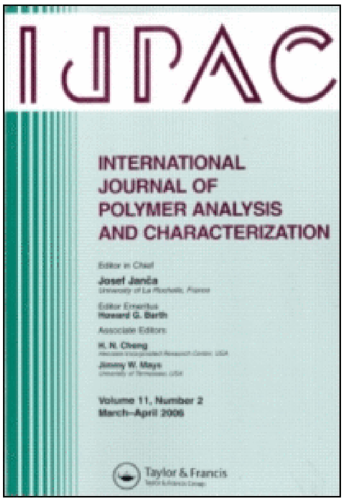

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Conducting Composites and Blends of Polythiophene and Polyoxymethylene

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Abstract: Conductive polyoxymethylene/polythiophene (POM/PT) composites and PT/POM blends were prepared by in situ chemical polymerization using $FeCl_3$ oxidant and mixing in solutions, respectively. It was found that the properties of the composites and blends were different from those of homopolymers and also from each other. Formation of polymer and composites was supported by FT-IR analyses. According to the results of thermal analyses (TGA), it was shown that polymers and composites have good thermal stability. The thermal degradation temperature of POM/PT composite containing 88% PT is higher than those of the other composites. The thermal degradation temperature of PT/POM blend containing 27% POM was described as higher than that of the other blends. The morphological structures of polymers and composites were studied by scanning electron microscopy (SEM). It was found that morphological structures of composites were smoother than that of PT. The crystal structures of polymers and composites were investigated by X-ray diffraction analysis. It was found that the crystal regions increased with increasing amount of POM in the composites and blends.

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Keywords: Blend; Composite; Polyoxymethylene; Polythiophene

INTRODUCTION

After 20 years' maturation, the world of conjugated polymers and oligomers has become established as an important branch of materials science with many opportunities for applications in electronics and photonics. Among conducting polymers, various derivatives of polythiophene (PT) have been investigated extensively because of their interesting semiconducting, electronic, and optical properties, combined with processing advantages and good mechanical characteristics. There are many application areas for the conductive polymers. The most exciting developments are the new class of semiconducting devices such as plastic batteries, sensors, conductive surfaces, magnetic recording, and solar cells.[1–4] However, better environmental and thermal stability and mechanical properties are desired for new developments in applications of conductive polymers. In order to improve these properties, one method was to prepare composites of the conducting polymers with selective nanodimensional inorganic oxides such as SiO_2, TiO_2, and zeolite.[5–7] Among other procedures a novel one involved preparations of composites, blends, or copolymers of the polythiophene with insulating polymers.[8–12]

Electrogenerated PT composites were reported such as PT-polystyrene, PT-polyvinylchloride, and PT-Nafion.[13] The idea was that such composites would be expected to possess a combination of outstanding optoelectronic and thermal stability characteristics of insulating polymers and conductivity of the constituent conducting polymers, which might lead to interesting advanced materials. Among insulating polymers, polyoxymethylene is a polymer showing good flexibility and mechanical properties. On the background of the above survey, we became interested in preparing a polyoxymethylene-based composite of polythiophene for which information appeared to be very meager.

In our work, we aimed to combine polyoxymethylene with polythiophene-insulating composite family. Polythiophene/polyoxymethylene (PT/POM) composites and blends with different contents of PT (wt.%) were synthesized using in situ polymerization of polythiophene into POM solution and blending method in solution, respectively. All the composites and the blends were characterized by using FT-IR, TGA, SEM, X-ray diffraction, conductivity, and magnetic susceptibility measurements.

EXPERIMENTAL SECTION

Materials

Polyoxymethylene (T_g: −13°C, T_m: 175°C, with acetate side group) was purchased from Aldrich. Thiophene (Ventron) was freshly distilled under reduced pressure. Anhydrous $FeCl_3$ (Aldrich), $CHCl_3$, and N,N-dimethyformamide (DMF) (Lab Scan AcronSci) were used as received.

Synthesis of Polythiophene

PT powder was obtained by thiophene polymerization in the presence of $FeCl_3$ as an oxidant. First, 18.7 mmol (1.5 mL) thiophene was dissolved in 60 mL $CHCl_3$ and stirred for 10 min at 55°C. Then 37 mmol of oxidant was added to the solution and stirred slowly. Polymerization was first carried out at 55°C for 3 h and then continued at room temperature for a further 17 h. The precipitated PT was washed with distilled hot water and ethanol and dried in a vacuum oven at 75°C for 24 h. The percentage yield of PT was calculated as 88 wt.%.

Synthesis of POM/PT Composites

First 1.4 g POM was dissolved in DMF at 135°C. Then, the temperature of the polymer solution was decreased to 55°C and $FeCl_3$ was added to this solution. Thiophene was dissolved in 5 mL DMF and added to the above POM + $FeCl_3$ solution. After 3 h at 135°C and 17 h at 55°C, the POM/PT composite was filtered, washed with water and ethanol, and finally dried at 50°C for 24 h in a vacuum oven. The content of PT in the composite was calculated as 14 wt.%. The POM/PT composites containing PT at different percentages (wt.%) were synthesized following the same procedure.

Preparation of PT/POM Blends

A known amount of PT was added to DMF at 55°C. POM dissolved in 15 mL DMF was added to PT suspension, and the mixture was stirred for 3 h at 55°C and 17 h at room temperature. After the preparation process was completed, PT/POM blend was exposed to filtering, washing, and drying processes. According to the same procedure, PT/POM blends at different percentages were prepared.

Characterization

Infrared spectra were recorded using a Fourier transform-infrared (FT-IR) spectrophotometer (Mattson-1000 model) to identify the chemical structure of polymers. The KBr technique was used to prepare the tested polymers. The morphology of the polymers was examined by a JEOL JSM-5600 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed from 20° to 900°C under N_2(g) atmosphere at a heating rate of 10°C/min using a Seteram (Groupe Sfim) Sys TG-DTA16 analyzer. X-ray diffraction patterns were measured by using a D8 Advance-Bruker-AXS. The conductivity of compressed pellets (4.9×10^6 Pa) of the polymers was determined using the standard four-point probe technique at room temperature. Magnetic susceptibility measurements were carried out by using a Sherwood Scientific model Gouy balance.

RESULTS AND DISCUSSION

Yield, Electrical Conductivity, and Magnetic Susceptibility Results

PT synthesized using $FeCl_3$ has a yield value of 88% and a conductivity of 1.90×10^{-3} Scm^{-1}. Additionally, PT homopolymer indicates positive magnetic susceptibility value showing polaron conductivity mechanism, i.e., it is of "polaron" nature.[14]

Table I shows the conductivity and magnetic susceptibility values of POM/PT composites including different percentages of PT. The conductivity values of POM/PT composites slightly increased with changing amount of PT up to 68% PT content. The POM/PT

Table I. Conductivity and magnetic susceptibility results for POM/PT composites

Composite	Content of PT in composite (g/g, %)	Conductivity (Scm^{-1})	Magnetic susceptibility (μ_e, BM[a])
POM/PT	14	1.99×10^{-4}	−27
POM/PT	29	2.32×10^{-4}	−20
POM/PT	42	2.34×10^{-4}	−27
POM/PT	68	2.87×10^{-4}	−29
POM/PT	72	2.66×10^{-4}	−23
POM/PT	88	2.59×10^{-4}	−21

[a] μ_e, effective magnetic moment; BM, Bohr magneton.

Table II. Conductivity and Gouy balance measurements of PT/POM blends

Blend	Yield of POM in blend (g/g,%)	Conductivity (Scm^{-1})	Magnetic susceptibility (μ_e, BM[a])
PT/POM	14	2.73×10^{-4}	−28
PT/POM	27	2.42×10^{-4}	−27
PT/POM	44	1.98×10^{-4}	−26
PT/POM	58	1.71×10^{-4}	−31
PT/POM	71	1.02×10^{-4}	−31
PT/POM	87	9.71×10^{-5}	−33

[a] μ_e, effective magnetic moment; BM, Bohr magneton.

composite containing 68% of PT has the highest conductivity, with a value of 2.87×10^{-4} Scm^{-1}. This value can be described as the percolation threshold point for the POM/PT composite.[15] The POM/PT composite exhibits diamagnetic properties. The conducting mechanisms of POM/PT composites are of "bipolaron" nature.[16]

The conductivity and magnetic susceptibility values of PT/POM blends are given in Table II. The blend containing 14% POM has the highest conductivity, with the value of 2.73×10^{-4} Scm^{-1}.

The conductivity of PT($FeCl_3$) was observed to decrease 10 times in POM/PT composites and PT/POM blends. Increasing the amount of POM in the composites and blends reduces electrical conductivity since POM is an insulating polymer which effects the electron delocalization and hopping in PT structure. PT/POM blends exhibit negative magnetic susceptibility values and diamagnetic properties.[16,17]

FT-IR Results

Figure 1 shows FT-IR spectra of PT homopolymer (spectrum a), POM/PT composite (spectrum b), and PT/POM blend (spectrum c). FT-IR spectrum of PT exhibited characteristic absorptions reported for polythiophene in the literature.[18–20] The bands at 2900–3100 cm^{-1} correspond to aromatic –C–H stretching, whereas the bands at 1420–1700 cm^{-1} belong to –C=C bands. Aromatic –C–H vibration bands and C-S stretching bands were identified at 820–850 cm^{-1} and at 750–800 cm^{-1}, respectively.

The appearance of peaks at 820 and 790 cm^{-1} in POM/PT composite (Figure 1(b)) and PT/POM blend (Figure 1(c)) confirmed the incorporation of PT homopolymer in the composite and polymer backbone. Also, the FT-IR spectrum of composite and blend clearly

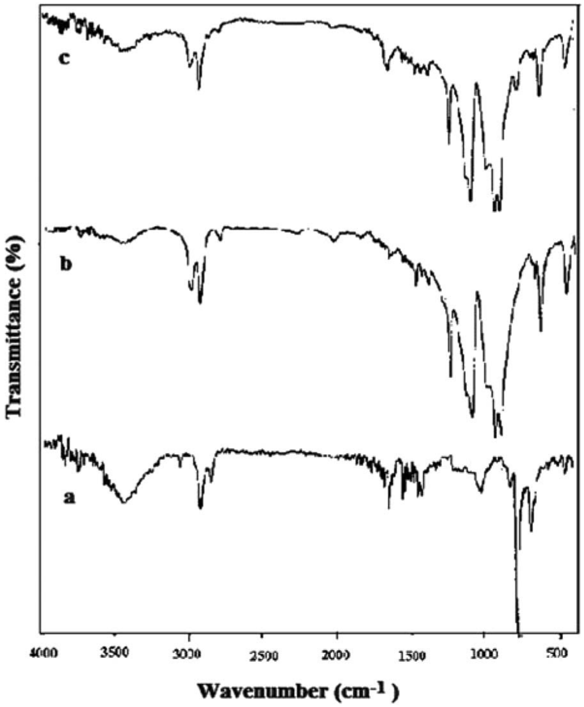


Figure 1. FT-IR spectra: (a) PT, (b) POM/PT composite, and (c) PT/POM blend.

shows the presence of characteristic peaks of POM in the range of 800–1400 cm^{-1} and 2800 cm^{-1}. These characteristic peaks in POM/PT composite are more intense than in the PT/POM blend. Thus, FT-IR data confirmed the incorporation of moieties in the structure of the composite and blend.

X-Ray Results

Figure 2 represents the X-ray diffraction (XRD) scans of PT, POM/PT composite, and PT/POM blend. The diffraction peak observed at a scattering angle of $2\theta = 18°$ seems to be a reflection of the polymer backbone.[21] Interestingly, the XRD pattern of PT ($2\theta = 20°$) suggesting a typical amorphous structure was modified to a slightly amorphous pattern of POM/PT composite and PT/POM blend by introducing amorphous characteristics. Significantly, similar XRD patterns were also observed in the case of a PT-zeolite composite prepared via the oxidative

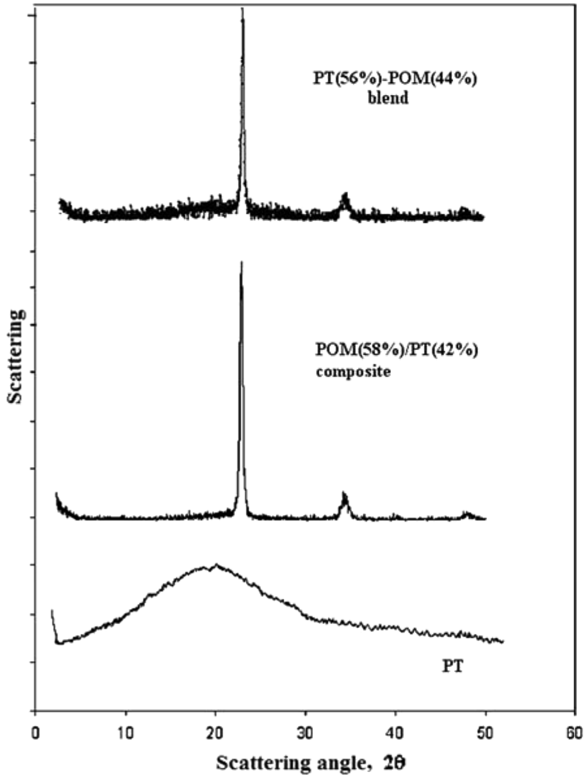
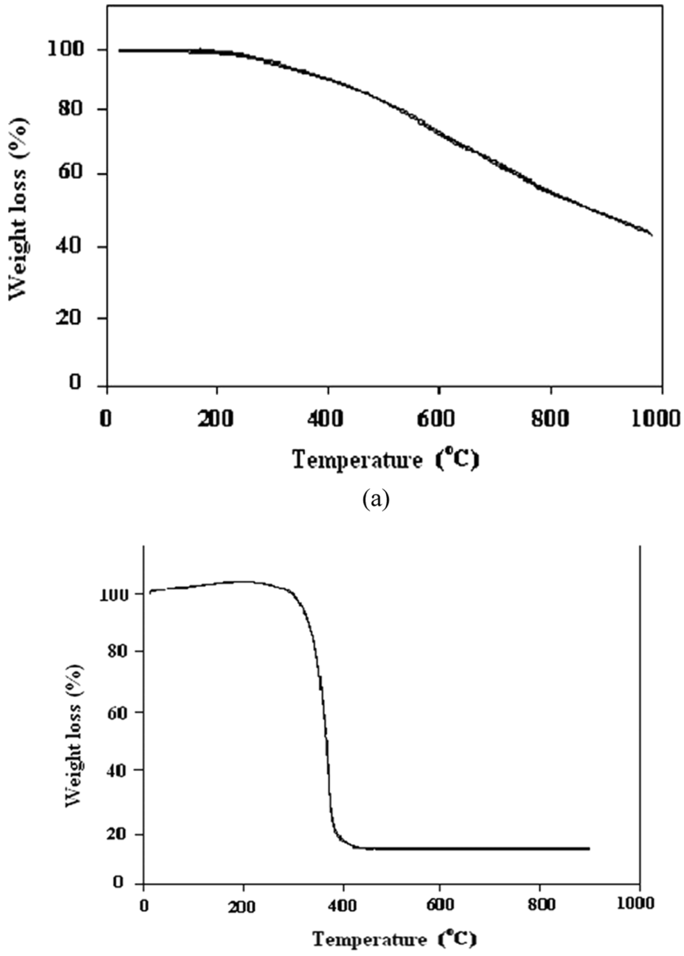


Figure 2. XRD patterns of PT, POM/PT composite, and PT/POM blend.

process as seen from polymerization.[7] The XRD patterns of the other POM/PT composites and PT/POM blends exhibited similar peaks in Figure 2.

TGA Results

The thermal stability of samples was examined by thermal analysis. Figure 3 shows TGA curves of PT (Figure 3(a)) and POM homopolymer (Figure 3(b)). PT (418°C), as characteristic of PT backbone,[22–24] has higher thermal stability than POM (323°C). Relevantly, the major thermal degradation of composite occurred at this temperature. Moreover, PT has 52% residue at 900°C whereas POM shows 11% residue at the same temperature. Figure 4 shows the TGA curves of POM/PT composite containing 42% of PT (Figure 4(a))



(a)

(b)

Figure 3. TGA curves of (a) PT and (b) POM.

and PT/POM blend containing 56% of PT (Figure 4(b)). The initial thermal degradation temperatures (T_i) of all the composites and blends were lower than those of the homopolymers. Some of the samples show thermal degradation with two-step removal of dopant anion and the decomposition of polymer structure,[7] whereas the others are one-step processes. In the PT/POM blends, the thermal degradation temperatures (T_i) increased from 179° to 211°C with increasing POM amount (14–87%). Moreover, T_i values of POM/PT composites also increased, from 175° to 221°C, with POM percentages changing between 12% and 86%. POM/PT composites and PT/POM blends exhibited

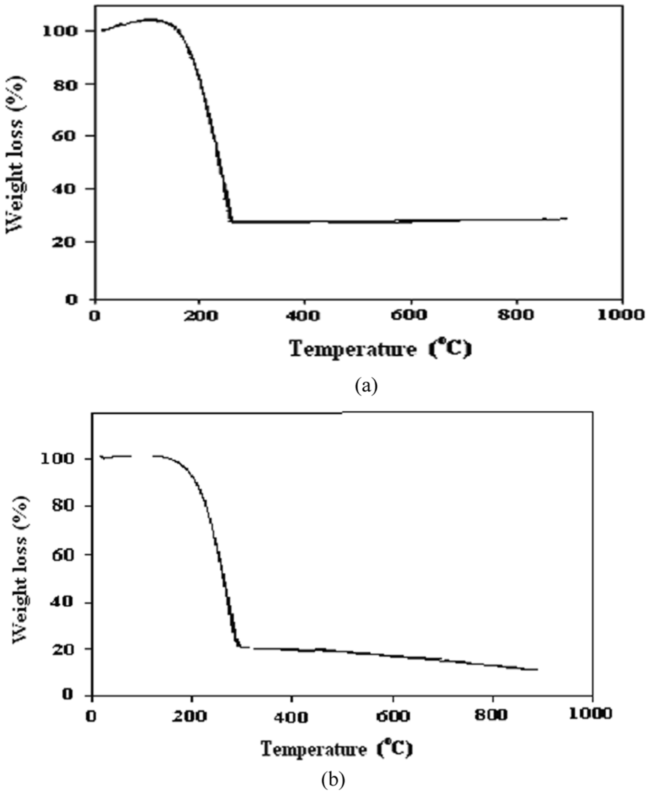
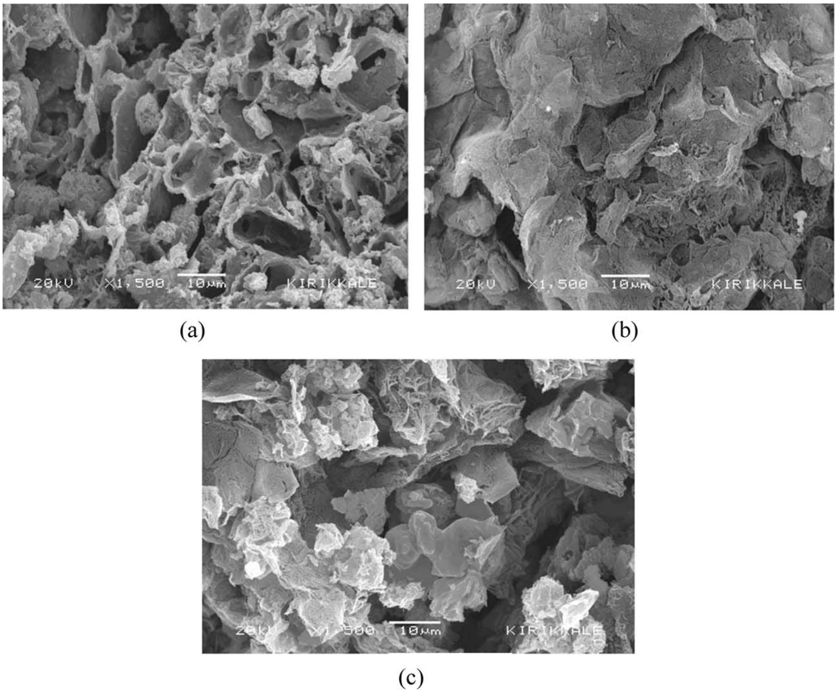


Figure 4. TGA curves of (a) POM(58%)/PT(42%) composite and (b) PT(56%)/POM(44%) blend.

thermal degradation temperatures after 56% and 68% value of PT in the composite and blend structure. This result can be interpreted as homogeneous interaction up to these percentages of PT and beyond these percentages, heterogeneous phase formation.

SEM Results

Figure 5 shows the SEM micrographs of PT($FeCl_3$) (Figure 5(a)), POM/PT (42%) composite (Figure 5(b)), and PT (56%)/POM blend (Figure 5(c)). PT shows a sponge-like and porous structure. When the morphologies of POM/PT composite and PT/POM blend were compared, it was observed that POM/PT composite has smoother layers than PT/POM blend. The differences in their conductivity values relating to morphology properties were also observed. Moreover, it may



(a) (b)

(c)

Figure 5. SEM micrographs of (a) PT($FeCl_3$), (b) POM(58%)/PT(42%), and (c) PT(56%)/POM(44%).

be concluded that POM and PT homopolymers provided compatible mixtures because of the interaction between PT and POM.

CONCLUSIONS

POM/PT composites and PT/POM blends were synthesized by in situ polymerization and blending in solution, respectively. The properties of the composites and blends were compared using SEM, conductivity, TGA, and X-ray measurements. POM/PT composite has smoother surface than PT/POM blends. This could explain slightly higher conductivity values of PT/POM composites than the blends. The crystallinity of PT increased in the presence of POM matrix for both composites and blends. All materials indicated bipolaron structure, which is more stable than a polaron structure. The conductivity of POM was improved with a small amount (14%) of PT for the POM/PT composite. A similar conductivity value could be obtained with a larger PT amount (56%) for the PT/POM blend. From conductivity, FT-IR, X-ray, and SEM results, we can say that the in situ composite system is more useful for applications of POM and PT materials.

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