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# Phosphorylated nano-diamond/ Polyimide Nanocomposites

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**Abstract.** In this study, a novel route to synthesize polyimide (PI)/phosphorylated nano-diamond films with improved thermal and mechanical properties was developed. Surface phosphorylation of nano-diamond was performed in dichloromethane. Phosphorylation dramatically enhanced the thermal stability of nano-diamond. Poly(amic acid) (PAA), which is the precursor of PI, was successfully synthesized with 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (4,4'-ODA) in the solution of N,N-dimethylformamide (DMF). Pure BTDA-ODA polyimide films and phosphorylated nano-diamond containing BTDA-ODA PI films were prepared. The PAA displayed good compatibility with phosphorylated nano-diamond. The morphology of the polyimide (PI)/phosphorylated nano-diamond was characterized by scanning electron microscopy (SEM). Chemical structure of polyimide and polyimide (PI)/phosphorylated nano-diamond was characterized by FTIR. SEM and FTIR results showed that the phosphorylated nano-diamond was successfully prepared. Thermal properties of the polyimide (PI)/phosphorylated nano-diamond was characterized by thermogravimetric analysis (TGA). TGA results showed that the thermal stability of (PI)/phosphorylated nano-diamond film was increased.

## 1. Introduction

Polyimide (PI) is known to be a high-performance material. Polyimides rank among the most heat-resistant polymers and are widely used in high temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials, membrane materials for separation etc. Additionally, polyimides are used in a diverse range of applications, coating, including the fields of aerospace; they are also used in liquid crystal alignments, composites, electroluminescent devices, electrochromic materials, polymer electrolyte fuel cells, polymer memories, gas separation membranes, Nanofiltration membranes, chemical sensor, fiber optics, etc [1-3].

Organic/inorganic nano-hybrid materials have rapidly received worldwide attention and become a new field on materials and membrane research because of their outstanding characteristics, such as excellent tensile strength, low thermal expansion coefficient and dielectric constant, better penetrant discrimination, and resistance to organic solvents. To prepare surface bound metal nanoparticles on polyimide surface would have great potential applications. Various nano-scale additives, such as Ag nanoparticles, TiO<sub>2</sub> nanoparticles, Au nanoparticles and platinum nanoparticles have been incorporated into the polyimide matrix [4-6].

Over the last 10 years, nano-sized diamond particles known as nano-diamonds (NDs) have attracted much attention because of their outstanding physical properties and low toxicity, as well as the possibility of modifying their surface chemistry [7].

In this work, we report the preparation of phosphorylated nano-diamonds/ polyimide (PI) nanocomposites.

## 2. Materials and methods

### 2.1. Materials

4,4'-Oxydianiline (ODA) and 3,3',4,4'-benzophenonetetracarboxylicdianhydride (BTDA) were purchased from Sigma Aldrich and used without further purification. Nano-diamond (ND), dimethyl

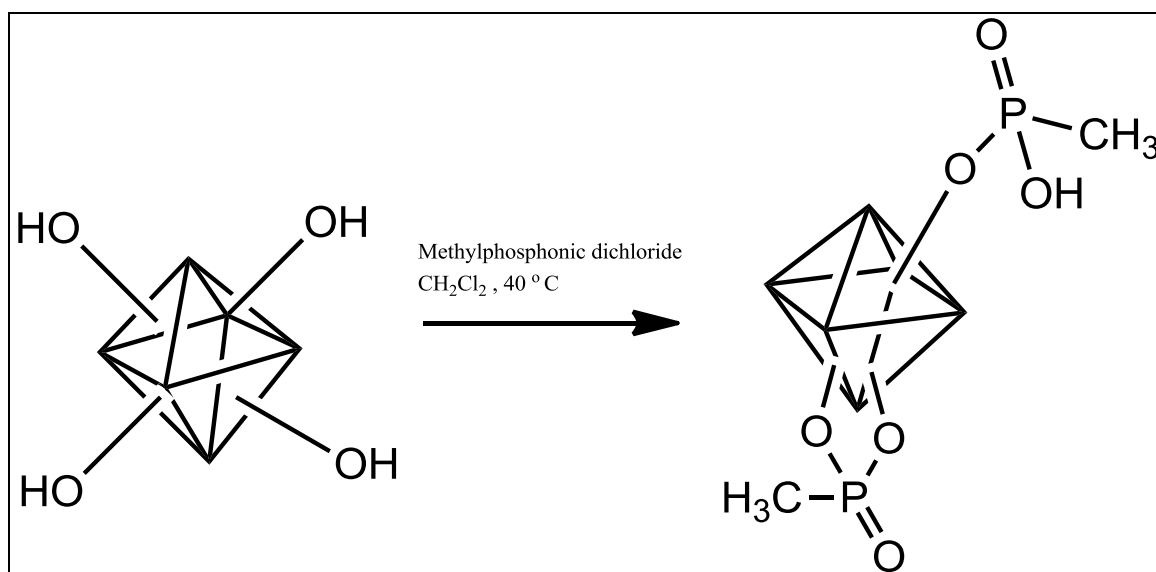


formamide (DMF), methylphosphonic dichloride and dichloromethane were also purchased from Sigma Aldrich.

## 2.2. Methods

### 2.2.1. Functionalization of nano-diamonds by phosphorylation

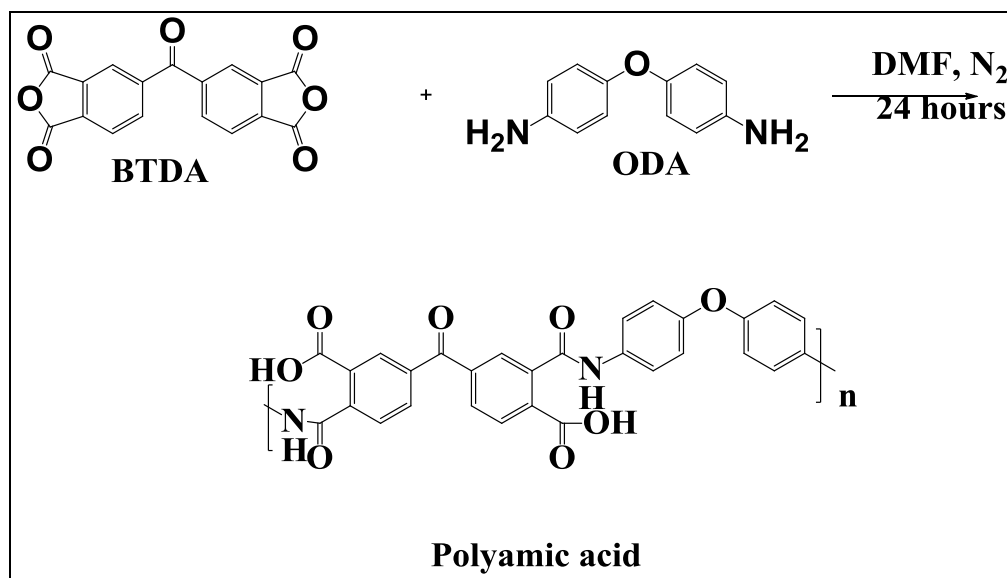
The procedure for the synthesis of nanodiamonds was adopted from reference [7]. Methylphosphonic dichloride (0.4 g) was added to a dispersion of nano-diamonds (1 g) in dry dichloromethane. The mixture was stirred for 3 days at 40 °C. The functionalized nano-diamonds were obtained after centrifugation (10.000 rpm for 10 minutes for 3 times) under ambient conditions, followed by a drying step at 150 °C under reduced pressure for 24 h. Phosphorylated nano-diamonds are shown in Scheme 1.



**Scheme 1.** Functionalization of nano-diamonds by phosphorylation

### 2.2.2. Synthesis of polyamic acids (PAA)

To synthesize polyamic acid (PAA) solutions, ODA (4 g) was first put into a flame dried three-neck flask containing (6.5 g) ml of DMF under a nitrogen purge. After ODA was completely dissolved in DMF, BTDA (42 g) was added to the flask. Procedure of polyamic acid synthesis is shown in Scheme 2. The mixture was stirred overnight at room temperature to obtain a viscous PAA solution. The resulting PAA solution was  $\approx 20$  wt %.



**Scheme 2.** Preparation of PAA

### 2.2.3. Synthesis of BTDA/ODA-phosphorylated nano-diamond

Composite membranes were prepared by adding appropriate amounts of phosphorylated nano-diamonds (0 wt% and 1 wt%) into PAA solutions. Membranes were prepared by casting viscous mixture solutions on clean dust-free glass plates. Then thermal imidization was performed stepwise at 100, 200, and 300 °C for 1 h at each temperature. The preparation of 1 wt% phosphorylated nano-diamond containing polyimide films were prepared by dispersing 0.02 g phosphorylated nano-diamond of in 10 g of PAA solution. The mixture was stirred for 24 h and these solutions were sonicated for 30 min. Then cast films were cured as described above. Hybrid films were removed from glass plates by immersing in distilled water at 80 °C.

### 2.2.4. Characterization methods

FTIR spectrum was recorded on Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer. Thermogravimetric analyses (TGA) of polyimide films were performed using a Perkin-Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 750 °C with heating rate of 10 °C/min under air atmosphere.

DSC measurements were performed using Pyris Diamond DSC. Samples were run from 30 to 300 °C with a heating rate of 10 °C/min. Glass transition temperatures were obtained from the second heating scan.

SEM imaging of the films were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a platinum coating.

## 3. Result and Discussion

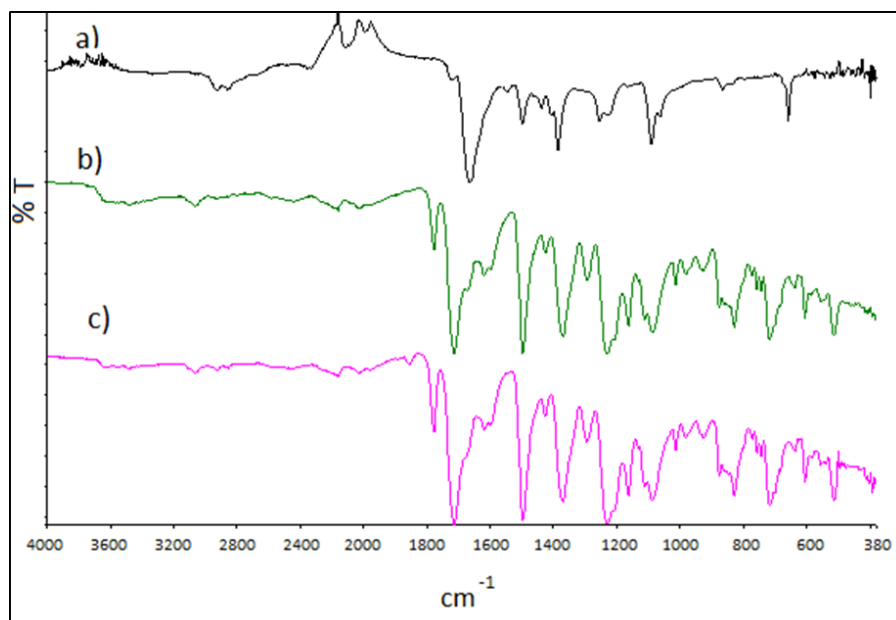
In this study BTDA/ODA polyimide film and phosphorylated nano-diamonds containing polyimide film were prepared and characterized. PNDs particles were successfully dispersed in polyimides up to 1 wt%.

### 3.1. FTIR studies

Fig. 1 shows the ATR-FTIR spectra of neat BTDA/ODA PAA, pure BTDA/ODA polyimide film and composite polyimide films. Pure polyimide film shows characteristic polyimide absorption bands at 1776  $\text{cm}^{-1}$  and 1713  $\text{cm}^{-1}$  which correspond to asymmetric and symmetric imide carbonyl stretchings, respectively. Also the peak at around 1370  $\text{cm}^{-1}$  is attributed to C-N bond stretchings.

Moreover, disappearance of  $-\text{NHCO}-$  peak at 1546  $\text{cm}^{-1}$  (which can be seen in the spectrum of PAA)

indicates that polyimides were synthesized successfully. In the ATR-FTIR spectra of composite film, peaks related with phosphorylated nano-diamonds can also be seen in addition to typical polyimide absorption bands.

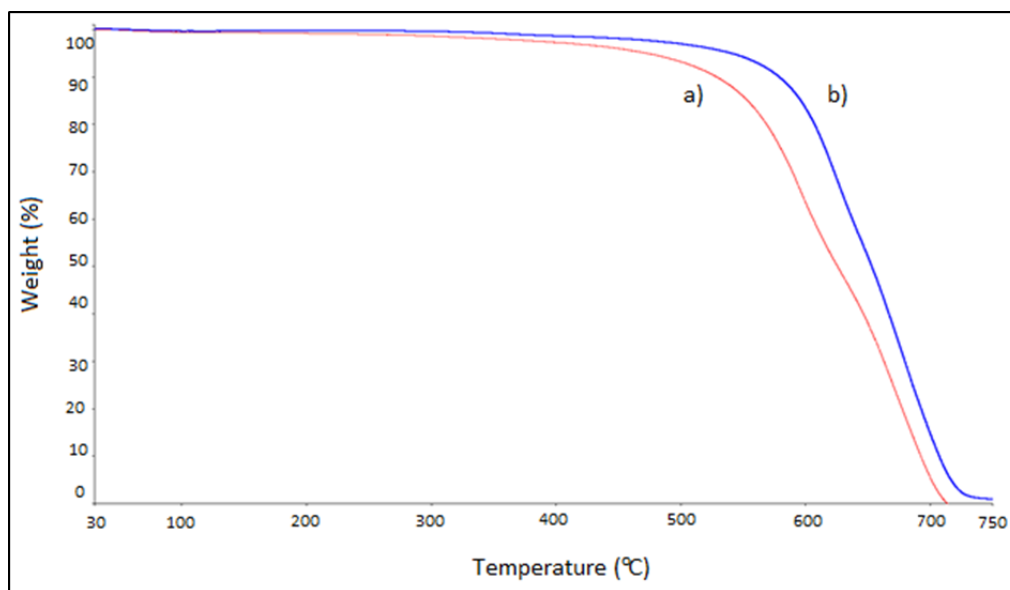


**Figure 1.** The FTIR spectra of a) PAA b) pure PI c) PI/PNDs

### 3.2. Thermal properties

Figure 2 show the thermal degradation behavior of hybrid film and pure polyimide film under air atmospheres. Under air atmosphere the onset weight loss temperature and the maximum weight loss temperature of pure BTDA/ODA polyimide were found as 546 and 619 °C respectively. From the results it can be seen that the addition of phosphorylated nano-diamonds significantly increases both the onset degradation and the maximum weight loss temperatures. As the amount of PNDs content was increased in the composite films, thermal properties were also increased. The addition of phosphorylated nano-diamonds greatly improves the thermostability of polyimide composites.

We found the glass transition temperature of pure BTDA/ODA polyimide film as 297 °C. When PNDs was incorporated into polyimide matrix, glass transition temperatures of hybrid composites decreased. The glass transition temperature of PI/PNDs was found as 268 °C.



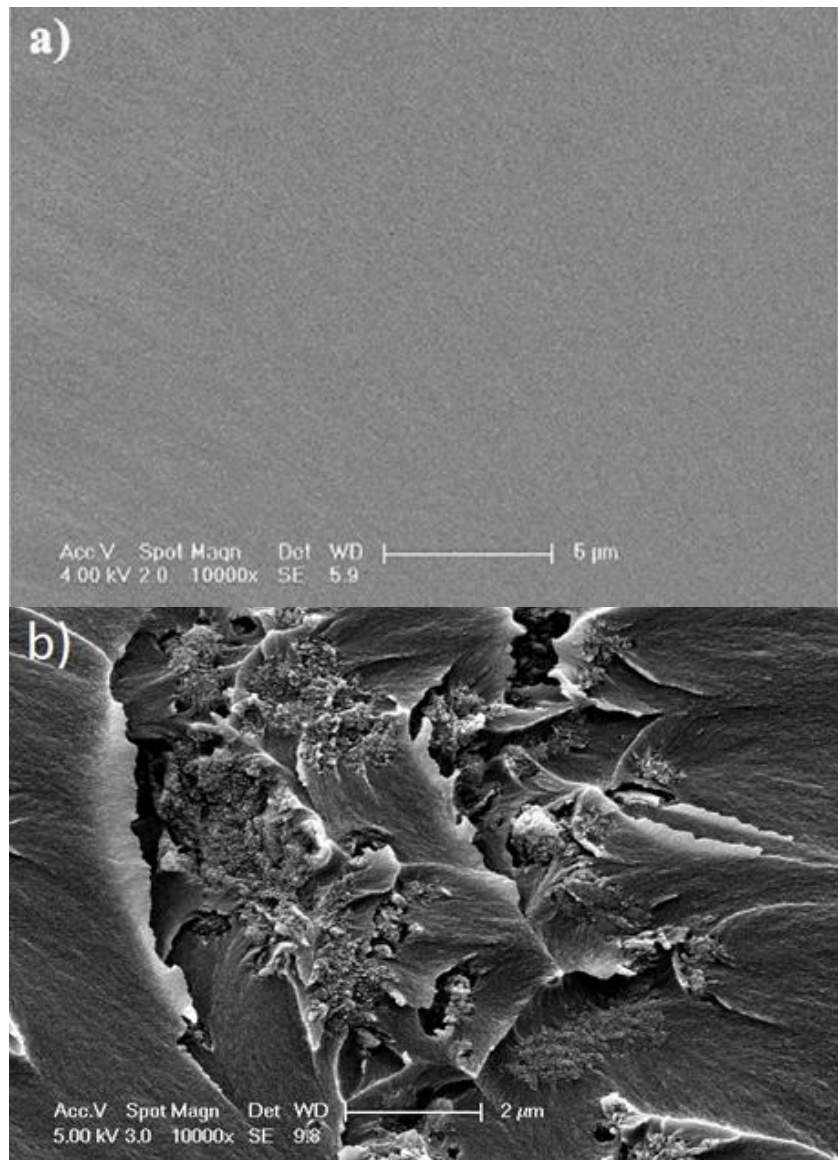
**Figure 2.** TGA thermograms of a) pure PI b) PI/PNDs films under air atmosphere

### 3.3. Morphology

Fig. 3a-b shows the fractured surface morphology of polyimide composites. We can see from SEM micrographs that pure polyimide has a homogenous, crack free, nonporous and a uniform surface (Fig. 3a). In the SEM images of phosphorylated nano-diamonds containing sample (Fig. 3b). Fig. 3b shows of the surface of PI/PNDs film and in this image it can be clearly seen that some phosphorylated nano-diamond particles were well entrapped in the polymer matrix.

### 4. Conclusions

In this study, pure BTDA-ODA polyimide films and phosphorylated nano-diamond containing BTDA-ODA PI films were prepared via thermal imidization of polyamic acid precursors. Surface phosphorylation of nano-diamond was performed in dichloromethane. Phosphorylation dramatically enhanced the thermal stability of nano-diamond. The effect of phosphorylated nano-diamonds of the composites was investigated.



**Figure 3.** SEM micrographs a) pure PI x10.000 b) PI/PNDs x10.000

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