ELECTRICAL CHARACTERISTICS AND THERMAL DIFFUSIVITY OF POLYPYRROLE-BASED CONDUCTING POLYMER

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ELECTRICAL CHARACTERISTICS AND THERMAL DIFFUSIVITY OF POLYPYRROLE-BASED CONDUCTING POLYMER

By

NORFAZLINAYATI OTHMAN

Thesis Submitted to the School of Graduate Studies, University Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

September 2009
DEDICATED TO MY HUSBAND AND PARENTS
Abstract of the thesis presented to the Senate of University Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

ELECTRICAL CHARACTERISTICS AND THERMAL DIFFUSIVITY OF POLYPYRROLE-BASED CONDUCTING POLYMER

By

NORFAZLINAYATI BINTI OTHMAN

September 2009

Chairman:  Associated Professor Zainal Abidin Talib, PhD

Faculty :  Science

Conducting polymer materials based on Polypyrrole (PPy) and Polypyrrole/Montmorillonite (PPy/MMT) clay composite were synthesis by using chemical reaction process with iron (III) chloride (FeCl₃) as oxidizing and dopant agent. During the mixing process of PPy, the solution changed from transparent to dark green indicating that the polymerization process took place instantaneously. The resulting powder was filtered, washed, grounded and press into pellet. The structural, thermal and electrical properties of the conducting polymer and conducting polymer composite were then investigated.

The structure of the samples was analyzed by using X-ray diffractometer (XRD) with the scanning was carried out at 2θ of 15° to 35° for doped PPy and at 2θ of 2° to 35° for PPy/MMT clay composite. The XRD spectra showed dopant and filler effect with
appearance of broad peak at around the 2θ value of 25 to 26° corresponded to highly disordered parts and new peak at low angle at around the 2θ value of 5 to 6° corresponded to successfully intercalation of PPy chain in the galleries of MMT clay. It was observed that all the peak angles shifted and the full width at half maximum (FWHM) values are difference with increasing in dopant concentrations and filler percentages indicate the strong interaction between dopant and filler with the conjugated polymer. The interchain separation showed good agreement with published data.

The thermal diffusivity of PPy and PPy/MMT clay composite was analyzed at room temperature by using photoflash technique. The results showed that the thermal diffusivity, \( \alpha_c \) for PPy increased with increasing dopant concentrations with \( \alpha_c \) from 1 to \( 4 \times 10^{-3} \text{ cm}^2\text{s}^{-1} \). On the other hand, the thermal diffusivity for PPy/MMT clay composite decreased with increasing MMT clay percentages loading in the PPy which is from 3 to \( 1 \times 10^{-3} \text{ cm}^2\text{s}^{-1} \) indicating some electron motion interruption. It also observed that a correlation between the thermal diffusivity and electrical conductivity for all the samples showed a similar trend.

The electrical conductivity studies were done by using four point probe technique and two probe technique with temperature dependence. At room temperature, the \( I-V \) characteristic for both techniques showed a linear behavior and obeys the Ohm’s law. From the results, the conductivity was calculated and showed a strongly dependent on dopant concentrations and filler percentages. To get more insight into the transport mechanism, various models have been used to fit the data from conductivity plots.
At low temperature range (100-300K), the charge carrier mechanism was dominated by 3-D variable range hopping, VRH transport. However, the electrical conduction transport is also apparently based on hopping of polarons. With regard to high temperature dependence (300-380K), the conductivity showed the same trend with observation in low temperature studies. Nevertheless, the electrical conduction showed a contribution of polarons and bipolarons mechanism which may due to some transformation at energy transport in the materials.
Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk penganugerahan ijazah Master Sains

**SIFAT-SIFAT ELEKTRIK DAN RESAPAN TERMA BAGI POLIMER PENGALIR ELEKTRIK DARI POLIPIRROLE**

Oleh

NORFAZLINAYATI BINTI OTHMAN

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Polimer konduksi berasaskan pada bahan Polipirrole (PPy) dan Polipirrole/Montmorillonite (PPy/MMT) komposit telah disintesis dengan menggunakan proses tindakbalas kimia dengan iron (III) chloride (FeCl₃) sebagai agen pengoksidaan dan dopan. Semasa proses percampuran bagi PPy, sebatian telah bertukar dari jernih ke hijau gelap menandakan proses pempolimeran berlaku serta merta. Hasil serbuk kemudianya dituras, dibasuh, dihaluskan dan dimampatkan menjadi pelet. Sifat struktur, terma dan elektrik bagi polimer konduksi dan polimer konduksi komposit ini telah dikaji.

Stuktur sample-sampel ini telah dianalisis dengan menggunakan pembeluaan sinar-X (XRD) pada sudut 2θ ialah 15° hingga 35° bagi PPy dan 2° hingga 35° bagi PPy/MMT
clay composite. Spektra XRD menunjukkan kesan dopan dan penyendat dengan kemunculan puncak lebar iaitu pada 2θ ialah 25 hingga 26° yang merupakan bahagian yang sangat tidak tersusun dan puncak yang baru disudut rendah iaitu pada 2θ ialah 5 hingga 6° yang menunjukkan rantaian PPy telah masuk ke dalam galeri tanah liat MMT. Dapat diperhatikan bahawa semua puncak sampel telah berganjar dan separuh maksimum kelebaran puncak (FWHM) telah berubah-ubah dengan peningkatan kepekatan dopan dan peratusan tanah liat MMT menandakan tindak balas yang kuat diantara dopan dan penyendat dengan polimer. Nilai jarak pemisah rantaian menunjukan persamaan dengan nilai yang telah diterbitkan oleh penyelidikan yang terdahulu.

Proses resapan terma bagi PPy dan PPy/MMT komposit telah dianalisis pada suhu bilik dengan menggunakan teknik fotokilat. Keputusannya menunjukkan resapan terma, $\alpha_c$ bagi PPy meningkat dengan peningkatan kepekatan dopan iaitu $\alpha_c$ dari 1 hingga $4 \times 10^{-3}$ cm²s⁻¹. Manakala, resapan terma bagi PPy/MMT komposit menurun dengan peningkatan peratusan tanah liat MMT didalam PPy iaitu $\alpha_c$ dari 3 hingga $1 \times 10^{-3}$ cm²s⁻¹ dimana ia menandakan pergerakan elektron terganggu. Walaubagaimanapun, perkaitan antara resapan terma dan kekonduksian elektrik bagi kesemua sampel menunjukan bentuk yang sama.

Kajian kekonduksian elektrik tdijalakan dengan menggunakan teknik penduga empat titik dan penduga dua dalam mengkaji sifat permukaan dan pukal dengan penggantungan suhu. Pada suhu bilik, sifat $I-V$ bagi kedua-dua teknik telah menunjukan garis lurus dan menepati hukum Ohm. Melalui keputusan ini, kekonduksian elektrik telah dikira dan menunjukkan bahawa sangat bergantung kepada kepekatan dopan dan peratusan
penyendat. Untuk mengkaji lebih jauh lagi tentang pergerakan mekanisma, pelbagai
modul telah digunapakai untuk memandankan data dari plot kekonduksian.

Pada julat suhu rendah (100-300K), mekanisma cas pembawa telah didominasi oleh
pergerakan pelbagai julat lompatan (VRH). Walau bagaimanapun, pergerakan
kekonduksian elektrik juga kelihatan melibatkan lompatan polaron. Berkenaan dengan
suhu tinggi pula (300-380K), kekonduksiannya menunjukkan corak yang sama dengan
pemerhatian pada suhu rendah. Namun begitu, kekonduksian elektriknya menunjukkan
penglibatan mekanisma polaron dan bipolaron dimana ia mungkin disebabkan oleh
perubahan pergerakan tenaga dalam bahan tersebut.
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I certify that an Examination Committee met on date of viva to conduct the final examination of Norfazlinayati Hj. Othman on her Master of Science thesis entitled “Electrical Characteristics and Thermal Diffusivity of Polypyrrole Based Conducting Polymer” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination are as follows:

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Date: 8 April 2010
DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations that have been duly acknowledge. I also declare that it has not been previously of concurrently submitted for any other degree at UPM or other institutions.

______________________________
NORFAZLINAYATI HJ. OTHMAN

Date: 14 September 2009
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5.12 Conductivity of doped PPy for four-point probe technique and two probe technique at various MR

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5.41 Plot of Ln ($\sigma_{\text{four-point probe}}$ ($T$)) versus 1000/$T$ of doped PPy/MMT clay composite with 6% of MMT clay

5.42 Plot of Ln ($\sigma_{\text{two probe}}$ ($T$)) versus 1000/$T$ of doped PPy/MMT clay composite with 6% of MMT clay

5.43 Plot of Ln ($\sigma_{\text{four-point probe}}$ ($T$)) versus 1000/$T$ of doped PPy/MMT clay composite with 8% of MMT clay
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5.45 Plot of \( \ln(\sigma_{\text{four-point probe}}) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 10% of MMT clay

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5.53 Plot of \( \ln(\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy with 0.5MR

5.54 Plot of \( \ln(\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy with 0.5MR

5.55 Plot of \( \ln(\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy with 1.0MR

5.56 Plot of \( \ln(\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy with 1.0MR

5.57 Plot of \( \ln(\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy with 1.5MR

5.58 Plot of \( \ln(\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy with 1.5MR

5.59 Plot of \( \ln(\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy with 2.0MR

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5.60 Plot of \( \ln (\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy with 2.0MR

5.61 Plot of \( \ln (\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy with 2.5MR

5.62 Plot of \( \ln (\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy with 2.5MR

5.63 Plot of \( \ln (\sigma_{\text{four-point probe}}(T^{1/2})) \) versus \( 1000/T \) of doped PPy with 2.5MR

5.64 Plot of \( \ln (\sigma_{\text{two probe}}(T^{1/2})) \) versus \( 1000/T \) of doped PPy with 3.0MR

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5.66 \( \sigma_{\text{two probe}} \) value of doped PPy/MMT clay composite at high temperatures with various MMT clay percentages

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5.68 Plot of \( \ln \sigma_{\text{two probe}} \) versus \( 1000/T \) of doped PPy/MMT clay composite at high temperatures and various MMT clay percentages

5.69 Plot of \( \ln (\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 2% of MMT clay

5.70 Plot of \( \ln (\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 2% of MMT clay

5.71 Plot of \( \ln (\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 4% of MMT clay

5.72 Plot of \( \ln (\sigma_{\text{two probe}}(T)) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 4% of MMT clay

5.73 Plot of \( \ln (\sigma_{\text{four-point probe}}(T)) \) versus \( 1000/T \) of doped PPy/MMT clay composite with 6% of MMT clay