

PREPARATION OF POLYIMIDE NANOCOMPOSITES REINFORCED WITH VARIOUS MODIFIED

KEIYA OBARA¹ and Seira MORIMUNE-MORIYA¹

¹ Department of Applied Chemistry, Graduate School of Engineering, Chubu University, Matsumoto,
Kasugai, Aichi 487-8501, JAPAN
Email: seiram@isc.chubu.ac.jp

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Abstract

Polyimide (PI) is one of super engineering plastics and is used in various applications such as electronic devices and artificial satellites. In this study, Nanodiamond (ND) was used as a filler for PI nanocomposites. ND is composed of core-shell structure with core of diamond primary particle and shell of graphite-like layer and oxygen containing groups. ND shows excellent properties such as high hardness, low friction coefficient and high thermal conductivity derived from diamond core. Since the size of ND is below 10 nm, it is expected to impart excellent properties to PI by the addition of a small amount of ND because of its large specific surface area. Due to the functional oxygen groups on surface, various chemical modifications can be applied to manipulate the ND surface properties. We prepared polyimide nanocomposites reinforced with various modified nanodiamonds. And the structures and properties of the PI/ND nanocomposites were investigated. As a result, PI nanocomposites reinforced with nanodiamonds showed excellent mechanical and thermal properties. It was revealed that the chemical modifications of ND largely improved these properties of the nanocomposites. In particular, the incorporation of ND modified with octadecylamine (ODA) increased the elastic modulus by about 1.5 times and the thermal decomposition temperature by 30 °C with only 0.1 wt% of ND-ODA.

1. Introduction

Polyimide (PI) is one of super engineering plastics and shows excellent thermal, mechanical and chemical properties. PI has extensively been used in various applications such as electronic devices and artificial satellites. However, processability of PI is low because of the insolubility and infusibility due to imide bond which is a strong intermolecular interaction. Therefore, PI has often been converted by imidization after forming precursor (polyamide, etc.). Recently, downsizing and weight saving of materials have advanced in various industries and alternatives to metals have been required. PI composites have been expected as potential materials to achieve the desired properties [1], [2].

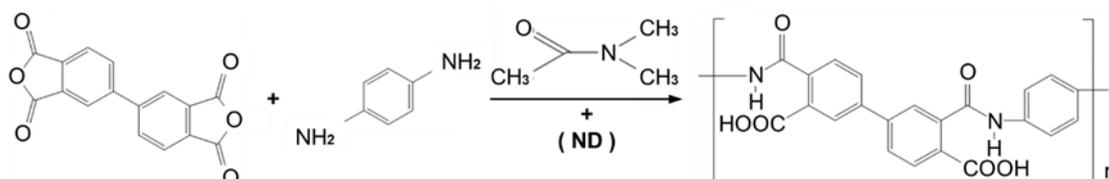
In this study, Nanodiamond (ND) was used as a filler for PI nanocomposites. ND is composed of core-shell structure with core of diamond primary particle and shell of graphite-like layer and oxygen containing groups. ND shows excellent properties such as high hardness, low friction coefficient and high thermal conductivity derived from diamond core. Since the size of ND is below 10 nm, it is expected to impart excellent properties to PI by the addition of a small amount of ND because of its large specific surface area. Due to the functional oxygen groups on surface, various chemical modifications can be applied to manipulate the ND surface properties.

In this study, we conducted chemical modification of ND and prepared ND-COOH and ND-ODA [3]-[5]. The structures and properties of the PI/ND nanocomposites were investigated.

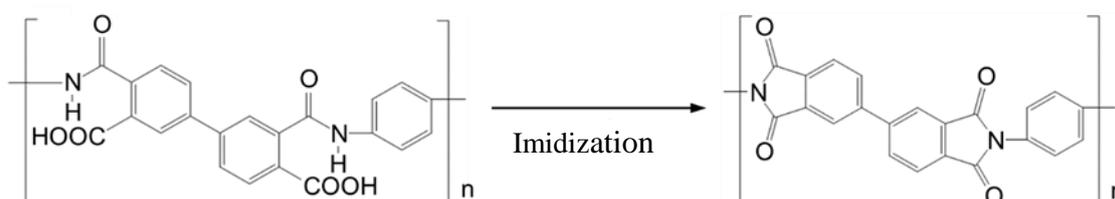
2. Experimental

2.1. Sample preparation

Polyamide (PA) /ND was synthesized by In-situ polymerization. ND was dispersed in N,N-dimethylacetamide (DMA) and 3,4-3',4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (PPD) were added. The reaction of PA synthesis is shown in Scheme 1. Subsequently, PA/ND was molded into a film shape. PA/ND film as heated stepwisely upto 300 ° C. In this process, PA was imidized as shown in Scheme 2 and PI/ND nanocomposites were obtained.



Scheme 1 Synthesis of PA.



Scheme 2 Imidization of PA.

2.2. Characterization

2.2.1 Fourier-transform infrared spectroscopy (FT-IR)

For the measurement, an infrared absorption spectrum was obtained by a KBR method using a Fourier transform infrared spectrophotometer (FT/IR-4200 manufactured by JASCO Corporation).

2.2.2 Differential scanning calorimetry (DSC)

For the measurement, a melting point and a DSC curve were obtained using a high sensitivity differential scanning calorimeter (THERMO PLUS EVO 2/DSC manufactured by Rigaku Corporation). Start measurement at 25 ° C under nitrogen gas atmosphere (flow rate 30 ml/min). The temperature was raised to 30 ° C at a rate of 5 ° C/MIN, held at 5 min, and then measured at 750 ° C at a heating rate of 10 ° C/min.

2.2.3 Thermo gravimetry (TG)

For the measurement, a 5% weight loss point and a thermogravimetric curve were obtained using a differential thermal balance (THERMO PLUS EVO2/TG-DTA, manufactured by Rigaku Corporation). Start measurement at 25 ° C under nitrogen gas atmosphere (flow rate 30 ml/min). The temperature was raised to 30 ° C at a rate of 5 ° C/MIN, held at 5 min, and then measured at 750 ° C at a heating rate of 10 ° C/min.

2.2.4 Tensile test

For the measurement, stress-strain curves, elastic modulus, tensile strength and fracture strain were determined using a small desk-top tensile tester (EZ-L 500N made by Shimadzu Corporation). At that

time, the measurement sample was prepared in a rectangular shape of 40 mm × 5 mm, and measurement was performed with a chuck distance of 20 mm, a width of 5 mm, and a test speed of 2 mm/min.

3. Results

FTIR spectra and Characteristic peaks of PI and various PI/ND nanocomposites were shown in Figure 1 and Table 1. In the spectrum of PI, amide (C=O), imide ring, aromatic ring (C-C), and imide C-N were appeared at 1650-1515 cm⁻¹, 1520-1500 cm⁻¹, 1350-1320 cm⁻¹ and 1190-1170 cm⁻¹, respectively. OH bond, CHO and COO bond and OH bond were appeared at 3500-3400 cm⁻¹, 1700 cm⁻¹, 1780-1770 cm⁻¹ and 1000-850 cm⁻¹, respectively[6].

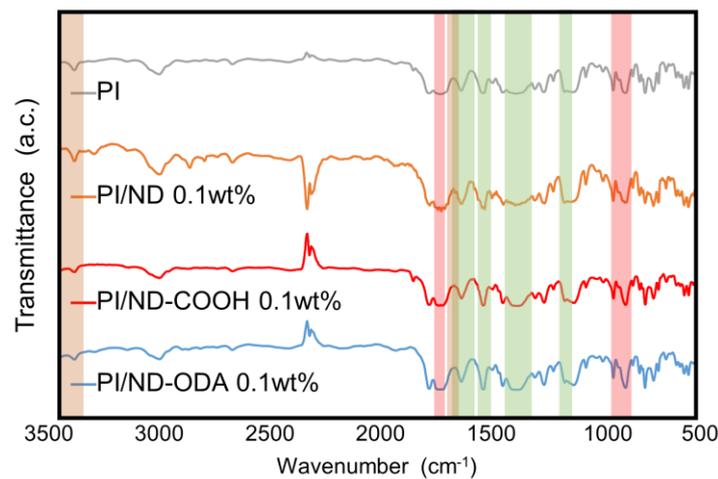


Figure 1. FTIR spectra of PI and various PI/ND nanocomposites.

Table 1. Characteristic peaks of FTIR spectra.

Amide C=O	1650-1515 cm ⁻¹	OH	3500-3400 cm ⁻¹
Imide ring	1520-1500 cm ⁻¹	CHO, COO	1700 cm ⁻¹
Aromatic ring C-C	1350-1320 cm ⁻¹	C=O	1780-1770 cm ⁻¹
Imide C-N	1190-1170 cm ⁻¹	-OH (deformation)	1000-850 cm ⁻¹

DSC curves and thermogravimetric traces of PI and various PI/ND nanocomposites were shown in Figure 2 and Figure 3, respectively. Melting temperature (T_m) and thermal decomposition temperature (T_d) of PI and various PI/ND is shown in Table 2. T_d was determined as a temperature at 5 wt% weight loss. It was revealed that T_m and T_d were increased by the incorporation of small amount of NDs, especially by ND-ODA.

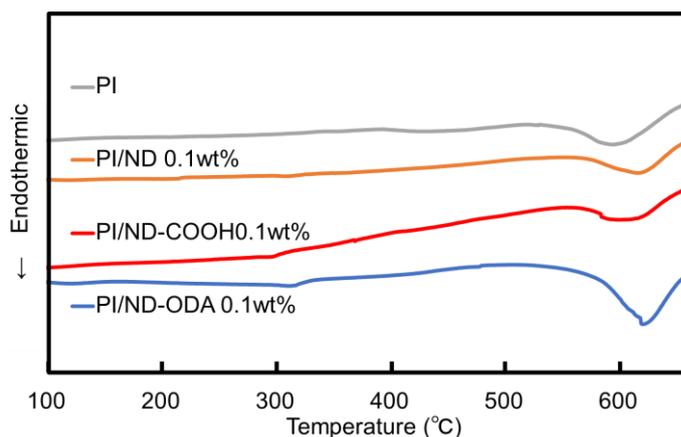


Figure 2. DSC curves of PI and various PI/ND nanocomposites.

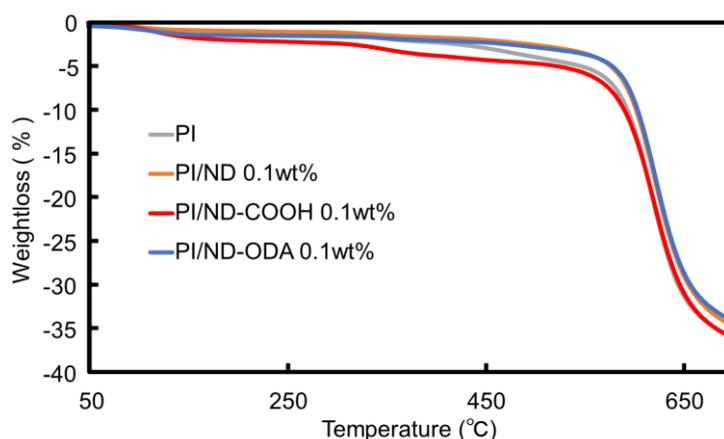


Figure 3. Thermogravimetric traces of PI and various PI/ND nanocomposites.

Table 2. Melting temperature (T_m) and thermal decomposition temperature (T_d) of PI and various PI/ND nanocomposites.

	T_m (°C)	T_d (°C)
PI	593	544
PI/ND	617	575
PI/ND-COOH	604	521
PI/ND-ODA	619	577

Stress-strain curves of PI and various PI/ND nanocomposites were shown in Figure 4. The Young's modulus, tensile strength and elongation at break obtained from the curves were shown in Table 3. The Young's modulus and the tensile strength remarkably increased by the incorporation of only 0.1 wt% of various NDs. The nanocomposite reinforced by ND-ODA showed the highest mechanical properties showing that the strong interaction between PI and ND-ODA was achieved in the nanocomposite.

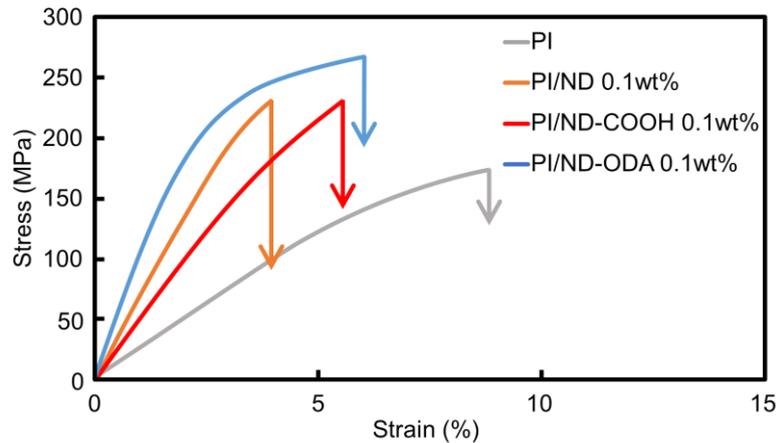


Figure 4. Stress-strain curves of PI and various PI/ND

Table 3. Young's modulus (E), Tensile strength (σ_{max}) and Elongation at break (ϵ) of PI and various PI/ND

	E (GPa)	σ_{max} (MPa)	ϵ (%)
PI	4.7	216	8.1
PI/ND	6.5	260	6.8
PI/ND-COOH	6.3	235	7.0
PI/ND-ODA	7.4	265	7.2

4. Conclusions

COOH and ODA were introduced on the ND surface by chemical modification. The PI nanocomposites reinforced by various NDs were prepared by in-situ polymerization. It was revealed that the mechanical properties and thermal properties remarkably increased with only 0.1 wt% of various NDs. ND-ODA showed highest reinforcement effect among the NDs.

References

- [1] Oxford University Press, POLYMER DATA HANDBOOK, 1999
- [2] Yoshio IMAI, Structure-Property Relationship in Polyimides *JIEP* Vol.4 No. 7, 2001
- [3] Vadym N. Mochalin, Ioannis Neitzel, Bastian J. M. Etzold et al., Covalent Incorporation of Aminated Nanodiamond into an Epoxy Polymer Network *J. Am. Chem. Soc.* VOL. 5, NO. 9, 7494–7502, 2011.
- [4] Ho, D., Nanodiamond Applications in Biology and Nanoscale Medicine, *Springer New York*, 2010 p 286.
- [5] Lang Ma, Guojian Wang, Jinfeng Dai, Influence of structure of amines on the properties of amines-modified reduced graphene oxide/polyimide composites, *J. APPL. POLYM. SCI.* 43820, 2016

- [6] Mayo, D. Miller, F. A. Hannah, R. W. Course Notes on the Interpretation of Infrared and Raman Spectra *John Wiley & Sons, Inc.* New York, 2004.