

Synthesis and Characterization of Poly(dimethylsiloxane)–Polythiophene Composites

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ABSTRACT: The synthesis was performed by the electropolymerization of thiophene on a poly(dimethylsiloxane) (PDMS)-coated platinum electrode at 2.2 V with tetrabutylammoniumtetrafluoroborate (TBAFB) as a supporting electrolyte and with acetonitrile as a solvent. The characterization of the PDMS–polythiophene (Pth) composites was carried out with cyclic voltammetry, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis, and conductivity measurements. The observed conductivities of the PDMS composites were 2.2–5.2 S/cm. The con-

ductivity of Pth did not change appreciably with the addition of up to 30% insulating PDMS, but its processability improved. FTIR, SEM, and DSC studies showed the existence of a strong interaction, rather than physical adhesion, between PDMS and Pth. Highly flexible and foldable PDMS–Pth composites were obtained. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2113–2119, 2003

Key words: conducting polymers; electrochemistry; synthesis; composites

INTRODUCTION

Electrically conducting polymers have attracted much attention since their discovery barely 2 decades ago.¹ Among the many application areas of conductive polymers, the most exciting developments are the new classes of semiconducting materials, including plastic batteries, sensors, conductive surfaces, and magnetic recording.^{2–5} Imparting flexibility to conductive polymers is desired for these applications. Preparing composites or copolymers of a conducting polymer with a nonconducting polymer with the desired properties is one way of achieving this goal.^{6–10}

In this study, we obtained a flexible and foldable conducting polymer by preparing composites of a conducting polythiophene (Pth) with a flexible polymer, poly(dimethylsiloxane) (PDMS).

EXPERIMENTAL

Materials

Acetonitrile, thiophene, and tetrahydrofuran (THF) were obtained from Merck (Darmstadt, Germany), and TBAFB was acquired from Aldrich (Steinheim, Germany). PDMS (molecular weight = 5×10^5) was pur-

chased from Polyscience Chemical Co. (Warrington, PA).

Electrochemical synthesis of the composites

The oxidation potential of the thiophene monomer was determined on a bare platinum electrode and a PDMS-covered platinum electrode. All scans were performed between 1.6 and 2.6 V with TBAFB as a supporting electrolyte and with acetonitrile as a solvent. The system was previously rendered inert by a nitrogen atmosphere. The thiophene monomer was converted into thiophene chains and finally into Pth on the platinum electrodes at an anodic potential of 2.1 V [Fig. 1(a)].

Figure 1(b) shows a cyclic voltammogram of thiophene on a PDMS-covered electrode. This system permitted electrochemical polymerization, despite the insulating matrix on the electrode. A 2.2-V anodic potential was used for the synthesis of the PDMS–Pth composites. The 0.1-V difference in the oxidation potential was needed to force the monomer to the electrode through the PDMS matrix.

For the electrochemical polymerization, silver wire was used as a reference electrode. The supporting electrolyte and solvent were TBAFB (0.1M) and acetonitrile, respectively.

The electrochemical potentials was determined with a PS95D potentiostat (Ankara, Turkey). Cyclic voltammograms were recorded with software from Pico

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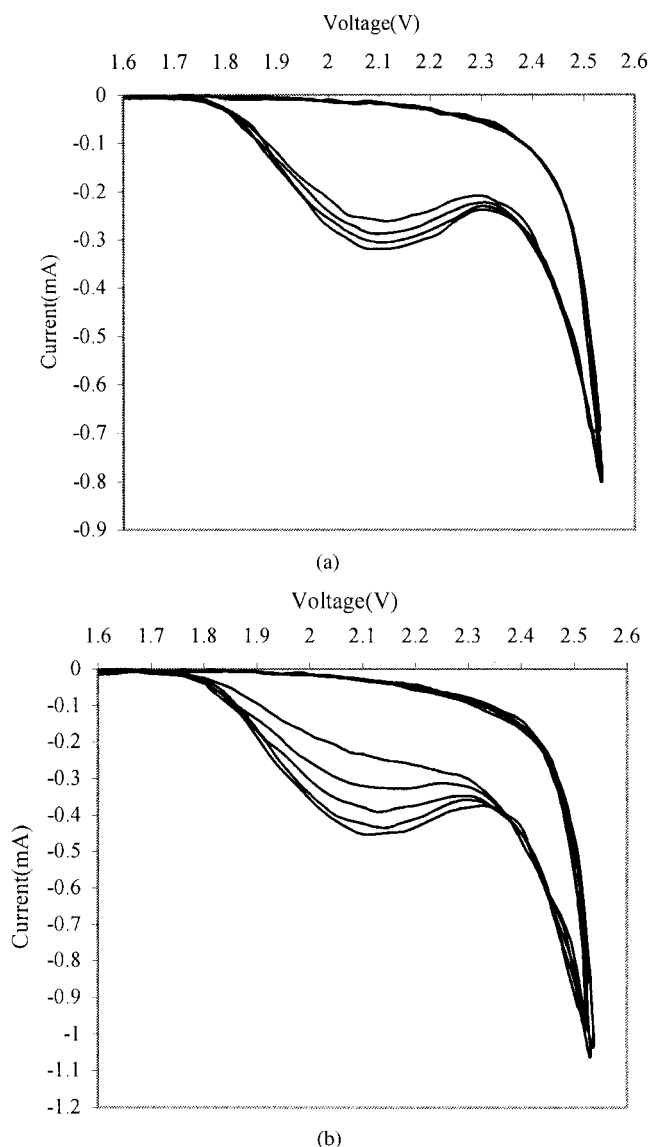


Figure 1 Cyclic voltammograms of thiophene (a) in a 0.1M TBAFB-CH₃CN solution (scan rate = 100 mV/s) and (b) on a PDMS-coated electrode in a 0.1M TBAFB-CH₃CN solution (scan rate = 100 mV/s).

Electronic Ltd. (UK). The electrical conductivity measurements were made with a four-point probe connected to a Keithley (Cleveland, OH) constant-current source system under atmospheric conditions at room temperature. Fourier transform infrared (FTIR) spectra were measured with a Nicolet DX 510 FTIR spectrometer (Madison, WI). A TA DSC 910S differential scanning calorimeter (New Castle, DE) and a DuPont 951 thermogravimetric analyzer (Wilmington, DE) were used for the thermal characterization. A JEOL JSM-6400 scanning electron microscope (Tokyo, Japan) was used for the morphological studies of the composites.

Washing process

The composites were left standing for 1 day and then were washed several times with the solvent of PDMS, THF.

RESULTS AND DISCUSSION

Preparation and conductivities of the composites

Black, conductive, freestanding films were obtained after the constant potential electrolysis of thiophene on a PDMS-coated electrode. The overall rate of the electrochemical polymerization of thiophene was affected by the amount of PDMS coated on the electrode. This insulating matrix was prepared up to 30% because a PDMS content higher than 30% prevented Pth formation on the electrode.

The compositions and conductivities of the composites are given in Table I. The electrical conductivity decreased as the weight percentage of PDMS in the composite increased for the PDMS-Pth composites (Table I). However, the decrease in the conductivity was not much, although the PDMS content increased within a large range. The composites containing 30% PDMS were just 3.7 S/cm less conductive than pure Pth.

The conductivities of the PDMS-Pth composites were tested once a week for 3 months under atmospheric conditions. The decrease in the conductivity of the samples was less than 10%. Therefore, the conductivity of the composites was environmentally stable.

FTIR spectra of the composites

The FTIR spectrum of the PDMS-Pth composite is given in Figure 2. The characteristic bands of the electrochemically synthesized Pth were 2927 cm⁻¹ for C-H symmetrical stretching and 1640 cm⁻¹ for C=C ring stretching, and an intense band at 1083 cm⁻¹ resulted from BF₄⁻, which was the anion of the supporting electrolyte.¹¹ When the characteristic bands of PDMS were examined, the following bands were observed: at 2962 cm⁻¹, C-H stretching in methyl groups; at 1260 cm⁻¹, Si-CH₃ bending; at 1090 and

TABLE I
Conductivities of PDMS-Pth Composites

PDMS (wt %) : Pth (wt %)	Conductivity (S/cm)
0 : 100	5.9
9 : 91	5.2
15 : 85	4.0
21 : 79	3.6
25 : 75	3.3
30 : 70	2.2

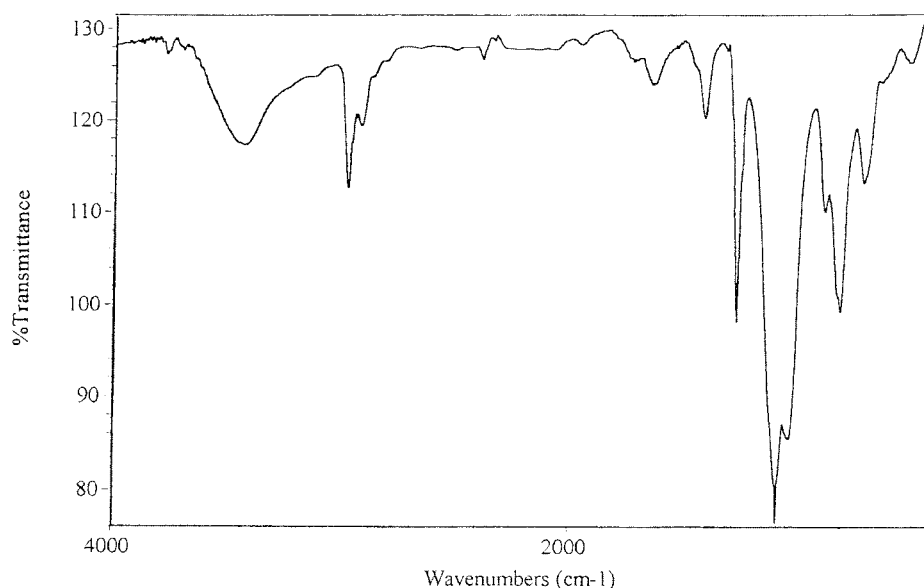


Figure 2 FTIR spectrum of the PDMS-Pth composite.

1026 cm^{-1} , Si—O—Si asymmetric stretching; and at 802 cm^{-1} , Si—CH₃ rocking.¹¹

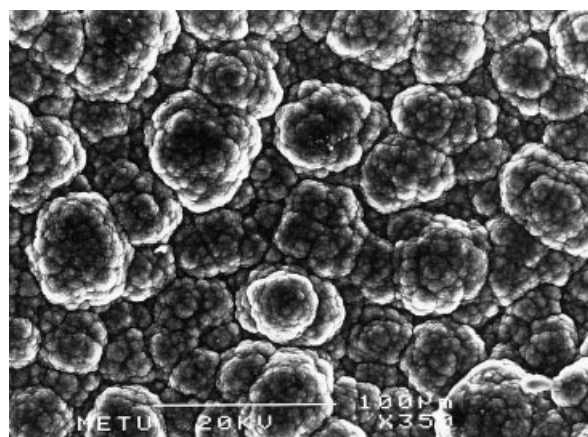
We observed peaks coming from both PDMS and Pth in the IR spectrum of the PDMS-Pth composites. Bands originating from PDMS were at 2964, 1261, and 802 cm^{-1} , and bands originating from Pth were at 2940, 1637, and 1083 cm^{-1} . This shows that the washing process could not remove PDMS from the composites.

Scanning electron microscopy (SEM) of the composites

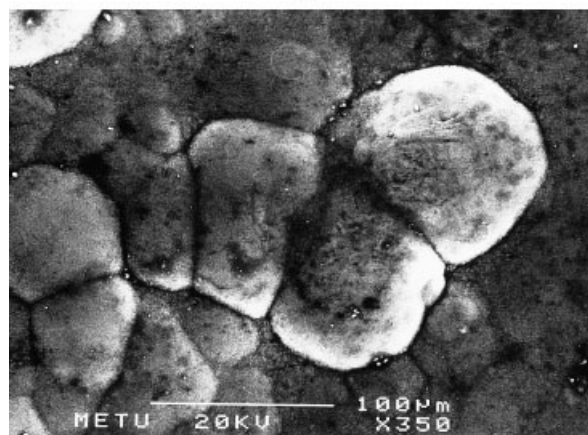
A standard cauliflower structure was observed in SEM micrographs of the PDMS-Pth composites. Moreover, we observed a distortion of the cauliflower structure when the PDMS content of the composites was changed from 10 to 30 wt % [Fig. 3(a,b)]. A washing process was also performed for the SEM studies, and SEM micrographs of washed and unwashed composites for both the solution and electrode sides were compared. No differences were observed between the washed and unwashed samples [Figs. 4(a) and 5(a) and Figs. 4(b) and 5(b), respectively].

Thermal analysis of the composites

The electrochemically synthesized conductive Pth did not have any thermal transition, except a decomposition peak at 234°C (Fig. 6). We observed a melting peak at about -40°C for PDMS (Fig. 7). For PDMS-Pth composites, an endothermic peak at about 107°C was detected (Fig. 8). This endothermic



(a)



(b)

Figure 3 (a) Standard cauliflower structure for a sample with 10% PDMS and (b) distorted cauliflower structure for a sample with 30% PDMS.

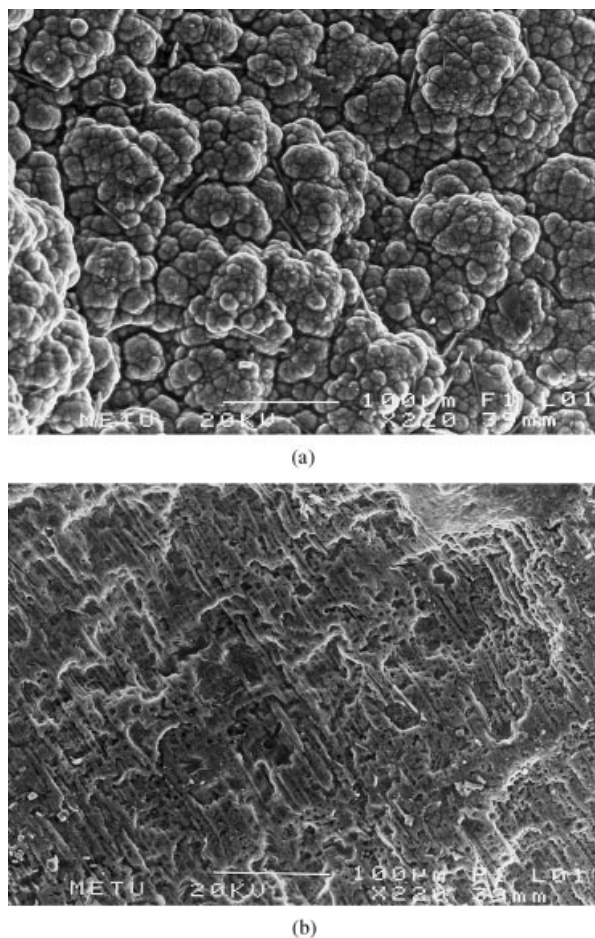


Figure 4 SEM images of (a) the solution side of an unwashed sample and (b) the electrode side of an unwashed sample.

peak might have originated from the Coulombic interactions between the positive charges on the conductive polymer and the dopant anion. Coulombic interactions might also have existed between the partial negative charges of oxygen atoms of PDMS and the positive charges arising from cations of the supporting electrolyte and cations already present on the conductive chain.

To prove that Coulombic interactions were the reason for the endothermic peak, we prepared mechanical mixtures of PDMS and TBAFB. The melting peaks of both PDMS (-40°C) and TBAFB (162°C) were detected during differential scanning calorimetry (DSC) studies of these mixtures (Fig. 9). In addition to these melting peaks, a new peak was detected at about 70°C . This peak could be attributed to the endothermic process, which broke the Coulombic interactions between the partial negative charges of oxygen and the tetrabutylammonium cation. That is, the energy needed to break the Coulombic interactions caused this kind of endothermic peak.

Thermogravimetric analysis (TGA) thermograms of Pth-PDMS composites are given in Figure 10. The small weight loss at 75°C might be due to a loss of the solvent. About a 10% weight loss was observed near 250°C . This could be attributed to the removal of the dopants. The DSC thermograms of the electrochemically synthesized Pth exhibited an endothermic peak at this temperature. Therefore, the TGA results confirmed the DSC results.

CONCLUSIONS

PDMS-Pth composites, which were highly flexible and foldable up and down by 180° , were obtained electrochemically. Because the washing process was not able to remove PDMS, there must have been strong interactions between the components. FTIR and SEM results also supported this conclusion. The conductivity of Pth did not decrease appreciably despite the addition of insulating PDMS (up to 30%). The electrical conductivity of the PDMS-Pth composites was stable under atmospheric conditions. The com-

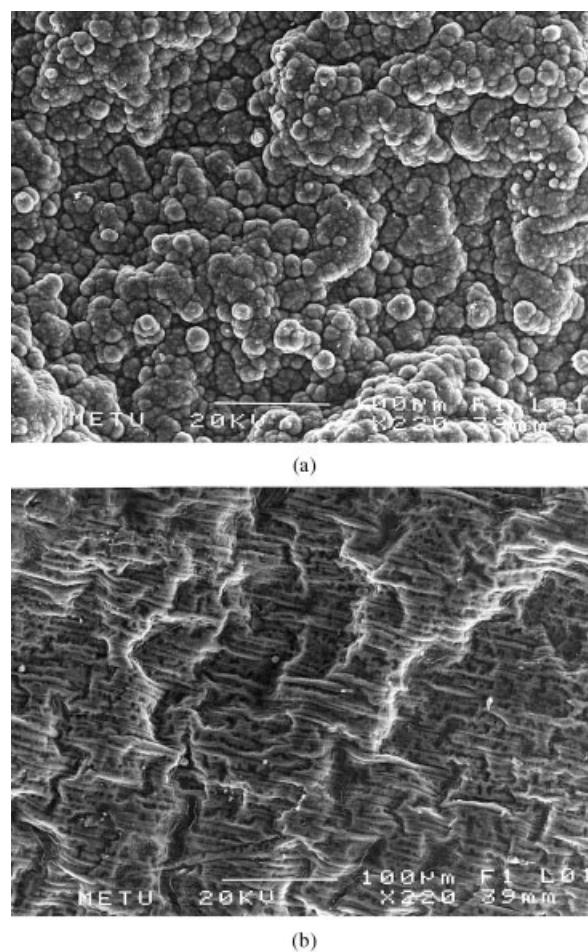


Figure 5 SEM images of (a) the solution side of a washed sample and (b) the electrode side of a washed sample.

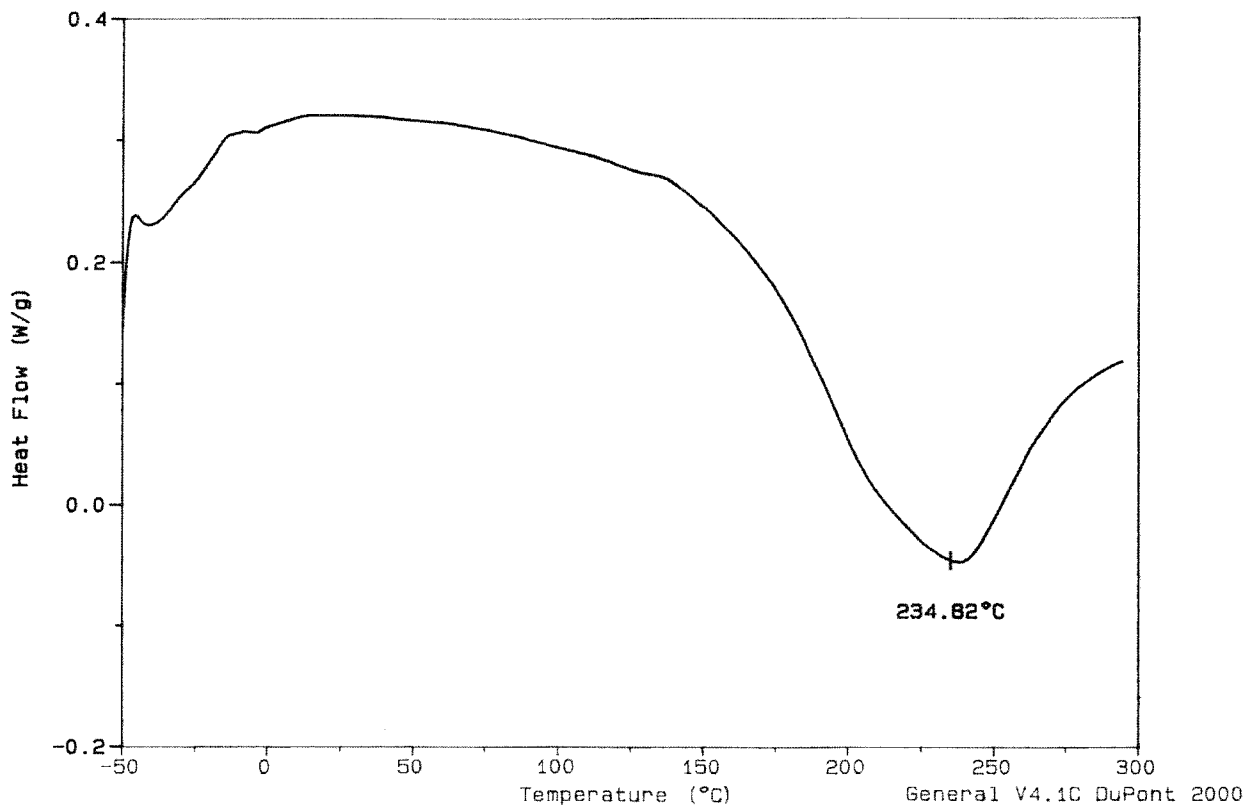


Figure 6 DSC thermogram of Pth.

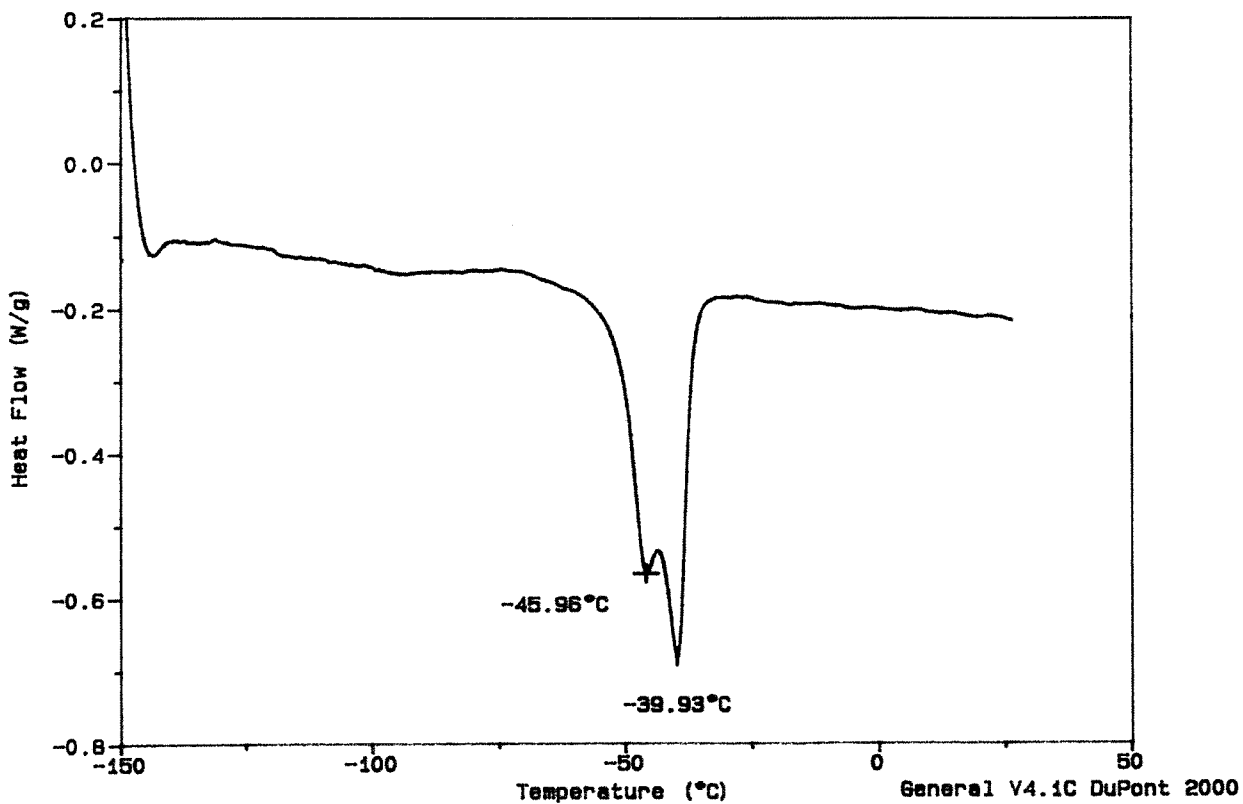


Figure 7 DSC thermogram of PDMS.

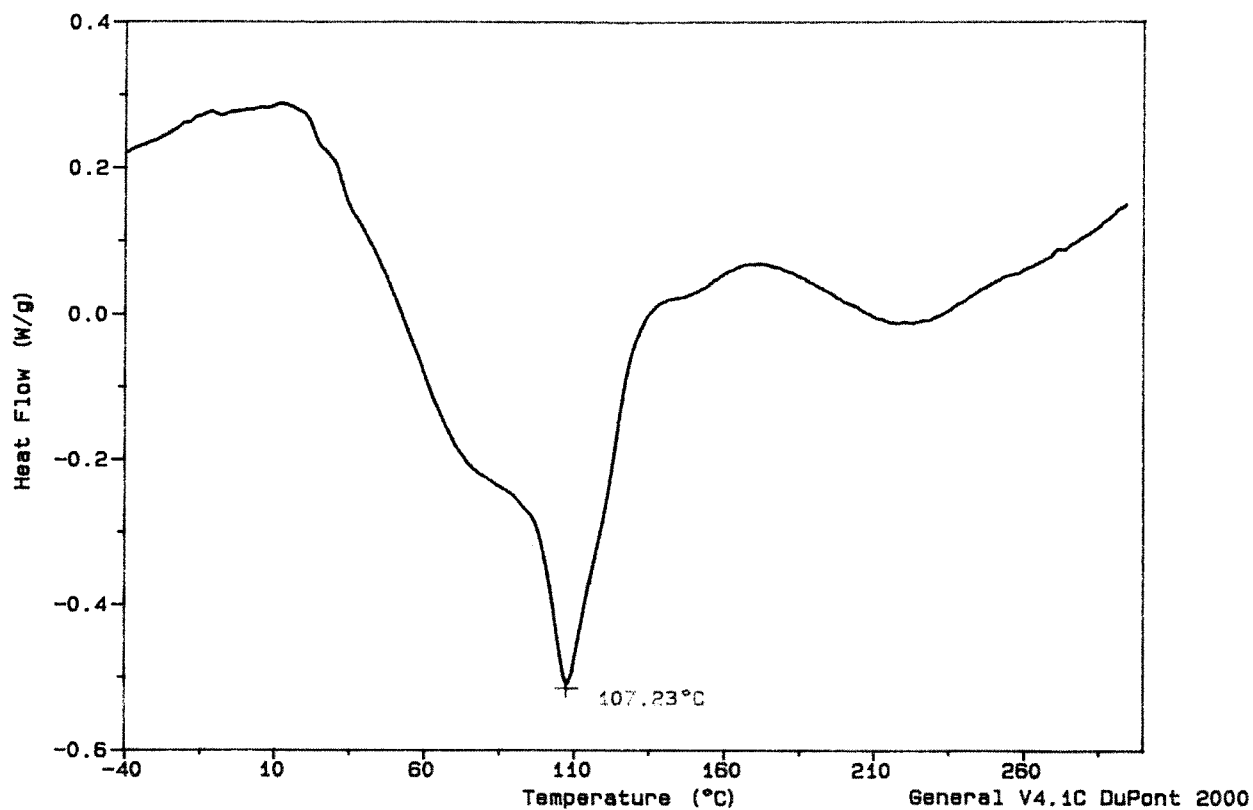


Figure 8 DSC thermogram of the PDMS-Pth composite.

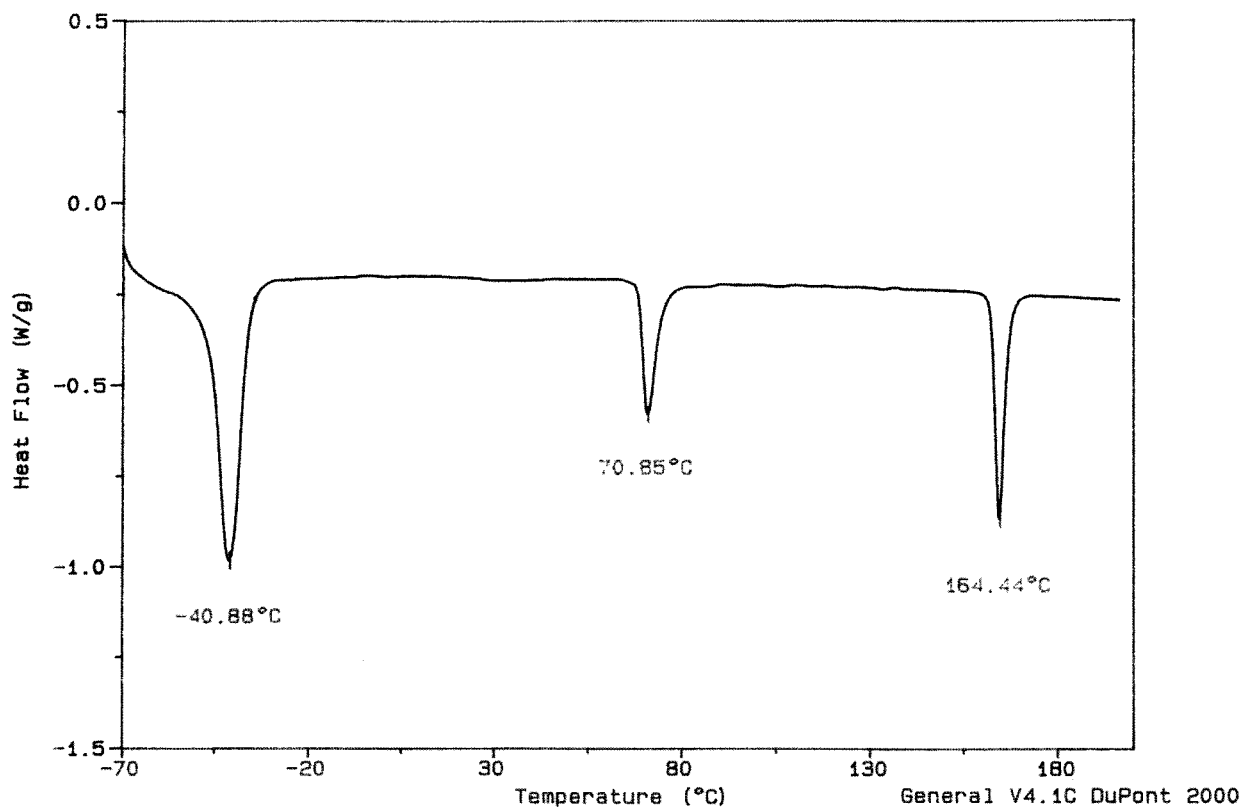


Figure 9 DSC thermogram of a mechanical mixture of PDMS and TBAFB.

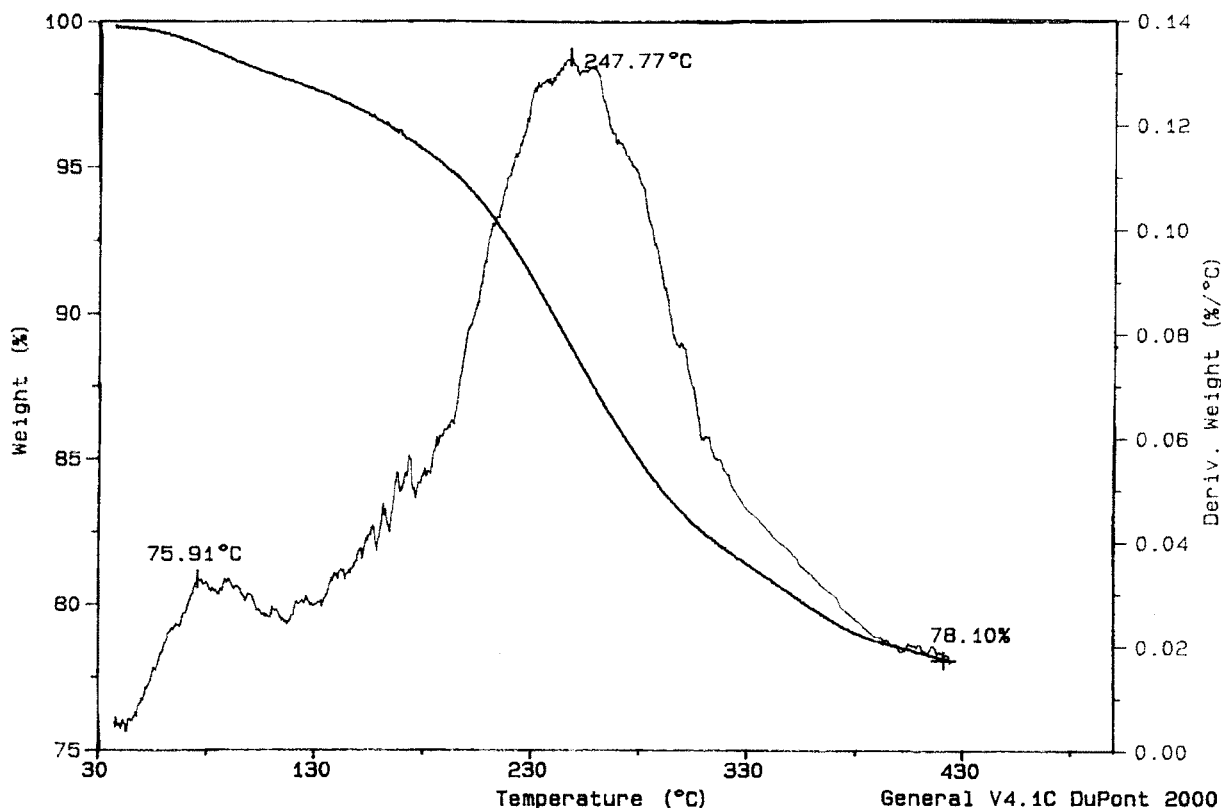


Figure 10 TGA thermogram of the PDMS-Pth composite.

posites were also heat-stable up to 400°C, at which point about 80% of the weight remained. The PDMS-Pth composites had a cauliflower structure. However, the cauliflower structure was destroyed when the content of the insulating matrix was increased to 30%.

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