Nuclear Inst, and Methods in Physics Research B 421 (2018) 13–17

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Toward advanced gamma rays radiation resistance and shielding efficiency with phthalonitrile resins and composites

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ARTICLE INFO

Keywords:
Phthalonitrile
Polymeric composites
Nanocomposites
Nuclear shielding

ABSTRACT

The phthalonitrile resins have claimed the leading place in the field of high performance polymers thanks to their combination of outstanding properties. The present work explores for the first time the gamma rays radiation resistance and shielding efficiency of the phthalonitrile resins and its related tungsten-reinforced nanocomposites. The primary goal of this research is to define the basic behavior of the phthalonitrile resins under highly ionizing gamma rays. The obtained results confirmed that the neat phthalonitrile resins can resist absorbed doses as high as 200 kGy. Meanwhile, the remarkable shielding efficiency of the phthalonitrile polymers was confirmed to be easily improved by preparing lead-free nanocomposites. In fact, the gamma rays screening ratio reached the exceptional value of 42% for the nanocomposites of 50 wt% of nano-tungsten loading. Thus, this study confirms that the remarkable performances of the phthalonitrile resins are not limited to the thermal and mechanical properties and can be extended to the gamma rays radiation and shielding resistances.

1. Introduction

Phthalonitrile (PN) resins, as a newly developed high performance polymer materials, present some interesting features such as an outstanding thermal stability, superior flame resistance, absence of a glass transition temperature (T_g) before their thermal decomposition, low water absorption, and excellent corrosion protective properties [1–7]. All these striking properties promote the phthalonitrile resins over the currently in use polymeric materials especially in aerospace and military applications. The phthalonitrile resins were effectively used as matrices for micro and nanocomposites and ameliorations in the neat resins properties were obtained. The resulting composites also exhibited better performances than those prepared by other high performance resins and reinforced with the same fillers [8,9].

Being designated for extremely exigent applications, the PN resins need to be fully investigated for their behavior and shielding performances under high energy ionizing radiations such as gamma rays. The strong penetration of the gamma rays can do great damage to the instruments and human beings. Therefore, the maximum absorption dose, before PN molecular structure changes occurs as well as the screening ratios need to be precisely determined. Moreover, using nontoxic "lead-free" fillers, such as tungsten nanoparticles to improve the shielding properties of the neat resin is more than suitable considering the numerous supplementary improvements that can be obtained in the mechanical and thermal properties [10–12]. Till now, there have been no reports on the effect of any type of high ionizing radiations on the radiation damage and shielding behavior of the PN resins. Therefore, we seized the opportunity to prepare tungsten-based PN nanocomposites and investigate their properties.

In this work, the tungsten nanoparticles were first treated with silane coupling agent, and then used to reinforce a typical bisphenol-A based PN (BAPh) resin at different amounts ranging from 30 to 50 wt%. The BAPh resin has been the most extensively studied type of PN precursors. Thus, it becomes important to assess its radiation resistance and shielding efficiency prior to extending the investigations to other PN monomers or oligomers. The maximum absorption dose was determined and its impact on the thermal and mechanical properties was investigated. The screening ratios of the PN and its related tungsten based nanocomposites were also investigated at different nanofillers loadings and thicknesses.

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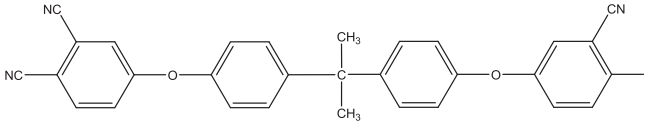
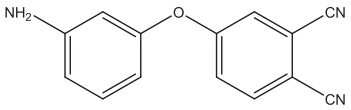
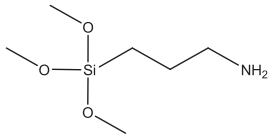
https://doi.org/10.1016/j.nimb.2018.02.017
Received 1 November 2017; Received in revised form 9 January 2018; Accepted 15 February 2018



2, 2-bis [4-(3,4-dicyanophenoxy)phenyl] propane (BAPh)



3-Aminophenoxy phthalonitrile (3-APN)



Aminopropyl trimethoxy silane (GX-540)

Fig. 1. Chemical structures of the BAPh, 3-APN, and GX-540 silane coupling agent.

2. Experimental

2.1. Materials

3-Aminophenol, 2,2-bis(4-hydroxyphenyl)propane, and 4-nitrophthalonitrile was obtained from Shanghai Aladdin Reagents. N,N-Dimethyl sulfoxide and potassium carbonate was purchased from Tianjin Kermel Chemical Reagent. The tungsten (W) nanoparticles were purchased from Shanghai Aladdin Reagents. These nanofillers are in the form of a black powder having an average diameter of particles of 100 nm. The silane coupling agent GX-540 ($(CH_3O)_3SiC_3H_6NH_2$) was friendly supplied from GBXF SILICONES CO., Ltd. 3-Aminophenoxy phthalonitrile (3-APN) and 2,2-bis [4-(3,4-dicyanophenoxy)phenyl] propane (BAPh) monomers were synthesized in our laboratory according to the literature [13,14]. The chemical structures of the as such synthetized monomers as well as the silane coupling agent are shown in Fig. 1.

2.2. Preparation of phthalonitrile/W nanocomposites

The W nanoparticles were mixed with GX-540 silane coupling agent (6 wt% of filler) in ethanol and stirred for 3 h. The collected nanoparticles from filtration were then dried under vacuum at 80 °C overnight. BAPh monomers and 3-APN curing agent were mixed thoroughly at a weight ratio of 90:10 respectively, then the proper amount of the treated nanoparticles of W was added ranging from 30 to 50 wt% with an increment of 10 wt%. The mixture compounds were melted, stirred vigorously and then quenched to room temperature. Owing to obtain a void free thermosets, the mixtures were first dried in a vacuum oven at 120 °C for 5 h, and then transferred into the appropriate steel mold according to the dynamic mechanical analyzer (DMA) and tensile shapes requirements. The samples were finally cured by a hot compression molding technique with a curing procedure of 240 °C for 2 h, 260 °C for 3 h, 280 °C for 6 h, 320 for 6 h and 340 °C for 6 h. Hereafter, the cured nanocomposites were noted as P(BAPh)/W.

2.3. Characterization techniques

The radiation behavior of the neat PN resin was studied by exposing the samples to different gamma ray radiation doses at an ambient humidity and temperature at the Technical Physics Institute of Heilongjiang Academy of Science (Harbin, China). The radiation doses of 50, 100, 150, and 200 kGy were applied, at the dose rate of 6 kGy/h, using a Co-60 gamma rays as the radiation source (3.7×10^{15} Bq). Thermogravimetric (TG) tests were performed on a TA Instruments Q50 at a heating rate of 20 °C/min from 50 to 820 °C under nitrogen atmosphere at a flow rate of 50 mL/min. The thermomechanical properties were investigated using a TA Q800 DMA. The tensile tests were carried out using Instron 5569 instrument, at the crosshead speed of 1 mm/min using a specimen size of about (50 mm × 10 mm × 2 mm), all tests were repeated four times to assure the repeatability and accuracy of the presented data. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the range of 4000–500 cm^{-1}, which was equipped with a deuterated triglycine sulfate (DTGS) detector and KBr optics. Transmission spectra were obtained at a resolution of 4 cm^{-1} after averaging two scans by casting a thin film on a KBr plate for the neat and irradiated samples. The gamma rays shielding efficiency of the P(BAPh)/W nanocomposites were studied by measuring the radiation dose absorbed through several samples thicknesses. Generally, the gamma rays interact with the materials either by absorption or scattering away. This interaction can be expressed as follow:

$$I/I_0 = e^{-\mu x} \quad (1)$$

Or

$$-Ln(I/I_0) = \mu x \quad (2)$$

where I_0 (herein equal to 1.17 MeV) represents the radiation dose without the shielding material, I refers to the radiation dose through a thickness x(cm) of shielding material, μ is the total linear attenuation coefficient of a specific material for gamma-rays in a specific energy.

The screening or shielding ratio (S) is defined as follows,

$$S = (I_0 - I/I_0) \times 100 \quad (3)$$

A half-value layer (HVL) is used to a thickness where the dose after absorbing is half of the original.

$$HVL = Ln2/\mu \quad (4)$$

3. Results and discussion

3.1. Irradiation resistance properties

3.1.1. Thermomechanical properties

The impact of various gamma radiations doses on the thermomechanical properties of the neat PN resin were investigated by DMA and the results are displayed in Fig. 2. The neat PN resin showed a storage modulus value at 50 °C of 1.8 GPa with a T_g of 380 °C.

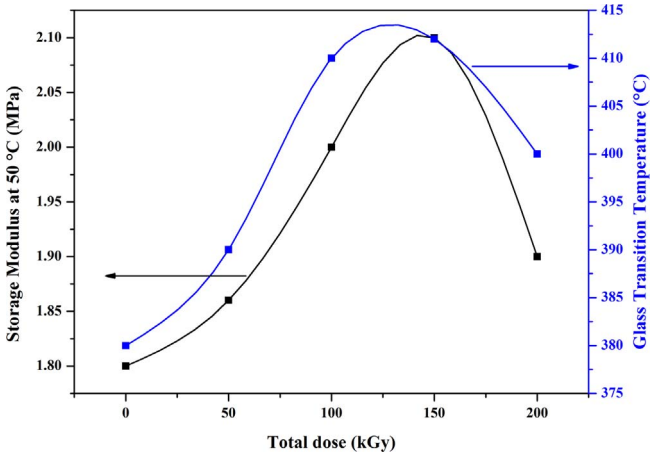


Fig. 2. Storage modulus and *Tg* variations of the P(BAPh) resin at various radiation doses.