Research Paper

Highly filled boron nitride-phthalonitrile nanocomposites for exigent thermally conductive applications

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HIGHLIGHTS

- First ever investigation of the phthalonitriles thermal conductivity.
- The thermal conductivity reached 4.69 W/m K at 30 wt.% silane treated BN.
- TEM analysis confirmed the formation of a conductive network.
- The 5 wt.% weight loss temperature reached the outstanding value of 551 °C.

GRAPHICAL ABSTRACT
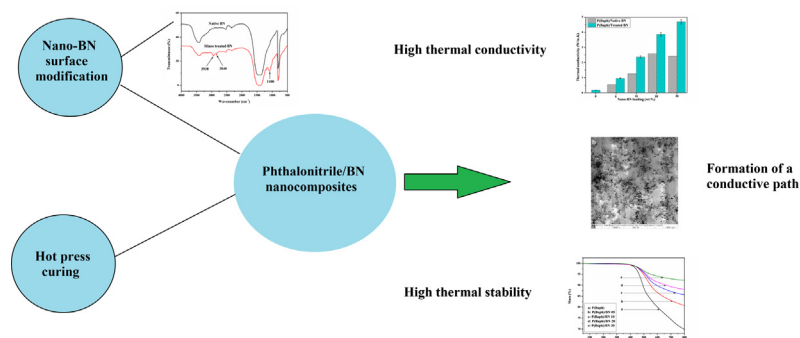
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ABSTRACT

Highly filled phthalonitrile nanocomposites, reinforced with both native and silane surface modified nano-BN were investigated for their mechanical and thermal properties. The nanocomposites were prepared by a solution blending technique followed by compression molding. The thermal conductivity was investigated as the core of the study along with a bending test, a morphological behavior, thermal stability investigations, and thermomechanical properties measurements. The highest thermal conductivity value of 4.69 W/m K was obtained at the maximum nanofillers loading of 30 wt.% treated BN. A high resolution TEM confirmed that the exceptional enhancements in the thermal conductivity are related to the formation of an effective conductive path assured by the silane surface modified nano-BN. The bending test also revealed consequent improvements in both the strength and modulus as the amount of the nanofillers increased. The SEM investigations revealed positive changes in the surface morphology of the neat resin, with a rougher and homogeneous state of surfaces for the hybrids. Moreover, the thermal stability at the maximum fillers loading was found to be one of the best ever reported in the field of high performance polymer-based composites, with a 5 wt.% weight loss temperature of 551 °C.

1. Introduction

Phthalonitrile (PN) resins are a class of high performance thermosets well-known for their combination of excellent physical and chemical properties such as an outstanding structural stability at high temperatures, superior flame resistance, low water absorption, and excellent corrosion protective properties [1–7]. The PN resins are superior in many ways to the traditional high performance polymers and present an interesting alternative to these materials especially in extremely exigent applications such as aerospace and military. However, PN as any other polymeric

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material suffers from a poor thermal dissipation affecting the performance, lifetime, and reliability of the PN-based electronic devices. Hence, developing thermally conductive PN materials is of a primary importance to help address this challenge. One effective and easy way to enhance the thermal conductivity of these materials is to prepare composites by introducing thermally conductive inorganic particles. Different kind of fillers were successfully incorporated into various polymeric matrices some of which are boron nitride (BN), silica (SiO_2), graphene oxide (GO), alumina (Al_2O_3), aluminum nitride (AlN), silicon nitride (Si_3N_4), barium titanate ($BaTiO_3$), and diamond [8–13]. Among these materials, hexagonal BN possesses the greatest potential due to its high thermal conductivity, low dielectric constant along with a good thermal stability and an excellent resistance to oxidation and chemical corrosion [14,15]. It is also important to point that inorganic particles were also extensively used to enhance the thermal properties of heat transfer fluids [16–20]. Although, large differences in the thermal behavior between fluids and polymers exist, however, both systems were effectively reinforced with inorganic particles to improve some of their physical properties.

The filler loading level is another important parameter influencing the thermal conductivity of the hybrids. Generally, the conductivity increases as the amount of the fillers increases. Hence, several highly filled polymer composites were successfully prepared [21,22]. The aim of adding a high amount of filler is to overcome the phonon scattering problems which are the main causes of low thermal conductivities in polymeric materials. At high filler amounts, the particles tend to form conductive paths and therefore reduce the thermal resistance [11]. However, high filler loadings may affect the processability by increasing the viscosity. One solution is to cure the composites by a hot-press molding technique; this method of curing also proved its efficiency during the preparation of multiple ceramic-based phthalonitrile micro- and nanocomposites. Moreover, the high thermal stability of the PN resins, which can be operated at elevated temperature without any degradation, promotes the formation of the conductive networks during the hot-press curing.

The thermal conductivity is also closely related to the size of the fillers. The general idea was that the composites with small particles tend to exhibit a lower thermal conductivity mainly caused by the large interfacial area resulting in phonon scattering and hindering the phonon transport [23]. However, recent developments in the field reported controversial effects of particle size, in particular, when nano-sized particles are used [24,25]. For instance, at the same amount of filler and processing conditions, epoxy filled with silver nanoparticles had up to a 50-fold higher thermal conductivity than composites prepared from micro-sized particles [26]. Moreover, micro-sized particles have a negative impact on the mechanical properties, and due to the difference in density between the filler and the polymeric matrix, the particles tend to agglomerate at the bottom on the structure making the formation of the conductive paths difficult to achieve. Hence, preparing thermally conductive polymer nanocomposites appears to be a good choice to obtain simultaneous enhancements in the thermal and mechanical properties.

Overcoming the interfacial resistance between the polymeric matrix and the fillers is also a key factor for improving the thermal conductivity. The thermal resistance can be reduced by treating the surface of the fillers. Several surface modifiers have been used to decrease the interfacial resistance, including silane coupling agents, functional polymers, and inorganic coatings [27]. Among them, the silane coupling agents are the most popular and effective surface modifiers, especially in the field of PN-based composites in which amino-based silanes were successfully used to treat the nanoparticles of SiC, Si_3N_4, Al_2O_3, TiO_2, ZnO and ZrO_2 [28–33]. The silane nanoparticles treatment improved both the dispersion of the nanofillers into the matrix and the state of adhesion between the two phases. The treated nanoparticles were found to be more effective than the native ones in enhancing the mechanical and thermal properties of the neat PN matrices.

PN resins are relatively newly developed materials and their thermal conductivities have not yet been investigated. This work relates for the first time ever the thermal conductivity investigations of a high performance PN resin and its related highly filled BN nanocomposites. Taking into account the previous studies in the field, it appeared to us that the most effective way to achieve a high thermal conductivity is by preparing highly filled PN nanocomposites based on silane surface modified hexagonal BN and cured by a hot compression molding technique. Our experimental approach consisted on first effectively modify the surface of the nanofillers, investigate the thermal conductivity of the nanocomposites from both native and silane surface modified BN nanoparticles, and then further explore the impact of the nanofillers on the flexural, thermal, and thermomechanical properties of the PN matrix. Indeed, our goal was to prepare high thermal conductive materials with enhanced mechanical and thermal properties. Hence, in this study, a high performance bisphenol-A based PN resin was chosen as the matrix for preparing two kinds of nanocomposites from different weight ratios of the native and silane surface modified BN nanoparticles, ranging between 5 and 30 wt.%. Samples of the neat PN resin and its subsequent nanocomposites were cured by hot pressing and their thermal and mechanical properties were investigated in terms of their nano-BN loading and state of surface.

2. Materials and experimental procedure

2.1. Materials

All the materials used in this study are listed in Table 1. The detailed synthesis procedure and chemical structures of the bisphenol-A based PN monomer (2, 2-bis [4-(3,4-dicyanophenoxy) phenyl] propane), commonly termed Baph, and the curing agent 3-Aminophenoxy phthalonitrile (Apph), can be found in the literature [34,35].

2.2. Preparation of phthalonitrile/BN nanocomposites

A GX-540 silane coupling agent was used to treat twenty grams of the raw BN nanoparticles. The treatment procedure was performed as follows: the native BN nanoparticles were placed in a vacuum oven for over 5 h to remove any moisture adsorbed on their surfaces. The dried nanoparticles and 1.2 mg of the silane coupling agent (6 wt.% of the nanofillers) were mixed in dry ethanol, sonicated for 20 min, and vigorously stirred for 10 h. The

Table 1
Names, detailed descriptions, and provenances of all the materials used in this study.

Name and description	Manufacturer	Purity (%)
3-Aminophenol 2,2-Bis(4-hydroxyphenyl)propane	Shanghai Aladdin Reagents (China)	99
4-Nitrophthalonitrile	Shijiazhuang Chemical Technology (China)	98
N,N-Dimethyl sulfoxide (DMSO) Acetone	Tianjin Kermel Chemical Reagent (China)	99.9
Potassium carbonate (K_2CO_3)	Tianjin Fengchuan Chemicals (China)	99
Boron nitride (BN), average particles diameter of 60 nm	Shanghai Aladdin Reagents (China)	N/A
Aminopropyl trimethoxy silane (GX-540)	GBXF Silicones CO., LTD (China)	98