Multiscale-void-containing low-density polyethylene/waste plastic porous carbon composites with electromagnetic shielding interference and thermal management capabilities

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1. Experiment

1.1. Raw material

Waste plastic powder (WP), from Yiyuan County Botuo Technology Co., LTD., Zibo City, Shandong Province, is produced by PVC composite plate production of defective products and scraps. It mainly contains calcium powder ($CaCO_3$) and polyvinyl chloride (PVC). Melamine is a product of Shanghai McLean Biochemical Technology Co., LTD. Its CAS number is 108-78-1. Graphite tail is a solid waste produced during the processing of graphite products by Henan Ruifeng New Materials Co., LTD. Low-density polyethylene (LDPE) was purchased from National Energy Group. Salt template agent (TEM) is a product of Beijing Food Group, and its main component is NaCl. Carbon fiber (CF) is T300 type PAN carbon fiber chopped filament from Toray, Japan. Polyethylene glycol (PEG) was purchased from Hermaclean Biochemical Technology Co., Ltd. with CAS number 25322-68-3.

1.2. Synthesis of nitrogen-doped waste plastic-based porous carbon nanoparticles (WPPC)

Firstly, precision electronic balance (FA2004B, Shanghai Yueping Scientific Instrument Co., LTD., China) was used to weigh WP (including waste PVC: $CaCO_3$= 4:6) and melamine according to the ratio of formula (10:0, 10:1, 10:2, 10:3 and 10:4). Next, both ingredients were placed in a mortar and ground for 10 min. Then, the mixed product was placed in a porcelain boat located in the tube furnace (ZHK-G06163, Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd, China) and sintered under nitrogen atmosphere according to a preset temperature-time curve (Figure 1b). The sintered product, which is waste plastic carbon (WPC), was placed into 3 mol/L hydrochloric acid solution to fully etch to remove CaO generated after decomposition of $CaCO_3$ as a self-sacrificing template agent. After washing with deionized water several times, the etching product was dried in a 120 ℃ blast drying oven (101A-2, Shanghai Experimental Instrument Factory, China) for 3 h. Based on the above process, waste plastic porous carbon (WPPC) was successfully prepared and recorded as WPPC-0, WPPC-1, WPPC-2, WPPC-3, and WPPC-4, respectively.

1.3. Preparation of Multi-scale structure pore (MSP) LDPE-based functional composites

The preparation process of MSP composite material includes the preparation of LDPE-based homogeneous composite material and pore-making. The preparation process of LDPE-based

homogeneous composites is as follows. First of all, according to the ratio of the formula (**Table S1**), the filler, LDPE matrix, and TEM were put into a laboratory-packaged high-speed mixer (J-2B, Hebi Tianguan Instrumentation Co., Ltd., China), uniformly mixed for 10 min and removed. Next, the mixture was fully melted and mixed for 10 min, with the aid of an open mixer (X(S)K-160, Jiangdu Tianyuan Test Machinery Co., Ltd., China), at 170 ℃. Finally, LDPE matrix composites are obtained after being molded by a vulcanizer (YT-LH20B, Dongguan Yitong Testing Equipment Technology Co., Ltd., China) at 170 ℃. To obtain the matrix pore structure, the pore-making process was carried out. Ultrasonic treatment was performed with the help of laboratory ultrasound equipment (LC-50, Shandong Lianchao Electronic Equipment Co., Ltd, China) for 5 h. After that, the composite material was taken out and dried in a blast drying oven at 105 ℃ for 1 h. At this point, the MSP composite material was obtained.

1.4. Preparation of PEG-based thermal management composites

MSP composites were placed into beakers containing PEG and thoroughly mixed at 60 ℃ for 3 h with the help of a magnetic stirrer (78HW-1, Changzhou Jintan Wanhua Experimental Instrument Factory, China). Thereafter, the beaker was placed into a vacuum-drying oven for 12 hours to facilitate the effective filling of the internal pores of the MSP composite with PEG. After that, the exposure experiment was carried out in a blast drying oven at 70 ℃ for 30 min to ensure that there was no PEG leakage. After removal, MSP-WPPC/PEG composites were prepared.

1.5. Characterization

The characterization of self-made WPPC involved scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy (Raman), X-ray Photoelectron Spectroscopy (XPS), contact Angle measurement test (CA), EMI test, automatic specific surface and porosity analyzer (BET), energy dispersive X-ray spectroscopy (EDS), conductivity and resistivity. SEM (GeminiSEM 300, ZEISS, Germany) was used to observe the micromorphology of WPPC. The mineral composition of WPPC was analyzed with XRD (D8 ADVANCE, Bruker, Germany) in the range of 10-80°. Raman (Evolution, Horiba LabRAM HR, Japan) determined the chemical bond type of WPPC. XPS (K-Alpha, Thermo Scientific, USA) characterized the elements on the surface of the sample and their electron orbital distribution. CA (OCA50, Dataphysics, Germany) demonstrated the effect of N doping amount on sample wettability. Based on the transmission line theory, the coaxial EMI test was carried out with the vector network analyzer (E5071C, Agilent., USA) in the range of 1-18 GHz,

and the S-parameter was obtained. This will be used to calculate EMI performance. BET (ASAP 2460, Micromeritics, USA) measured the specific surface area and porosity of WPPC in a nitrogen atmosphere. EDS (GeminiSEM 300, ZEISS, Germany) was used to determine the proportion and distribution of C and N elements in WPPC-3. An automated powder resistivity tester (four-probe method) (ST2742B, Suzhou Lattice Electronics Co., Ltd., China) was applied to test the electrical conductivity and resistivity of sample powders.

The testing of the composites covered tensile strength, scanning electron microscopy (SEM), thermal conductivity, differential calorimetry (DSC), thermogravimetric (TG), derivative thermogravimetric (DTG), and EMI efficiency test. The tensile strength of the sample was tested by a universal testing machine (CTM-2500, Shanghai Xieqiang Instrument Manufacturing Co., China) at a rate of 5 mm/min. According to Chinese standards GB/T 10401-2018. The microstructure of the tensile section was observed with the help of a scanning electron microscope (GeminiSEM 300, ZEISS, Germany) to analyze the internal structural differences of the composite. The thermal conductivity test was performed via a thermal conductivity meter (TC3100, Xi 'an Xiaxi Electronic Technology Co., Ltd., China). DSC was accomplished with the help of a dynamic thermal analyzer (GmbH STA449F5, NETZSCH, Germany) at a temperature range of 30 ℃-180 ℃ at a temperature rise/fall rate of 10 ℃/min. Based on Equation 1, the crystallinity of the composite can be calculated.

$$\chi_c = \Delta H_m/((1 - \varphi) \times \Delta H_0) \quad (1)$$

Where χ_c is the crystallinity of Pure LDPE and its composite, ΔH_m is the enthalpy of melting of the sample to be measured, φ is the proportion of filler in the composite, and ΔH_0 is the enthalpy of melting of completely crystalline Pure LDPE (293.6 $J \cdot g^{-1}$). TG and DTG analyses were carried out in the temperature range of 30 to 750 ℃ to measure the thermal stability of the composites with the help of a dynamic thermal analyzer (STA449F5, NETZSCH GmbH, Germany). The bulk conductivity of the composite was measured by an LCR digital bridge (UTR2830E, UNI-T, China). EMI efficiency tests were performed with a vector network analyzer (E5071C, Agilent, USA) to compare EMI functional differences of LDPE-based composites.

2. Test method for EMI interference effectiveness

2.1. Coaxial method with the help of a vector network analyzer

The vector network analyzer Can be regarded as an electromagnetic wave emission source. Two ports

are defined at the same time, one as a transmitting port and the other as a receiving port; On the contrary, one is used as a receiving port and the other as a transmitting port. The transmitting port detects reflected waves and the receiving port detects transmitted waves. The coaxial method relies on the scattering parameters of the reflected wave and transmitted wave measured by two ports. The scattering parameter, also known as the S-parameter, is denoted as S_{ij}, meaning the electromagnetic wave emitted by the j port from the i port (Figure 1c). When the optical cable on the left is connected to the electromagnetic wave transmitting port, $Input_1$ is the incident wave, Output1 is the reflected wave, $Output_2$ is the transmitted wave, S_{11} is the emission parameter, and S_{21} is the transmission parameter. When the right optical cable is connected to the electromagnetic wave transmitting port, $Input_2$ is the incident wave, $Output_2$ is the reflected wave, $Output_1$ is the transmitted wave, S_{22} is the emission parameter, and S_{12} is the transmission parameter.

Based on the S-parameter and Shekunov theory, the relative reflectance (R), relative transmittance (T), and relative absorptivity (A) of EMI materials can be calculated by the following Equation 2-4.

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

$$T = (S_{21})^2 = (S_{12})^2 \quad (3)$$

$$A = 1 - R - T \quad (4)$$

With the help of R and T, the total electromagnetic shielding efficiency (EMI SE or SE_T), emission shielding effectiveness (SE_R), and absorption shielding effectiveness (SE_A) of the shielding material can be specifically calculated by Equation 5-7.

$$SE = SE_T = 10 \lg(\frac{1}{T}) = 10 \lg(\frac{1}{|S_{12}|^2}) \quad (5)$$

$$SE_R = 10 \lg(\frac{1}{1 - R}) = 10 \lg(\frac{1}{1 - |S_{11}|^2}) \quad (6)$$

$$SE_A = 10 \lg(\frac{1 - R}{T}) = 10 \lg(\frac{1 - |S_{11}|^2}{|S_{12}|^2}) \quad (7)$$

2.2. EMI testing with Bluetooth devices

Bluetooth devices in electronic products such as commercially available mobile phones and Bluetooth headsets are used to detect the EMI function of MSP-WPPC/PEG. The connection status of the two

Bluetooth devices is used as a test index to measure the electromagnetic shielding capability of the sample.

3. Computing and simulation

3.1. DFT calculation methods

The DFT calculation of WPPC was carried out using the Gaussian 09w platform and the Vienna Ab initio Simulation Package (VASP), respectively. To calculate the relaxation structure, Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), molecular electrostatic potential (ESP) and dipole moment (DM), the B3LYP generalization, 6-31G basis group, and DFT-D3 dispersion correction method were set, based on the DFT principle, in the Gaussian 09w program. In the post-processing phase, Multiwfn[1-3] and VMD programs are used to analyze and visualize the results of the calculations. To calculate the charge density, Fermi energy, state density, and band structure of WPPC-0 and WPPC-3, Perdew-Burke-Ernzerhof (PBE) of functional of generalized gradient approximation (GGA) is used in VASP, also based on the DFT principle. The specific parameter setting involved Brillouin region k point density (3×3×1), plane wave cutoff energy (400 eV), electronic self-consistent calculation of the maximum number of steps (100), self-consistent field energy threshold (1E-05 eV), and force convergence (-1E-02 eV/AA).

3.2. Finite element simulation methods

The finite element simulation was carried out by Abaqus and Ansys HFSS software respectively. For uniaxial tensile simulations, the dynamic analysis mode and plastic damage evolution were set up in the Abaqus software, accompanying displacement as the feed. The simulation was carried out using pure LDPE and LDPE/TEM composites as models and was mutually verified by experiments. The specific formulas (Equation 8-15) of model construction are shown below.

$$m_{TEM}:m_{LDPE} = a:(10 - a) \tag{8}$$

$$\rho_{TEM}:\rho_{LDPE} = 2.64:0.92 \tag{9}$$

$$V = \frac{m}{\rho} \tag{10}$$

$$\eta = \frac{V_{TEM}}{V_{LDPE}} = \frac{m_{TEM}}{\rho_{TEM}}:\frac{m_{LDPE}}{\rho_{LDPE}} = \frac{0.92a}{2.64(10 - a)} \tag{11}$$

$$V_{all} = L \times W \times H = 1600\ mm^3 \tag{12}$$

$$V_{TEM} = \frac{\eta}{\eta + 1} \times V_{all} = \frac{0.92a \times (L \times W \times H)}{0.92a + 2.64(10 - a)} = \frac{0.92 \times 1600}{0.92 + 23.76} = 59.64 \tag{13}$$

$$V_{LDPE} = V_{all} - V_{TEM} \tag{14}$$

$$a \times n \times l_{TA}^3 = V_{TEM} \tag{15}$$

Where m_i is the quality of different raw materials i; ρ_i is the density of different raw materials i (**Table S2**). V_i is the volume of different raw materials i; L is the length of the sample to be measured (40.0 mm); W is the width of the sample to be measured (20.0 mm); H is the thickness of the sample to be measured (2.0 mm); a is the TEM mass ratio in every 10 parts of the formula mixture, n is a constant, where a is a positive integer from 0 to 8, and n is an integer 100. Based on Equation8-15 and the value of a, the parameters (**Table S3**) can be calculated for model construction (Figure 1d). The model after meshing by Hypermesh software (Figure 1e) was used for uniaxial tensile simulation.

Concentric rings (inner diameter 3.05mm, outer diameter 6.98mm) were constructed based on the experimental air line specification of the coaxial method (Figure 1f) for EMI simulation. To complete the simulation scene setup (Figure 1g), ideal conductive and magnetic boundary conditions and dual port excitation were set in the Ansys HFSS module. After that, the EMI finite element simulation of four materials, including Pure LDPE, LDPE/GT-10, LDPE/GT-40, and LDPE/GT-70, in the frequency range of 1-18 GHz was accomplished.

Table S1 Experimental formulations of LDPE based composites.

Formulation		Experimental raw materials					
		LDPE	TEM	GT	CF	WPPC	PEG
TEM content / wt%	00.0	100.0	00.0	/	/	/	/
	10.0	90.0	10.0				
	20.0	80.0	20.0				
	30.0	70.0	30.0				
	40.0	60.0	40.0				
	50.0	50.0	50.0				
	60.0	40.0	60.0				
	70.0	30.0	70.0				
	80.0	20.0	80.0				
GT content / wt%	00.0	100.0	/	00.0	/	/	/
	10.0	90.0		10.0			
	20.0	80.0		20.0			
	30.0	70.0		30.0			
	40.0	60.0		40.0			
	50.0	50.0		50.0			
	60.0	40.0		60.0			
	70.0	30.0		70.0			
CF content / wt%	00.0	60.00	/	40.00	0.00	/	/
	10.0	54.55		36.36	9.09		
	20.0	50.00		33.33	16.67		
	30.0	46.15		30.77	23.08		
	40.0	42.86		28.57	28.57		
WPPC content / wt%	0.00	36.59	14.63	24.39	24.39	/	/
	/	36.59	14.63	12.20	24.39	12.20	
PEG content / wt%	0.00	36.59	14.63	12.20	24.39	12.20	/
	/	36.59	14.63	12.20	24.39	12.20	Filling

Table S2 Density of raw materials.

Samples	Density / g·cm^{-3})
Template agent (TEM)	2.63
LDPE	0.92

Table S3 Specific parameters for finite element simulation of LDPE/TEM composites.

Value of a	V_{TEM} / mm^3	V_{LDPE} / mm^3	l / mm
0	0	1600	
1	59.64	1540.36	
2	119.28	1480.72	
3	178.92	1421.08	
4	238.56	1361.44	0.8417
5	298.2	1301.8	
6	357.84	1242.16	
7	417.48	1182.52	
8	477.12	1122.88	

Table S4 Scattering intensity ratio of D and G peaks about WPPC-0/1/2/3/4.

Name of sample	D peak		G peak		I_D/I_G
	Raman shift / cm^{-1}	I_D / a.u.	Raman shift / cm^{-1}	I_G / a.u.	
WPPC-0	1346.90	6114.63	1584.63	7870.47	0.78
WPPC-1	1344.17	7081.63	1579.16	7808.94	0.91
WPPC-2	1340.07	8354.07	1583.26	7862.2	1.06
WPPC-3	1340.07	8012.13	1581.89	7902.84	1.01
WPPC-4	1333.24	7886.07	1587.36	8487.44	0.93

Table S5 Specific parameters of C 1s and N 1s orbital split-peak for WPPC-0/1/2/3/4.

Orbital	Peak name	Peak position (eV)				
		WPPC-0	WPPC-1	WPPC-2	WPPC-3	WPPC-4
C 1s	C-C/C=C	284.8	284.8	284.8	284.8	284.8
	C-N/C=N	/	285.9	285.9	286.0	284.7
	C-O/C=O	286.4	288.9	287.4	288.3	287.2
	Π-Π* satellite	290.2	291.7	290.8	291.1	290.0
N 1s	Pyridine N	/	398.8	398.4	398.5	398.7
	Pyrrole N		400.7	400.2	400.3	400.5
	Graphite N		402.6	401.8	403.1	402.5

Table S6 Surface area and porosity parameters of WPPC-3.

Material	Surface area and porosity parameters		
	BET surface area: / $m^2 \cdot g^{-1}$	Pore volume / $cm^3 \cdot g^{-1}$	Pore size / nm
WPPC-3	45.54	0.14	12.09

Table S7 Specific parameters of DSC for Pure LDPE and LDPE/GT composites.

Samples	T_c [a] / ℃	T_m [b] / ℃	T_{pc} [c] / ℃	T_{pm} [d] / ℃	ΔH_m [e] / $J \cdot g^{-1}$	χ_c [f] / %
Pure LDPE	110.2	114.0	105.5	128.2	90.20	30.72
LDPE/GT-10	116.4	115.6	109.5	128.2	78.21	29.60
LDPE/GT-40	118.4	113.8	112.6	125.1	41.34	23.47
LDPE/GT-70	119.6	106.5	110.6	121.9	22.22	25.23

[a] T_c is the initial crystallization temperature; [b] T_m is the melting point temperature; [c] T_{pc} is the crystallization peak temperature; [d] T_{pm} is the melting peak temperature; [e] ΔHm is the enthalpy of melting; [f] χc is the crystallinity.

Table S8 Parameters of TG-DTG of Pure LDPE and LDPE-based composites.

Name of sample	Temperature / ℃		
	$T_{5\ wt\%}$ [a]	T_r [b]	$T_{50\ wt\%}$ [c]
Pure LDPE	445.93	478.77	476.18
LDPE/GT-10	455.25	481.82	480.97
LDPE/GT-40	458.78	483.43	489.31
LDPE/GT-70	458.30	473.34	/

[a] $T_{5\ wt\%}$ is the temperature when the sample to be tested loses 5 wt%; [b] T_r is the temperature when the sample to be tested loses the fastest burning rate; [c] $T_{50\ wt\%}$ is the temperature when the sample to be tested loses 50 wt%.

Table S9 Specific parameters of EMI Simulation for Pure LDPE and LDPE/GT composites.

Indicators	Samples		
	Pure LDPE[a)]	LDPE/GT-40	LDPE/GT-70
Relative Permittivity	2.25	3.62	10.90
Relative Permeability	1	1.02	0.16
Bulk Conductivity / $S \cdot m^{-1}$	0	0.77	5.94
Dielectric Loss Tangent	0.01	0.05	0.31
Magnetic Loss Tangent	0	0.04	3.22

[a)]Pure LDPE-related parameters are from the Ansys HFSS database.

Table S10 Specific parameters of DSC for LDPE-based functional composites.

Samples	T_c / ℃	T_m / ℃	T_{pc} / ℃	T_{pm} / ℃	ΔH_m / $J \cdot g^{-1}$	χ_c / %
LDPE/GT-40	118.4	113.8	112.6	125.1	41.34	23.47
LDPE/GT/CF-30	119.1	113.2	113.2	124.3	32.18	23.75

Table S11 Parameters of TG-DTG of Pure LDPE and LDPE-based composites.

Name of sample	Temperature / ℃		
	$T_{5\ wt\%}$	T_r	$T_{50\ wt\%}$
LDPE/GT-40	458.78	483.43	489.31
LDPE/GT/CF-20	452.47	476.75	497.51
LDPE/GT/CF-40	455.88	476.21	/
MSP-GT	446.75	475.63	/
MSP-WPPC	432.31	476.06	/

Table S12 Price parameters of each material.

Items	Ton price / yuan	Mean value / yuan
WP	1,000 to 3,000	2,000
GT	300 to 800	550
Melamine	6,000 to 9,000	7,500
By-product Hydrochloric Acid (Industrial Grade)	200 to 500	350
Salt template (Industrial grade)	300 to 600	450
LDPE (Injection grade)	9,000 to 11,000	10,000
Ni-Zn ferrite	20,000 to 50,000	35,000
CF	250,000 to 300,000	275,000
Graphene oxide (GO)	500,000 to 1,200,000	850,000

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