Research Article

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A lightweight polyurethane-carbon microsphere composite foam for electromagnetic shielding

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Abstract: In this study, we have produced a lightweight foam composite material by a simple freeze-drying method, which is composed of carboxylated multi-walled carbon nanotubes (MWCNTs), mesoporous carbon hollow microspheres (MCHMs), water-based polyurethane (WPU), and polyvinyl alcohol (PVA). MCHMs were prepared by a novel and facile method. We found that the electromagnetic shielding performance of foam composites can be adjusted by adjusting the density of foam composites, and the electromagnetic shielding performance of composites can be enhanced through the synergistic effect of hollow mesoporous carbon and MWCNTs. The composite material with a density of $232.8042 \text{ mg}\cdot\text{cm}^{-3}$ and 40 wt% MWCNT has a δ of $30.2 \text{ S}\cdot\text{m}^{-1}$ and SE of 23 dB. After adding 10 wt% MCHMs to the composite material, δ reaches $33.2 \text{ S}\cdot\text{m}^{-1}$, and SE reaches 28 dB. Both absorption losses accounted for 70%. The increase in the content of MWCNT, the increase in density, and the introduction of MCHMs all have a positive effect on the δ and SE of the composite material.

Keywords: mesoporous carbon hollow microspheres, electromagnetic shielding performance, WPU, MWCNT, foam

1 Introduction

With the rapid growth of a new generation of industries such as aviation, aerospace, and automobiles, miniaturized electronic products are developing rapidly, which brings the problem of electromagnetic radiation, which

will seriously reduce the performance of nearby precision equipment and threaten human health (1–3). Therefore, it is essential to find efficient materials to suppress the electromagnetic interference pollution. High magnetic permeability or high electrical conductivity is essential for effective electromagnetic shielding (4,5). Traditionally, various forms of metal structures (sheets/films, coatings, etc.) can be used for electromagnetic shielding (6–8). However, metal shielding has the disadvantages of high density, poor corrosion resistance, and expensive processing costs, which limit its use in the modern electronic world (9). In contrast, conductive polymer composites (CPCs) formed by insulating polymers and conductive fillers have attracted more and more attention from industry and academia (10–12). These materials usually have the advantages of low density, high flexibility, good chemical stability, and easy processing and molding (13). Choosing a suitable conductive filler can help transform the electromagnetic shielding mechanism from reflection loss to absorption loss, which will not cause secondary pollution. For porous conductive polymers, the air in the internal cavity of the material can reduce the real part of the dielectric constant, thereby reducing the reflectivity of the material surface. Adding the microporous structure to the electromagnetic shielding material can not only effectively reduce electromagnetic pollution but also promote the transformation of the electromagnetic interference shielding mechanism from reflection loss to absorption loss, to achieve effective electromagnetic shielding even at low density. Mesoporous carbon hollow microspheres (MCHMs), which has a unique hollow mesoporous structure, is conducive to changing electromagnetic shielding from reflection loss to absorption loss, so it is very suitable for use as a filler for electromagnetic shielding composite materials to achieve better electromagnetic shielding performance (14–17). Both water-based polyurethane (WPU) (18,19) and polyvinyl alcohol (PVA) (20) have the advantages of good fluidity, non-toxicity, flame retardancy, and non-volatility in aqueous media, so they are very suitable as the base material of CPCs. Compared with other functional group-modified multi-walled carbon nanotubes (MWCNT), carboxylated MWCNT can be uniformly dispersed in water and are environmentally friendly,

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so they are very suitable for blending with WPU and PVA (21–23). There are many methods for preparing foamed materials, such as the supercritical fluid foaming method (24,25), melt mixing method, extrusion method (26,27), phase separation method (28,29), aerogel preparation technology (30,31), and so on. A simple aerogel preparation technology is adopted. After WPU and PVA are mixed with water to form a gel, the water in the system is removed by freeze-drying technology to form a foaming material. This method is environmentally friendly and low in cost. By controlling the moisture content, the density of the foam material can be controlled, so it is suitable for large-scale applications.

2 Materials and methods

2.1 Chemicals and materials

Concentrated ammonia aqueous solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25%), hydrofluoric acid (HF, 25%), resorcinol formaldehyde (37%), tetraethyl orthosilicate (TEOS), MWCNT (inner diameter: 5–10 nm, outer diameter: 20–40 nm, and length: 10–30 μm), polyethylene glycol (PEG, $M_n = 400$), 2-hydroxy-2-methylpropiophenone, isophorone diisocyanate (IPDI), hydroxyethyl acrylate (HEA), 2,2-dimethylolpropionic acid (DMPA, vacuum dried at 90°C before use), triethylamine, 2,6-di-*tert*-butyl *p*-cresol, 1,4-butanediol (BDO, 99%), dibutyltin dilaurate (99%), 2-hydroxy-1-[4-(2-hydroxyethyl)phenyl]-2-methyl-1-propiophenone (Irgacure 2959, 95%), acetone (Ac), PVA ($M_n = 600$), and absolute ethanol (EtOH) were of analytical grade. All chemicals were purchased from Aladdin Company. Polycaprolactone diol (PCLD, $M_n = 2,000$) was purchased from Japan Daicel Corporation.

2.2 Preparation of MCHMs

The MCHMs were prepared according to our previous work with some minor modifications (32). In stage 1, we manufactured colloidal silica spheres by a method of the hard template. 1 mol TEOS was added to the solution containing 40 mL of ethanol, 8 mL of deionized water, and 3 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$. Then, magnetic stirring of the solution was carried out for 20 min at indoor temperature. In stage 2, 0.2 mol of formaldehyde and 3.84 mmol of resorcinol were added to the previous solution while stirring for 8 h. During this stage, the molar ratio of formaldehyde to resorcinol remains constant. In stage 3, $\text{SiO}_2@\text{SiO}_2/\text{phenolic}$ resin was centrifuged and washed several times through

ethanol and deionized water. Afterward, the sediment was dried in a vacuum oven for 12 h at 60°C. In stage 4, the compounds were heated for 6 h under N_2 atmosphere at 700°C. Finally, $\text{SiO}_2@\text{SiO}_2/\text{carbon}$ was etched by HF (25%) for removing the silica scaffold.

2.3 Preparation of WPU

In a 500 mL four-necked round bottom flask equipped with a magnetic stirrer, thermometer, nitrogen protection device, and condensing reflux device, PCLD, DMPA, and IPDI were added in a metered ratio, slowly increasing the temperature to 90°C, and carrying out the reaction under the protection of N_2 . At the same time, the $-\text{NCO}$ content in the system was measured by di-*n*-butylamine-hydrochloric acid titration. When the theoretical value was reached, the temperature of the system was reduced to 40°C, the calculated amount of BDO was added to extend the chain and a small amount of BHT inhibitor was added to prevent the reactant from explosion. Then, slowly the temperature was increased to 80°C and allowed to react until the isocyanate ($-\text{NCO}$) content reached the theoretical value. During the reaction process, an appropriate amount of Ac needs to be added dropwise to reduce the viscosity of the system. After cooling the reactant to 40°C, the calculated amount of HEA and appropriate amount of Ac were added and then the temperature was increased to 60°C and allowed to react until the $-\text{NCO}$ reaction is complete. The reactant was lowered to room temperature, and the solvent Ac was removed by distillation under reduced pressure.

2.4 Preparation of MWCNT/MCHMs/WPU/PVA foam

After dissolving a certain amount of WPU and PVA in water, stir vigorously to emulsify, then add MCHMs and MWCNT uniformly dispersed by ultrasonic, and stir it magnetically for 3 h. After mixing uniformly, pour it into the mold and freeze-dry for 36 h to get a foam material of 30 mm $\times$ 30 mm $\times$ 2.5 mm. The density of the prepared sample is shown in Table 1.

2.5 Characterization

The sample was sprayed with gold, and the morphology of the sample was studied by the Hitachi SU800 scanning electron microscope. The acceleration voltage

Table 1: Density of samples

Sample	Density (mg·cm ⁻³)	MWCNT (wt%)	MCHMs (wt%)
MWCNT/foam-20	280.3819	20	0
MWCNT/foam-40a	232.8042	40	0
MWCNT/foam-40b	198.9865	40	0
MWCNT/foam-40c	157.1455	40	0
MCHMs/MWCNT/foam-40	258.9581	40	10

during the test is 5 kV. Density test is performed on the MWCNT/MCHMs/WPU/PVA composite material sample, the weight is weighed with an electronic balance, the length and width of the cube sample are measured with a ruler, the thickness of the sample is measured with a spiral micrometer, and the volume of the sample is calculated. The average of three values measured for each sample was taken. The density of samples was calculated by the Eq. 1:

$$\rho = m/V \quad (1)$$

where ρ refers to the density; m is the mass; and V is the volume.

The VictorVC890D digital multimeter was used to test the volume resistivity of the sample. The test method is as follows: use a copper sheet with a diameter of 1 cm to clamp the relative positions on both sides of the sample as a circular electrode and use the positive and negative probes of the multimeter to measure the volume resistance of the sample. Generally, three different parts of the sample are measured, and the average value is calculated. Eqs. 2 and 3 are used to calculate the conductivity:

$$\rho_v = R_v \frac{S}{h} \quad (2)$$

$$\delta = 1/\rho_v \quad (3)$$

where S is the area of the test electrode, h is the thickness of the sample, ρ_v is the volume resistivity, and δ is the volume conductivity.

The N5224A vector network analyzer was used to test the electromagnetic shielding performance of the composite material under the X band (8.2–12.4 GHz), and the sample was cut into a rectangle of size 22.86 mm × 10.16 mm × 2 mm to measure the scattering parameters (S_{11} , S_{12} , S_{21} , and S_{22}), the calculation formula are Eqs. 4–8:

$$SE_R = 10 \times \lg\left(\frac{1}{1-R}\right) \quad (4)$$

$$SE_A = 10 \times \lg\left(\frac{1-R}{T}\right) \quad (5)$$

$$R + A + T = 1 \quad (6)$$

$$R = S_{11}^2 = S_{22}^2 \quad (7)$$

$$T = S_{12}^2 = S_{21}^2 \quad (8)$$

Among them, R stands for reflection coefficient, T stands for transmission coefficient, A stands for absorption coefficient, SE_A stands for absorption loss, SE_R stands for reflection loss, and SE_M stands for multiple reflection loss. When $SE > 15$ dB, SE_M is ignored.

The WDW-50E microcomputer-controlled electronic universal testing machine was used to test the compressive strength of the sample. The sample was made into a size of 30 mm × 30 mm × 25 mm, and the indenter moving speed was 10 mm·min⁻¹. The average of five groups of tests for each sample was taken, and the compressive strength δ_p can be calculated by the Eq. 9:

$$\delta_p = F/S \quad (9)$$

where F is the maximum force when the sample is broken, S is the cross-sectional area of the sample, and δ_p is the compressive strength.

3 Result and discussion

Carbon nanotubes (CNTs) are carbon materials with cylindrical or tubular nanostructures containing six-membered carbon rings. Polymer matrix composites containing CNT fillers usually have excellent electrical conductivity, thermal conductivity, and mechanical properties. And compared with the conventional carbon-based fillers, MWCNTs have a high aspect ratio, so they have greater advantages in preparing electromagnetic shielding materials (33). The internal cavity and mesoporous shell structure of MCHMs have a significant impact on dielectric loss and impedance matching. Compared with solid carbon spheres and hollow carbon spheres, MCHMs show better microwave absorption performance, and as a supplementary filler, it can further improve the electromagnetic shielding performance of the foam (32).

Figure 1 is the scanning electron microscope (SEM) image of the samples. Both WPU and PVA are hydrophilic polymers with good fluidity in water. The freeze-drying method transforms the water in the mixed solution into ice crystals, and the growing ice crystals exclude the particles from the freezing peak, resulting in the formation of cell walls of the MWCNT/MCHMs/WPU/PVA composite material. The space template occupied by ice crystals forms a porous structure, but the growth direction of the hydrogel is not controlled during the ice sublimation process, so the cell walls are anisotropic. When MCHMs are not added, the MWCNTs in the cell walls are dispersed as reinforced nanofibers in the WPU/PVA matrix. As a rigid fiber, MWCNT can play a supporting role in the polymer matrix. Therefore, an appropriate amount of MWCNT is beneficial to porous conductive polymers. According to

the heterogeneous nucleation effect, MWCNT and MCHMs will be dispersed along the cell wall. However, due to the increase in the filler content, the filler will aggregate. Affected by the physical barrier effect of MWCNT, the bubbles cannot increase freely. So irregular cells are formed, which induced the breaking of the closed-cell structure.

In the X-band (8.2–12.4 GHz), the imaginary part of the dielectric constant (ϵ'') of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40 varies with frequency as shown in Figure 2, ϵ'' is usually used to indicate power loss. According to the Maxwell–Wagner polarization theory in heterostructures, interface polarization will cause the accumulation of virtual charges at the interface between different media with different conductivity and dielectric constants (34). The ϵ'' of MWCNT/foam-40a is higher than

Figure 1: SEM images of: (a) MWCNT/foam-20, (b) MWCNT/foam-40a, (c) MWCNT/foam-40b, (d) MWCNT/foam-40c, and (e) MCHMs/MWCNT/foam-40; the scale bar is 10 μm and 1 μm .

Figure 2: The value of ϵ'' of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40.

MWCNT/foam-20. With the content of conductive filler increasing, the dielectric loss will increase, because a large number of cells and cavities exist in the foam material, which can be regarded as a miniature capacitor. The conductive filler acts as the electrode, the insulating WPU as matrix, and the air acts as the dielectric layer. After the MWCNT content increases from 20 to 40 wt%, the local concentration exceeds the percolation threshold, and the adjacent conductive fillers are close to each other to form a perfect conductive network, which causes a sudden increase in ϵ'' . At the same time, it can be found that as the density increases, the ϵ'' of MWCNT/foam-40c, MWCNT/foam-40b, and MWCNT/foam-40a will also increase. When the carrier concentration of MWCNT per unit volume increases, a complete conductive network is formed, following which the gap between them is reduced, and the concentration of carriers per unit volume is increased, which causes an increase in dielectric loss. When 10 wt% MCHMs is added to the foam composite material, ϵ'' will also increase. The increase in amplitude is mainly due to the augment in conductivity loss caused by the increase in the carrier concentration per unit volume, and the increase in polarization loss due to the polarization of the interface between MCHMs and WPU, which leads to the increase in the dielectric loss and ϵ'' value.

Figure 3 shows the conductivity of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40. Similar to the change trend of ϵ'' , when the MWCNT content is 20 wt%, even if the density is $280.3819 \text{ mg}\cdot\text{cm}^{-3}$, the conductivity is only $2.3 \text{ S}\cdot\text{m}^{-1}$. But when the MWCNT filler content was increased to 40 wt%,

Figure 3: Conductivity of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40.

the conductivity increased to 25.4 , 27.3 , and $30.2 \text{ S}\cdot\text{m}^{-1}$. Because when the content of MWCNT is low, the conductive filler is isolated by the isolation WPU matrix and the air in the cell structure and cannot exceed the percolation threshold. For the sake of forming a complete conductive network, free electrons can only conduct electricity through the tunneling effect, so the conductivity of MWCNT/foam-20 is low. When the content of MWCNT filler was increased to 40 wt%, on the one hand, the number of conductive fillers increases, so in the base, the conductive fillers in the body will be physically connected to form a complete conductive network, the continuity of the conductive network is enhanced, and the conductivity has a sudden change. On the other hand, the number of free charge carriers increases. When the carriers between adjacent conductive filler concentrations is high enough, and the gap between adjacent conductive fillers is reduced, carriers can cross the energy barrier and undergo transitions, thus causing a sudden increase in conductivity. In addition to the increase in filler content, the increase in density will also cause conductivity. When the density increases, the concentration of MWCNT per unit volume increases, causing the concentration of carriers per unit volume to increase, and the gap between adjacent conductive fillers decreases, causing the jump current to increase, which causes an augment in electrical conductivity. Compared to MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40 have higher conductivity with a larger conductive filler content and density.

Electromagnetic shielding refers to the isolation or shielding of external electromagnetic waves by shielding

the main body to reduce or eliminate the influence of electromagnetic waves on electronic equipment or the human body.

$$SE = 10 \times \lg\left(\frac{P_i}{P_o}\right) = 20 \times \lg\left(\frac{E_i}{E_o}\right) = 20 \times \lg\left(\frac{H_i}{H_o}\right) \quad (10)$$

where P represents power, E represents electric field, H represents magnetic field, and the subscripts “I” and “O” represent incident wave and transmitted wave, respectively. All electromagnetic waves consist of two basic components perpendicular to each other, namely the magnetic field and the electric field (35). When electromagnetic waves radiate to the shielding material, surface reflection, internal absorption, transmission, and multiple scattering occur. This causes reflection loss, absorption loss, and multiple reflection loss. Reflection loss is when the electromagnetic radiation is incident on a shielding material with active charge carriers and the radiation interacts with electrons and holes and then is reflected. Generally, materials with better conductivity, such as metal materials, attenuate electromagnetic waves by reflection loss. According to the absorption mechanism, absorption loss is for materials with electric dipoles and magnetic dipoles, the radiation energy interacts with the electric dipoles and magnetic dipoles and consumes energy during the polarization process to achieve effective electromagnetic wave attenuation. Multiple reflection losses generally occur on materials with a layered structure and a modified interface, and generally occur inside the shield. When the absorption loss is the main factor, the value of multiple reflection loss is generally small and can usually be ignored.

Figure 4 shows the SE value of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40, which shows similar conductivity and ε'' . It can be seen that the electromagnetic shielding performance of MWCNT/MCHMs/WPU/PVA composites is positively correlated with electrical conductivity. The SE_T value of MWCNT/foam-20 is only 12 dB, which cannot achieve effective electromagnetic shielding performance. The content of MWCNT does not reach the percolation threshold, and physical connections cannot be formed in the polymer matrix to form a complete conductive network. Therefore, electromagnetic waves cannot excite free electrons for transfer and transition, so effective electromagnetic shielding performance cannot be achieved. When the MWCNT filling amount reaches 40 wt%, the SE_T values of MWCNT/foam-40a, MWCNT/foam-40b, and MWCNT/foam-40c are 23, 20, and 18 dB, respectively. It can be found that MWCNT/foam-40a and MWCNT/foam-40b can achieve effective shielding effectiveness except for the MWCNT/foam-40c

with a lower density. It shows that with the increase in MWCNT content, a complete conductive network can be formed in the structure. When electromagnetic waves are incident, it will promote free electron transfer and transition. Free electrons collide in the process of transfer and transition, which will cause the conversion of electrical energy into heat, which leads to energy loss. Similarly, when 10 wt% MCHMs were added, the electromagnetic shielding effectiveness will also be significantly improved. On the one hand, it is possible that MCHMs can overlap dispersed MWCNTs together, thereby increasing the concentration of carriers per unit volume, strengthening the continuity of the conductive network, and enhancing the conduction loss. On the other hand, due to the mismatch between MCHMs and WPU matrix interface, the interface polarization generated on the interface will increase the polarization loss. Therefore, the increase in dielectric loss will cause the electromagnetic wave to be attenuated and lost when it is incident. In addition, when electromagnetic waves are incident, most of the electromagnetic waves will enter the MCHMs instead of being reflected on the surface. The incident electromagnetic waves will continue to be reflected and scattered in the hollow and mesoporous cavities, thereby being attenuated because of the special hollow mesoporous structure and impedance matching. Therefore, the SE_T of MCHMs/MWCNT/foam-40 is 28 dB, which can effectively shield electromagnetic waves.

In order to further analyze the electromagnetic shielding mechanism of MWCNT/MCHMs/WPU/PVA foam materials, Figure 5 shows SE_A , SE_R , and SE_T values of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40 at 9.04 GHz. By calculation, the SE_A/SE_T value of MWCNT/foam-20 is about 0.58. When the MWCNT content was increased to 40 wt%, the SE_A/SE_T of MWCNT/foam-40a, MWCNT/foam-40b, and MWCNT/foam-40c increased, respectively, to 0.68, 0.71, and 0.72. As a result, the absorption loss plays a dominant role in the electromagnetic shielding mechanism. This is mainly because MWCNTs, as a conductive filler, are cross-linked along the cell walls and prisms to form a conductive network. When the electromagnetic waves are incident, the free electrons in MWCNT collide and lose energy during the process of migration and transition. In addition, when electromagnetic waves are incident inside the foam composite material, there are a lot of interfaces with unmatched impedance due to the large amount of air inside the cells. On the one hand, the incident electromagnetic waves continue to scatter and reflect on the cell walls and attenuate. On the other hand, because MWCNT and WPU/PVA matrix have different conductivities and polarities, large amount of accumulated and uneven charges on the composite

Figure 4: SE of: (a) MWCNT/foam-20, (b) MWCNT/foam-40a, (c) MWCNT/foam-40b, (d) MWCNT/foam-40c, and (e) MCHMs/MWCNT/foam-40.

interface of MWCNT and WPU/PVA, electromagnetic waves produce polarization loss; however, because the content of the filler is too high, the filler is aggregated, so a complete cell structure cannot be formed, and electromagnetic waves

are easy to escape. Therefore, after adding 10 wt% MCHMs, SE_A , and SE_T both increased significantly, mainly because of the microstructure of MCHMs. Because the internal cell structure of the composite material is imperfect, the

Figure 5: SE_R and SE_A of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40 at 9.04 GHz.

electromagnetic wave cannot be greatly weakened when it enters the composite material. The electromagnetic waves that cannot be attenuated will continuously undergo multiple reflections and scattering in the hollow mesoporous cavity of MCHMs, resulting in double attenuation, which makes it difficult for the electromagnetic waves to escape

and improves the effectiveness of electromagnetic shielding. In addition, the conductivity and polarity of MCHMs and WPU/PVA are not the same. Under the action of electromagnetic waves, the free carriers in the composite material will be trapped by the traps and interfaces in the material. Therefore, the difference between MCHMs and WPU/PVA ions and electrons will accumulate on the interface, which will cause interface polarization and increase the dielectric loss, which will also enhance the electromagnetic shielding effectiveness. Obviously, the introduction of MCHMs effectively compensated for the adverse effects of imperfect cell structure caused by excessive filler content.

In order to further explain the electromagnetic shielding mechanism of the porous materials, according to the transmission line theory of electromagnetic waves in electromagnetic shielding materials, the schematic diagram is shown in Figure 6. When electromagnetic waves are incident on the surface of the shielding material, due to the inherent properties of the conductive filler, impedance mismatches are caused. At this time, a part of the electromagnetic waves will be reflected on the surface of the shielding material, resulting in reflection loss. The remaining electromagnetic waves are incident into the shielding material. On the one hand, the electric dipole of the conductive filler itself

Figure 6: Schematic illustration of electromagnetic shielding mechanisms for foam composite.

Table 2: Electromagnetic shielding performance of different carbon-based materials

Sample (substrate-filler)	Density (mg·cm ⁻³)	Filler content (wt%)	Bandwidth (GHz)	SE (dB)	Reference
WPU/PVA-MWCNT	230	40%	8.2–12.4 (X-band)	23	This work
WPU/PVA-MCHMs/MWCNT	260	10% + 40%	8.2–12.4 (X-band)	28	This work
NRF-MXene	—	2%	8.2–12.4 (X-band)	6	(36)
PU-AgNWs/MXene	150	1.2% + 7.61%	8.2–12.4 (X-band)	50	(37)
EP-RGO/MWCNT	—	5%	8.2–12.4 (X-band)	22.6	(38)
PVDF-CNT	—	7.5%	8.2–12.4 (X-band)	29.1	(2)
PU-Graphene	—	5%	8.2–12.4 (X-band)	15	(39)

NRF: natural rubber latex foam; AgNW: Ag Nano wire; EP: epoxy; RGO: reduced graphene oxide; PVDF: polyvinylidene fluoride.

interacts with the electromagnetic waves, free electrons are excited to transfer or transition, and the free electrons produce energy loss during the collision. The electromagnetic wave is lost after being converted into heat. On the other hand, electromagnetic waves are constantly reflected on the cell walls, and the interface polarization caused by the impedance mismatch between the conductive filler and the polymer matrix will also cause dielectric loss of the electromagnetic waves. Therefore, strong absorption loss is generated inside the shielding material, which leads to the improvement of electromagnetic shielding effectiveness.

Table 2 lists the electromagnetic shielding properties of other carbon-based/polymer composites. Compared with other materials, the composite material obtained by this work can obtain effective electromagnetic shielding performance at a lower density.

Figure 7 shows the compression modulus of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40. MWCNT/foam-20 has the highest compressive strength. Because as the filler increases, the dispersibility of the filler in the matrix is poor, and the compressive load is not effectively transmitted at the interface between the filler and the polyurethane matrix. With the increase in stress, the fillers contained in the cell walls and prisms are stressed and separated from the matrix, which result in a decrease in compressive strength. The compressive strength of MWCNT/foam-40a, MWCNT/foam-40b, and MWCNT/foam-40c increases with the decrease in density. Because as the density increases, MWCNTs entangle and agglomerate, which triggers physical hindrance, which leads to the destruction of the cell structure, hidden defects, and stress concentration points. The large pore size leads to a low number of internal prisms. When subjected to stress, the cell structure first collapses, and the compressive strength also decreases. Therefore, the increase in carbon fillers will also adversely affect the mechanical properties of the composite materials.

4 Conclusion

Using MWCNT and MCHMs as conductive fillers and WPU/PVA as matrix, foam composite materials were prepared by controlling the moisture content and freeze-drying methods. The effects of MWCNT content, conductive filler, and density on the electrical conductivity, electromagnetic shielding performance, and mechanical properties of the composite were studied. The study found that the increase in MWCNT content will lead to the improvement of material

Figure 7: Stress–strain curves of MWCNT/foam-20, MWCNT/foam-40a, MWCNT/foam-40b, MWCNT/foam-40c, and MCHMs/MWCNT/foam-40.

conductivity and electromagnetic shielding performance, and the decrease in compressive strength. The conductivity of the composite material with a density of $232.8042 \text{ mg}\cdot\text{cm}^{-3}$ and 40 wt% MWCNT/WPU is $30.2 \text{ S}\cdot\text{m}^{-1}$. The electromagnetic shielding efficiency under the wave band is 23 dB, and the thickness is only 2.5 mm. The compressive strength of the composite with a density of $280.3819 \text{ mg}\cdot\text{cm}^{-3}$ and 20 wt% WPU is 3 MPa. At the same time, the decrease in density will cause a decrease in electrical conductivity, an increase in electromagnetic shielding performance, and an increase in compression strength. The addition of MCHMs will provide free electrons in the three-dimensional conductive network, making the conductive network more closely connected, and therefore will also lead to the improvement in conductivity and electromagnetic shielding performance. The density of $258.9581 \text{ mg}\cdot\text{cm}^{-3}$, 40 wt% MWCNT/10 wt% MCHMs/WPU composite material has a conductivity of $33.2 \text{ S}\cdot\text{m}^{-1}$, and its electromagnetic shielding effectiveness in the X-band is 28 dB. The MWCNT/MCHMs/WPU/PVA foam material has good compression resistance, easy preparation, and environmental friendliness, so it can be used for large-scale applications as a three-dimensional electromagnetic shielding material.

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