

Synthesis and Characterization of PT/PS/SiO₂ Nanocomposite in Nonaqueous Medium by Chemical Method

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Received 22 January 2004; accepted 16 August 2004

DOI 10.1002/app.21513

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The PT/PS/SiO₂ nanocomposite of polythiophene (PT), polystyrene (PS), and SiO₂ with a grain size of 100–150 nm was synthesized by chemical polymerization using FeCl₃ oxidant in nanoaqueous medium (CHCl₃). The properties of PT/PS/SiO₂ synthesized were compared to those of PT, PT/PS, and PT/SiO₂ synthesized in the same conditions. The synthesized materials were subsequently characterized by FTIR spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The incorporation of PT in the composite was endorsed by FTIR studies. TGA revealed enhanced thermal stability of

the PT/PS/SiO₂ nanocomposite compared to that of PT. SEMs showed globular particles and the presence of clusters of composite particles. The conductivity of the PT/PS/SiO₂ nanocomposite was measured as $1.30 \times 10^{-7} \text{ Scm}^{-1}$ and the conductivity value of PT ($1.02 \times 10^{-4} \text{ Scm}^{-1}$) decreased with entering PS and SiO₂ to PT structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 746–752, 2005

Key words: conducting polymers; nanocomposites; polythiophene; silicas

INTRODUCTION

During the past decade, there has been growing interest in electrically conducting polymers due to their potential applications.^{1–4} Speciality polymers such as polypyrrole (PPY),⁵ polyaniline (PANI),⁶ and polythiophene (PT)⁷ display outstanding conductivity and other interesting bulk properties, but suffer from processibility limitations due to their intractable nature. There are many approaches to significantly improve these intractable materials.

Of all the different modification techniques available, one of the most widely studied and applied in this respect is the formation of composites of different origins. Conducting polymer composites are in fact some suitable compositions of a conducting polymer with one or more insulating materials so that their desirable properties are combined successfully.^{8–11} In recent years, composites of a special category, termed “nanocomposites” have been studied with growing interest. There is numerous literature describing the preparation and properties of these materials, which are in fact some hybrid materials in which organic polymers and inorganic oxides or salts of different metals with nanometer dimensions combine in some special fashion to give rise these nanocomposites.^{12–15}

Recently, the composites and nanocomposites of PT was prepared using both insulating and nanomatrix substances. A review by Rancali¹⁶ refers to the work on some PT–polymer [poly(methyl methacrylate), poly(vinyl chloride), polystyrene] composites by direct electropolymerization of thiophene in the presence of the respective host polymer and on other PT composites using multistep methods. In a series of publications, many researchers recently have reported the preparation and evaluation of nanocomposites of PT with TiO₂,¹⁷ Al₂O₃.¹⁸

To the best of our knowledge, no report dealing with the preparation of PT nanocomposites, including both insulating and nanostructure properties, seems to be available. In this study, we prepared polythiophene/polystyrene/silica nanocomposite (PT/PS/SiO₂) and PT/SiO₂ materials by dispersing the inorganic nanomatrix SiO₂, an organic thiophene matrix, by *in situ* oxidative polymerization. The as-synthesized materials were characterized by FTIR spectroscopy, scanning electron microscopy, and thermal analysis. The properties of composites and nanocomposites obtained were compared with that of PT homopolymer.

EXPERIMENTAL PROCEDURES

Materials

Thiophene (Aldrich, USA) was freshly distilled under pressure before use. Nanodimensional SiO₂ powder

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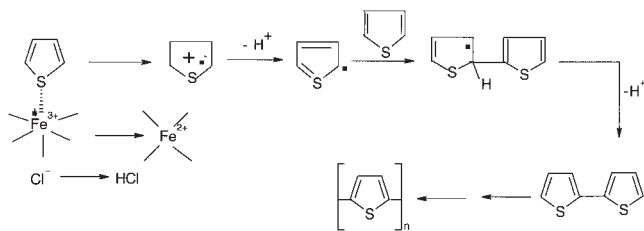


Figure 1 Proposed mechanism of thiophene oxidative polymerization with FeCl₃ in CHCl₃.

(average particle size 150 nm) and polystyrene ($M = 200,000$) were purchased from Aldrich. All other reagents and chemicals [FeCl₃, chloroform, ethanol, *N*-methyl pyrrolidinone (NMP), sulfuric acid (H₂SO₄)] were of analytical grade.

Chemical polymerization of thiophene using FeCl₃

A known mass of thiophene (TP) was placed into a round-bottomed flask containing 50 ml CHCl₃ and a particular quantity of FeCl₃ was added to this at one time. The reaction mixture was stirred for 4 h at room temperature. The product was washed thoroughly with chloroform and ethanol. The deep brownish-black mass was then dried at 70°C under vacuum.

Preparation of composites

Synthesis of the PT/PS composite

A solution of PS and thiophene in chloroform was placed in a three-neck round flask. To this solution, a solution of FeCl₃ in CHCl₃ was added dropwise with vigorous stirring. The polymerization reaction was allowed to proceed for 4 h with stirring. The solvent of polymerization solution then was evaporated and precipitated powder was washed with ethanol, filtered, and finally dried in vacuum at 70°C.

Synthesis of the PT/SiO₂ composite

A known mass of SiO₂ was finely dispersed into 50 ml of CHCl₃, after which a known quantity of TP was injected and the solution was stirred for 1 h. A particular amount of FeCl₃ was then added to the solution at one time. The reaction mixture was magnetically stirred at room temperature for 4 h. The separated mass was thoroughly washed with chloroform and ethanol.

Synthesis of the PT/PS/SiO₂ nanocomposite

A certain amount of SiO₂ was dispersed together with thiophene in approximately 60 ml polystyrene–chloroform solution and the solution was stirred for 1 h.

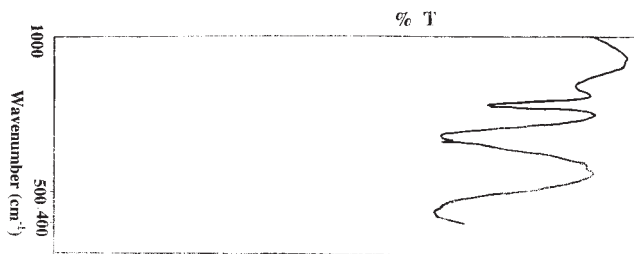


Figure 2 FTIR spectrum of PT obtained by FeCl₃.

This procedure is necessary for thiophene to absorb onto the oxide particles. 50 ml of a saturated solution of FeCl₃ in chloroform was added to this dispersion. After stirring for 1–2 h, the color of mixture changed from gray to deep black, producing hydrogen chloride. Finally, the solvent of the dispersion was evaporated and the separated product was washed with ethanol. The nanocomposite was dried at 70°C for 24 h.

Characterization

FTIR spectra were taken on a Perkin–Elmer BX model instrument by the KBr pellet technique. Thermogravimetric analyses were performed at a heating rate of 10°C min⁻¹ under nitrogen atmosphere on a Perkin–Elmer Thermogravimetric Analyzer. Surface morphologies of homopolymers and composites were studied by taking scanning electron micrographs on a JEOL 5600-LV model instrument. The conductivities of polymers were determined on pressed pellets by using a four-probe technique with a direct current (dc) measurement at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the proposed mechanism for thiophene oxidative polymerization. The reaction starts by complexation between the thiophene sulfur and the FeCl₃ to form a cation radical, which upon deprotonation yields the initiating radical. The mechanism also proposes that the combination of thiophene radicals gives mainly the 2,5-disubstituted thiophene moieties in the PT chains.¹⁹

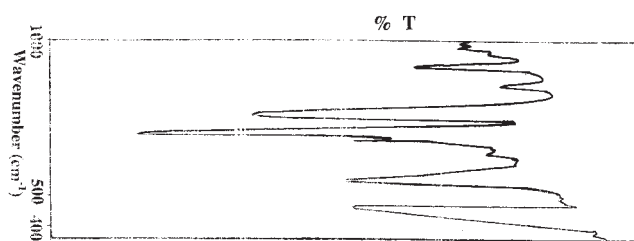


Figure 3 FTIR spectrum of PT/PS/SiO₂ nanocomposite.

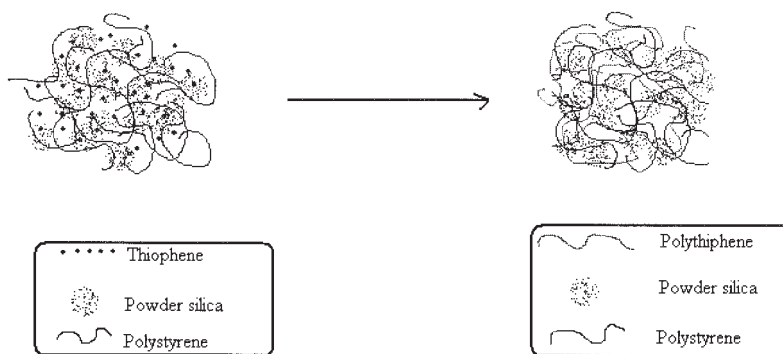


Figure 4 Schematic representations of synthesis of PT/PS/SiO₂.

Figure 2 shows the FTIR spectrum of PT synthesized with FeCl₃ in CHCl₃. The formation of PT was readily determined by the IR absorption peaks at 682 and 787 cm⁻¹ usually ascribed^{16, 20, 21} to the C–H out-of-plane stretching vibration.

The incorporation of PT in the composite was seen at the FTIR spectrum (Fig. 3) of the PT/PS/SiO₂ nanocomposite. We observed peaks coming from each PT, PS, and SiO₂ at the FTIR spectrum of the PT/PS/SiO₂ nanocomposites. The intercalation of PT in the PS and SiO₂ system is confirmed by the presence of characteristic peaks of PT. Similar results were obtained for PPy–MMT²² and poly(*o*-methoxyaniline)–MMT²³ systems.

Figure 4 is a schematic representation of the formation of the PT/PS/SiO₂ nanocomposite. Organic thiophene monomers were intercalated into PS chains and SiO₂ particles as host structures and were followed by a one-step oxidative polymerization.

Table I compares the conductivity values of PT, PT/PS, PT/SiO₂, and PT/PS/SiO₂ polymers. The conductivity at room temperature of PT is higher

TABLE I
Conductivity Values of Polymers

Polymer	Conductivity (Scm ⁻¹)
PT	1.02×10^{-4}
PT/PS	2.89×10^{-5}
PT/SiO ₂	6.44×10^{-5}
PT/PS/SiO ₂	1.30×10^{-7}

TABLE II
Solubility of the Polymers

Solvents	Dielectric constant	Polarity index	Solubility ^a of polymers and solution color ^b				
			PT	PT/SiO ₂	PT/PS	PT/PS/SiO ₂	PS
NMP	32	6.7	PS(RO)	PS(YM)	MS(MR)	MS(MR)	IS
H ₂ SO ₄	101	—	SS(LB)	IS	SS(LG)	SS(LG)	IS

^a MS, mainly soluble; PS, partially soluble; SS, slightly soluble; IS, insoluble.

^b The letters in parentheses indicate solution color: RO, red-orange; LB, light-blue; YM, yellow-maroon; MR, maroon-red; LG, light-gray.

than that of PT/PS, PT/SiO₂, and PT/PS/SiO₂ composites. The conductivity of PT/PS/SiO₂ nanocomposite is lower than that of PT homopolymer. The PT/PS/SiO₂ sample is a more insulating state than the PT one, which implies that the SiO₂ particles intercalated by the conducting PT induce a weak interchain interaction between the polymerized PT chains.²⁴

The electrical conductivities of PT/SiO₂ and PT/PS are smaller than that of PT. This was expected because the PS and SiO₂ are not electrically conductive and the incorporation of PS molecules and SiO₂ particles into the PT matrix contributes to the decrease of electrical conductivity. As shown in the literature,^{25, 26} the conductivity of a chemically synthesized nanocomposite of polyaniline intercalated into Na⁺–montmorillonite was decreased. This phenomenon was attributed to the clay layer intercalated by a polyaniline layer inducing a weak interchain interaction between the polyaniline chains.

Poor processability is a serious problem for most of the π -conjugated polymers. The improvement of the processability of the conducting polymers, especially PT, should depend on the enhancement of the polymer solubility by chemical modification, because the solubility is one of the most important performances deciding the feasibility of the solution-processing method. The solubility of PT and its composites in NMP and H₂SO₄ solvents with characteristic parameters is summarized in Table II. The

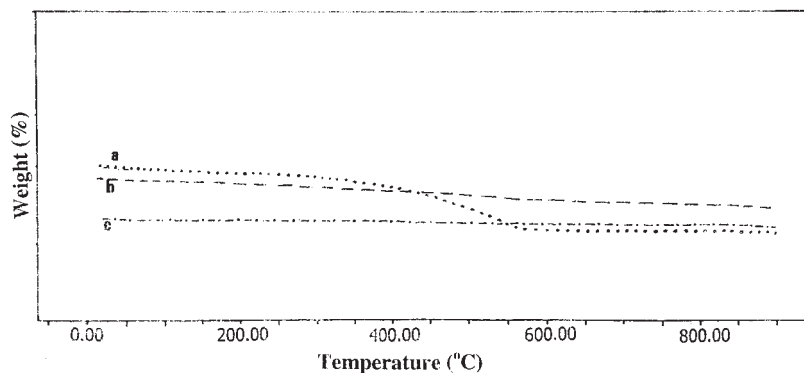


Figure 5 TGA thermogram of (a)PT (.), (b)PT/SiO₂ (- - -), (c) SiO₂ (- . - .).

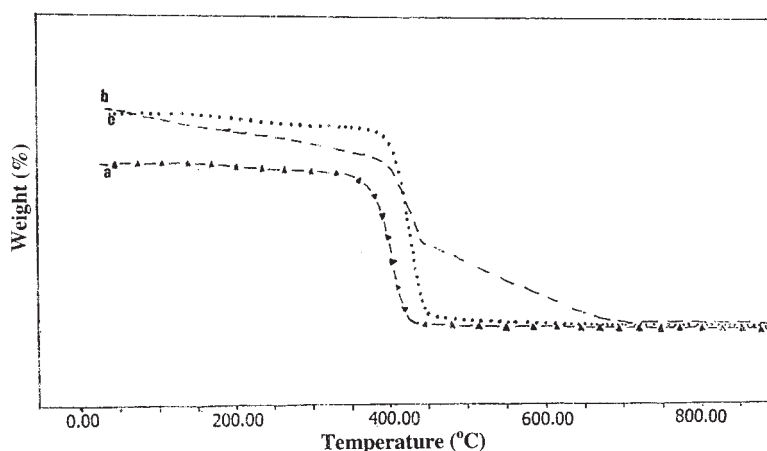


Figure 6 TGA thermogram of (a)PS (-△-△-△), (b) PT/PS (- - -), (c) PT/PS/SiO₂(. . . .).

solubilities of composites are better than homopolymers and composites are more soluble in NMP than H₂SO₄.

Figures 5(a-c) and 6(a-c) show TGA curves of PT, PT/SiO₂, SiO₂ and PS, PT/PS, and PT/PS/SiO₂ patterns, respectively. The decomposition temperatures obtained from these thermograms are compared in Table III.

PT/PS composite shows two decomposition steps whereas PT, PS, SiO₂, PT/SiO₂, and PT/PS/SiO₂ show degradation with one step. In these degradation temperatures the pattern starts to degrade, removing dopant anions.²⁷ When T_i are compared, SiO₂ has the highest thermal stability. The thermal stability analysis of SiO₂ indicated a 5% weight loss at 568°C due to probable loss of the volatile impurities.¹⁵

The thermal stability of PT is increased from 299 to 366 and 359 °C, respectively, preparing PT/PS composite and PT/PS/SiO₂ nanocomposite. In the PT/SiO₂ nanocomposite, its % weight loss decreased to 28% at 500°C, whereas % weight loss of PT was 55% at 500°C. Thus, these data readily confirmed the enhanced thermogravimetric stabilities

for the PT/PS composite and PT/PS/SiO₂ nanocomposite relative to PT.

Figure 7(a-d) represents the SEM images of PT, SiO₂, PS, and PT/PS/SiO₂ polymers. A scanning electron micrograph of PT is presented in Figure 7(a). In general, the PT particles were characterized by globular morphology; also, particles were not of uniform size and exhibited a tendency to form clusters.¹⁸ The SEM micrograph of SiO₂ particles is

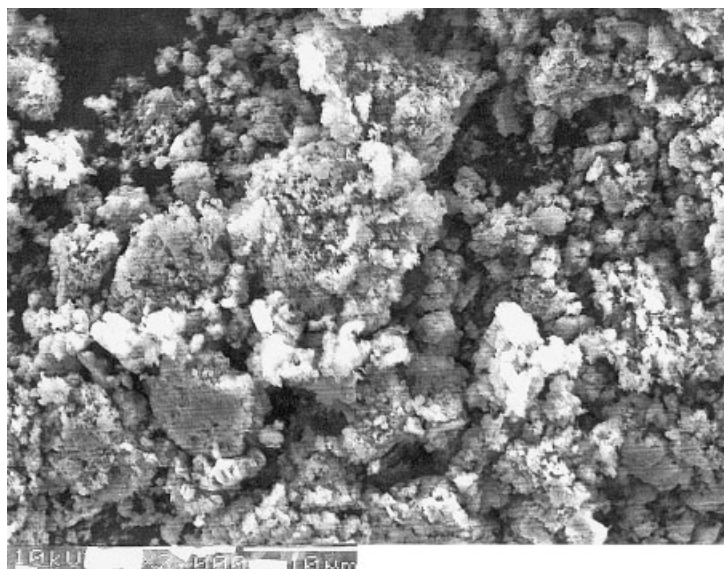
TABLE III
Results of TGA Analysis of Polymers

Polymer	T_i^a (°C)	T_m^b (°C)	T_f^c (°C)	% wt loss
PT	299	472	576	55
PS	354	401	432	98
PT/PS	366	421	451	35
	460	551	704	28
SiO ₂	379	476	568	5
PT/SiO ₂	128	323	519	28
PT/PS/SiO ₂	359	422	464	90

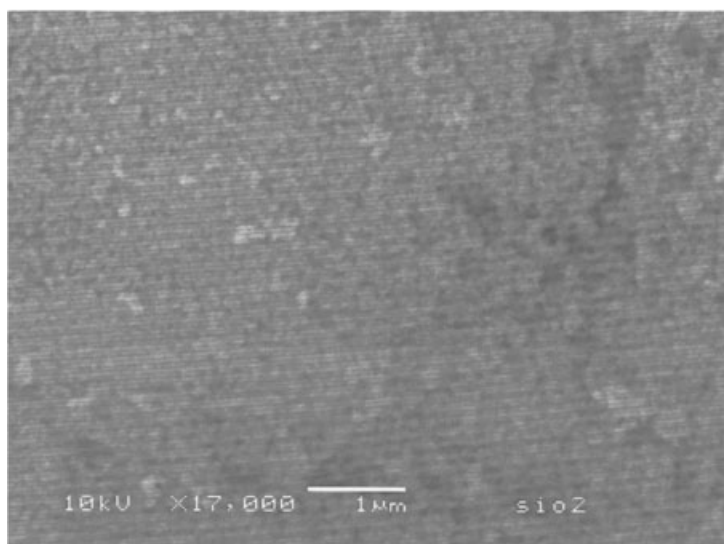
^a T_i , initial temperature.

^b T_m , maximum decomposition temperature.

^c T_f , final temperature.



(a)



(b)

Figure 7 SEM micrograph of (a) PT (magnification $\times 2,000$, bar = $10 \mu\text{m}$), (b) SiO_2 (magnification $\times 17,000$, bar = $1.0 \mu\text{m}$), (c) PS (magnification $\times 33,000$, bar = $0.5 \mu\text{m}$), (d) PT/PS/ SiO_2 (magnification $\times 5,000$, bar = $5.0 \mu\text{m}$).

shown in Figure 7(b). The average size of the particles is 100–150 nm. Figure 7(c) shows uniform surface morphology with white color of PS film. The SEM image of PT/PS/ SiO_2 nanocomposite is presented in Figure 7(d). It shows a nonporous and uniform structure in the underlayer and a granular and sponge-like structure on the upper surface. In addition, the formation of irregular particles (both spherical as well as nonspherical) included some clusters. The SEM micrograph of the nanocomposite showing the presence of PT with black color covering the surface of PS with color [in Fig.

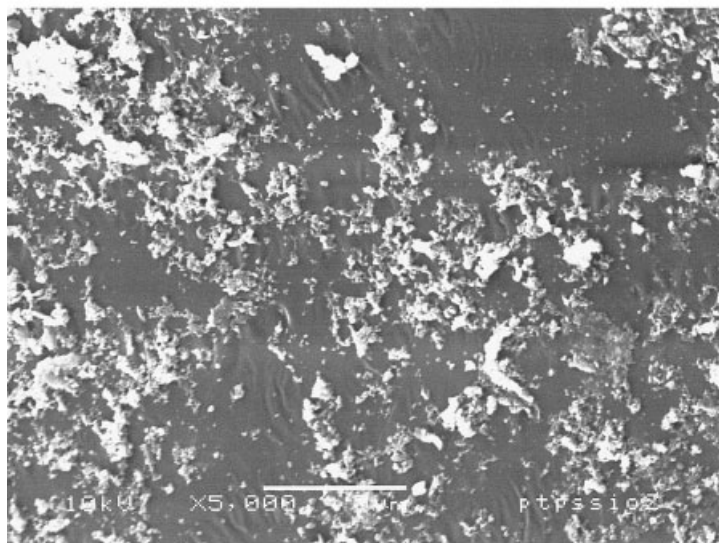
7(d)] includes all together the PS, PT, and SiO_2 structures.

CONCLUSION

A PT/PS/ SiO_2 conducting nanocomposite with conducting, insulating, and nanomatrix properties was prepared by a simple chemical method. The PT/PS/ SiO_2 nanocomposite showed improved thermogravimetric stability compared to the PT homopolymer. The solubility of PT was enhanced by preparing its nanocomposite. Morphological images of as-



(c)



(d)

Figure 7 (Continued from the previous page)

synthesized materials were investigated by scanning electron microscopy. It was seen that all patterns synthesized showed different conductivities, thermal stabilities, and morphological structures. PT/PS/SiO₂ nanocomposite is expected to present a material with versatile commercial utilization.

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