Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Raju, M. Padmanabha and Alam, Sarfaraz(2009) 'Synthesis of Polyimide Nanocomposites', Journal of Macromolecular Science, Part A, 46: 11, 1136 — 1141
To link to this Article: DOI: 10.1080/10601320903256695
URL: http://dx.doi.org/10.1080/10601320903256695

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 1136–1141

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903256695

Synthesis of Polyimide Nanocomposites

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Received January 2009, Accepted May 2009

A series of polyimide nanocomposite (PINC) films were prepared by using poly(amic acid) and Ba, Sr, Sn, TiO_3 nanoparticles via in-situ polymerization method. Poly(amic acid) was synthesized from benzophenone tetracarboxylic anhydride and diamino diphenyl ether by ring-opening polyaddition reaction. The PINC films were characterized by FTIR spectroscopy. The thermal properties of PINC films were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) methods. The prepared PINC showed major weight loss in the range of 550–600°C in nitrogen atmosphere. These had char yield in the range of 50–60% at 800°C. The morphological studies of PINC films were carried out using SEM method.

1 Introduction

Aromatic polyimides are well established as high performance polymeric materials because of their excellent heat resistance, electrical insulating properties as well as mechanical characteristics and are widely used as electronic materials, adhesives, composite materials, fiber and film materials (1–5). Polymer/inorganic filler nanocomposites belong to a relatively new class of advanced materials with improved properties (6–10). Polymer nanocomposites have attracted substantial attention from academic and industrial researchers because of their superior thermal and mechanical properties compared to those of their micro- and macrocomposite counterparts containing an equivalent volume fraction of inorganic filler. Presently, polymer nanocomposites reported in the literature are typically based on polymer matrices reinforced by nanofillers such as montmorillonite (MMT) platelets or carbon nanotubes. Because of their excellent heat resistance, chemical stability, and superior electrical properties, polyimide (PI) based nanocomposites are desirable candidates for use in corrosive and aggressive environments where current polymer nanocomposites are not useable. It has been reported that PI nanocomposites can exhibit increased modulus and strength, high-heat distortion temperature, decreased thermal expansion coefficient, and increased solvent resistance compared to the pure (unfilled) polymer.

Polymer–ceramic composites on the other hand offer excellent materials characteristics including low temperature processability, flexibility, high temperature resistance, outstanding solvent resistance etc. One of the most attractive features of filled composites is that their dielectric properties can be varied over a wide range by the choice of the shape, size and connectivity of the constituents in the polymeric matrix. A number of methods, such as solution mixing, melt blending, and in situ polymerization, for preparing PI nanocomposites have been reported (11–13).

In the present study, polyimide nanocomposite (PINC) films were prepared by using poly (amic acid) and Ba, Sr, Sn, TiO_3 nanoparticles via *in situ* polymerization method. The PIN films were characterized by FTIR spectroscopy. The thermal properties of PIN films were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) methods.

2 Experimental

2.1 Materials

Benzophenone tetracarboxylic anhydride (BTDA) was recrystallized from acetic anhydride. Oxy dianiline (ODA) was recrystallized from ethanol before use. N,N-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over phosphorous pentoxide and stored over 4 Å molecular sieves.

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2.2 Synthesis of Poly(amic acid)

Equimolar amounts of diamine and dianhydrides monomers were reacted in nitrogen atmosphere. A representative polymerization procedure is as follows.

A round-bottom flask equipped with a nitrogen inlet, a stir bar was charged with 0.01 mol of diamine (ODA) and 20 ml of DMAc. The solution was stirred until the diamine dissolved completely. 0.01 mol of dianhydride (BTDA) was added to this solution under effective stirring. The reaction mixture was stirred under magnetic stirring for 24 h at room temperature to obtain poly (amic acid) resin.

2.3 Synthesis of Polyimide Nanocomposites Films

Ba, Sr, Sn, TiO_3 nanoparticles having a size of $\sim$ 50 nm (1%) were taken into poly(amic acid) and stirred for 4 h to get a homogenous mixture. The reaction mixture was poured onto a clean and dry glass plate and then thermal imidization was carried out in an oven at 100°C for 1 h and at 150°C, 200°C, 250°C for 30 min at each temperature. The pale-yellow transparent films were obtained by a thermal imidization process. Further various proportions (2%, 3%, 4% and 5%) of polyimide nanocomposites films were synthesized through above the mentioned procedure.

2.4 Measurements

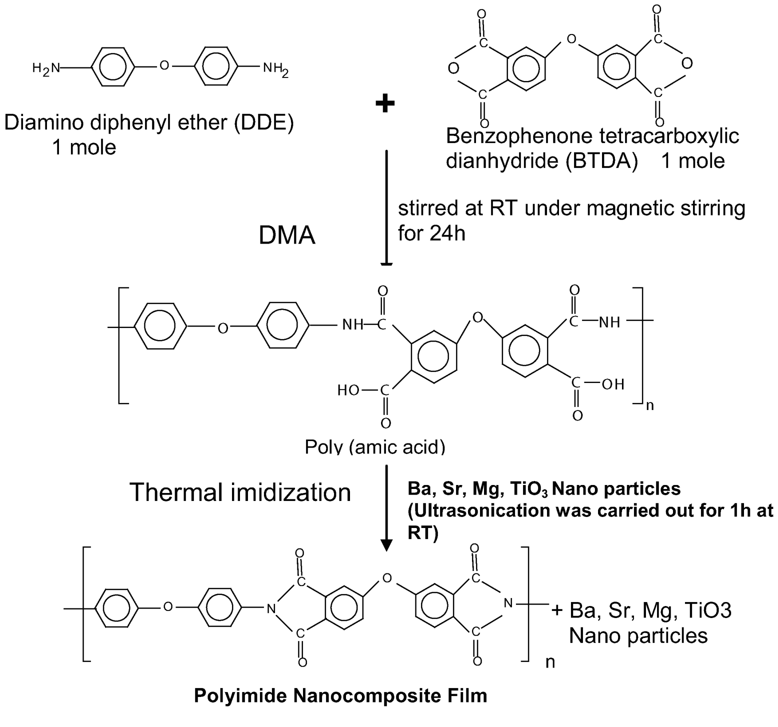
The infrared spectra were recorded using Nicolet 750 Fourier transform infrared spectrophotometer. Glass transition temperatures (T_g) were obtained using differential scanning calorimetry, using TA Instruments, USA (Model No. DSC 2910) at a heating rate of 10°C min^{-1} under N_2 atmosphere. The degradation temperatures (T_d) were recorded using a Hi-Res TGA 2950 instrument at a heating rate of 20°C min^{-1} under N_2 atmosphere. The water uptake was determined by the change of the mass in vacuum dried film specimens before and after immersion in water at room temperature for 24 h.

3 Results and Discussion

3.1 Imidization of PINCs

The synthesis of PINC films were synthesized via poly (amic acid) intermediate. Initially, diamine was dissolved in measured amount of dry DMAc and then dianhydride was added portion wise to obtain poly (amic acid). The 15% solid content of poly(amic acid) was obtained. Ba, Sr, Sn, TiO_3 nanoparticles containing poly(amic acid) solutions were cast on clean glass plates and heated through various stages upto 250°C to remove solvent and water formed during the process of imidization. The complete imidization was occurred at 250°C. The reaction procedure is shown in Scheme 1.

FTIR spectroscopy allows monitoring of the imide ring formation during thermal imidization. From the spectra, the characteristic absorption band of the imide ring was observed near 1780, 1720 cm^{-1} (asymmetrical and



Sch. 1. Preparation of polyimide nanocomposite films.

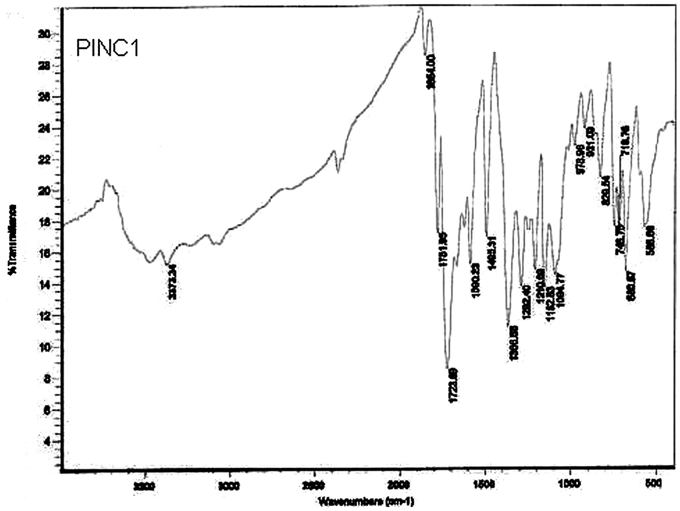


Fig. 1. Typical FTIR spectrum of polyimide nanocomposite film.

symmetrical C=O stretching vibration), 1350 cm^{-1} (C—N stretching vibration), and those of amide and carboxyl groups in the region of 3000–3500 and 1500–1700 cm^{-1} disappeared, indicating a virtually completed conversion of the PAA precursor into PINC film. A typical FTIR spectrum of poly(amic acid) and PINC film is shown in Figure 1.

3.2 Thermal Behavior of PINC Films

The thermal behavior of the PINC films was evaluated by using the differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) and results were presented in Table 1. DSC measurements were conducted at a heating rate of 10°C min^{-1}. The glass transition temperatures (Tg) were taken as the midpoint of the change in slope of the baseline in DSC curve. The PINC films showed glass transition temperatures (T_g) in the range of 320–350°C. Further it is observed that the incorporation of nanoparticles does not affect the thermal imidization of poly (amic acid). The decomposition temperatures (T_d) were recorded using TG measurements conducted at a heating rate 20°C min^{-1} in inert atmosphere. TG studies reveal that the prepared PIN films were showed single step decomposition. From TG studies, the initial mass loss (IDT) was observed in the temperature range of 500–520°C and maximum loss (T_{max}) was observed in the temperature range of 530–550°C. The resulting PINC films had char yield 75–65% at 700°C in inert atmosphere.

3.3 SEM Studies

The morphological studies of PIN films carried out using SEM method. Figures 2–5 show the pure polyimide and Ba, Sr, Sn, TiO_3 nanoparticles containing polyimide films. The SEM studies show that as the Ba, Sr, Sn, TiO_3 nanoparticles increased more than 0.4% the agglomeration of nanoparticles was observed. PINC 5 film was difficult to carry out SEM studies due its brittle nature.

3.4 Water Uptake

Water uptake of the PINC films was measured by immersing films into deionized water for 24 h at room

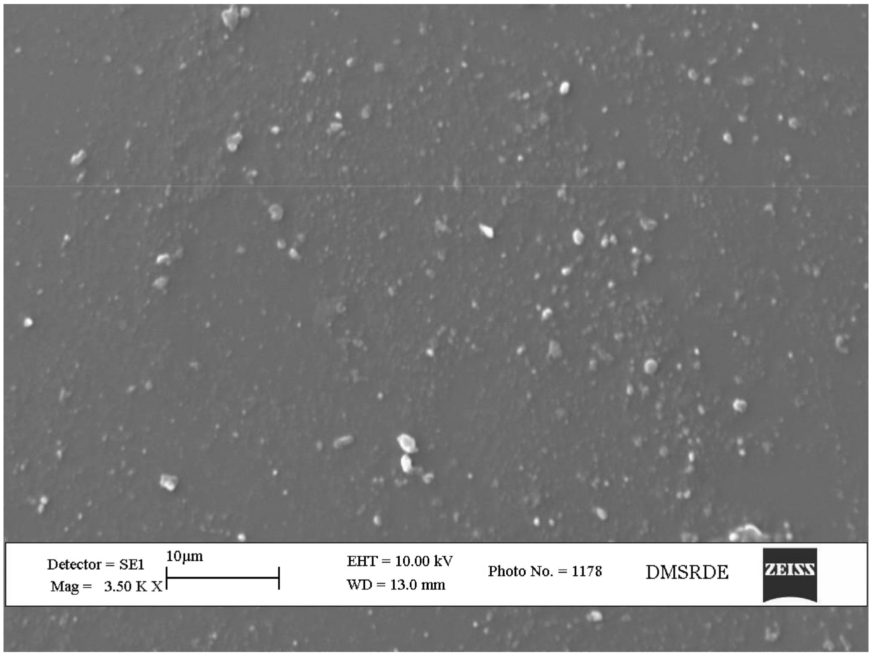


Fig. 2. SEM image of Polyimide Nanocomposite films (2) PINC 1 (%).

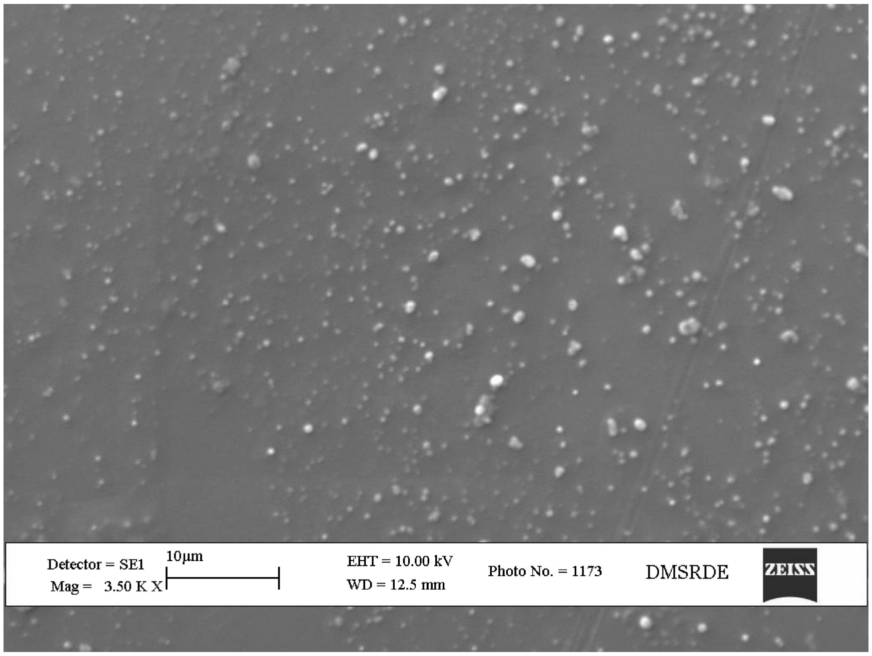


Fig. 3. SEM image of polyimide nanocomposite films (3) PINC 2 (%).

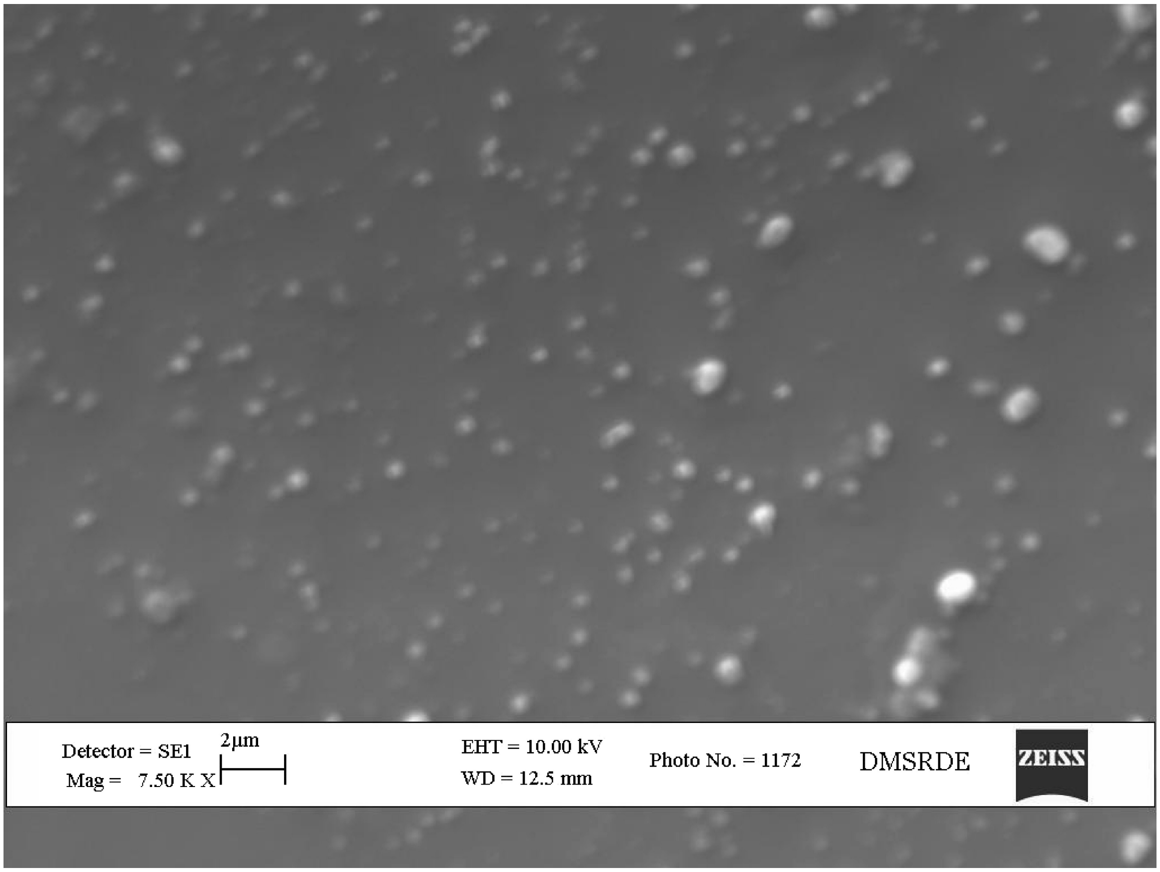


Fig. 4. SEM image of polyimide nanocomposite films (4) PINC 3 (3%).

Table 1. Thermal and Physical properties of PINC films

Polymer Code	*Major thermal decomposition temp. (TGA)*	*Char yield % (TGA)*	*Curing temperature (DSC)*	*Water absorption %*	*Film property*
PI	643	68	185	2.5	Flexible
PINC1 (0.1%)	645	70	184	2.4	Flexible
PINC2 (0.2%)	650	71	185	2.4	Flexible
PINC3 (0.3%)	667	72	185	2.3	Flexible
PINC4 (0.4%)	668	74	184	2.3	Brittle
PINC5 (0.5%)	674	76	188	2.2	Highly Brittle

temperature. The films were then taken out, wiped with tissue paper and quickly weighed on a microbalance. The water uptake of the film was calculated form the following equation.

$$\text{Water uptake}\,(\%) = \frac{W - W_0}{W_0} \times 100$$

W_0 – is the initial mass of the PIN film

W– is the mass of the PIN film after immersion in water for 24 h.

The water uptake of PIN films was in the range of 1.26–1.84 wt%. They exhibited low water uptake values due to the presence of Ba, Sr, Sn, TiO_3 nanoparticles.

4 Conclusions

Polyimide nanocomposite (PINC) films were prepared by using poly(amic acid) and Ba, Sr, Sn, TiO_3 nanoparticles via in-situ polymerization method. Poly(amic acid) was synthesized from benzophenone tetracarboxylic anhydride and diamino diphenyl ether by ring-opening polyaddition reaction. The PINC films were characterized by FTIR spectroscopy. The thermal properties of PINC films were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) methods. The prepared PINC showed major weight loss in the range of 550–600°C in nitrogen atmosphere. These had char yield in the range of 75–65% at 800°C. The thermal stability of PI films were increased as the percentage of nanoparticles increased. PINC 4 and PINC 5 films are highly brittle in nature due to higher loading of Ba, Sr, Sn, TiO_3 nanoparticles

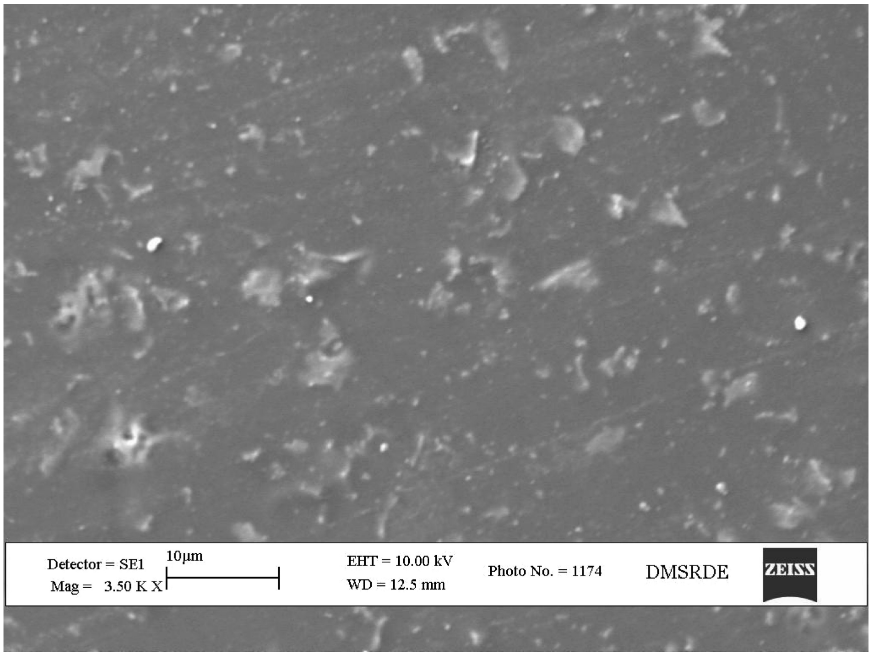


Fig. 5. SEM image of polyimide nanocomposite films (5) PINC 4 (4%).

into the polyimide films. The morphological studies of PINC films were carried out using SEM method. The SEM studies represents that as the Ba, Sr, Sn, TiO_3 nanoparticles increased more than 0.4% the agglomeration of nanoparticles was observed. Further electrical studies of PINC films are under progress.

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