三维石墨烯网络复合材料的电磁波屏蔽性能研究

段　岩，李进松

（北京航空航天大学物理科学与核能工程学院，北京 100191）

[摘要]　通过溶剂热法与电泳法制备了以碳纳米管膜为基底的三维石墨烯 / 碳纳米管 / 四氧化三铁膜状复合材料，然后以环氧树脂为基体制备出多层电磁波屏蔽复合材料。分析了电场强度和沉积时间对氧化石墨烯层结构形貌、复合材料电导率和屏蔽效能的影响。研究结果表明：当复合材料为 4 层时，厚度仅为 1.4mm，在 X 波段频率范围内的最高电磁屏蔽效能为 49.7dB，比屏蔽效能高达 35.5dB/mm，超过目前大多数碳基复合材料，抗拉强度为 53.2MPa，是兼具高屏蔽性能和力学性能的石墨烯电磁波屏蔽材料。

关键词：石墨烯；电磁波；屏蔽性能；复合材料；环氧树脂

Design of 3D Graphene Network Composites for Optimal Performance of Electromagnetic Wave Interference Shielding

DUAN Yan , LI Jinsong

(School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, China)

[ABSTRACT]　A thin 3D reduced graphene oxide(rGO)/CNT/Fe_3O_4 composite based on carbon film with outstanding electromagnetic wave interference shielding capability was fabricated by solvothermal method and electrophoresis. Then, multi-layered composites were prepared based on epoxy resin. The influence of electric field and deposition time on the morphology of the graphene oxide nanosheet and conductivity and shielding efficiency of 3D rGO/CNT/Fe_3O_4/epoxy composites was analyzed. 3D rGO/CNT/Fe_3O_4/epoxy composite with 4-layer has a thickness of 1.4mm, and its shielding effectiveness is up to 49.7dB in the X-band frequency range. More significantly, its specific shielding effectiveness is as high as 35.5dB/mm, which surpasses the value of most of the current carbon-based composites, and its tensile strength is 52MPa. Therefore, the successful fabrication of this novel material signifies the potential of the use of graphene as a thin and high-performance EMI shielding material.

Keywords:　Graphene; Electromagnetic wave; Interference shielding; Composites; Epoxy resin

DOI:10.16080/j.issn1671-833x.2018.10.084

现代航空电子设备和无线电技术的发展导致了严重的电磁辐射，这严重影响了高精度电子设备的正常运转，因此设计和探索具有抗电磁波干扰性能的屏蔽材料对于现代航空装备有重大意义。材料的电磁波屏蔽效能（SE）满足[1]：

$$SE = 10\lg(P_i/P_t) \qquad (1)$$

其中，P_i 为入射电磁波功率；P_t 为透射电磁波功率。

对于电磁波屏蔽材料而言，屏蔽效能应当大于 20dB。其中，材料的反射效能（SE_R）与吸收效能（SE_A）是电磁屏蔽效能的重要组成部分[2–6]。尽管反射增强了材料对电磁波的屏蔽性能，但是反射回去的电磁波依然对其他灵敏电子设备造成影响，因此具有较高电磁屏蔽性能的材料必须同时减少反射和透射。而反射效能与透射效能及屏蔽材料自身的电导率（σ）、介电常数（ε）、磁导率（μ）以及比表面积又有着非常重要的关系[2–10]。碳纳米管（CNT）和石墨烯等碳系材料具有非常卓越的力学、电学等物理性能[11–17]，可以应用于树脂基屏蔽复合材料[1,4,6,7,18–25]。但是由于碳纳米管与石墨烯纳米片层在复合材料中分散性差，导致碳纳米管以及石墨烯复合材料的电磁屏蔽性能不能达到预期效果。

CNT 膜中单根 CNT 排列固定，解决了分散问题，已经被用于半导体[14]、超级电容器[26]、集成电路[27]和传感器[12]。对石墨烯而言，三维交联石墨烯网络结构是现今研究的重点[28–30]。如当石墨烯的添加量为 0.8%（质量分数）时，石墨烯泡沫 / 聚二甲基硅氧烷复合材料的电磁屏蔽效能达到 30dB[7]。然而，其高介电常数导致石墨

烯泡沫的阻抗与空间阻抗严重不匹配，而增强其对电磁波的反射。因此，将磁性金属或者磁性金属氧化物沉积或者通过官能团链接在碳纳米管和石墨烯上是提高其阻抗匹配性以及电磁波损耗的有效方法[31–34]。其中，四氧化三铁（Fe_3O_4）因为具有在过渡金属氧化物中的高电导率（$\sigma = 2\times10^2$S/cm）[35]和饱和磁化强度以及低剩余磁化强度和矫顽力[36]，因此常被用来提高碳纳米管和石墨烯的屏蔽效能。

本研究设计与制备了具有高电磁波屏蔽性能的三维还原氧化石墨烯（3D rGO）/CNT/Fe_3O_4/环氧树脂膜状复合材料。通过溶剂热法在CNT膜上生长Fe_3O_4颗粒，而后通过电泳法在膜的表面组装3D rGO交联网络结构。研究发现当所制备复合材料为4层时，其电磁屏蔽效能高达49.7dB，而且比电磁屏蔽效能（电磁屏蔽效能与厚度的比值）为35.5dB/mm，超过了大多数碳/树脂基复合材料。

1　试验及方法

1.1　CNT/Fe_3O_4复合材料的制备

CNT膜通过浮动催化化学气相沉积法（FCCVD）制得，具体工艺如下：将含有体积分数为1.2%的Fe^{2+}和体积分数为0.4%的噻吩加入乙醇中，由Ar或H_2承载，以20mL/h的速度在高温（约1300℃）下注入管式炉，形成质地轻薄的CNT气凝胶。其中，乙醇、Fe^{2+}和噻吩分别作为碳源、催化前体和促进剂。最后，将CNT气凝胶从管式炉中连续吹出，并沿垂直于气流方向旋转收集，形成具有无规则取向的宏观CNT膜（厚度2μm；密度807mg/cm^3）。然后采用溶剂热法制备出CNT/Fe_3O_4复合材料，具体工艺如下：首先将浓度为0.05mol/L的六水合三氯化铁溶液（$FeCl_3\cdot6H_2O$）溶于50mL乙二醇（EG）中，加入3.0g醋酸钠溶液（NaAc，作为保护剂）和10mL乙二胺溶液（EDA），通过磁力搅拌形成均匀溶液。然后将混合物转移到聚四氟乙烯衬里的不锈钢高压釜（100mL，ChangLong Instrument）中，并将面积为30cm^{2}的CNT膜完全浸入溶液中，在200℃下进行溶剂热反应10h。最后将制得的产物用去离子水洗涤数次，70℃真空干燥20min。

1.2　3D rGO/CNT/Fe_3O_4/树脂基复合材料的制备

首先，将氧化石墨烯（N002-PS-1.0，Angstron Materials Co.，Ltd.，厚度1~1.2nm，横向尺寸为554nm）分散在浓度为0.1mol/L的高氯酸锂溶液（$LiClO_4$，pH=3）中制备成浓度为3mg/mL的混合溶液。接下来的电泳试验在三电极系统中进行。CNT/Fe_3O_4复合材料作为工作电极[37]，铂片作为对电极，Ag/AgCl作为参比电极。工作电极和对电极之间的距离是3cm。还原电位分别为–0.3V、–0.6V、–0.9V、–1.2V和–1.5V，对应的电场分别为10V/m、20V/m、30V/m、40V/m和50V/m。然后，将制得的3D rGO/CNT/Fe_3O_4复合材料冷冻干燥24h。最后，利用旋涂法将环氧基剂（EPONTM Resin 862）、固化剂（DETDA）与丙酮按10∶1∶10的比例稀释成的环氧树脂稀释溶液分布在3D rGO/CNT/Fe_3O_4/复合材料表面，依次叠加，将所制备的复合材料放入真空烘箱中，在100℃下固化2h。

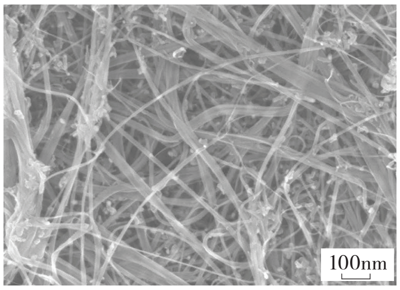
1.3　性能测试

红外光谱测试在Thermo NEXUS 670变换红外分光光度计上进行。扫描电子显微成像（SEM）在Zeiss Auriga 60 FIB-SEM上进行。材料通过四探针法（Agilent 34411A）测量复合材料的电导率，使用Agilent E8363B在8~12GHz（X波段）测量电磁屏蔽效能。使用50kN SANS电子万能试验机测试抗拉强度。复合材料样品的尺寸为22.9mm×10.2mm。

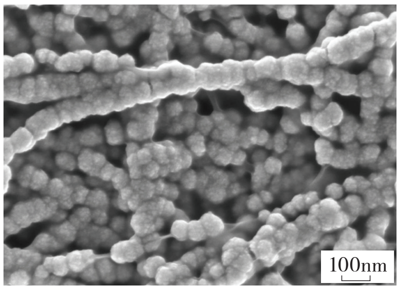
2　试验结果与讨论

图1为所制备CNT膜和CNT膜/Fe_3O_4的SEM照片。图1（a）所示为CNT各向均匀分布，其直径为10~30 nm，Fe_3O_4纳米颗粒沿CNT轴向均匀分布，其直径为50~100nm。

在直流电场中，GO纳米片层旋转的同时，会沿电场线排列并向CNT膜/Fe_3O_4负电极移动[38]。当GO与CNT膜/Fe_3O_4负电极间的距离足够近能够使电子发生转移时，GO开始被还原。最终形成rGO网状结构并从



（a）CNT膜

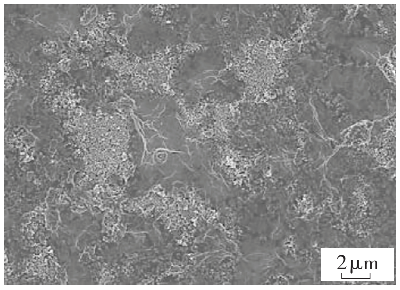


（b）CNT膜/Fe_3O_4

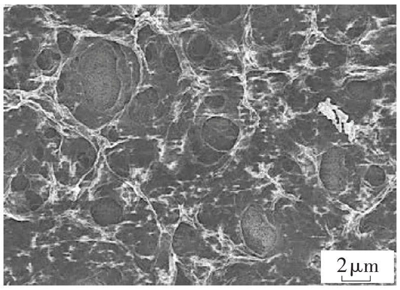
图1　CNT膜和CNT膜/Fe_3O_4扫描电镜照片

Fig.1　SEM images of CNT film and CNT film/Fe_3O_4

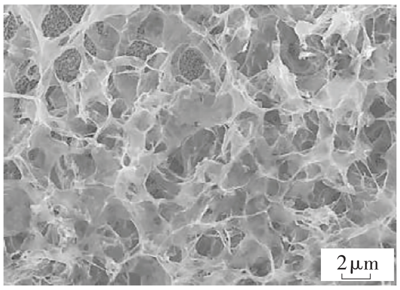
CNT 膜 /Fe_3O_4 向外延伸。从图 2 可以看出沉积时间为 10min 时，rGO 网络的微观结构会随着电场强度变化。如图 2（a）所示，当直流电场电压为 10V/m 时，rGO 基本为二维平面结构，在此过程中羟基（-OH）脱离而羧基（-COOH）形成。当电压从 20V/m 增大到 40V/m，如图 2（b）和（c）所示，rGO 网络随着厚度的增加逐渐组成了三维交联结构，同时，O=C-OH 被还原成为 C=O。如图 2（d）所示，当电压增加到 50V/m，伴随着 C=O 的形成，越来越多的 rGO 纳米片层堆积到了 CNT 膜 /Fe_3O_4 上。



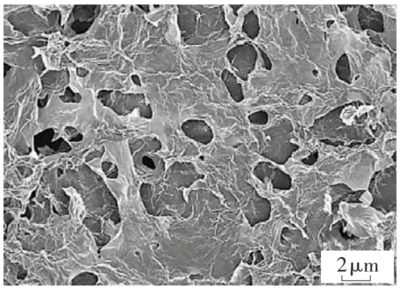
（a）电场强度为 10V/m



（b）电场强度为 20V/m



（c）电场强度为 40V/m



（d）电场强度为 50V/m

图2　不同电场强度下 rGO/CNT/Fe_3O_4复合材料形貌

Fig.2　SEM images of rGO/CNT/Fe_3O_4 composites prepared at different electric field

如图 3 所示，伴随着电场强度与沉积时间增加，rGO 的质量也随之增加。电场强度为 50V/m，沉积时间为 15min 时，沉积的 rGO 质量最多。如图 4（a）所示，当沉积时间仅为 5min 时，复合材料的电导率就高达 6.2S/cm，为化学气相沉积法制备石墨烯泡沫的 3 倍[7]。在相同沉积时间内，随着电场强度的增大，电导率增大；

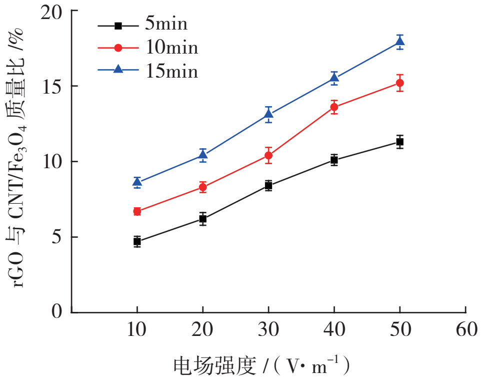
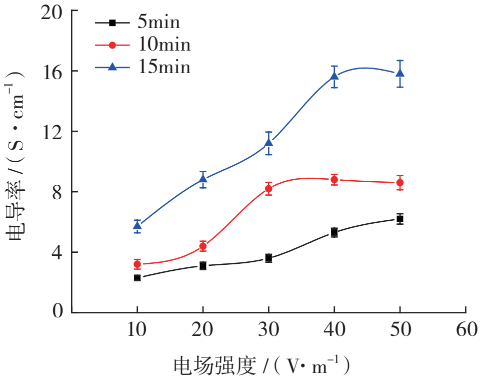
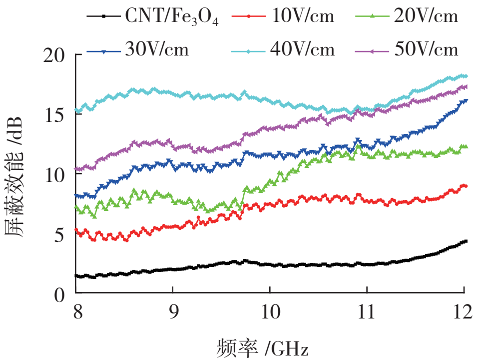


图3　rGO与CNT/Fe_3O_4的质量比-电场强度曲线

Fig.3　Weight ratio of rGO to CNT/Fe_3O_4 composites



（a）电导率－电场强度曲线



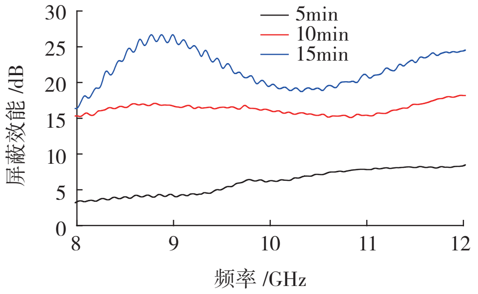
（b）屏蔽效能－频率曲线

图4　单层3D rGO/CNT/Fe_3O_4/环氧树脂复合材料电导率和屏蔽效能曲线

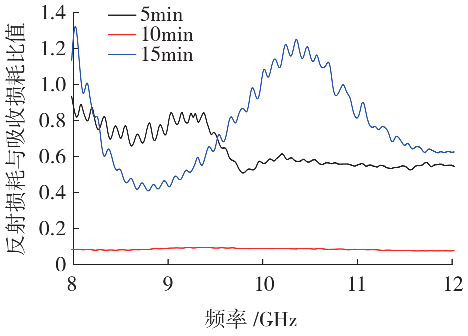
Fig.4　Electric conductivity and EMI SE of the monolayer 3D rGO/CNT/Fe_3O_4 composite

当电场强度增大到 40V/m 后，电导率趋于平缓。因此，选择在电场强度为 40V/m 条件下，制备出 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料，并测量 8~12GHz（X 波段）的电磁波屏蔽效能。如图 4（b）所示，与不含石墨烯的 CNT/Fe_3O_4/ 环氧树脂复合材料相比，单层 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料显示了更高的电磁屏蔽性能。当电压为 40V/m 时，在 8~12GHz 范围内，屏蔽效能达到最大值 15.1~18.2dB，随着电场强度增大，屏蔽效能随之下降。如图 5（a）所示，当电压为 40V/m 时，屏蔽效能随着电泳时间增加而增加，这主要是由于电导率增大导致反射增强引起的。如图 5（b），反射效能与吸收效能之比（SER/SEA）随沉积时间变化，在沉积时间为 10 min 时达到最小值 0.08，这说明在 X 波段，复合材料的屏蔽效果主要来源于材料对材料的吸收。

由上述可以看出，当电场强度为 40V/m 和沉积时间为 10min 时，单层 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料的屏蔽性能最优，但是屏蔽效能仍然小于 30dB。为了进一步提高 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料的电磁波屏蔽性能，在电场强度为 40V/m、沉积时间为 10 min 的条件下，将单层 3D rGO/CNT/Fe_3O_4/ 环氧树脂膜叠加成多层结构。如图 6（a）所示，相比单层复合材料，多层 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料显示了更高的电磁波屏蔽效能。当层数超过两层时，在 X 波段，复合材料的电磁屏蔽效能就高于 30dB。



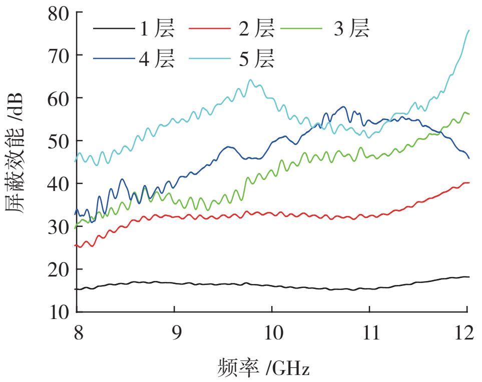
（a）屏蔽效能－频率曲线



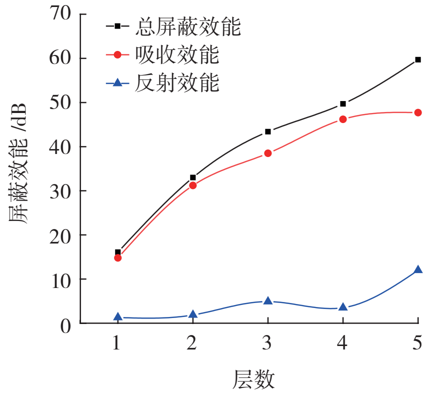
（b）反射效能与吸收效能比值－频率曲线

图5　单层3D rGO/CNT/Fe_3O_4/环氧树脂复合材料屏蔽效能曲线

Fig.5　EMI SE of the monolayer 3D rGO/CNT/Fe_3O_4 composite



（a）屏蔽效能－频率曲线



（b）屏蔽效能－层数曲线

图6　多层3D rGO/CNT/Fe_3O_4/环氧树脂复合材料屏蔽效能曲线

Fig.6　EMI SE of multilayer 3D rGO/CNT/Fe_3O_4/epoxy composites with different layers

材料的总电磁屏蔽效能（SE_T）由 3 部分组成：反射效能（SE_R）、吸收效能 SE_A 与多重反射效能（SE_M）。这些都与自由电荷、电（磁）偶极子、不同表面以及内表面的反射有关[3]。总电磁屏蔽效能满足[2]：

$$SE_T = SE_A + SE_R + SE_M \tag{2}$$

而吸收效能又满足[2]：

$$SE_A(-dB) = 8.68t\left(\frac{\sigma\omega\mu_r}{2}\right)^{1/2} \tag{3}$$

其中，t 为屏蔽材料厚度，σ 为屏蔽材料电导率，ω 为电磁波角频率，μ_r 为屏蔽材料的相对磁导率。由于 CNT 膜和 rGO 的磁导率很小，因此多层 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料的 μ_r 几乎由 Fe_3O_4 提供，从而提高了吸收效能。

当屏蔽效能大于 15dB 时，多重反射效能一般情况下忽略不计。如图 6（b）所示，多层 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料的屏蔽效能、反射效能、透射效能随层数的变化而变化。复合材料的屏蔽效能与吸收效能都随着层数的增加而增加，但是反射效能在层数为 5 层时突然增加。4 层复合材料的总屏蔽效能、吸收效能和反射效能分别为 49.7dB、46.2dB 和 3.5dB，而 5 层复合材

料的总屏蔽效能、吸收效能和反射效能分别为 59.7dB、47.7dB 和 12.0dB。正如上文提到，对于材料的屏蔽效果而言，必须尽可能增加电磁波的吸收同时降低反射。因此，综合上述结果，得出复合材料的优化参数：电场强度 40V/m、电泳沉积时间为 10min 和层数为 4 层。

与屏蔽效能相比，比屏蔽效能更适合评价更轻薄的材料[39]。如表 1 所示，4 层的 3D rGO/CNT/Fe_3O_4/ 环氧树脂复合材料的比屏蔽效能高达 35.5dB/mm，高于树脂基碳纳米管复合材料与树脂基石墨烯复合材料的比屏蔽效能。（树脂基碳纳米管复合材料的比屏蔽效能为 20dB/mm[24]，树脂基石墨烯复合材料的比屏蔽效能为 30dB/mm[7]）。

如图 7 所示，4 层 3D rGO/CNT/Fe_3O_4 复合材料的抗拉强度为 53.2MPa，是 4 层聚氯乙烯 /CNT 复合材料的 4 倍[48]。因此，本文所研究的 rGO/CNT/Fe_3O_4 复合材料是兼具优异电磁屏蔽性能和力学性能的理想材料。

表1　树脂基复合材料屏蔽性能的比较

材料	最大屏蔽效能 SE/dB	厚 d/mm	最大比屏蔽效能 /（dB·mm^{-1}）	参考文献
环氧树脂 / 碳纳米管	33	2	16.5	[24]
聚碳酸酯 / 多壁碳纳米管	26	2	13	[40]
聚氨酯 / 多壁碳纳米管	29	1.5	19.3	[41]
聚甲基丙烯酸甲酯 / 多壁碳纳米管	32	5	6.4	[42]
多壁碳纳米管 / 四氧化三铁	32.5	5	6.5	[43]
环氧树脂 / 单壁碳纳米管	20	1.5	13.3	[44]
聚二甲基硅氧烷 / 石墨烯	30	1	30	[7]
聚甲基丙烯酸甲酯 / 氧化石墨烯	19	2.4	7.9	[45]
聚甲基丙烯酸甲酯 / 氧化石墨烯	30	3.4	8.8	[46]
聚苯乙烯 / 氧化石墨烯	45.1	2.5	18	[47]
环氧树脂 / 石墨烯 / 碳纳米管 / 四氧化三铁	49.7	1.4	35.5	本文

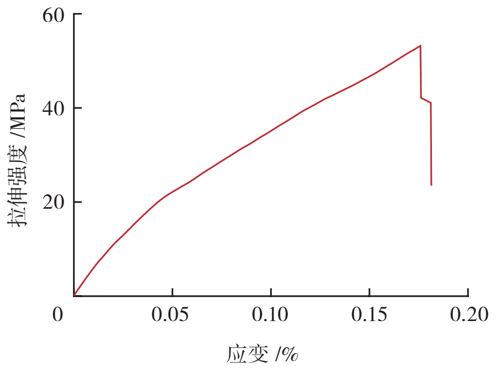


图7　4层rGO/CNT/Fe_3O_4复合材料抗拉强度–应变曲线

Fig.7　Tensile strength of 4–layer rGO/CNT/Fe_3O_4 composite

3　结论

综上所述，本文通过溶剂热法与电泳法制备了以碳纳米管膜为基底的 3D rGO/CNT/Fe_3O_4/ 环氧树脂膜状复合材料。该材料复合材料厚度仅为 1.4mm，在 X 波段频率范围内最大屏蔽效能和比屏蔽效能分别达 49.7dB 和 35.5dB/mm，超过目前大多数碳基复合材料，抗拉强度为 53.2MPa，是兼具高屏蔽性能和力学性能的电磁波屏蔽材料。

参考文献

[1]　CHEN M, ZHANG L, DUAN S, et al. Highly conductive and flexible polymer composites with improved mechanical and electromagnetic interference shielding performances[J]. Nanoscale, 2014, 6(7): 3796–3803.

[2]　PAWAR S P, BISWAS S, KAR G P, et al. High frequency millimetre wave absorbers derived from polymeric nanocomposites[J]. Polymer, 2016, 84(1): 398–419.

[3]　THOMASSIN J M, JEROME C, PARDOEN T, et al. Polymer/carbon based composites as electromagnetic interference (EMI) shielding materials[J]. Materials Science and Engineering Reports, 2013, 74(7): 211–232.

[4]　THOMASSIN J M, PAGNOULLE C, BEDNARZ L, et al. Foams of polycaprolactone/MWNT nanocomposites for efficient EMI reduction[J]. Journal of Materials Chemistry, 2008, 18(7): 792–796.

[5]　ZHANG H, XIE A, WANG C, et al. Novel rGO/α–Fe_2O_3 composite hydrogel: synthesis, characterization and high performance of electromagnetic wave absorption[J]. Journal of Materials Chemistry A, 2013(30): 8547–8552.

[6]　ZHAO D L, LI X, SHEN Z M. Electromagnetic and microwave absorbing properties of multi–walled carbon nanotubes filled with Ag nanowires[J]. Materials Science and Engineering B, 2008, 150(2): 105–110.

[7]　CHEN Z, XU C, MA C, et al. Lightweight and flexible graphene foam composites for high–performance electromagnetic interference shielding[J]. Advanced Materials, 2013, 25(9): 1296–1300.

[8]　SUN H, CHE R, YOU X, et al. Cross–stacking aligned carbon–nanotube films to tune microwave absorption frequencies and increase absorption intensities[J]. Advanced Materials, 2014, 26(48): 8120–8125.

[9]　SUN X, HE J P, LI G X, et al. Laminated magnetic graphene with enhanced electromagnetic wave absorption properties[J]. Journal of Materials Chemistry C, 2013(4): 765–777.

[10]　ZHENG Z, XU B, HUANG L, et al. Novel composite of Co/carbon nanotubes: synthesis, magnetism and microwave absorption properties[J]. Solid State Sciences, 2008, 10(3): 316–320.

[11]　BAUGHMAN R H, ZAKHIDOV A A, DE H W, et al. Carbon nanotubes—the route toward applications[J]. Science, 2002, 297(5582): 787–792.

[12]　LI Z, DHARAP P, NAGARAJAIAH S, et al. Carbon nanotube film sensors[J]. Advanced Materials, 2004, 16(7): 640–643.

[13]　NOVOSELOV K S, GEIM A K, MOROZOV S V, et al. Electric

field effect in atomically thin carbon films[J]. Science, 2004, 306(5696): 666–669.

[14] ZHOU Y, GAUR A, HUR S H, et al. P–channel, n–channel thin film transistors and p–n diodes based on single wall carbon nanotube networks[J]. Nano Letters, 2004, 4(10): 2031–2035.

[15] GEIM A K, NOVOSELOV K S. The rise of graphene[J]. Nature Materials, 2007, 6(3): 183–191.

[16] BALANDIN A A, GHOSOH S, BAO W, et al. Superior thermal conductivity of single–layer graphene[J]. Nano Letters, 2008, 8(3): 902–907.

[17] CASTRO N A, GUINEA F, PERES N, et al. The electronic properties of graphene[J]. Review of Modern Physics, 2009, 81(1): 109–162.

[18] MEI H, HAN D, XIAO S, et al. Improvement of the electromagnetic shielding properties of C/SiC composites by electrophoretic deposition of carbon nanotube on carbon fibers[J]. Carbon, 2016, 109(1): 149–153.

[19] XIAO S, MEI H, HAN D, et al. Ultralight lamellar amorphous carbon foam nanostructured by SiC nanowires for tunable electromagnetic wave absorption[J]. Carbon, 2017, 122(1): 718–725.

[20] QIN F, BROSSEAU C. A review and analysis of microwave absorption in polymer composites filled with carbonaceous particles[J]. Journal of Applied Physics, 2012, 111(6): 061301.

[21] WEN B, CAO M, LU M, et al. Reduced graphene oxides: light–weight and high–efficiency electromagnetic interference shielding at elevated temperatures[J]. Advanced Materials, 2014, 26(21): 3484–3489.

[22] YOUSEFI N, SUN X, LIN X, et al. Highly aligned graphene/polymer nanocomposites with excellent dielectric properties for high–performance electromagnetic interference shielding[J]. Advanced Materials, 2014, 26(31): 5480–5487.

[23] YAN D X, PANG H, LI B, et al. Structured reduced graphene oxide/polymer composites for ultra–efficient electromagnetic interference shielding[J]. Advanced Functional Materials, 2015, 25(4): 559–566.

[24] CHEN Y, ZHANG H B, YANG Y, et al. High–performance epoxy nanocomposites reinforced with three–dimensional carbon nanotube sponge for electromagnetic interference shielding[J]. Advanced Functional Materials, 2016, 26(3): 447–455.

[25] ZENG Z, JIN H, CHEN M, et al. Lightweight and anisotropic porous MWCNT/WPU composites for ultrahigh performance electromagnetic interference shielding[J]. Advanced Functional Materials, 2016, 26(2): 303–310.

[26] YU J, LU W, PEI S, et al. Omnidirectionally stretchable high–performance supercapacitor based on isotropic buckled carbon nanotube films[J]. ACS Nano, 2016, 10(5): 5204–5211.

[27] CAO Q, KIM H S, PIMPARKAR, et al. Medium–scale carbon nanotube thin–film integrated circuits on flexible plastic substrates[J]. Nature, 2008, 454(7203): 495–500.

[28] LEE S H, KIM H W, HWANG J O, et al. Three–dimensional self–assembly of graphene oxide platelets into mechanically flexible macroporous carbon films[J]. Angewandte Chemie International Edition, 2010, 49(52): 10084–10088.

[29] XU Y, SHENG K, LI C, et al. Self–assembled graphene hydrogel via a one–step hydrothermal process[J]. ACS Nano, 2010, 4(7): 4324–4330.

[30] CHEN Z, REN W, GAO L, et al. Three–dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition[J]. Nature Materials, 2011, 10(6): 424–428.

[31] ZHENG X L, FENG J, ZONG Y, et al. Hydrophobic graphene nanosheets decorated by monodispersed superparamagnetic Fe$_3$O$_4$ nanocrystals as synergistic electromagnetic wave absorbers[J]. Journal of Materials Chemistry C, 2015, 3(17): 4452–4463.

[32] LIU P B, HUANG Y, YAN J, et al. Magnetic graphene@PANI@porous TiO$_2$ ternary composites for high–performance electromagnetic wave absorption[J]. Journal of Materials Chemistry C, 2016(26): 6362–6370.

[33] LIU P, HUANG Y, ZHANG X. Superparamagnetic NiFe$_2$O$_4$ particles on poly(3,4–ethylenedioxythiophene) – graphene: synthesis, characterization and their excellent microwave absorption properties[J]. Composites Science and Technology, 2014, 95(1): 107–113.

[34] SINGH B P, SAKET D K, SINGH A P, et al. Microwave shielding properties of Co/Ni attached to single walled carbon nanotubes[J]. Journal of Materials Chemistry A, 2015, 3(25): 13203–13209.

[35] ZHANG W M, WU X L, HU J S, et al. Carbon coated Fe$_3$O$_4$ nanospindles as a superior anode material for lithiumion batteries[J]. Advanced Functianal Materials, 2008, 18(24): 3941–3946.

[36] GE J, HU Y, BIASINI M, et al. Superparamagnetic magnetite colloidal nanocrystal clusters[J]. Angewandte Chemie International Edition. 2007, 46(23): 4342–4345.

[37] GAO M, XU Y, WANG X, et al. Analysis of electrochemical reduction process of graphene oxide and its electrochemical behavior[J]. Electroanalysis, 2016, 28(6): 1377–1382.

[38] LI J, LUO R, YAN Y. Densification kinetics and matrix microstructure of carbon fiber/carbon nanofiber/pyrocarbon composites prepared by electrophoresis and thermal gradient chemical vapor infiltration[J]. Carbon, 2011, 49(1): 242–248.

[39] SALIMBEYGI G, NASOURI K, SHOUSHTARI, et al. Microwave absorption properties of polyaniline/poly(vinyl alcohol)/multi–walled carbon nanotube composites in thin film and nanofiber layer structures[J]. Macromolecular Research, 2015, 23(8): 741–748.

[40] ARJMAND M, MAHMOODI M, GELVES G A, et al. Electrical and electromagnetic interference shielding properties of flow–induced oriented carbon nanotubes in polycarbonate[J]. Carbon, 2011, 49(11): 3430–3440.

[41] GUPTA T K, SINGH B P, DHAKATE S R, et al. Improved nanoindentation and microwave shielding properties of modified MWCNT reinforced polyurethane composites[J]. Journal of Materials Chemistry A, 2013(32): 9138–9149.

[42] KAR G P, BISWAS S, BOSE S. Simultaneous enhancement in mechanical strength, electrical conductivity, and electromagnetic shielding properties in PVDF–ABS blends containing PMMA wrapped multiwall carbon nanotubes[J]. Physical Chemistry Chemical Physics, 2015, 17(22): 14856–14865.

[43] PAWAR S P, MARATHE D A, PATTABHI K, et al. Electromagnetic interference shielding through MWNT grafted Fe$_3$O$_4$

（下转第99页）

参考文献

[1] 蒲永伟，宋扬，齐芳，等．U型多区域蜂窝夹层复合材料构件制造工艺探究[C]// 第十届沈阳科学学术年会论文集（信息科学与工程技术分册）．沈阳，2013.

PU Yongwei, SONG Yang, QI Fang, et al. Research on manufacturing process of U-shaped honeycomb sandwich composite materials[C]// Proceedings of the 10th Annual Meeting of the Shenyang Scientific Academic Conference (Information Science And Engineering Technology Branch). Shenyang, 2013.

[2] 李勇．直九机用Nomex蜂窝研究[J]．航空材料学报，1996(1): 47–54.

LI Yong. Research on Nomex honeycomb applied in the Helicopter 9[J]. Journal of Aviation Materials, 1996(1): 47–54.

[3] PARIS I L, HOJJATI M, CHEN J. Characterization of composites sandwich ramp failure under tensile loading[EB/OL].[2018-05-07]. http://www.iccm-central.org/Proceedings/ICCM17proceedings/Themes/Applications/SANDWICH%20STRUCTURES/B6.19%20Paris.pdf

[4] 柳敏静，武湛君．复合材料蜂窝夹层结构在飞机中的应用[J]．科技导报，2016, 34(8): 21–25.

LIU Minjing, WU Zhanjun. The application of composite honeycomb sandwich structure in aircraft[J]. Science & Technology Review, 2016, 34(8): 21–25.

[5] 肖军，李勇，文立伟，等．树脂基复合材料自动铺放技术进展[J]．中国材料进展，2009, 28(6): 28–32.

XIAO Jun, LI Yong, WEN Liwei, et al. Progress in automatic laying of resin matrix composite materials[J]. Progress of Chinese Materials, 2009, 28(6): 28–32.

[6] 李勇，肖军．复合材料纤维铺放技术及其应用[J]．纤维复合材料，2002(3): 39–41.

LI Yong, XIAO Jun. The technology and application of composite fiber laying technology[J]. Fiber Composite, 2002(3): 39–41.

[7] LICHTINGER R, LACALLE J, HINTERHÖLZL R. Simulation and experimental validation of gaps and bridging in the automated fiber placement process[J]. Science & Engineering of Composite Materials, 2015, 22(2): 131–148.

[8] SCHLEDJEWSKI. In first international symposium automated composites manufacturing[C]. Keynote Lecture: Montreal, 2013.

[9] PARIS I L, HOJJATI M, CHEN J, et al. In proceedings of the 17th international conference on composite materials ICCM-17 2009, Edinburgh, 2009.

[10] 台元月，卞航．复杂曲面夹层结构复合材料制件成型工艺研究[J]．科技创新与应用，2016(28): 15–16.

TAI Yuanyue, BIAN Hang. Study on the forming process of complex surface sandwich structure compositematerials[J]. Technological Innovation and Application, 2016(28): 15–16.

[11] 毕红艳，段友社，谢凯文．共固化成型蜂窝夹层结构缺陷分析及工艺改进[J]．航空制造技术，2014, 57(15): 106–109.

BI Hongyan, DUAN Youshe, XIE Kaiwen. Study on process improvement and production defects of co-cured sandwich composite structure[J]. Aeronauetical Manufacturing Technology, 2014, 57(15): 106–109.

[12] 赵渠森，郭恩明．先进复合材料手册[M]．北京：机械工业出版社，2003.

ZHAO Qusen, GUO Enming. Advanced composite material manual[M]. Beijing: China Machine Press, 2003.

[13] 吴鑫．NOMEX蜂窝材料超声切割直刃刀具设计与性能研究[D]．大连：大连理工大学，2016.

WU Xin. Study on the design and performance of ultrasonic cutting edge tool of NOMEX cellular material[D]. Dalian: Dalian University of Technology, 2016.

[14] 赵聪，肖军，王显峰，等．丝束张力对自动铺丝成型工艺的影响[J]．航空学报，2016, 37(4): 1384–1392.

ZHAO Cong, XIAO Jun, WANG Xianfeng, et al. The effect of tow tension on the forming process of automatic wire laying[J]. Acta Aeronautica et Astronautra Sinica, 2016, 37(4): 1384–1392.

[15] 梁滨，刘清方，陶树宇，等．蜂窝夹层结构面板胶粘剂的研究[J]．中国胶粘剂，2001, 10(5): 11–13.

LIANG Bin, LIU Qingfang, TAO Shuyu, et al. Research on the adhesive of honeycomb sandwich panel[J]. China Adhesives, 2001, 10(5): 11–13.

[16] 汪海，沈真．复合材料手册：复合材料夹层结构[M]．上海：上海交通大学出版社，2016.

WANG Hai, SHEN Zhen. Composite material handbook: structural sandwich composites [M]. Shanghai: Shanghai Jiao Tong University Press, 2016.

[17] 朱攀星，杨绍昌．X850树脂预浸料材料工艺性研究[J]．科技展望，2016(24): 70–72.

ZHU Panxing, YANG Shaochang. Study on the technology of X850 resin preimpregnated materials[J]. Technology Outlook, 2016(24): 70–72.

通讯作者：王显峰，博士、副教授，研究方向为复合材料自动化成型软件技术，E-mail: wangxf@nuaa.edu.cn。

（责编 铃兰）

（上接第89页）

nanoparticles in PC/SAN blends[J]. Journal of Materials Chemistry A, 2015, 3(2): 656–669.

[44] LI N, HUANG Y, DU F, et al. Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites[J]. Nano Letters, 2006, 6(6): 1141–1145.

[45] ZHANG H B, YAN Q, ZHENG W G, et al. Tough graphene-polymer microcellular foams for electromagnetic interference shielding[J]. ACS Applied Materials Interfaces, 2011, 3(3): 918–924.

[46] HANG H B, ZHENG W G, YAN Q, et al. The effect of surface chemistry of graphene on rheological and electrical properties of polymethylmethacrylate composites[J]. Carbon, 2012, 50(14): 5117–5125.

[47] YAN D X, PANG H, LI B, et al. Structured reduced graphene oxide/polymer composites for ultra-efficient electromagnetic interference shielding[J]. Advanced Functional Materials, 2015, 25(4): 559–566.

[48] GAO X Y, LI J, GAO Y, et al. Microwave absorbing properties of alternating multilayer composites consisting of poly (vinyl chloride) and multi-walled carbon nanotube filled poly (vinyl chloride) layers[J]. Composites Science and Technology, 2016, 130(1): 10–19.

通讯作者：李进松，博士、讲师，研究方向为碳基复合材料、吸波材料和储能材料，E-mail: lijinsong@buaa.edu.cn。

（责编 铃兰）