (36):

$$R = \left(\frac{\sum_{i=1}^{N_0} r_i^3}{N} \right)^{1/3}, \quad (3)$$

where r_i is the cell size of each cell counting by Image Pro-plus software.

2.3.5 Foaming property characterizations

The electrical conductivities of BPLA/CNT foams were measured by the method of electrical resistivity with a double electric four-probe resistance ratio test. The electrical resistivity was measured by applying a voltage across the sample and measuring the resulting current. The resistivity is calculated from the geometry of the electrodes and the thickness of the sample. To ensure the good contact between electrodes and samples, two copper threads of electrodes ($d = 0.3$ mm, resistance 0Ω at 20°C) were stuck on the sample surfaces by silver paint.

3 Results and discussion

3.1 Dispersion morphology

The dispersion morphologies of BPLA/CNT were observed by TEM as shown in Figure 2. Viewing the TEM images of BPLA/CNT8, 12, and 16 shows that CNT had formed an efficient conductive network, which contrasts sharply with the separate structure of CNT in BPLA/CNT4. For BPLA/CNT16, many agglomerates were visible, which indicated that CNT was easy to agglomerate because of the high dosage and high specific surface area. However, for BPLA/CNT8, 12, and 16, the CNT was overall dispersed uniformly in BPLA matrix because that effective conductive pathway could be distinguished. This could benefit the electrical conductivity of BPLA foams.

3.2 Thermal analysis

Figure 3 and Table 1 depict the DSC curves and thermal parameters of BPLA/CNT, respectively. It could be seen that the T_g of BPLA samples, which were similar to those

of LPLA at about 60°C , was not obviously affected by inducing CNT. The T_{cc} of LPLA was at 120°C . For the case of BPLA/CNT, with the increasing content of CNT, the T_{cc} shifted to the low temperature, from 119°C to 106°C . Interestingly, DSC curves of BPLA/CNT exhibited two melting peaks, with a higher temperature melting peak at around 157°C and a lower temperature peak at around 149 – 152°C . It indicated that two different crystalline (α and α' crystalline) formed in the cooling step. Sasaki et al. provide that α crystalline with two anti-parallel-oriented 10^3 helical chain segments in every orthorhombic cell unit would form at a crystallization temperature of 120°C (37,38), whereas the imperfect α' crystalline with hexagonal cell unit would form below 100°C (39). If crystallization temperature was between 100°C and 120°C , both α and α' crystalline would form (40). As the cold crystallization occurred at a foaming temperature range, it was easy to induce α' crystalline in the foaming process. Specifically, the heterogeneous nucleation function of CNT accelerated the cold crystallization process of PLA and shifted the melting temperature to low temperature. With the increase in CNT content, cold crystallization temperature decreased from 119°C to 106°C .

On the contrary, the crystallinity of PLA also was affected by inducing CNT. With the increase in CNT content, its crystallinity increased from 1.17% to 3.03%. As shown in Figure 3, the reason for the increase in crystallinity was the decrease in α' crystallinity. The thin and imperfect α' lamella generated attributed to the crystallization nucleation function of branching structure, and this α' lamella would melt at a lower temperature. However, the existing CNT would react with BPLA and thus would hinder the formation of α' crystalline. With the increasing CNT content, the melting peak at higher temperature gradually becomes major melting peak, whereas the melting peak at lower temperature tends to be a shoulder melting peak. Crystallinity has profound influence on controlling the cellular morphology and the final mechanical performance of foams. A faster crystallization rate and proper crystallinity would help in solidifying the cells in a short time during the foaming processes. A light-weight BPLA/CNT foams could be stably produced by controlling crystallinity (41).

Figure 4 shows the POM images of different BPLA/CNTs. In these images, the BPLA fractions were the bright and ringless spherulites with Maltese-cross pattern. The average size of spherulites in BPLA was over $270 \mu\text{m}$, and it could only observe limited spherulites in the photo. Compared with that, the spherulite numbers of other BPLA/CNTs were increased, and the spherulite size was decreased to $45 \mu\text{m}$. This was attributed to the

Figure 2: TEM images of BPLA/CNT composites.

heterogeneous nucleation effect of CNT. The spherulite morphology characterized had a similar trend as the results of isothermal crystallinity previously.

3.3 Dynamic rheological measurements

The dynamic shear rheological analysis was used to study the viscoelasticity of BPLA/CNT in the foaming process. These rheological parameters are highly sensitive to molecular chain architecture and CNT dispersion structure. When differential blending ratios of BPLA/CNT were induced, the topological structure of molecular chains was changed, and the rheological parameters of BPLA/CNT were subsequently changed. To investigate the foaming behaviors of BPLA/CNT more accurately, three techniques, i.e., plots of storage modulus, complex viscosity, and loss factor versus various frequency, were used. Figure 5a displays the influence of CNT on G' of BPLA. This value played an important role in controlling foaming process (42,43). G' represented the melt elastic behavior of polymer melt. For foaming purpose, melt elasticity is usually considered as a key indicator of

foamability. The higher the G' value, the better the melt elasticity is. The G' of BPLA was higher than that of LPLA, which implied that its melt elasticities were enhanced (44). Moreover, a plateau could be observed at a low frequency of ~ 0.1 rad/s in case of BPLA/CNT. Hingmann et al. proved that both the increment of G' and the existence of plateau zone were signatures of existing long-

Figure 3: DSC curves of different PLA samples.

Table 1: Thermal property parameters of different PLA samples

Samples	T_g (°C)	T_{cc} (°C)	H_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	H_m (°C)	χ_a (%)
LPLA	62	126	16	152	—	21	5.05
BPLA	60	—	—	155	—	1	1.27
BPLA/CNT4	60	119	27	152	157	28	1.17
BPLA/CNT8	60	116	22	152	158	23	1.64
BPLA/CNT12	60	109	22	150	158	24	2.02
BPLA/CNT16	60	106	20	149	157	22	3.03

chain-branched polymer (45). However, the G' of the BPLA/CNT decreased with the increasing CNT content. As shown in Figure 2, this was because of the aggregation of CNT, which decreased the entanglement degree of branched molecules. Figure 5b shows the complex viscosity of BPLA/CNT, and this value is equivalent to melt viscosity relevant to cell nucleation and growth during foaming process (46). Obviously, different BPLA/CNT samples all displayed representative shear-shinning behaviors. Compared with LPLA, BPLA/CNT had higher complex viscosity value, especially at low-frequency zone of 0.1–1 rad/s, which was caused by the same reason for increase in G' . Loss factor is another rheologic parameter to estimate the molecular structure and viscoelasticity of BPLA/CNT. The smaller the $\tan \delta$, the faster the elastic response of the sample is, and thus the higher the melt elasticity is. Compared with G' , $\tan \delta$ value accurately reflected the factor of melt elastic response rather

than the magnitude of melt elasticity. As shown in Figure 5c, it was obvious that the $\tan \delta$ of BPLA was smaller than that of LPLA, which showed the superior melt elasticity enhancing effect of branched structure. Moreover, adding CNT would lead to a higher value than that of BPLA, and the $\tan \delta$ value could be further increased with the increase in CNT content.

3.4 Cellular morphology

The resultant cellular morphology and the relevant cellular structure parameters of BPLA/CNT foams are shown in Figure 6a and Table 2, respectively. Due to the poor melt elasticity of LPLA, its cells ruptured easily in the foaming process; thus the cellular morphology of LPLA was not shown in Figure 6. After the branching

Figure 4: POM images of BPLA/CNT foams.

Figure 5: Rheological curves of BPLA/CNT: (a) storage module curves, (b) complex viscosity curves, and (c) loss factor curves.

reaction, BPLA's melt elasticity, complex viscosity, and loss factor were greatly enhanced as shown in Figure 5, which relief the cell rupture and combination. As a result, a cellular morphology with pentagonal dodecahedron cells was obtained as shown in Figure 6a. With the increase in CNT content, the cells of BPLA/CNT foam were likely evolved from polyhedron to sphere, which was a consequence of the decreasing melt elasticity. Moreover, the cross-sectional morphology and cell surface of cell wall in Figure 6b also displayed the impact of CNT content on the foaming process. The section and surface of BPLA cells were smooth. For BPLA/CNT4, many small burrs appeared on the cross section of cell wall. These small burrs were the CNT yarns. With further increase in the CNT content, the number of small burrs increased, and the surface became rough. The main reason for this phenomenon is that the

aggregated CNT remained steady in cell growth when cell rupture and combination occur.

Table 2 shows the cellular morphology parameters of BPLA/CNT foams. The expansion ratio of BPLA could reach 9.92 because of the enhanced melt elasticity. Furthermore, inducing CNT to BPLA led to the decrement in expansion ratio from 7.13 to 3.99. The cell growth was controlled by rheological properties, which in turn affected the cell size and cell wall thickness of PLA foam. As shown in Table 2, the high melt elasticity of BPLA melt could withstand the stretching force during cell growth, avoiding the collapse of the foamed structure. Thus, its cell size was the largest of 115 μm , and its cell wall thickness was the smallest of 7 μm . With the increase in CNT content, the cell size of BPLA/CNT decreased to 68 μm , and its cell wall thickness increased to 32 μm .

Figure 6: (a) Cellular structure of BPLA/CNT foams; (b) cellular wall of BPLA/CNT foams.

By comparing the cell density of BPLA foam, the cell density of BPLA/CNT foams increased from 7.42×10^6 to 1.59×10^7 cell/cm³ and then decreased to 4.51×10^6 cell/cm³, eventually. The reason is that the foaming temperature was set to 140°C, and this temperature was between

T_{cc} and T_m for all PLA samples. According to the thermal properties of BPLA/CNT at 140°C, amorphous phase, spherulites, and CNT existed in the matrix. Thus, besides homogeneous cell nucleation, heterogeneous cell nucleation also occurred at the spherulite–amorphous phase

Table 2: Cellular morphology parameters of BPLA/CNT foams

Samples	Density (g/cm ³)	Expansion ratio	Cell density (cell/cm ³)	Cell size (μm)	Cell wall thickness (μm)
BPLA	0.125	9.92	7.42×10^6	115^{+104}_{-42}	7
BPLA/CNT4	0.174	7.13	1.55×10^7	87^{+52}_{-41}	15
BPLA/CNT8	0.204	6.08	1.59×10^7	76^{+22}_{-27}	18
BPLA/CNT12	0.263	4.72	9.25×10^6	72^{+34}_{-22}	22
BPLA/CNT16	0.311	3.99	4.51×10^6	68^{+57}_{-26}	32

interfaces and at the interface between BPLA and CNT in the foaming process. The twofold cell density of BPLA/CNT foam as that of BPLA foam was attributed to the cell nucleation effect of CNT. However, the aggregations would be generated when the concentration of CNT is higher than 8 wt%, which compromised the cell nucleation effect. The formation of the cellular structure might affect the electrical conductivity of BPLA/CNT.

3.5 Electrical resistivity

The electrical resistivity of unfoamed and foamed BPLA/CNTs is shown in Figure 7a. For the unfoamed samples, the increase in the CNT content in the BPLA led to a sharp decrease in electrical resistivity from 1.10×10^9 to $3.51 \times 10^4 \Omega/\text{m}$, whereas the electrical resistivity of foamed BPLA/CNT also depends on the CNT content. At the same CNT content, the electrical resistivity of foamed BPLA/CNT was similar to that of the unfoamed one. However, the foamed BPLA/CNT with high CNT content presents a lower electrical resistivity compared with the unfoamed counterpart. For instance, the electrical resistivity of foamed and unfoamed BPLA/CNT16 was

3.51×10^4 and $4.80 \times 10^4 \Omega/\text{m}$, respectively. The main reason was because of the aggregation and secondary dispersion of CNT inside the cell wall. It could further induce an aligning structure and a decrease in the average distance between CNTs by secondary dispersion as shown in Figure 8. Thomassin et al. also found that the foamed polycaprolactone/CNT had a higher conductivity (47). Lin et al. reported that the percolation threshold of PLA/CNT was ~ 0.75 wt% (48). In this study, the CNT contents were above the electrical percolation threshold and showed quite low mean resistivity values between 4.30×10^6 and $3.51 \times 10^4 \Omega/\text{m}$; thus, the percolation threshold values were not characterized.

The conducting performance of BPLA/CNT foams was also indicated by serving as a conductor in a circuit to light up a light-emitting diode (LED) powered by a 3V button battery as shown in Figure 7b. Compared with unfoamed BPLA/CNT, the LED became more brighter when foaming materials were contained in the circuit, suggesting elongated conducting paths in cell walls and decreased resistance. This change implied the BPLA/CNT foams could serve as a pressure sensor.

In brief, the mechanism of enhancement of electrical conductivity in BPLA/CNT foams can be concluded in

Figure 7: (a) Electrical resistivity of BPLA/CNT composite foamed and unfoamed in function of CNT content; (b) conductive effect of BPLA/CNT foamed and unfoamed samples.

Figure 8: Cross section of cellular wall of BPLA/CNT foams.

Figure 9: Schematic illustration for the dispersion morphologies of BPLA/CNT foams.

Figure 9. The CNT was difficult to produce uniformly oriented structure in polymer matrix; thus, CNT tends to aggregate during the melt blending process, and the CNTs and the spherulites could serve as cell nucleation sites. More cells would nucleate in the BPLA matrix, which brought about more cell growth in the foaming process. At this stage, the BPLA resin surrounding the

cell walls withstood an intensive bi-axial tension, and the aggregated CNTs embedded in cell walls also further form an oriented and efficient conductive network as shown in Figure 8. The higher the CNT content, the more efficient the formation of oriented structure. As a consequence, the LED is brighter when foam was in series in the circuit.

4 Conclusion

As described above, an effective method was developed to prepare highly electrically conductive BPLA/CNT foams. In the process, epoxy-based acrylic/styrene copolymer can serve as an efficient chain extender for the formation of BPLA. The adding of CNT could increase the crystallinity of BPLA from 1.17% to 3.03%. The thermal results indicated that α' crystalline was the major crystalline form of BPLA, and the existence of CNT induced more formation of α crystalline in BPLA. However, an increase in the content of CNT in BPLA resulted in slightly lower rheological parameters. Thus, the densities of BPLA/CNT foams were between 0.174 and 0.311 g/cm³. The electrical resistivity of unfoamed BPLA/CNT16 could reach $3.51 \times 10^4 \Omega/\text{m}$, and its foamed counterpart further decreased to $4.80 \times 10^4 \Omega/\text{m}$. In terms of cost-effectiveness, compared to PLA (2.20 \$/kg), CNT is an expensive substance (i.e., 42.00 \$/kg). Compared with 100 wt% CNT aerogel or foams, CNT accounts for up to ca. 16 wt% in BPLA foam (7.49 \$/kg, only 17.83% of the cost of CNT), which could offer a well-percolated CNT network structure. A bio-degradable, electrically conductive, and light-weight BPLA could be obtained. Thus, the BPLA/CNT foams have the potential of stimulating the development of useful high-end electronic applications.

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References

- (1) Huang W, Dai K, Zhai Y, Liu H, Zhan P, Gao J, et al. Flexible and lightweight pressure sensor based on carbon nanotube/thermoplastic polyurethane-aligned conductive foam with superior

compressibility and stability. *ACS Appl Mater Interfaces*. 2017;9(48):42266–77.

- (2) Jiang S, Reich S, Uch B, Hu P, Agarwal S, Greiner A. Exploration of the electrical conductivity of double-network silver nanowires/polyimide porous low-density compressible sponges. *ACS Appl Mater Interfaces*. 2017;9(39):34286–93.
- (3) Verma P, Saini P, Malik RS, Choudhary V. Excellent electromagnetic interference shielding and mechanical properties of high loading carbon-nanotubes/polymer composites designed using melt recirculation equipped twin-screw extruder. *Carbon*. 2015;89:308–17.
- (4) Zhang H, Liu N, Shi Y, Liu W, Yue Y, Wang S, et al. Piezoresistive sensor with high elasticity based on 3D hybrid network of sponge@CNTs@Ag NPs. *ACS Appl Mater Interfaces*. 2016;8(34):22374–81.
- (5) Kar M, Saha S, Sarkar R, Pal S, Sarkar P. Comparative study on the photovoltaic properties of ZnX (X = S, Se, Te) QD/CNT inorganic/organic hybrid nanocomposites. *J Phys Chem C*. 2020;124(14):7652–60.
- (6) Liu Y, Li F, Xia Q, Wu J, Liu J, Huang M, et al. Conductive 3D sponges for affordable and highly-efficient water purification. *Nanoscale*. 2018;10:4771–8.
- (7) Li Z, Liu Z, Sun H, Gao C. Superstructured assembly of nanocarbons: fullerenes, nanotubes, and graphene. *Chem Rev*. 2015;115(15):7046–117.
- (8) Li Y, Kang Z, Yan X, Cao S, Li M, Guo Y, et al. A three-dimensional reticulate CNT-aerogel for a high mechanical flexibility fiber supercapacitor. *Nanoscale*. 2018;19:9360–8.
- (9) Wang D, Wang J, Liu Z, Yang X, Hu X, Deng J, et al. High-performance electrochemical catalysts based on three-dimensional porous architecture with conductive interconnected networks. *ACS Appl Mater Interfaces*. 2016;8(42):28265–73.
- (10) Flores J, Pavía-Sanders A, Chen Y, Pochan DJ, Wooley KL. Recyclable hybrid inorganic/organic magnetically active networks for the sequestration of crude oil from aqueous environments. *Chem Mater*. 2015;27(10):3775–82.
- (11) Zou J, Liu J, Karakoti AS, Kumar A, Joung D, Li Q, et al. Ultralight multiwalled carbon nanotube aerogel. *ACS Nano*. 2010;4:7293–302.
- (12) Li Y, Zhou B, Zheng G, Liu X, Li T, Yan C, et al. Continuously prepared highly conductive and stretchable SWNT/MWNT synergistically composited electrospun thermoplastic polyurethane yarns for wearable sensing. *J Mater Chem C*. 2018;6:2258–69.
- (13) Bekyarova E, Thostenson ET, Yu A, Kim H, Gao J, Tang J, et al. Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites. *Langmuir*. 2007;23:3970–4.
- (14) Li L, Li B, Hood MA, Li CY. Carbon nanotube induced polymer crystallization: the formation of nanohybrid shish-kebabs. *Polymer*. 2009;50:953–65.
- (15) Romeo HE, Hoppe CE, Lopez-Quintela MA, Williams RJJ, Minaberry Y, Jobbagy M. Directional freezing of liquid crystalline systems: from silver nanowire/PVA aqueous dispersions to highly ordered and electrically conductive macroporous scaffolds. *J Mater Chem*. 2012;22:9195–201.
- (16) Wu D, Lv Q, Feng S, Chen J, Chen Y, Qiu Y, et al. Polylactide composite foams containing carbon nanotubes and carbon black: synergistic effect of filler on electrical conductivity. *Carbon*. 2015;95:380–7.

- (17) Safdari M, Al-Haik MS. Synergistic electrical and thermal transport properties of hybrid polymeric nanocomposites based on carbon nanotubes and graphite nanoplatelets. *Carbon*. 2013;64:111–21.
- (18) Shah T, Vasava D. A glimpse of biodegradable polymers and their biomedical applications. *e-Polymers*. 2019;19(1):385–410.
- (19) Baimark Y, Rungseesantivanon W, Prakymoramas N. Synthesis of flexible poly(l-lactide)-b-polyethylene glycol-b-poly(l-lactide) bioplastics by ring-opening polymerization in the presence of chain extender. *e-Polymers*. 2020;20(1):423–9.
- (20) Donate R, Monzón M, Elena M, Domínguez A. Additive manufacturing of PLA-based scaffolds intended for bone regeneration and strategies to improve their biological properties. *e-Polymers*. 2020;20(1):571–99.
- (21) Pretula J, Slomkowski S, Penczek S. Polylactides – methods of synthesis and characterization. *Adv Drug Delivery Rev*. 2016;107(15):3–16.
- (22) Armentano I, Bitinis N, Fortunati E, Mattioli S, Rescignano N, Verdejo R. Multifunctional nanostructured PLA materials for packaging and tissue engineering. *Prog Polym Sci*. 2013;38(10–11):1720–47.
- (23) Raquez JM, Habibi Y, Murariu M, Dubois P. Polylactide (PLA)-based nanocomposites. *Prog Polym Sci*. 2013;38(10–11):1504–42.
- (24) Wang X, Mi JG, Wang J. Multiple actions of poly(ethylene octene) grafted with glycidyl methacrylate on the performance of poly(lactic acid). *RSC Adv*. 2018;8(60):34418–27.
- (25) Li Y, Mi JG, Fu H. Nanocellular foaming behaviors of chain-extended poly(lactic acid) induced by isothermal crystallization. *ACS Omega*. 2019;4:12512–23.
- (26) Yin DX, Mi JG, Zhou HF, Wang XD, Tian HF. Fabrication of branching poly (butylene succinate)/cellulose nanocrystal foams with exceptional thermal insulation. *Carbohydr Polym*. 2020;247:116708–18.
- (27) Nofar M, Ameli A, Park CB. A novel technology to manufacture biodegradable polylactide bead foam products. *Mater Des*. 2015;83(15):413–21.
- (28) Saurabh C, Inderdeep S, Jung S. Recyclability analysis of PLA/Sisal fiber biocomposites. *Compos Part B Eng*. 2019;173(15):106895–10903.
- (29) Rudresh BM, Kumar BN, Madhu D. Combined effect of micro- and nano-fillers on mechanical, thermal, and morphological behavior of glass-carbon PA66/PTFE hybrid nano-composites. *Adv Compos Hybrid Mater*. 2019;2:176–88.
- (30) Sun H, Fang Z, Li T, Lei F, Jiang F, Li D, et al. Enhanced mechanical and tribological performance of PA66 nanocomposites containing 2D layered α -zirconium phosphate nanoplatelets with different sizes. *Adv Compos Hybrid Mater*. 2019;2:407–22.
- (31) Liu Y, Kumar S. Polymer/carbon nanotube nano composite fibers: a review. *ACS Appl Mater Interfaces*. 2014;6:6069–87.
- (32) Liu W, Li H, Wang X. Effect of chain extension on the rheological property and thermal behaviour of poly (lactic acid) foams. *Cell Polym*. 2013;32(6):323–33.
- (33) Chen Y, Qi Y, Tai Z, Yan X, Xue Q. Preparation, mechanical properties and biocompatibility of graphene oxide/ultrahigh molecular weight polyethylene composites. *Eur Polym J*. 2012;48(6):1026–33.
- (34) Ameli J, Nofar M, Jung P, Park CB. Development of high void fraction polylactide composite foams using injection molding: mechanical and thermal insulation properties. *Compos Sci Technol*. 2014;90(2):88–95.
- (35) Najafi N, Heuzey MC, Carreau PJ, Theriault D, Park CB. Mechanical and morphological properties of injection molded linear and branched-polylactide (PLA) nanocomposite foams. *Eur Polym J*. 2015;73:455–65.
- (36) Barmouz M, Behraves AH. Statistical and experimental investigation on low density microcellular foaming of PLA-TPU/cellulose nano-fiber bio-nanocomposites. *Polym Test*. 2017;61:300–13.
- (37) Alemán C, Lotz B, Puiggali J. Crystal structure of the α -form of poly(l-lactide). *Macromolecules*. 2001;34:4795–801.
- (38) Sasaki S, Asakura T. Helix distortion and crystal structure of the α -form of poly(l-lactide). *Macromolecules*. 2003;36:8385–90.
- (39) Kawai T, Rahman N, Matsuba G, Nishida K, Kanaya T, Nakano M, et al. Crystallization and melting behavior of poly-(l-lactic acid). *Macromolecules*. 2007;40:9463–9.
- (40) Androsch R, Schick C, Lorenzo ML. Kinetics of nucleation and growth of crystals of poly(l-lactic acid). In *synthesis, structure and properties of poly(lactic acid)*. New York: Springer; 2017. p. 235–72.
- (41) Wang J, Zhu W, Zhang H. Continuous processing of low-density, microcellular poly (lactic acid) foams with controlled cell morphology and crystallinity. *Chem Eng Sci*. 2012;75:390–9.
- (42) Ahmed J, Auras R, Kijchavengkul T, Varshney SK. Rheological, thermal and structural behavior of poly (ϵ -caprolactone) and nanoclay blended films. *J Food Eng*. 2012;111(4):580–9.
- (43) Qu Z, Yin D, Zhou H, Wang X, Zhao S. Cellular morphology evolution in nanocellular poly (lactic acid)/thermoplastic polyurethane blending foams in the presence of supercritical N₂. *Eur Polym J*. 2019;116:291–301.
- (44) Liu W, Li HQ, Wang XD, Du ZJ, Zhang C. Effect of chain extension on the rheological property and thermal behaviour of poly (lactic acid) foams. *Cell Polym*. 2013;6:343–67.
- (45) Hingmann R, Marczinke. BL. Shear and elongational flow properties of polypropylene melts. *J Rheology*. 1994;38(3):573–87.
- (46) Kuang T, Mi H, Fu D, Jing X, Chen B, Mou W. Fabrication of poly (lactic acid)/graphene oxide foams with highly oriented and elongated cell structure via unidirectional foaming using supercritical carbon dioxide. *Ind Eng Chem Res*. 2015;54(2):758–68.
- (47) Thomassin JM, Pagnoulle C, Bednarz L, Huynen I, Jerome R, Detrembleur C. Foams of polycaprolactone/MWNT nanocomposites for efficient EMI reduction. *J Mater Chem*. 2008;18(7):792–6.
- (48) Lin L, Suksut B, Schlarb AK. Process–structure–property relationships in semicrystalline polymer – based nanocomposites. *Manufacturing of nanocomposites with engineering plastics*. Cambridge: Woodhead Publishing; 2015. p. 279–98.