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学位の種類	博士（　工学　）
学位記番号	甲　第　７１５　号
学位授与の日付	２０１９年9月３０日
学位授与の要件	信州大学学位規程第５条第１項該当
学位論文題目	Fabrication of functional micro/nano-carbon composites based on structural design for electromagnetic shielding (構造設計による機能性マイクロ・ナノコンポジットの開発および電磁波遮蔽への応用)
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論　文　内　容　の　要　旨

Presently, increasing demand for advanced electromagnetic (EM) shielding devices brought on the development of smart EM shielding materials. In this doctoral research, by using shape memorable polyurethane (SMPU) as supporting matrix, varieties of nano/micro-carbon based composites with different three dimensional structures were designed and fabricated for stimuli-responsive controllable electromagnetic shielding. These functional shielding composites include thickness-adjustable graphite micro-flakes@SMPU sponge (G@SMPU), vapor grown carbon fiber (VGCF) based polyurethane foam (VGCF@PUF), gradient VGCF based shape memory polyurethane foam (VGCF@SMPUF), and unidirectional nonwoven VGCF based polyurethane fibrous membrane (VGCF@PUFM). Shape memory effect was mainly utilized for thickness fixing and bending actuation of those functional shielding composites.

To better understand the memory effect of SMPU on shape driving, multi-layer graphene oxide (MLGO) coated shape memory polyurethane (MLGO@SMPU) was fabricated for adjustable shape memory switching devices. The MLGO, which stacked together in parallel, evenly covered the surface of the SMPU. Stress strain testing indicated that the coating of GO improved the mechanical strength of these MLGO@SMPU composites in the stretching stage below the strain of approximately 6 %. Adhesive force testing suggested that the first GO layer could adhere well to the SMPU surface, but the interaction force between GO layers was weak. The angle recovery ratio and time, bending recovery force, and angle fixity ratio of these MLGO@SMPU composites were evaluated using homemade evaluation apparatus. Results indicated that with the increase of GO layers from one to five layers, the MLGO@SMPU gave an angle recovery ratio reduced to 83.2 %, recovery time decreased to 7.6 s, bending recovery force increased to 18.3 mN, and angle fixity ratio decreased to 83.3 %. This novel and straightforward approach of dipping graphene oxide onto shape memory substrates for adjustable recovery ratio, time and force has the potential to be applied to smart switching devices including sensors and actuators.

Then, by using shape memory effect as driving force, thickness adjustable graphite (G) micro-flakes@shape memory polyurethane (G@SMPU) sponge was fabricated by two-step dipping separately in G-dispersed aqueous solution and SMPU/THF solution for high-performance microwave shielding. The sponge exhibited an ultrahigh G loading ratio (G/sponge, wt/wt) up to 490 wt.%. For the first time, dipping coating of SMPU onto the sponge was proposed, and the obtained G@SMPU sponge exhibited a good recovery effect at least above 90 % after thorough compression. And also, the thickness could be adjusted by utilizing its shape memory property. For microwave shielding, G-9@SMPU and G-18@SMPU sponges achieved the shielding effectiveness over 20 and 30 dB, respectively. Moreover, varying thickness or compressing repeatedly even up to 100 times would not obviously decrease the shielding effect of the G@SMPU sponge. This suggests the steady distribution and adhesion of G micro-flakes inside the three-dimensional sponge substrate due to the fixing of SMPU. This shape memory driving thickness-adjustable G@SMPU sponge could be expected for use in compressible electromagnetic shielding devices.

After that, VGCFs having higher electrical conductivity was used as carbon fillers of polyurethane instead of graphite micro-flakes. By way of dipping coating, VGCF based polyurethane foam was fabricated based on H_2O-DMF solvent exchange for compression-adjusted high-performance microwave shielding. The obtained VGCF@PUF specimens with different thicknesses were obtained by hot compression at 120 ^oC in the pressure range of 0-20 MPa. The tensile test indicated that the hot compression enhanced both the mechanical strength and elongation of the VGCF@PUF. Moreover, with increasing compression, the electrical conductivity of the VGCF@PUF was improved for orders of magnitude. This indicated that the effective inter-connection of VGCFs, achieved by hot compression, is vital for enhancing the electrical conductivity of the VGCF@PUF. In the end, microwave shielding of the VGCF@PUF specimens with different degrees of compression was evaluated by coaxial transmission line method in the frequency range of 0.5-18 GHz. The shielding result showed that increasing compression greatly improved the microwave shielding performance of the VGCF@PUF. For example, the VGCF@PUF specimen with the weight content of approximately 25 %, which had the thicknesses of 1.96 mm and 0.45 mm before and after hot-compression, revealed the difference of shielding effectiveness from 10-15 dB to 35-50 dB. As for the reason, the hot-compression was considered to be able to efficiently improve the electrical inter-connection of the nanoscale carbon fibers in the VGCF@PUF. This research demonstrated the structure optimization of shielding materials is of great importance for improvement of electrical conductivity and microwave shielding performance.

Continually, gradient VGCF based shape memory polyurethane foam (VGCF@SMPUF) was fabricated by alternative dipping in a gradually diluted VGCF@SMPU/DMF solution and distilled water for directional microwave shielding. Shape memory performance for this VGCF@SMPUF was achieved by heat transfer of thermal conductive VGCF. Shielding effectiveness was adjusted through different degrees of angle recovery. A consistent shielding effect from either side indicated that electromagnetic reflection may take place at both the surface and inside of the non-homogeneous composite shield. For shape memory effect, hot compression made VGCF@SMPUF achieve a faster recovery time and higher recovery ratio owing to improved thermal conductivity. Moreover, the VGCF@SMPUF, which was bent to the positive side (PS) with a higher VGCF content, showed shorter recovery time and higher recovery ratio than that bent to the negative side (NS) with a lower VGCF content. We attribute this result to the relatively small mechanical compression strength of the negative side with the lower VGCF content at the bending point when expanding from the positive side. Furthermore, hot compression obviously improved the shielding effectiveness (SE) of the VGCF@SMPUF, mainly through a considerable increase of the electrical conductivity. The VGCF@SMPUF hot compressed to a thickness of 0.11 mm achieved a SE value of ~30 dB, corresponding to a shielding efficiency of ~99.9 %.

Following with the gradient carbon composites, anisotropic structure was designed for direction-dependent EM shielding. In this part, unidirectional nonwoven VGCF based polyurethane (PU) fibrous membrane (VGCF@PUFM) was fabricated by rotation spinning based on DMF-H2O exchange for directional microwave shielding. This VGCF@PUFM showed obviously different electrical conductivity and mechanical strength in parallel and perpendicular directions. Variational microwave shielding effectiveness (SE) could be observed by changing the crossing angles of VGCF@PUFM with vibrational direction of EM wave. There was the shielding difference more than 10 dB (above 20 dB in 0°, below 8 dB in 90°). Greater shielding effectiveness could be expected by enhancing the anisotropy of electrical conductivity of the VGCF@PUFM. In addition, oriented alignment of VGCF in fibre is promising for further improvement of the electrical conductivity in fibre direction.

In summary, three types of carbon based composite structures, foam structure, gradient structure, and unidirectional structure were successfully designed by using graphite micro-flakes or VGCF as fillers, and SMPU as filling matrix. Shape memory effect played the role of thickness fixing and bending actuation. By varying thickness or angles, those unique structures showed adjustable EM shielding in the decibel range of 0-40 dB. These functional EM shielding composites opened up a new insight for development of smart EM shielding devices.