Study on Dielectric and Thermal Properties of ABS / multilayer graphene Composites

Bo Song
Jiangmen Polytechnic, Jiangmen 529090, Guangdong, China
sb8099@126.com

Abstract: ABS / multilayer graphene (MLGN) composites were prepared by melt blending ABS and multilayer graphene masterbatch, and their dielectric and thermal properties were studied. The results show that the dielectric constant, dielectric loss, conductivity, thermal decomposition temperature and thermal conductivity of ABS / MLGN composites increase with the increase of MLGN content. The content of MLGN in ABS /MLGN composites with conductive percolation is between 7-8%. When the mass content of MLGN increased to 7%, the dielectric constant of the composite increased from 3.01 to 103.23, the dielectric loss increased from 0.058 to 0.83 at 100Hz, the 5% mass loss temperature of the composite increased by 17.0℃ and the thermal conductivity increased by 1.9 times. The research results can provide reference for the preparation of thermally conductive polymer dielectric composites.

1. Introduction
Polymer dielectric materials have attracted more and more attention because of their good processability and flexibility, but their applications are limited by their low dielectric constant and poor thermal conductivity. Inorganic ceramic materials [1, 2] and conductive particles [3, 4] are usually required for modification. Among them, graphene has been studied more because of its excellent electrical properties. The research method is mainly to blend graphene oxide with polymer solution and then reduce graphene oxide. The process flow of this method is complex, solvent is needed, and graphene is expensive, which is unfavorable for industrial application. In terms of polymers, PVDF with high dielectric constant is most used, but PVDF has the disadvantages of high relative price and large proportion (1.77~1.80g/cm³).

This paper uses the general electrical plastic ABS (specific gravity 1.05~1.10g/cm³) as the matrix resin, modified with multilayer graphene(MLGN) masterbatch, and prepared composites with high dielectric constant and improved thermal conductivity through melt blending. This method is simple and low cost, which provides a useful reference for the preparation of new polymer dielectric composites.

2. Experimental

2.1 Materials
MLGN masterbatch (ABS matrix, graphene content 20%), Jiangsu carbon Feng graphene Technology Co., Ltd.; ABS, 757, Taiwan Qimei Industrial Co., Ltd.
2.2 Sample preparation
Firstly, ABS and ABS / MLGN masterbatch were dried by hot air at 100 °C for 2 h. Then mix according to the mass ratio, melt and blend in the torque rheometer (Harpo 200C, Harbin Harpo Electric Technology Co., Ltd.) for 10 min, the mixing temperature is 190 °C, and the rotating speed is 60 rpm after granulation, press it into 2 mm thin sheets in a small manual tablet press (ZG-50t, Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd.).

2.3 Test
The material is subjected to thermogravimetric analysis (DTG-60, Shimadzu Corporation, Japan) under the protection of nitrogen at a heating rate of 10°C/min. High insulation resistance meter is used (ZG-90G, Shanghai Taiou Electronics Co., Ltd.) tested the volume resistivity of the material. The thermal conductivity of the composite was tested with the drl-2a thermal conductivity tester of Xiangtan Xiangyi Instrument Co., Ltd. and the AC dielectric properties were tested. (WY2858, Shanghai Wuyi Electronic Equipment Co., Ltd).

3. Results and discussion

3.1 volume resistivity and AC conductivity of ABS /MLGN Composites

Fig.1 DC electrical resistivity of ABS /MLGN composites as a function of graphite content

Fig.1 is a graph showing the relationship between the content of multilayer graphene (MLGN) and the logarithm of the volume resistivity of the ABS/MLGN composite. It can be seen from the graph that the volume resistivity of composites decreases nonlinearly with the increase of mass content, decreases slowly when the mass content is less than 7%, and decreases significantly between 7-8%. It shows that MLGN content forms a conductive channel between 7-8%, the resistivity decreases significantly, and percolation occurs.

Fig.2 AC electrical conductivity of ABS/MLGN composites with difficult MLGN contents as a function of frequency
Fig. 2 is the double logarithm relationship between AC conductivity and applied electric field frequency of ABS / MLGN composites with different mass MLGN content. It can be seen from the figure that under the same applied electric field frequency, the conductivity of the composite increases with the increase of MLGN content. Under the condition of constant composition, the conductivity of the composite increases with the increase of applied electric field frequency, but the increase amplitude decreases with the increase of MLGN content, showing the characteristics of conductive filled composites. When the mass content of MLGN is 8%, the increase in conductivity does not exceed an order of magnitude. The results show that MLGN forms a conductive network structure in the composite when the mass content is 8%, which further indicates that the percolation transition of the system is between 7-8% of MLGN.

3.2 Dielectric constant and dielectric loss of ABS / MLGN Composites

Fig. 3 Dielectric constant of ABS/MLGN composites with difficult MLGN contents as a function of frequency

Fig. 4 Dielectric loss of ABS/MLGN composites with difficult MLGN contents as a function of frequency

Fig. 3 and 4 show the dielectric constant $\varepsilon_r$ and dielectric loss factor $\tan\delta$ of ABS/MLGN composites with different qualities of MLGN content versus frequency. As can be seen from the figure, under the same applied electric field frequency $\varepsilon_r$ and $\tan\delta$ All increased with the increase of MLGN content. Taking 100Hz as an example, when the MLGN content is 7%, the $\varepsilon_r$ of the composite material increases from 3.01 to 103.23, an increase of more than 30 times; the $\tan\delta$ increases from 0.058 to 0.83, but still less than 1.

It can also be seen from the figure that when the content of MLGN is low, $\varepsilon_r$ and $\tan\delta$ do not change much with frequency. When the MLGN content is higher, the $\varepsilon_r$ and $\tan\delta$ of the composite material decrease with increasing frequency, and the more MLGN content, the more sensitive $\varepsilon_r$ and $\tan\delta$ change with frequency. For example, when the MLGN content is 8%, as the electric field frequency increases from $10^2$ Hz to $10^6$Hz, the $\varepsilon_r$ of the composite material rapidly decreases
from 247.28 to 25.41, and the tanδ decreases from 80.77 to 0.97. The reason is that when the MLGN content is small, the dielectric properties are mainly generated by the dipole polarization of the matrix, and the dipole polarization time is about \(10^{-9}\) seconds, so it is not affected by the frequency. With the increase of MLGN, the interface polarization increases. The time of interface polarization is \(10^{-2} - 10^{-6}\) seconds [5], which is within the frequency range of the experimental electric field. Therefore, it is greatly affected by the frequency of the electric field, resulting in an increase in tanδ. In addition, the micro capacitance composed of two conductive MLGN particles in the system increases, and the combined action of the two makes the material more stable \(\varepsilon_r\) increase. When the MLGN content reaches the percolation threshold, the MLGN is interconnected to form a conductive network structure in the matrix, resulting in a sharp increase in leakage current and conductivity loss, tan δ was a significant increase [6].

3.3 Thermal stability of ABS / MLGN Composites

Fig. 5 shows the thermogravimetric analysis of ABS / MLGN composites with different MLGN contents. It can be seen from the figure that the thermogravimetric curves of the composites are similar, indicating that MLGN does not change the thermal degradation mechanism of ABS. The thermogravimetric curve shifted to the right with the increase of MLGN content, indicating that the addition of MLGN increased the thermal decomposition temperature of ABS. Generally, the characteristic temperature is 5% mass loss of material. The temperature of pure ABS with 5% mass loss is 388.6 °C, 394.6 °C with 3% MLGN, an increase of 6.0 °C, and 405.6 °C with 7% MLGN, an increase of 17.0 °C. The reason may be that there is a strong force between ABS and MLGN. MLGN with excellent heat resistance inhibits the thermal degradation of ABS and improves the thermal stability of the composites.

3.4 Thermal conductivity analysis of composites

Fig. 6 Thermal conductivity of ABS / MLGN composites as a function of graphite content
Fig. 6 shows the effect of MLGN content on the thermal conductivity of the composite. It can be seen from the figure that the overall thermal conductivity of the composite shows a nonlinear upward trend with the increase of the filler filling amount. This is because when the content of MLGN is small, it exists in the continuous ABS matrix resin phase in the form of a single particle, does not form an interactive and contact heat conduction network, has limited effect on improving the thermal conductivity of the material, and the thermal conductivity is very low. With the increase of graphite content, isolated graphene is gradually lapped together, the thermal conductivity network is gradually formed and increased, and the thermal conductivity is gradually increased. The thermal conductivity of pure ABS is 0.18 W/(m.K). When the addition of graphite increases to 7%, the thermal conductivity increases to 0.35 W/(m.K), an increase of 91%.

4. Conclusion
(1) The conductive percolation range of ABS / MLGN composites is 7-8% of MLGN mass content.
(2) At the same frequency of applied electric field, the $\varepsilon_r$ and tan$\delta$ all increased with the increase of MLGN. At 100Hz and MLGN mass content of 7%, $\varepsilon_r$ increased from 3.01 to 103.23, tan$\delta$ increased from 0.058 to 0.83.
(3) When the content of MLGN was 7%, the 5% mass loss temperature of the composite increased by 17.0$^\circ$C.
(4) The addition of MLGN improves the thermal conductivity of the composites. When the content is 7%, the thermal conductivity increases by 91%.

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