Effect of Graphene Encapsulated Styrene-butyl Acrylate Copolymer Microspheres on Enhancing the Dielectric Properties of Polymethyl Methacrylate

Feng You

Wuhan Institute of Technology <https://orcid.org/0000-0001-6622-9965>

Cong Zhou

Wuhan Institute of Technology

Zitong Peng

Wuhan Institute of Technology

Xueliang Jiang (✉ Jiangxl@wit.edu.cn)

Wuhan Institute of Technology

Chu Yao

Wuhan Institute of Technology

Junlong Yao

Wuhan University of Technology

Pei Zhao

Wuhan Institute of Technology

Research Article

Keywords: Styrene-butyl acrylate copolymer, Dielectric constant, Segregated network

Posted Date: March 31st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-353941/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In this work, the dielectric properties of polymethyl methacrylate (PMMA) were obviously improved by using graphene encapsulated microspheres through soap-free emulsion polymerization technique. Scanning electron microscope (SEM) observation implied that styrene-butyl acrylate copolymer (SBA) microspheres and reduced graphene oxide encapsulated SBA microspheres (rGO@SBA) was successfully obtained through using soap-free emulsion polymerization. The dielectric constant of PMMA/rGO@SBA could reach 46.64 at 1000 Hz by incorporating only 0.26 wt% rGO. On the other hand, three different PMMA based composites were also prepared by adding rGO and SBA through conventional emulsion polymerization and simple physical blending. The dielectric constant results revealed that all these composites presented low dielectric constant compared with composites through soap-free emulsion polymerization technique. The possible reason was that the isolated rGO sheets can interconnect with each other to form three-dimensional segregated network structure through hot pressing technique. SEM results demonstrated that the rGO encapsulated SBA structure could be retained after hot pressing. Therefore, soap-free emulsion polymerization technique can favorably fabricate rGO encapsulated polymer microspheres with high dielectric properties.

Introduction

With the development of electronic technology, the demand for dielectric materials is pressing and the ultimate performance requirements are high^[1–3]. Dielectric composites range from dielectric-dielectric composites to dielectric-conductive composites and then composite fillers are added to the composites to improve the dielectric constant of the composites and control the dielectric loss and percolation threshold of the composites^[4–7]. The so-called dielectric-dielectric composite material is to add ceramic fillers to the composite material. However, the dielectric-dielectric composites usually need to be filled with high content of ceramic fillers in order to improve the dielectric properties of the composites^[8–11]. Later, dielectric-conductive composites have been gradually developed, that is, conductive fillers were added to polymer matrix composites to control the amount of fillers^[12]. Owing to the leakage current caused by the polarization of conductive fillers in composites, the dielectric loss of composites is increased. Thereafter, composite fillers with core-shell structure have been further developed^[12]. Because of the existence of isolation shell, the leakage current of composite materials in interfacial polarization can be constrained, thus the dielectric loss of composite materials can be effectively controlled^[14–16].

Many researchers have been committed to the core-shell structure of composite materials and their dielectric properties^[17–19]. Zhang and co-workers have investigated the effect of metal-semiconductor Zn-ZnO core-shell structure on the dielectric properties of polyvinylidene fluoride (PVDF) composites^[20]. Their results found that Zn-ZnO/PVDF composites have higher dielectric constant than that of Zn/PVDF composites. This can be attributed to duplex interfacial polarizations induced by metal-semiconductor interface and semiconductor-insulator interface. Liang^[21] et al. have prepared a composite material by embedding a core-shell Ag@TiO₂ filler in polytetrafluoroethylene. Ag nanoparticles were homogeneously

coated with TiO_2 to give a shell thickness of approximately 810 nm. The composite containing Ag@TiO_2 nanoparticles with rutile shells exhibited better dielectric properties than that of the composite containing Ag@TiO_2 nanoparticles with anatase shells. The relative permittivity (ϵ_r) of the composite containing 70 vol % filler was approximately 240 at 100Hz, which was more than 100 times higher than that of pure polytetrafluoroethylene.

The fabrication methods can affect the final dielectric properties of composite materials^[22–24]. Chao^[25] et al. have prepared $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) particles by sol-gel method (sg) and solid-state (ss) method respectively. The CCTO distribution obtained by the sg method is more uniform and the particle size is about 480nm. Thus, it can realize more stable chemical activation and lower crystallization temperature, which have improved the dielectric constant of the composites. The results showed that the dielectric constant of CCTO-sg/PVDF composites reaches 62.3 at 100 Hz when the content of CCTO-sg is 50 wt%. The dielectric constant of CCTO-sg/PVDF composites is twice as high as that of CCTO-ss/PVDF composites with the same filler content.

In this work, the dielectric properties of polymethyl methacrylate (PMMA) were obviously improved by using graphene encapsulated microspheres through soap-free emulsion polymerization technique. The composites microspheres were made of reduced graphene oxide (rGO) encapsulated styrene-butyl acrylate copolymer (SBA) microspheres. In our previous study, high dielectric constant rGO@SBA composites were obtained when the rGO loading was approximated to 2 wt%^[26]. Furthermore, the effect of other two different fabrication methods on the dielectric properties of composites was also compared. Namely, the conventional emulsion polymerization and simple physical blending of SBA and rGO was obtained. The three different composites fabricated by soap-free emulsion polymerization, conventional emulsion polymerization and simple physical blending were denoted as PMMA/rGO@SBA , PMMA/rGO-SBA and PMMA/rGO/SBA composites, respectively. The effect of rGO loading on the dielectric properties of these three different composites was discussed in detail.

Experimental

In this work, styrene butyl acrylate copolymer was prepared. Styrene-butyl acrylate (SBA) copolymer and styrene-butyl acrylate copolymer microspheres were obtained by conventional emulsion polymerization and soap-free emulsion polymerization, respectively. Graphene oxide was prepared by modified Hummers method^[27] to coat the outer layers of corresponding copolymer or copolymer microspheres. The coating effect was achieved by non-covalent π - π bonding. Then, graphene-styrene-butyl acrylate copolymer (rGO-SBA) and graphene@styrene-butyl acrylate copolymer microspheres (rGO@SBA) can be obtained. PMMA/rGO-SBA composites and PMMA/rGO@SBA composites were prepared by adding rGO-SBA and rGO@SBA into polymethyl methacrylate (PMMA) matrix, PMMA/rGO/SBA composites mean that the prepared SBA copolymer and rGO were directly added into PMMA matrix. In this paper, the effects of different preparation methods on the dielectric properties of PMMA composites were explored. The

effects of physical blending, conventional emulsion polymerization and soap-free emulsion polymerization on the structure of PMMA composites were compared.

The preparation procedure of rGO-SBA composite filler was as following. Firstly, a certain mass ratio of purified styrene (61.1g) and acrylic acid (28.9 g) monomer was poured into a three-necked flask, a small amount of sodium bicarbonate and sodium dodecyl sulfonate (SDS, emulsifier) was dissolved in a beaker containing deionized water. After stirring well, it was slowly dripped to a three-necked flask and mechanically stirred at 80 ° C for 1 h in a water bath. A small amount of an aqueous solution of ammonium persulfate (APS) was slowly added to a three-necked flask, then the reaction began at 70 ° C for 2 h to obtain an emulsion of SBA copolymer. An appropriate amount of 5% calcium chloride solution was slowly added to the emulsion, and reacted for 0.5 h under mechanical stirring. The emulsion was divided into two layers. After the supernatant was discarded, the SBA copolymer particles were freeze-dried to obtain SBA powders. On the other hand, a certain amount of graphene oxide powder was weighted and dissolved in an appropriate amount of deionized water, and sonicated for 2 h. Then, the SBA copolymer emulsion and the graphene oxide suspension were poured into a three-necked flask, further sonicated for 2 h, and 5 ml of hydrazine hydrate was slowly added dropwise to the reaction solution, and reacted at 95 °C for 3h under mechanical stirring and nitrogen protection. Finally, the rGO-SBA suspension was freeze-dried for several days to obtain rGO-SBA composite filler.

For the fabrication of rGO@SBA composite filler, the procedures were similar to our previous study [26]. The first step was to synthesize SBA microspheres, generally, purified styrene (20g) and butyl acrylate (3g) was poured into a three-necked flask with a water bath. Then a certain amount of deionized water was added with mechanically stirred under the condition of nitrogen protection. After the water bath temperature reached 70°C, the prepared APS aqueous solution was slowly dripped to this solution, and the reaction was carried out for 8 hours. Subsequently, the SBA microspheres emulsion was obtained by through freeze-drying for several days. Then the SBA microspheres powders were obtained. In addition, a certain amount of graphene oxide powder was weighed and dispersed in an appropriate amount of deionized water, and sonicated for 2h. Then, the SBA microspheres emulsion and the graphene oxide suspension were poured into a three-necked flask, further sonicated for 2h, and 5 ml of hydrazine hydrate was slowly added, and subjected to mechanical stirring with nitrogen protection at 65°C for 6h. Finally, the rGO@SBA suspension was freeze-dried for several days to obtain rGO@SBA powders.

The rGO-SBA and rGO@SBA powders as prepared above were mixed with PMMA powder by using a high speed mixer. 87 wt% PMMA with 13 wt% rGO-SBA or 13 wt% rGO@SBA composite filler was hot-pressed in a self-made mold at 180°C for 15 min under 15 MPa to obtain PMMA/rGO-SBA and PMMA/rGO@SBA composites. The diameter and thickness of sample were 10 mm and 1 mm, respectively. In addition, the as-prepared SBA microsphere powders and reduced graphene oxide were also added in PMMA matrix to fabricate PMMA/rGO/SBA by simple physical blending. The effects of physical blending, conventional emulsion polymerization and soap-free emulsion polymerization on the structure of PMMA composites were compared. The PMMA/rGO composites without SBA were also fabricated. The content of SBA and

rGO in all composites was fixed. Especially, the weight fraction of SBA in all composites was fixed at 13 wt%.

The prepared SBA and rGO coated SBA microspheres were characterized by JSM-5510LV scanning electron microscope manufactured by JEOL. The sample powder was placed on a glass slide, sprayed with gold for 2 min, and the accelerating voltage was 20kV. The dielectric properties of samples with dimension of 1 cm² were tested by Agilent 4294A impedance analyzer manufactured in the USA at room temperature, and the test frequency was at 10³ Hz ~ 10⁶ Hz.

Results And Discussion

The morphologies of SBA and rGO@SBA microspheres are given in Fig. 1. It can be seen that the diameter of SBA microsphere is uniform and the average dimension is about 500 nm. After encapsulating rGO, the diameter of rGO@SBA microspheres began to exhibit uneven distribution. The dimension of rGO@SBA microspheres is larger than that of SBA. Moreover, the surfaces of rGO@SBA microspheres become coarse and some wrinkled rGO flakes are embellished on the SBA microspheres.

The effect of rGO@SBA microspheres on the dielectric properties of PMMA was investigated. First, the effect of rGO content on the dielectric properties of PMMA/rGO@SBA and PMMA/rGO-SBA composites was discussed.

As shown in Fig. 2, the incorporation of rGO-SBA or rGO@SBA could affect the dielectric properties of PMMA. For PMMA/rGO-SBA composites by using conventional emulsion polymerization, both the dielectric constant and dielectric loss did not elevate. On the contrary, the dielectric constant of PMMA/rGO@SBA composites was increased greatly with the rGO loading. After incorporating 0.26 wt% rGO, the dielectric constant reached 46.64 at 1000 Hz, which was 11 times of PMMA/SBA blends without rGO. Taking the low addition of rGO for consideration, the enhancing effect is remarkable. The dielectric constant of composites began to decrease when the weight fraction of rGO exceeded 0.26 wt%. Therefore, the threshold percolation of dielectric constant for PMMA/rGO@SBA system can be ensured to about 0.26 wt%. The possible reason is that the rGO encapsulated SBA microspheres is in a segregated dispersion in PMMA matrix. The successful encapsulation of rGO on SBA microspheres resulted from the non-covalent π - π stacking effect^[28]. An interconnected three-dimensional network structure could be formed among the isolated rGO through hot pressing technique. These segregated rGO@SBA domains can be served as large amount of microcapacitors. On the other hand, the dielectric loss of PMMA/rGO@SBA composites was also obviously enhanced with rGO loading.

As shown in Fig. 3a, the dielectric loss of PMMA/rGO@SBA with 0.26 wt% rGO is increased to 4.8 at 1000 Hz. This is because that the rGO content reaches the percolation threshold, and the perfect three-dimensional network structure formed in the composite material generates a large amount of leakage current, which increases the dielectric loss of the composite material. In addition, the incorporation of rGO@SBA composite filler can increase the electrical conductivity of PMMA/rGO@SBA composites,

which further exacerbates the increase of dielectric loss. Therefore, the incorporation of rGO should be controlled in a low level to avoid the high dielectric loss.

At the same time, the effect of different fabrication methods on the dielectric properties was also analyzed. The results are presented in Fig. 4 by taking the 0.26 wt% weight fraction of rGO for an example. The dielectric constant of all composites is higher than that of PMMA/SBA blends (the dielectric constant is 4.36 at 1000 Hz). However, the enhancement of dielectric constant is in a low level except PMMA/rGO@SBA composites. Compared with other three composites, the dielectric constant of PMMA/rGO@SBA composites with 0.26 wt% rGO can reach 46.64 at 1000 Hz, indicating the segregated structure of rGO@SBA microspheres in PMMA matrix can generate the three-dimensional network. In addition, the dielectric loss results also exhibited similar tendency. The dielectric loss of PMMA/rGO@SBA composites through soap-free emulsion polymerization exceeds much than that of other three composites. Obviously, these different dielectric properties were resulted from their different dispersion of SBA and rGO in PMMA matrix, their related morphologies can be found in Fig. 5. Obvious disparities can be found for these composites. Though the conventional emulsion polymerization can fabricate SBA microspheres, the dimension distribution of SBA is unevenly for PMMA/rGO-SBA composites. In addition, the improper diameter of SBA is also not suitable for rGO to interconnect with each other. Subsequently, the enhancement of dielectric properties is limited. Compared with PMMA/SBA/rGO and PMMA/rGO composites, the dispersion of rGO@SBA microspheres in PMMA matrix exhibited a segregated structure, which would benefit for the formation of percolation pathway. The rGO encapsulated SBA structure could be retained after hot pressing. The wrinkled rGO sheets can be found to locate around the SBA microspheres. Thus, the rGO sheets on SBA microspheres can interconnect with each other to generate percolation pathway. Consequently, the dielectric properties of PMMA matrix could be remarkably enhanced by incorporating little amount of rGO. Therefore, composites with high dielectric properties can be obtained through appropriate structure design by controlling their fabricating procedures.

Conclusions

The effect of rGO encapsulated SBA microspheres (SBA) on the dielectric properties of PMMA was investigated. rGO@SBA microspheres were successfully fabricated through soap-free emulsion polymerization technique. Dielectric measurement revealed that the dielectric constant of PMMA/rGO@SBA composites with 0.26 wt% rGO was 11 times than that of PMMA/SBA blends at 1000 Hz. In addition, three different PMMA based composites were also prepared by adding rGO and SBA conventional emulsion polymerization. Results illustrated that all three composites presented lower dielectric constant than that of PMMA/rGO@SBA composites at the same content of rGO. The fabricated dielectric composites through incorporating segregated structure of rGO encapsulated microspheres will be a favor approach to obtain high dielectric properties. This preparation method has potential application value and prospect in the preparation of composite materials in the field of embedded electronics equipment.

Declarations

Acknowledgements This work was financially supported by the National Natural Science Foundation of China(No. 51972241), Natural Science Foundation of HuBei Province (No. 2017CFB289) and Guangdong Basic and Applied Basic Foundation (No. 2019A1515110465). We also want to thank for the friendly technical support from Professor Zhimin Dang, Tsinghua University.

Conflict of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- 1 Z. H. Dai, T. Li, Y. Gao, J. Xu, J. L. He, Y. X. Weng and B. H. Guo, *Compos. Sci. Technol.*, **169**, 142 (2019).
- 2 P. Xu, W. J. Fu, Z. P. Cui, and Y. S. Ding, *Appl. Phys. Lett.*, **112**, 6 (2018).
- 3 M. H. Yang, H. Zhao, D. L. He, and J. B. Bai, *Appl. Phys. Lett.*, **109**, 7 (2016).
- 4 P. F. Ma, L. L. Du, Y. M. Wang, R. Jiang, Q. Xin, Y. X. Li, and A. Song, *Appl. Phys. Lett.*, **112**, 2 (2018).
- 5 R. Moucka, M. Sedlacik, and M. Cvek, *Appl. Phys. Lett.*, **112**, 12 (2018).
- 6 M. Savinov, V. Bovtun, E. Tereshina-Chitrova, A. Stupakov, A. Dejneka, and M. Tyunina, *Appl. Phys. Lett.*, **112**, 5 (2018).
- 7 N. H. Wan, S. Mouradian, and D. Englund, *Appl. Phys. Lett.*, **112**, 14 (2018).
- 8 A. Zyane, A. Belfkira, F. Brouillette, P. Marchet, R. Lucas, J. Appl. Polym. Sci., **133**, 48 (2016).
- 9 B. H. Fan, Y. Liu, D. L. He, and J. B. Bai, *Appl. Phys. Lett.*, **112**, 5 (2018).
- 10 F. Wen, J. F. Ye, L. L. Li, Z. Xu, W. Wu, Z. C. Zhang, G. F. Wang, *Ceram. Int.*, **45**, 1 (2019).
- 11 D. R. Wang, Y. R. Bao, J. W. Zha, J. Zhao, Z. M. Dang, and G. H. Hu, *ACS Appl. Mater. Inter.*, **4**, 12 (2012).
- 12 J. Yu, Y. D. Lian, W. Xu, C. L. Wang, X. L. Chang, T. B. Tang, and M. Gu, *Appl. Phys. Lett.*, **112**, 17 (2018).
- 13 Y. Huang, J. P. Xu, L. Liu, Z. X. Cheng, P. T. Lai, and W. M. Tang, *Appl. Phys. Lett.*, **111**, 5 (2017).
- 14 H. Y. Wang, Q. Fu, J. Q. Luo, D. M. Zhao, L. H. Luo, and W. P. Li, *Appl. Phys. Lett.*, **110**, 24 (2017).
- 15 G. X. Tong, Y. Liu, T. T. Cui, Y. N. Li, Y. T. Zhao, *Appl. Phys. Lett.*, **108**, 7 (2016).

- 16 H. B. Sun, H. L. Zhang, S. T. Liu, N. Y. Ning, L. Q. Zhang, M. Tian, Y. Wang, *Compos. Sci. Technol.*, **154**, 145 (2018).
- 17 Y. Feng, W. L. Li, J. P. Wang, J. H. Yin, and W. D. Fei, *J. Mater. Chem. A.*, **3**, 40 (2015).
- 18 D. L. He, Y. Wang, X. Q. Chen, and Y. Deng, *Compos. Part. A-Appl. S.*, **93**, 137 (2017).
- 19 X. H. Zhang, S. D. Zhao, F. Wang, Y. H. Ma, L. Wang, D. Chen, C. W. Zhao, W. T. Yang, *Appl. Surf. Sci.*, **403**, 71 (2017).
- 20 Y. Zhang, Y. Wang, Y. Deng, M. Li, and J. B. Bai, *ACS Appl. Mater. Inter.*, **4**, 1 (2012).
- 21 F. Liang, L. Zhang, W. Z. Lu, Q. X. Wan, and G. F. Fan, *Appl. Phys. Lett.*, **108**, 7 (2016).
- 22 A. P. Sobha, and S. K. Narayanankutty, *IEEE. T. Nanotechnol.*, **13**, 4 (2014).
- 23 Z. H. Peng, P. F. Liang, X. Wang, H. Peng, Y. C. Xiang, X. L. Chao, Z. P. Yang, *Ceram. Int.*, **44**, 7(2018).
- 24 D. Wang, X. Zhang, J. W. Zha, J. Zhao, Z. M. Dang, and G.-H. Hu, *Polymer.*, 54, 7 (2013).
- 25 X. L. Chao, P. Wu, Y. Zhao, P. F. Liang, Z. P. Yang. *J. Mater. Sci: Mater. Electron.*, **26**, 6 (2015).
- 26 X. L. Jiang, W. W. Guo, F. You, Z. M. Dang, C. Yao, J. L. Yao, F. J. Liu and Y. H. Zhang, *Synthetic Metals.*, **259**, 116229 (2020).
- 27 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, *ACS Nano*, **4**,8(2010).
- 28 L. F. Wei, W. B. Zhang, J. Z. Ma, S. L. Bai, Y. J. Ren, C. Liu, D. Simion, J. B. Qin, *Carbon.*, **149**, 679 (2019).

Figures

Figure 1

SEM images of SBA(a) and rGO@SBA microspheres with 2 wt% rGO (b)

Figure 2

Frequency dependence of dielectric constant of PMMA/rGO@SBA (a) and PMMA/rGO-SBA (b) composites with different rGO loadings

Figure 3

Frequency dependence of dielectric loss of PMMA/rGO@SBA (a) and PMMA/rGO-SBA (b) composites with different rGO loadings

Figure 4

Comparison of different fabricating methods on the dielectric properties of composites: (a) dielectric constant, (b) dielectric loss

Figure 5

SEM images of fracture surfaces for four different composites with 0.26 wt % rGO: (a) PMMA/rGO-SBA, (b) PMMA/rGO/SBA, (c) PMMA/rGO, (d) PMMA/SBA@rGO