

**Improving thermal conductivity of polyethylene/polypropylene by styrene-ethylene-propylene-styrene wrapping h-BN at the phase interface**

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**Abstract**

In this work, the polyethylene (PE) and polypropylene (PP) percentage is controlled at 50:50 to make the composite form a co-continuous structure; the hexagonal boron nitride (h-BN) is wrapped by thermoplastic elastomer styrene-ethylene-propylene-styrene (SEPS). This approach enables the localized distribution of h-BN at the interface of the co-continuous structure of PE/PP/SEPS/h-BN composite material, allowing the construction of a heat conduction path, thereby improving the thermal conductivity of PE/PP. Theoretical calculation predicted the localized distribution of SEPS at the interface of the PE/PP composite co-continuous structure.

The thermal conductivity of the composites can be improved by 57.7% by adding 10 wt% h-BN, presenting a commercial potential of such composites in heat dissipation applications.

**Keywords:** Hexagonal boron nitride; thermal conductivity; co-continuous phase; phase interface.

## 1. Introduction

The miniaturization of electronic components has led to high density heat generation in a limited volume. For electronic devices, such as light-emitting diodes (LEDs) and integrated circuits, high thermal conductivity and electric-insulating materials are often required to promote heat dissipation of electronics [1]. Effectively addressing the heat dissipation problem of high-power devices and highly integrated electronic components can significantly improve their stability and service life [2-6]. Three typical methods have been adopted to improve the thermal conductivity of composites. The first one is the filler compounding. For example, Cao *et al.* [7] obtained high thermal conductivity and high electrical resistance of polyvinylidene fluoride (PVDF)/polystyrene (PS) composites by the localization of both fillers in the minor phase. The 2<sup>nd</sup> is the filler modification. To increase the dispersion of dropped epoxy resin on the top of SiC cake, a surface oxidation treatment was applied to the SiC particles. The introduction of hydroxyl groups on the surface greatly increases the wettability between epoxy matrix and SiC, which reduces the interfacial voids and improves the thermal conductivity of the composites [8]. The third one is the processing technology. For example, Agari *et al.* [9] compared the powder mixing, solution mixing,

roll mixing and melting mixing methods in preparing polypropylene (PP)/graphite composites. It was found that the powder mixing method has the highest thermal conductivity.

Polymer blending can not only improve the material performance, but also reduce the cost of products [10-14]. However, single polymer blending cannot achieve high thermal conductivity, even with the addition of inorganic fillers. Therefore, it is necessary to design and construct thermal conductive pathway in the composite system with a desired material structure.

The thermal conductivity of most polymers is around 0.2 W/mK [15-17], which is far below the requirements of practical applications. The advantages of polymers are also obvious such as excellent electrical insulation, light weight, easy processing, corrosion resistance and moisture resistance in various electronic packaging applications. Therefore, polymer-filler compounding has been explored as a feasible approach to address the thermal conduction issue [18-24]. The thermal conduction of polymer composites is analogous to the "percolation threshold" in the electrical conduction process. Without fillers, the thermal conduction of polymer relies on photon transfer between intra- and inter- polymer chains, which is typically a low-efficient process. When adding fillers to certain amount, the fillers get in touch with each other to form a heat conduction channel, which plays a major role in heat transfer. Since photon scattering is easy to occur at the polymer/filler interface, it is often preferred to align the fillers into oriented structure for better thermal conduction [25-27].

The performance of polymer blends is not only determined by the molecular structure, but also depends on the phase morphology [28-30]. For example, the droplet structure usually appears

in the toughening system of the blend, the fiber structure is commonly seen in the blend reinforcement system, and the co-continuous structure is more common in the conductive and thermal polymer materials. When adding fillers to the polymer blending system, the difference in the affinity of the fillers to different components in the blending system can be used to promote the filler distribution. When the filler is selectively positioned in one of the two phases or at the interface, higher thermal conductivity can be achieved by fewer fillers [31]. In this way, the filler required to establish a permeable thermal network is minimized [32].

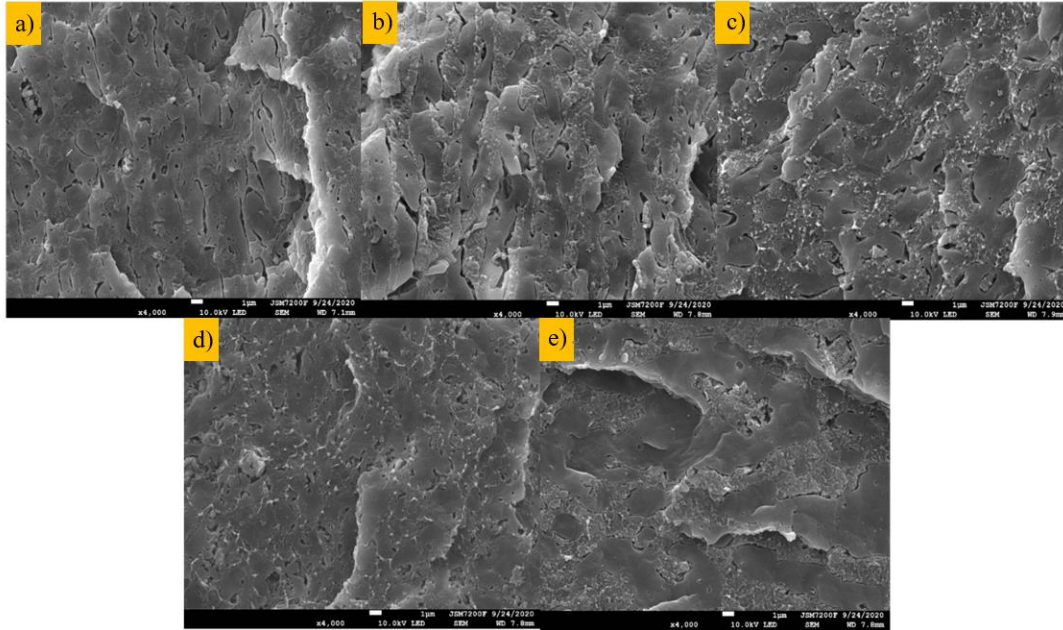
In this work, both high thermal conductivity and insulating composite materials were achieved in the binary PE and PP matrix by a novel strategy to realize the positioning of the filler by wrapping the filler with a carrier. That is, the SEPS/h-BN composite material was prepared first, and then the SEPS/h-BN composite material was used as the masterbatch, and PE/PP/SEPS/h-BN composite materials are prepared by melt blending SEPS/h-BN composite materials with PE and PP. The composite material prepared in this experiment can be used in many applications that require high thermal conductivity insulating materials.

## **2. Results and discussion**

### **2.1. Microstructure of PE/PP/SEPS/h-BN composite**

SEM images of PE/PP/SEPS/h-BN composite materials are shown in **Figure 1**, it can be seen that SEPS is continuously connected in the composite material. Combining the contact angle test and the continuity calculation, it shows that SEPS is distributed at the phase PE-PP interface of

the co-continuous structure of PE/PP/SEPS/h-BN composites. According to the analysis of Figure 2a-e diagram, with the increase of h-BN content, the continuity of SEPS does not change too much.

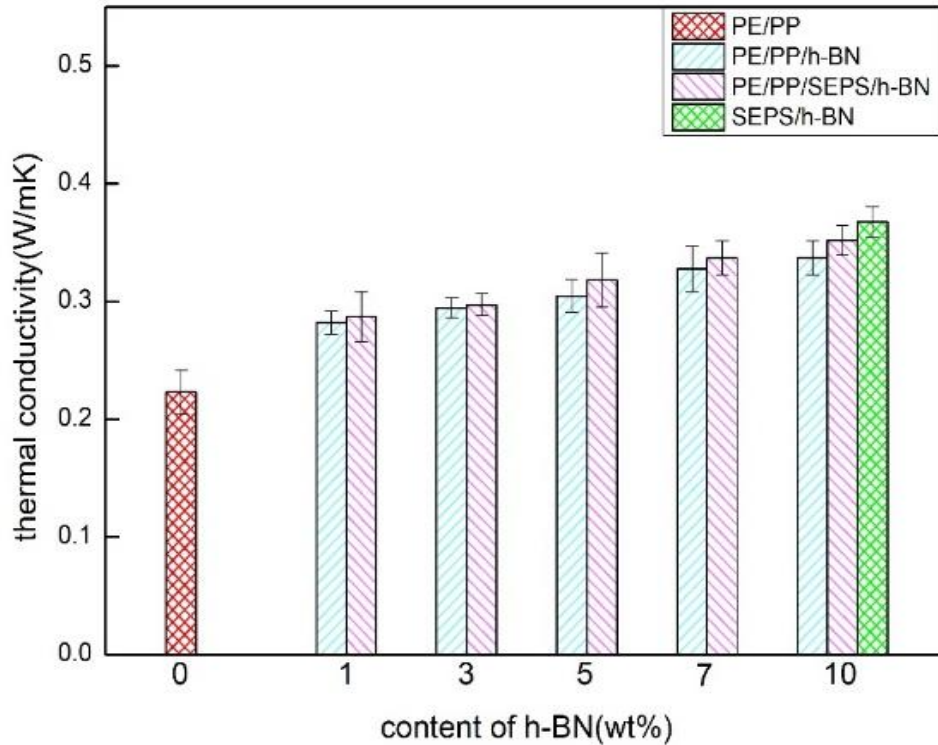


**Figure 1.** SEM micrograph of PE/PP/SEPS/h-BN composite. Mass ratio of PE/PP is 50/50, SEPS is 17.5 wt% of PE/PP, h-BN ratios are (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, (d) 7 wt%, and (e) 10 wt%. The SEPS phase has been etched by xylene.

When the mass ratio of PE/PP is 50/50 and the mass ratio of SEPS is 17.5 wt%, the co-continuity of the composite material forming a co-continuous structure after etching by xylene is the best, and the calculated co-continuity degree (refer to the supporting materials) reaches 99.5%. Therefore, the mass ratio of SEPS used in this experiment is 17.5% by weight. In order to study the distribution of h-BN, the PE/PP/SEPS/h-BN composite material was made into a cube sample with a side length of 2 mm and soaked in xylene for several days until the sample had a constant weight. When the mass of SEPS is 17.5% of the total mass of PE and PP, and the mass of h-BN is 10% of the total mass of PE and PP, the continuity of SEPS and h-BN in the PE/PP/SEPS/h-BN

composite is calculated by the continuity formula. The calculated degree of 97.6% indicates that h-BN is mostly distributed in the SEPS after the processing.

## 2.2. Thermal conductivity of PE/PP/SEPS/h-BN composite

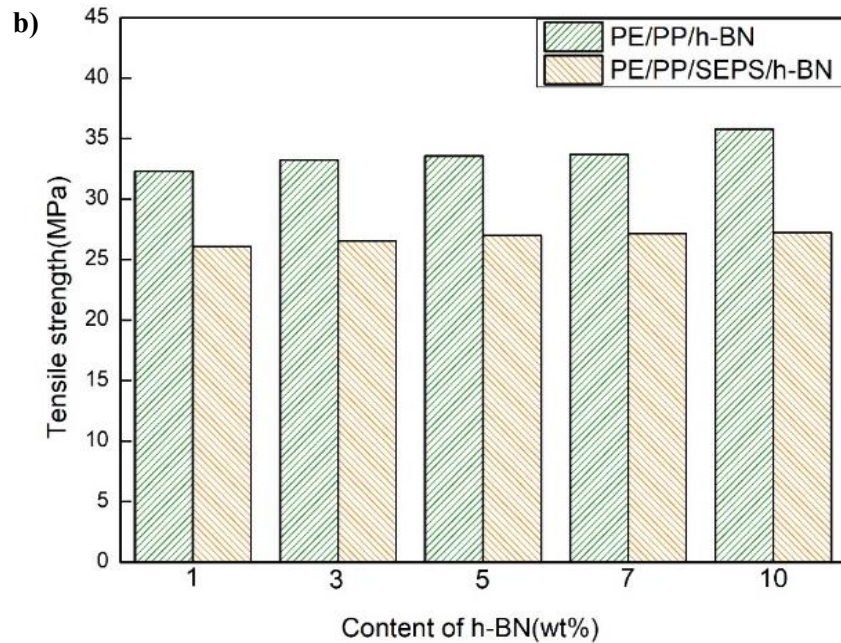


**Figure 2.** Thermal conductivity of PE/PP/SEPS/h-BN composites. Mass ratio of PE/PP is 50/50, SEPS is 17.5 wt% of PE/PP, h-BN ratios are 1, 3, 5, 7 and 10 wt%.

**Figure 2** shows the thermal conductivity ( $K$ ) of PE/PP/SEPS/h-BN composites. According to the thermal conductivity test, the  $K$  of PE/PP/SEPS/h-BN composite materials increases with the increase of h-BN content. The  $K$  of the PE/PP/SEPS/h-BN composite with 10 wt% h-BN is about 0.3520 W/mK, and the  $K$  of the h-BN/SEPS composite is about 0.3674, indicating that the carrier wraps the filler. The method can achieve a thermal conversion rate of about 96%. The reason is that when the mass ratio of PE to PP is 50:50, the PE/PP composite will form a co-

continuous structure. The contact angle test and continuity calculation show that the PE/PP/SEPS/h-BN composite is prepared when SEPS and h-BN are melt blended first, h-BN is mostly distributed in SEPS, and SEPS is mostly distributed at the phase interface of the co-continuous structure of PE/PP/SEPS/h-BN composites. Therefore, h-BN forms a heat conduction path at the PP/PE phase interface of PE/PP/SEPS/ H-BN composites with a co-continuous structure. Compared with filling a single matrix with thermal conductivity filler[33-35], this method can achieve higher thermal conductivity when the filler content is lower.

### 2.3. Mechanical properties of PE/PP/SEPS/h-BN composite

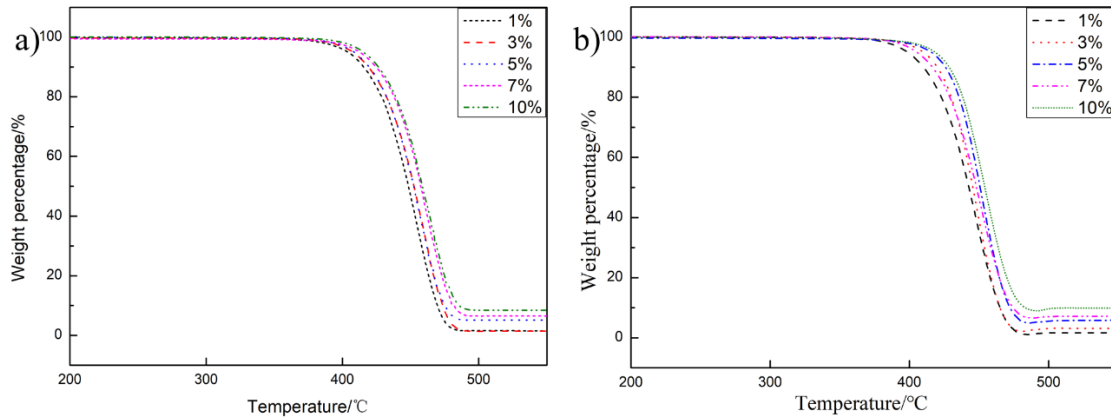


**Figure 3.** The tensile strength of PE/PP/SEPS/h-BN composite materia. Mass ratio of PE/PP is 50/50, SEPS is 17.5 wt% of PE/PP, h-BN ratios are 1 wt%、3 wt%、5 wt%、7 wt% and 10 wt%.

**Figure 3** shows the tensile strength of PE/PP/SEPS/h-BN composites. With the increase of h-BN content, it has little effect on the tensile strength of PE/PP/SEPS/h-BN composites. This is because in the PE/PP/SEPS/h-BN composite prepared by the two-step method, the h-BN is mostly

distributed in the SEPS phase, and the SEPS is mostly distributed at the phase PE/PP interface of the PE/PP/SEPS/h-BN composite co-continuous structure place. This is because when subjected to external force, the material tends to fracture at the interface of the two phases. The h-BN at the interface bears most of the stress, which reduces the impact of SEPS on the tensile strength, so it has little effect on the entire system. With the increase of filler content, this method can maintain better mechanical properties than that of a single thermal conductive composite[36].

#### 2.4. Thermal stability of PE/PP/SEPS/h-BN composites



**Figure 4** TGA curve of (a) PE/PP/SEPS/h-BN composites and (b) PE/PP/h-BN composite. Mass ratio of PE/PP is 50/50, SEPS is 17.5 wt% of PE/PP, h-BN ratios are 1, 3, 5, 7 and 10 wt%.

**Figure 4** shows the TGA curve of the PE/PP/SEPS/h-BN and PE/PP/h-BN composite. It can be seen from the figure that the mass after decomposition is the mass of h-BN and residual carbon in the composite, which is basically the same as the actual amount of h-BN added in the sample. As the content of h-BN increases, the thermal stability of PE/PP/SEPS/h-BN gradually increases. The reason is that the melting point and thermal conductivity of h-BN is larger than that of PE, PP



and SEPS, which is good for absorbing heat and transferring it out in time. It shows that h-BN forms a heat conduction path in the composite material.

### **3. Conclusion**

The polyethylene (PE) and polypropylene (PP) percentage of 50:50 makes the composite form a co-continuous structure; the hexagonal boron nitride (h-BN) is wrapped by thermoplastic elastomer SEPS. This approach enables the localized distribution of h-BN at the interface of the co-continuous structure of PE/PP/SEPS/h-BN composite, allowing the construction of a heat conduction path, thereby improving the thermal conductivity of PE/PP/SEPS/h-BN composites. With such a unique structure, the thermal conductivity of the composites can be improved by 57.7% by adding only 10 wt% of the h-BN filler. The thermal conductive composite was prepared by adjusting the filler distribution[37-39], the composite material obtained by positioning the carrier-wrapped filler at the phase interface possess high thermal conductivity and high toughness, and can be used in many applications that require thermally conductive and insulating materials.

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### **Compliance with ethical standards**

**Conflict of interest:** The authors declare no conflict of interest.

### **References :**

- [1] J. K. Han, et al., An Anisotropically High Thermal Conductive Boron Nitride/Epoxy Composite Based on Nacre-Mimetic 3D Network, *Adv. Funct. Mater.*, 29(2019), 1-9, 10.1002/adfm.201900412.
- [2] T. Morishita, H. Okamoto, Facile Exfoliation and Noncovalent Superacid Functionalization of Boron Nitride Nanosheets and Their Use for Highly Thermally Conductive and Electrically Insulating Polymer Nanocomposites, *ACS Appl. Mater. Interfaces*, 8(2016), 27064-27073, 10.1021/acsami.6b08404.
- [3] S. Wang, et al., Revisiting the Reduction of Thermal Conductivity in Nano- to Micro-Grained Bismuth Telluride: The Importance of Grain-Boundary Thermal Resistance, *Engineered Science*, 17(2021), 45-55, 10.30919/es8d513.
- [4] Y. Zhou, et al., Recent Advances in Thermal Interface Materials, *ES Materials & Manufacturing*, 7(2020), 4-24, 10.30919/esmm5f717.
- [5] Lilin He, Improve Thermal Conductivity of Polymer Composites via Conductive Network, *ES Materials & Manufacturing*, 13(2021), 1-2, 10.30919/esmm5f460.
- [6] J. Zhuang, et al., Multi-factor analysis on thermal conductive property of metal-polymer composite microstructure heat exchanger, *Advanced Composites and Hybrid Materials*, 4(2021), 27-35, 10.1007/s42114-021-00204-5.
- [7] J. P. Cao, et al., High thermal conductivity and high electrical resistivity of poly(vinylidene fluoride)/polystyrene blends by controlling the localization of hybrid fillers, *Composites Science and Technology*, 89(2013), 142-148, 10.1016/j.compscitech.2013.09.024.

- [8] Y. Hwang, et al., Fabrication of surface-treated SiC/epoxy composites through a wetting method for enhanced thermal and mechanical properties, *Chem. Eng. J.*, 246(2014), 229-237, 10.1016/j.cej.2014.02.064.
- [9] Y. A. A. U. S. Nagai, Thermal conductivities of composites in several types of dispersion *Journal of Applied Polymer Science*, 42(1991), 1665-1669, 10.1002/app.1991.070420621.
- [10] J. Huang, et al., Phase Morphology, Rheological Behavior, and Mechanical Properties of Poly (lactic acid)/Poly (butylene succinate)/Hexamethylene Diisocyanate Reactive Blends, *ES Energy & Environment*,12(2020), 86-94, 10.30919/esee8c1017.
- [11] H. Han, et al., Flexible Ethylene-vinyl Acetate Copolymer/Fluorographene Composite Films with Excellent Thermal Conductive and Electrical Insulation Properties for Thermal Management, *ES Materials & Manufacturing*, 15(2021), 53-64, 10.30919/esmm5f523.
- [12] X. Hu, et al., Improving thermal conductivity of ethylene propylene diene monomer/paraffin/expanded graphite shape-stabilized phase change materials with great thermal management potential via green steam explosion, *Advanced Composites and Hybrid Materials*, 4(2021), 478-491, 10.1007/s42114-021-00300-6.
- [13] Y. Xie, et al., Paraffin/polyethylene/graphite composite phase change materials with enhanced thermal conductivity and leakage-proof, *Advanced Composites and Hybrid Materials*, 4(2021), 543-551, 10.1007/s42114-021-00249-6.

- [14] F. Xu, et al., Copper nanoparticle-deposited graphite sheets for highly thermally conductive polymer composites with reduced interfacial thermal resistance, *Advanced Composites and Hybrid Materials*, 152(2021), 1-9, 10.1007/s42114-021-00367-1.
- [15] S. N. Leung, Thermally conductive polymer composites and nanocomposites: Processing-structure-property relationships, *Compos. Pt. B-Eng.*, 150(2018), 78-92, 10.1016/j.compositesb.2018.05.056.
- [16] M. Namasivayam, J. Shapter, Factors affecting carbon nanotube fillers towards enhancement of thermal conductivity in polymer nanocomposites: A review, *J. Compos Mater.*, 51(2017), 3657-3668, 10.1177/0021998317692398.
- [17] M. A. Vadivelu, et al., Polymer composites for thermal management: a review, *Compos. Interfaces*, 23(2016), 847-872, 10.1080/09276440.2016.1176853.
- [18] F. Chen, et al., Thermally conductive glass fiber reinforced epoxy composites with intrinsic self-healing capability, *Advanced Composites and Hybrid Materials*, 4(2021), 1048-1058, 10.1007/s42114-021-00303-3.
- [19] H. Y. Chen, et al., Thermal conductivity of polymer-based composites: Fundamentals and applications, *Prog. Polym. Sci.*, 59(2016), 41-85, 10.1016/j.progpolymsci.2016.03.001.
- [20] H. Cheng, et al., Ultrathin flexible poly(vinylidene fluoride)/MXene/silver nanowire film with outstanding specific EMI shielding and high heat dissipation, *Advanced Composites and Hybrid Materials*, 4(2021), 505-513, 10.1007/s42114-021-00224-1.

- [21] Q. Gao, et al., Flexible multilayered MXene/thermoplastic polyurethane films with excellent electromagnetic interference shielding, thermal conductivity, and management performances, *Advanced Composites and Hybrid Materials*, 4(2021), 274-285, 10.1007/s42114-021-00221-4.
- [22] Z. D. Han, A. Fina, Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review, *Prog. Polym. Sci.*, 36(2011), 914-944, 10.1016/j.progpolymsci.2010.11.004.
- [23] J. Li, et al., Enhanced Thermal Transport Properties of Epoxy Resin Thermal Interface Materials, *ES Energy & Environment*, 4(2019), 41-47, 10.30919/esee8c222.
- [24] H. Yan, et al., Flexible thermally conductive and electrically insulating silicone rubber composite films with BNNS@Al<sub>2</sub>O<sub>3</sub> fillers, *Advanced Composites and Hybrid Materials*, 4(2021), 36-50, 10.1007/s42114-021-00208-1.
- [25] A. Li, et al., Thermal Conductivity of Graphene-Polymer Composites: Mechanisms, Properties, and Applications, *Polymers*, 9(2017), 1-17, 10.3390/polym9090437.
- [26] M. Xiao, B. X. Du, Review of high thermal conductivity polymer dielectrics for electrical insulation, *High Volt.*, 1(2016), 34-42, 10.1049/hve.2016.0008.
- [27] C. Y. Xu, et al., Thermal conductive composites reinforced via advanced boron nitride nanomaterials, *Compos. Commun.*, 10(2018), 103-109, 10.1016/j.coco.2018.08.002.
- [28] W. James, Molecular structure and property: Product engineering. *Industrial and Engineering Chemistry Research*, 41(2002), 1917–1919. <https://doi.org/10.1021/ie0200398>.

- [29] X. Zhang, Applications of Kinetic Methods in Thermal Analysis: A Review, *Engineered Science*, 14(2021), 1-13, 10.30919/es8d1132.
- [30] X. Zhang, et al., Constructing dual thermal conductive networks in electrospun polyimide membranes with highly thermally conductivity but electrical insulation properties, *Advanced Composites and Hybrid Materials*, 4(2021), 1102-1112, 10.1007/s42114-021-00335-9.
- [31] C. Zhang, et al., Selective location and double percolation of short carbon fiber filled polymer blends: High-density polyethylene/isotactic polypropylene. *Materials Letters*, 36(1998), 186–190. [https://doi.org/10.1016/S0167-577X\(98\)00023-8](https://doi.org/10.1016/S0167-577X(98)00023-8).
- [32] J. R. Huang, et al., Massive enhancement in the thermal conductivity of polymer composites by trapping graphene at the interface of a polymer blend, *Composites Science and Technology*, 129(2016), 160-165, 10.1016/j.compscitech.2016.04.029.
- [33] H. Fang, et al., “White graphene” – hexagonal boron nitride based polymeric composites and their application in thermal management, *Compos. Commun.*, 2(2016),19-24, 10.1016/j.coco.2016.10.002.
- [34] J. Lee, J. Kim, Improved through-plane thermal conductivity of 3D structured composites via BN alignment and AlN surface modification, *Compos. Commun.*, 28(2021), 100935 10.1016/j.coco.2021.100935.
- [35] C. Y. Xu, et al., Thermal conductive composites reinforced via advanced boron nitride nanomaterials, *Compos. Commun.*, 10(2018), 103-109, 10.1016/j.coco.2018.08.002.

- [36] W. Yang, et al., Methods for enhancing the thermal properties of epoxy matrix composites using 3D network structures, *Compos. Commun.*, 12(2019), 14-20, 10.1016/j.coco.2018.12.004.
- [37] D. Pan, et al., Ice template method assists in obtaining carbonized cellulose/boron nitride aerogel with 3D spatial network structure to enhance the thermal conductivity and flame retardancy of epoxy-based composites, *Advanced Composites and Hybrid Materials*, (2021), 10.1007/s42114-021-00362-6.
- [38] G. Droval, et al., Conductive polymer composites with double percolated architecture of carbon nanoparticles and ceramic microparticles for high heat dissipation and sharp PTC switching, *Smart Mater. Struct.*, 17(2008), 10, 10.1088/0964-1726/17/2/025011.
- [39] H. Cheng, et al., PVDF-Ni/PE-CNTs Composite Foams with Co-Continuous Structure for Electromagnetic Interference Shielding and Photo-Electro-Thermal Properties, *Engineered Science*, 16(2021), 331-340 10.30919/es8d518.