

Formation of thermal conductive hydrogel network in boron nitride/polyvinyl alcohol by directional freezing assisted salting-out method for cryogenic application

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Abstract. Hydrogels are promising packaging materials for flexible electronic devices, where improving thermal conductivity is essential for reliable operation. In this work, a polyvinyl alcohol (PVA)-based hydrogel doped with 500 nm boron nitride nanosheets (BNNS) was prepared via directional freezing-assisted salting. The hydrogel exhibits a directional porous structure confirmed by SEM, with a tensile strength of 513.4 kPa and a thermal conductivity of $0.65 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature. Notably, its thermal conductivity remains $0.32 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 77 K, demonstrating effective heat dissipation under cryogenic conditions. Beyond direct encapsulation applications, the hydrogel serves as a template for constructing a three-dimensional BNNS skeleton, which can be impregnated with epoxy resin to form high thermal conductivity composites. The resulting epoxy composite achieves conductivities of $0.82 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature and $0.38 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 77 K, attributed to the continuous thermal conduction network established by the BNNS skeleton. Overall, this study presents a facile approach to develop flexible hydrogels with excellent mechanical and thermal performance and demonstrates their further utility in fabricating epoxy composites for advanced low-temperature electronic packaging.

1. Introduction

With the advancement of electronic technology, electronic components are progressing towards miniaturization, functionalization, integration and flexibility[1]. Highly integration leading to an increasingly prominent issue of heat generation. In conditions of high integration and power, the heat generated by electronic components rises significantly. Poor thermal conductivity of packaging materials can result in high temperatures within the device, affecting



its performance, service life, and posing security risks. Especially for devices operating in low-temperature environments, once excessive heat is generated while cannot dissipate, a significant impact on the working environment temperature of the devices may occur, thereby affecting the overall performance. Therefore, working in low-temperature environments places require higher demands on the heat dissipation performance of device packaging materials. Polymers, particularly hydrogels and epoxies, have been widely investigated due to their excellent processability, mechanical performance, and electrical insulation [2–6]. Hydrogel-based materials, owing to their flexibility, have shown promise in wearable sensors, electronic skin, personalized medical monitoring, and human–machine interfaces. Epoxy-based systems, in contrast, are extensively applied as encapsulation and coating materials for low-temperature electronics due to their inherent stability under cryogenic conditions. However, conventional hydrogels generally suffer from poor mechanical strength and low thermal conductivity, limiting their application in thermal management.

To address these limitations, various strategies have been explored, such as the incorporation of thermally conductive fillers (e.g., graphene, carbon nanotubes, and BNNS), polymer cross-linking, and structural orientation techniques. Among these, boron nitride nanosheets (BNNS) have attracted growing attention as highly effective thermally conductive fillers [7], owing to their high intrinsic thermal conductivity, chemical stability, and superior electrical insulation compared to carbon-based counterparts. Previous studies have shown that randomly dispersed BNNS can enhance the thermal conductivity of PVA or epoxy matrices; for instance, one study reported $\sim 150\%$ improvement in epoxy at just 7 wt% BNNS loading, along with enhanced Young's modulus and fracture toughness [8]. However, the enhancements were often limited by poor filler alignment and weak interfacial bonding. In contrast, orientation strategies such as directional freezing or vacuum filtration have demonstrated much more pronounced improvements: a BNNS/PVA aerogel fabricated via vacuum-assisted filtration achieved thermal conductivities up to $0.76 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ compared to $\sim 0.15 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for pure PVA. Similarly, vertically aligned 3D BNNS networks within epoxy boosted thermal conductivity from $\sim 0.32 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to over $1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, even at low filler contents [9]. These examples underscore both the potential and the limitations of existing systems and emphasize the need for methods that combine structural control with interfacial optimization—gaps that our directional freezing-assisted salting-out approach aims to fill.

Inspired by the work of Hua [10], we employed a directional freezing-assisted salting-out method to enhance the mechanical properties of hydrogels. This process involves directional freezing to form porous structures [11], followed by salting-out using high-concentration salts to induce polymer precipitation [12]. On this basis, boron nitride nanosheets (BNNS) were introduced to improve thermal conductivity. BNNS offers excellent electrical insulation, chemical stability, and thermal stability, making it a superior alternative to carbon-based fillers for electronic packaging. Moreover, the three-dimensional BNNS/PVA hydrogel scaffold can be further infiltrated with epoxy resin to construct a thermal conduction network, effectively improving the conductivity of epoxy materials while maintaining mechanical integrity.

In this paper, the thermal conductivity and the tensile properties at fracture of the hydrogel composites were tested under room temperature and 77K conditions. Besides, the thermal conductivity of the epoxy material with a hydrogel-based framework was also tested at room temperature and at 77K. The method can be used to prepare polymer composites with high thermal conductivity for flexible electronic device packaging and other fields. At the same time, a

kind of epoxy resin with high thermal conductivity can be prepared, which can be used in the field of electronic device coating and bonding under liquid nitrogen temperature zone.

2. Method

2.1 Materials

Commercially available boron nitride nanosheets (BNNS) powders (99% metal basis) with the size of 500 nm were purchased from Macklin(China). Polyvinyl alcohol (PVA) (95%, Mw89000~98000) and sodium citrate hydrate were purchased from Macklin(China). Bisphenol F type epoxy resin (BPF) (5.80~6.10 Eq/kg) were supplied from Huntsman(USA). Diethyltoluenediamine curing agent(DETD) were supplied from Yarui Chemical(China). The deionized water was obtained from Institute of Physics and Chemistry, CAS.

2.2 Preparation of BNNS/PVA composite hydrogel

The preparation process of the BNNS/PVA composite hydrogel is shown in Figure 1. 8 g PVA was added to 100 mL of deionized water, heated to 60°C in an oil bath and stirred until the PVA particles were completely dissolved, then BNNS was added to the solution and continued to be heated and stirred in an oil bath at 60°C until the BNNS were evenly dispersed in the solvent. The proportion of BNNS of PVA is 50 wt%, 100 wt%, 150 wt% and 200 wt% respectively, and the amount of BNNS is 4 g, 8 g, 12 g and 16 g. Then the mixed solution was poured into the mold for directional freezing. In this paper, a mold made of brass and polytetrafluoroethylene was used to achieve directional freezing. Then the mold was placed on a refrigeration platform constructed of liquid nitrogen, and its temperature was adjusted in a directional manner to control the solidification speed. As the solvent water nucleates on the surface of the cold source and grows directionally along the temperature gradient to form an ice crystal with an oriented structure, the solute PVA and BNNS are also repelled and squeezed to form a three-dimensional network between the ice crystals. After completely freezing, the BNNS/PVA composite was removed from the mold and placed in a dialysis bag, and then the dehydration treatment of BNNS/PVA composite was realized by immersed in 1.5 mol/L sodium citrate salt solution for 24 h to obtain the porous BNNS/PVA composite.

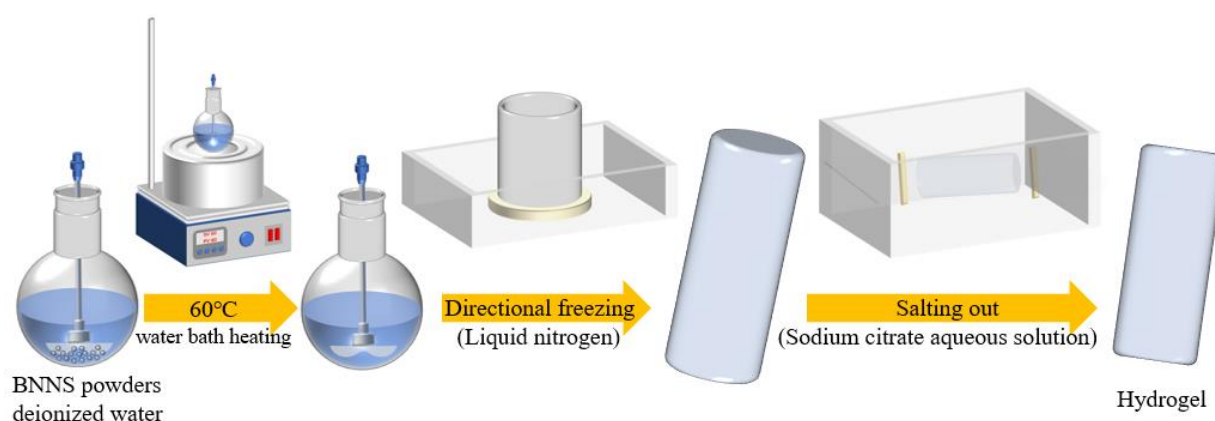


Figure 1. Preparation steps of hydrogels by directional freezing salting-out method.

2.3 Preparation of 3D-BNNS/epoxy composite

The preparation process of 3D-BNNS/epoxy composite material is shown in Figure 2. BNNS/epoxy nanocomposites were prepared by vacuum assisted epoxy resin impregnation method. First, the BNNS/PVA composite hydrogel was put into Muffle furnace and burned at 600°C for 3 h to remove PVA in the material and the BNNS skeleton was remained. Then the epoxy resin monomer and curing agent are evenly mixed under heating conditions, and the mass ratio of epoxy resin and curing agent is controlled at 100/24, and then the BNNS skeleton is completely immersed in the resin mixture. After soaking for 2 h, the sample was transferred to a vacuum oven at room temperature for 12 h to remove air. Finally, the composites were placed in an oven and cured at 80°C for 6 h and 150°C for 3 h to obtain epoxy resin /BNNS nanocomposites.

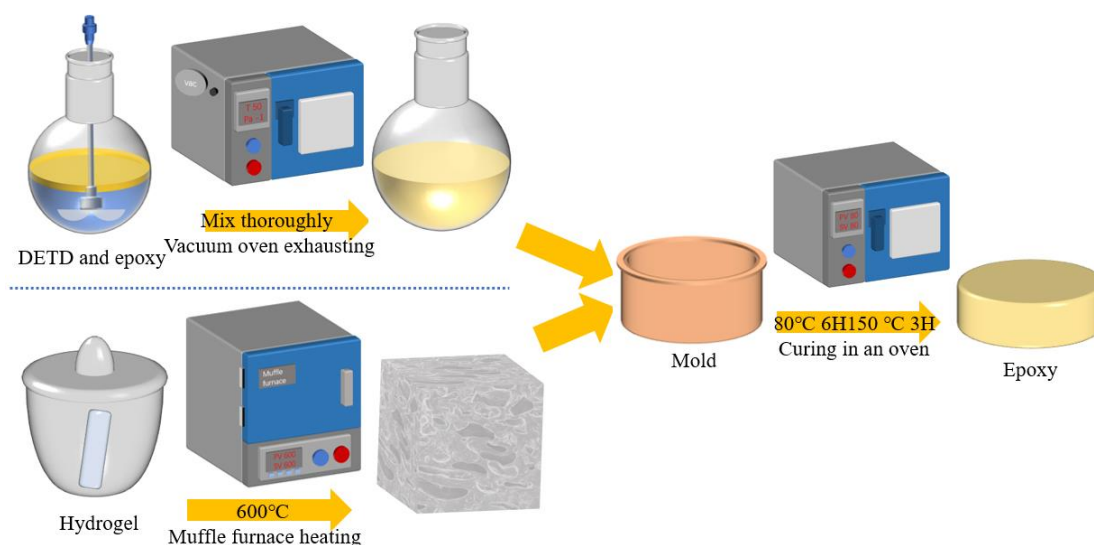


Figure 2. Preparation steps of high thermal conductivity epoxy resin.

2.4 Characterization

Scanning electron microscopy (SEM) images were taken by Hitachi S-4800. The stress and strain tests are performed using the UTM6503 electronic universal testing machine. The thermal conductivity test is achieved by the CTM-60K model of the steady-state thermal conductivity tester.

3. Result and discussion

Under the influence of permeable salt solution, the PVA chain and the original uniform phase of the phase separation gradually intensified with the passage of time, until the complex structure and crystallization gradually formed, and finally formed a network of nanofibers on the surface of the pore wall arranged in the micron scale. The morphology of the composite was observed under scanning electron microscope, and it was observed that the sample had obvious porous structure, and the three-dimensional network structure had obvious transverse orientation, as shown in Figure 3. In Figure 3. a, b shows the direction of water crystallization. Due to the shear direction of the sample, only a distinct direction of water crystallization was observed in the 150wt% hydrogel. In the 50wt% hydrogel (Figure 3. c,d), obvious pores could be observed, but the

direction of water crystallization was less obvious. It is proved that the method of directional freezing assisted salting-out can indeed construct three-dimensional porous network and the network structure is formed along the direction of ice crystal growth.

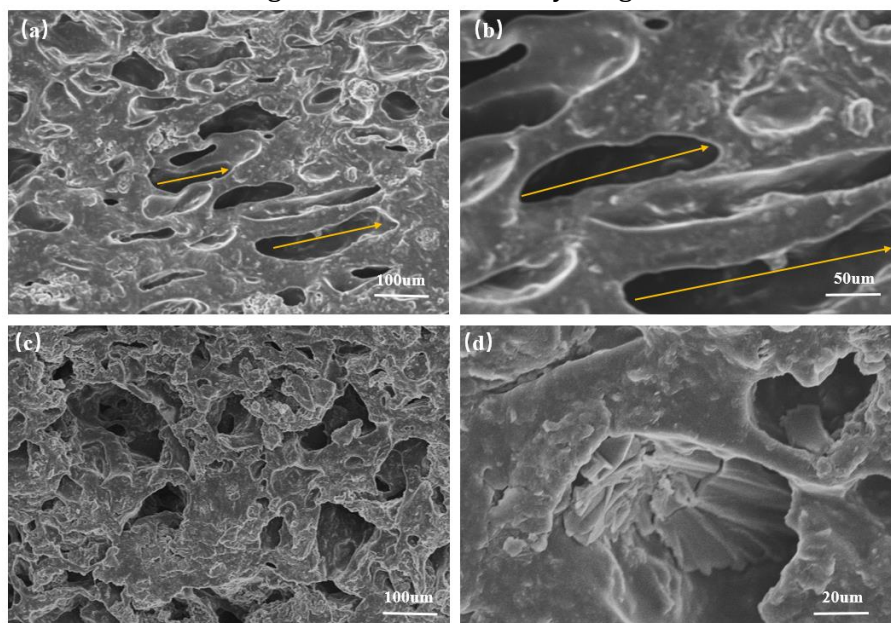


Figure 3. Scanning electron microscopic (SEM) images of BNNS/PVA hydrogel for (a, b)150wt%, (c, d)50wt%.

In addition, the thermal conductivity characteristics of hydrogel in a wide temperature range were studied. The thermal conductivity of traditional PVA hydrogels at room temperature is about $0.1 \text{ W/m}\cdot\text{K}$ [9], which is very low. The thermal conductivity of PVA hydrogels after adding BNNS is significantly improved. For BNNS/PVA composites, the thermal conductivity is tested at a wide temperature range of 77-300 K. It can be found that with the decrease of temperature, the thermal conductivity of hydrogel composites also decreases accordingly. Because the heat conduction of the composite mainly depends on the phonon vibration, the thermal conductivity of the BNNS/PVA composite decreases with the decrease of temperature. It can be seen from Figure 4 that the thermal conductivity of BNNS/PVA composites at room temperature is in the range of 0.3 to $0.65 \text{ W/m}\cdot\text{K}$, which is greatly improved compared with the $0.1 \text{ W/m}\cdot\text{K}$ thermal conductivity of pure PVA hydrogels. At the same time, the tensile test of hydrogel at room temperature is carried out. From figure 5, the hydrogel material with BNNS filler content of 50 wt% has the best tensile property, the tensile strength can reach 513.4kPa, and the elongation at break can reach 426.53%. The tensile properties of BNNS/PVA composites decreased with the increase of BNNS content. The tensile strength of samples with 100 wt% and 150 wt% filler content were 218.44kPa and 151.69kPa, respectively, and the elongation at break were 73.45% and 102.28%, respectively. Since the doping of BNNS filler can lead to the destruction of the integrity of the molecular chain segment structure in the hydrogel, an increase in the doping amount will result in the decline of the overall mechanical properties of the hydrogel.

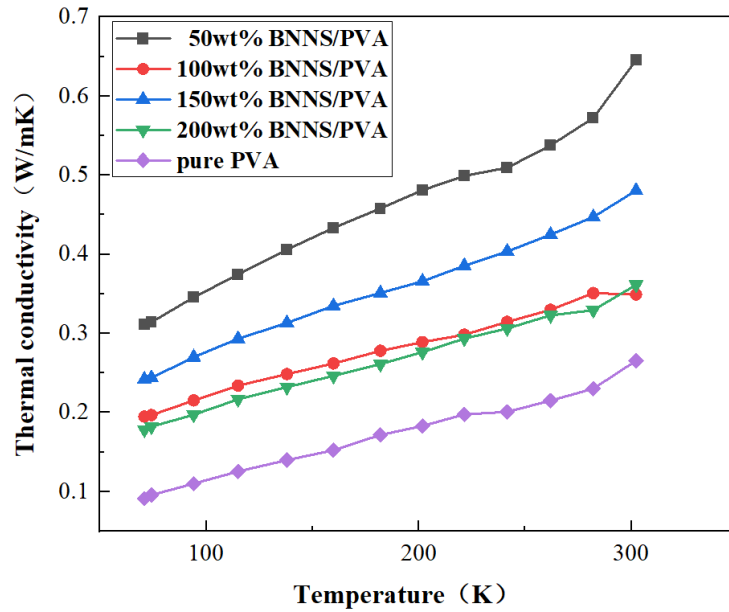


Figure 4. Thermal conductivity of BNNS/PVA hydrogel.

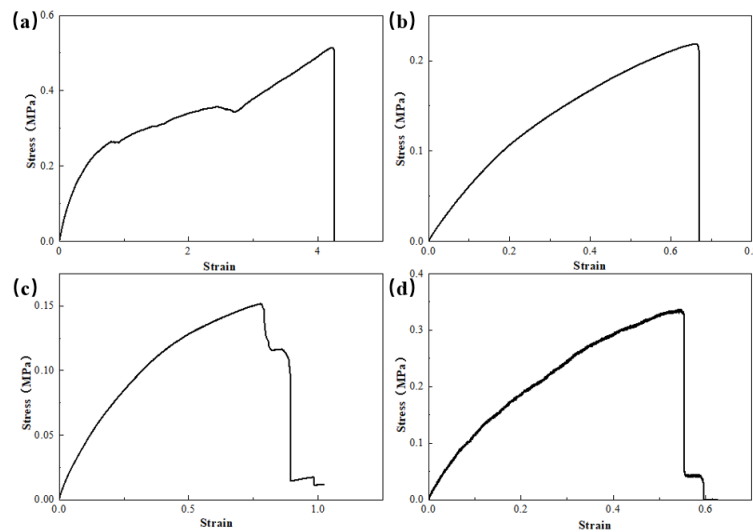


Figure 5. Stress-strain curve for (a)50wt%, (b)100wt%, (c)150wt%, (d)200wt%.

In the selection of electronic packaging materials and binders, epoxy resin occupies a place because of its excellent insulation properties, mechanical properties, chemical stability, thermal stability and easy processing [10]. However, the thermal conductivity of epoxy resin is very low, so improving the thermal conductivity of epoxy resin can greatly expand the scope of application, which has important practical significance. Building a thermal conductivity network with three-dimensional structure is one of the important means to improve the thermal conductivity of epoxy composite materials. The BNNS/PVA composite hydrogel material can form a three-dimensional thermal conduction skeleton of BNNS with good performance after sintering at high temperature, which can effectively improve the thermal conductivity of epoxy resin. The thermal conductivity of epoxy composites was also tested at a wide temperature range of 77-300 K, and the figure 6

showed that the thermal conductivity of epoxy composites at room temperature ranged from 0.35 to 0.83 W/m·K. Compared with the thermal conductivity of pure epoxy resin materials at 0.2 W/m·K, the thermal conductivity increased by 75%-315%. At a low temperature of 77K, the thermal conductivity of the composite is between 0.15-0.38 W/m·K, which is also significantly improved compared with pure epoxy resin materials. At the same time, it was found that the thermal conductivity of epoxy composite increased significantly with the increase of BNNS filler; and the thermal conductivity of epoxy composite had an obvious linear relationship with the content of filler.

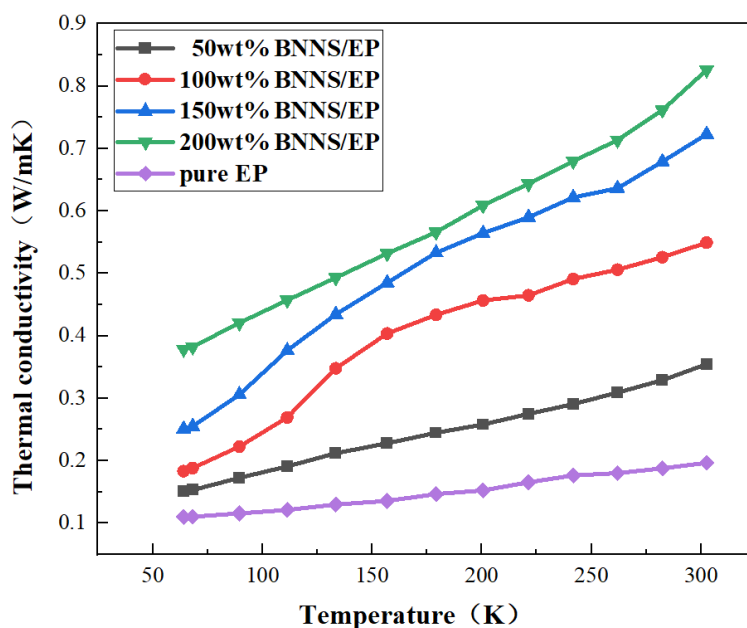


Figure 6. Thermal conductivity of BNNS/epoxy resin. (The mass fraction values presented in the figure correspond to the content of BNNS within the hydrogel matrix, whereas the BNNS loading in the epoxy resin is maintained at a constant level of 35 wt%.)

4. Conclusion

A method for forming a conductive hydrogel network in boron nitride/polyvinyl alcohol materials by means of a targeted freezing-assisted desalination technique was designed, and its performance and application under low-temperature conditions were investigated. The main conclusions are as follows:

(1) The thermal conductivity of hydrogel composites increased by more than 260% compared with pure PVA hydrogels. The thermal conductivity of composites with different filler ratios is distributed in the range of 0.36-0.65 W/m·K at room temperature, and in the temperature range of 77-300 K, the thermal conductivity improvement level of the materials is above 78%.

(2) The tensile strength of the hydrogel composite is in the range of 513.4-151.7 kPa, and the overall mechanical strength is good, but the mechanical strength of the composite decreases compared with that of the pure PVA material due to the addition of boron nitride filler.

(3) The hydrogel was sintered at high temperature to prepare a three-dimensional thermal conductivity network, and it was impregnated in epoxy resin to prepare an epoxy composite material with significantly improved thermal conductivity. In the temperature range of 77-300 K,

the thermal conductivity of the material is between 0.15-0.32 W/m·K, and the thermal conductivity of the material at room temperature is in the range of 0.35-0.82 W/m·K.

Application recommendation: Based on the above findings, the BNNS/PVA hydrogel composites exhibit relatively high thermal conductivity enhancement and flexibility, making them more suitable for use as flexible encapsulation materials in wearable sensors and low-temperature flexible electronic devices where mechanical compliance is essential. However, the decrease in tensile strength compared with pure PVA may limit their application in load-bearing scenarios. By contrast, the BNNS/EP composites derived from the hydrogel skeleton demonstrate superior structural stability and higher thermal conductivity at both room and cryogenic temperatures, making them particularly advantageous for rigid electronic packaging, coating, and bonding applications under liquid-nitrogen or other cryogenic environments. Therefore, for low-temperature technology, BNNS/PVA composites are more suitable for flexible, deformation-tolerant systems, while BNNS/EP composites are better suited for rigid, high-stability encapsulation systems.

Acknowledgments

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