Solid State Science and Technology, Vol. 18, No 1 (2010) 437-443
ISSN 0128-7389

CORRELATION BETWEEN THERMAL DIFFUSIVITY AND DC CONDUCTIVITY IN POLYPYRROLE/MONTMORILLONITE CLAY COMPOSITE

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ABSTRACT

Polypyrrole/montmorillonite, (PPy/MMT) clay composite was synthesized via chemical reaction method by adding 0.6M iron (III) chloride, ($FeCl_3$) as oxidizing and doping agent to 0.2M monomer of pyrrole with 2 to 12 % of MMT clay as filler. The insertion of conducting polymer PPy into layered MMT clay has been confirm by using X-Ray Diffraction, (XRD) technique in the 2θ range of 4° to 35°. The influence of various percentages of the filler on thermal diffusivity was investigated by using photoflash technique and to examine the dc conductivity in this conducting polymer composite, four-point probe technique was used at room temperature. Interestingly, correlation between the thermal diffusivity and the dc conductivity is qualitatively constant for all samples in which both characteristic showed decreasing trend with increased in percentages of MMT clay loading in the PPy.

INTRODUCTION

The discovery of the conductive polymer is unique in its accomplishment acting not as traditional insulators but as a semiconductor or metal behavior [1]. Electrical conductivity of the conducting polymer can be increased to as high as 15 orders of magnitude by changing dopant concentrations [2,3]. Since that, the conductive polymers belonging to polyaniline, polythiopene and polyacetylene have been studied extensively [4]. Between all the above classes, polypyrrole (PPy) is among the best candidate material used in commercial applications due to their good electronic properties, exhibit significant environmental stability and easy to synthesis [5, 6]. Nevertheless, in some extend the physical properties of PPy are not satisfactory for practical applications [7]. This has led much intensive research to overcome the drawback [8]. For that reason, Montmorillonite (MMT) clay is commonly used as filers because its environment friendly available used in large quantities with relatively low coast which is suitable in industry condition especially in the application of reinforcement materials with polymers [9, 10]. Beside that, MMT clay is the most active clay in terms of generates negative charges situated in the MMT clay galleries [11]. This type of interlayer is characterized by a moderate surface charge known as cation-exchange as showed in Figure 1 [12, 13]. The cation-exchange can provide

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functional groups that can react with the polymer chains and improve the strength of interface between the MMT clay and the polymer chains.

The analysis regarding the electrical conductivity measurement which is electrical transport of the polymer always gets much attention and available in the literatures [14]. Nevertheless, knowledge of the thermal transport is also important for their long term use in devices as well as from the mechanistic point of view. Therefore, there must be a correlation between the thermal and electrical transport. In the present study, in order to investigate the correlation between thermal diffusivity and dc conductivity in this conducting polymer composite, MMT clay was added to PPy as filler. Iron (III) chloride, ($FeCl_3$) was used as oxidizing and doping agent.

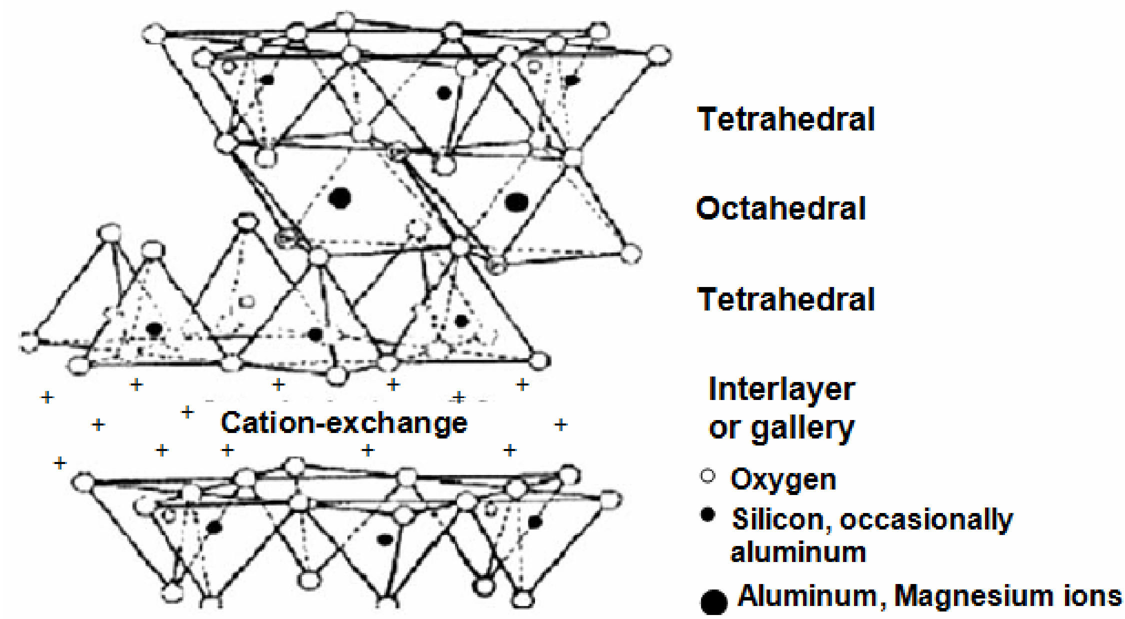

Figure 1: The structure of layered MMT clay

EXPERIMENTAL METHOD

The PPy/MMT clay composite was synthesized by chemical reaction method. Initially, the monomer pyrrole (Fluka) was distilled at a 131°C and stored at 4°C. A mixture solution containing pyrrole of 0.2M concentration and $FeCl_3$ (HmBG Chemicals) with 0.6M concentration was dissolved in distilled water. During the mixing process, the colour of the solution changed from transparent to dark green indicating the polymerization has taken place instantaneously and resulting PPy conducting polymer. After 5 minutes, 2 % of MMT clay (Fluka) was added into the solution. Then the mixture was stirred for 6 hours at room temperature. The resulting powders were filtered and dried at 40°C for 48 hours. The powdered was then grounded into fine powder and pressed into pellet at 7 tonne pressure. These steps were repeated for 4 to 12 % of MMT clay. The insertion of the PPy into the layered MMT clay is confirmed

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by using X-Ray Diffraction, (XRD) technique. The XRD analysis was carried out using a computer-controlled x-ray diffractometer (PANalytical X'pert PRO XRD System) in conjugation with a programmable control unit. A scanning was carried out at 2θ range of 4° to 35°. The characterization of thermal diffusivity was determine by using photoflash technique in which the thermal diffusivity is obtained by measuring the time corresponding to the half maximum of the temperature rise ($t_{1/2}$). In order to study the dc conductivity, four point probe technique (model DMV-001) with current source was applied from 5mA to 50mA.

RESULTS AND DISCUSSIONS

3.1 X-Ray Diffraction Characteristic

Figure 2 showed that all spectra become more polycrystalline structure due to the presence of sharp peaks. Three sharp peaks were observed for pure MMT clay and shifted to lower angle with decreasing MMT clay percentages in the PPy. It is observed that only for 10 and 12% of MMT clay loading in the polymer showed the existence of the first peak and for the rest of the samples samples, there is no such peak in that 2θ range. With the slight shifting for the all peaks confirmed that the PPy chains have intercalated into the MMT clay layers [15]. The values of *d*-spacing for PPy/MMT clay composite are tabulated in Table 1.

In the 2θ range between 26.40° to 26.98° there a formation of ion-pair (NaCl). The existence of the ion-pair is probably connected with the cation-exchange phenomena that occur during modification of sodium (Na^+) in polymerization process. The result has good agreement with Bricker, (1999), Thakur et al., (2006) and Mravcakova et al., (2006). They reported that the formation of the ion-pair provides evidence for very strong interaction between polymer chain and MMT clay network [16, 17,18]. The ion-pair also showed the presence of some ionic interaction network can be influence the mechanism of charge carrier in the composite.

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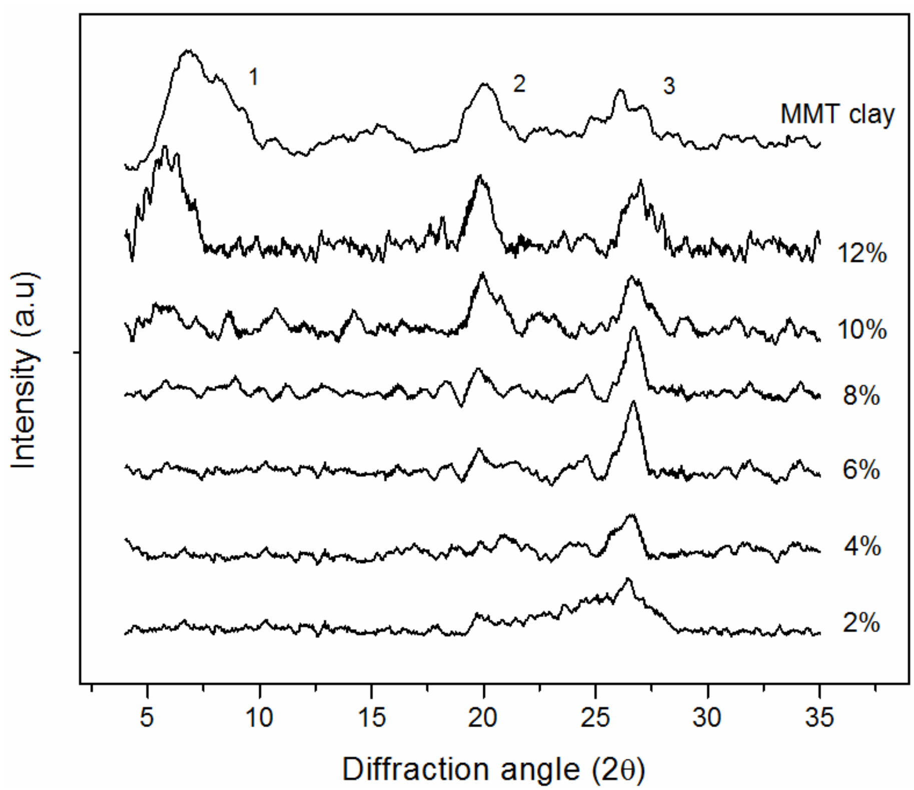

Figure 2: The effect of filling MMT clay to PPy/MMT clay composite

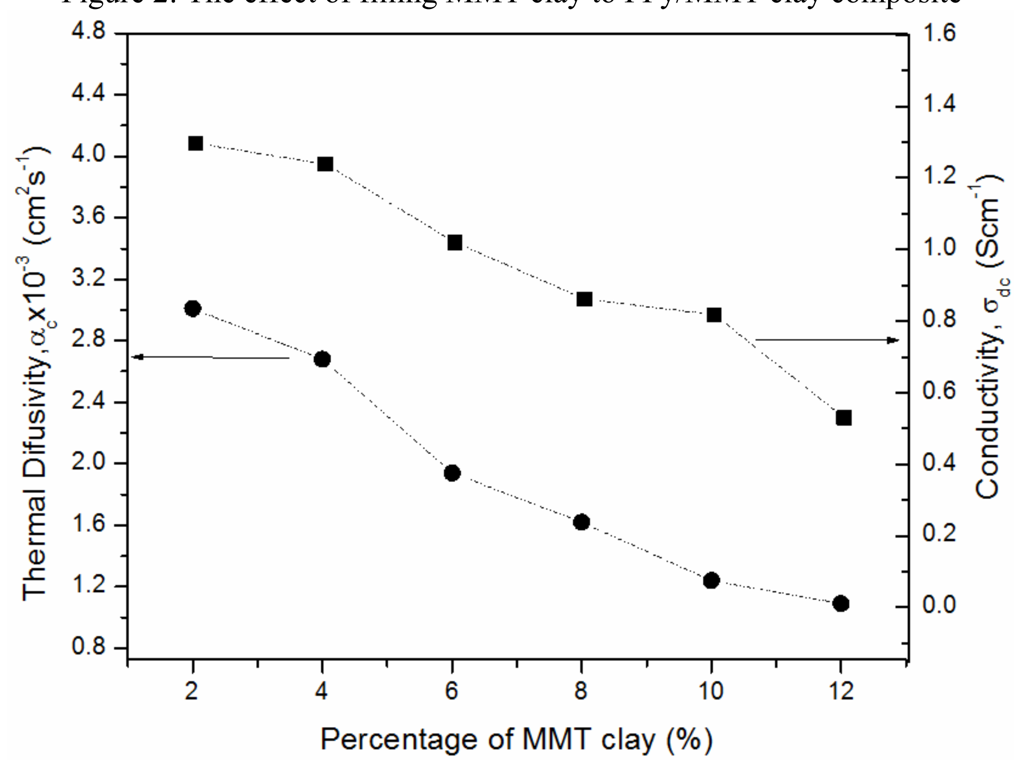

Figure 3: The thermal diffusivity and dc conductivity of PPy/MMT clay composite against different MMT clay percentage

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Table 1: Parameters of XRD data of PPy/MMT clay composite prepared with various MMT clay percentages.

PERCENTAGE OF MMT CLAY (%)	PEAK	2Θ (°)	*d*-SPACING (Å)
2	1	-	-
	2	19.79	4.48
	3	26.40	3.38
4	1	-	-
	2	19.59	4.53
	3	26.52	3.36
6	1	-	-
	2	19.72	4.50
	3	26.56	3.36
8	1	-	-
	2	19.86	4.47
	3	26.73	3.33
10	1	5.77	15.32
	2	19.99	4.44
	3	26.72	3.34
12	1	5.93	14.92
	2	19.95	4.41
	3	26.98	3.30
MMT Clay	1	6.75	13.10
	2	20.12	4.45
	3	26.69	3.34

Correlation between Thermal Diffusivity and DC Conductivity

The measured values of thermal diffusivity and dc conductivity for the PPy/MMT clay composite with various percentages of MMT clay are shown in Figure 3. A qualitative correlation between thermal diffusivity and dc conductivity can be obviously observed from the figure. Both thermal diffusivity and dc conductivity display a similar trend. The thermal diffusivity of the conducting polymer composite decreased from 3.01 to 1.09×10^{-3} cm^2s^{-1} and the dc conductivity also showed a decreasing trend from 1.29 to 0.53 Scm^{-1}. A more qualitative correlation between thermal diffusivity, α_c and dc conductivity, σ_{dc} can be obtained from the ratio of α_c / σ_{dc} [14]. As a results, the values are approximately constant with average ratio are 0.20 ±0.05 cm^2s^{-1} /Scm^{-1}.

What can be inferred from the both results is the decreasing trend may possibly because of the presence of the layered MMT clay. Thus, with the presence of silica and aluminum in nature (Figure 1) in the PPy/MMT clay composite may be a reason to become a resistance for the electron motion. Furthermore, with the formation of ion-

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pair, NaCl, as observed in the XRD, can reduce the number of available charge carrier. Consequently, it can lower the thermal diffusivity and the dc conductivity in the conducting polymer composite on further MMT clay addition [13, 16].

CONCLUSION

Bulk samples of PPy/MMT clay composites have been successfully prepared by chemical polymerization at various MMT clay percentages. XRD results suggest a strong interaction between polymer and MMT clay which showed the formation of ion-pair, NaCl in the 2θ range of 26.40° to 26.98°. A correlation between thermal diffusivity and dc conductivity has shown a similar trend where the average ratio (α_c /σ_{dc}) is approximately constant. Its also observed that the decreasing trend of thermal diffusivity and dc conductivity is because of the presence of the MMT clay layers which may influence the motion of electron.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial assistance given by The Ministry of Science Technology and Innovation and Ministry of Higher Education through e-Science Fund (5450040) and Fundamental Science Research Grant (5523123) and a scholarship from The National Science Foundation.

REFERENCES

[1]. Nina Hall (2003). Twenty-five years of conducting polymers, *Chem. Commun*, 1-4.

[2]. Bengt Norden and Eva Krutmeije (2000). The Nobel Prize in Chemistry, 2000: Conductive polymers, *The Royal Swedish Academy of Sciences,* 1-16.

[3]. B.D. Malhotra and Rahul Singhal (2003) Conducting polymer based biomolecular electronic devices, *Indian Academy of Sciences*, Vol. **61**, No. 2, 331–343.

[4]. D.Kumar and R.C Sharma (1998). Review article advances in conductive polymers, European Polymer Journal Vol. **34**, No.8, 1053-1060.

[5]. Aguilar-Hernandez et al., J Aguilar-Hernandez and K Potje-Kamloth (2001). Evaluation of the electrical conductivity of polypyrrole polymer composites*, J. Phys. D: Appl. Phys.* ***34***, 1700–1711.

[6]. Mun-Sik Kang, Kyo-Hyeok Kim, Il Sub Chung and Yongkeun Son (2006). Electrical properties of polypyrrole wires measured by scanning probe microscope, *Journal of Colloid and Interface Science, Article in Press,* 1-5.

[7]. Woo Jin Bae, Keon Hyeong Kim, Won Ho Jo and Yun Heum Park (2005). Fully exfoliated nanocomposite from polypyrrole graft copolymer/clay, *Polymer* ***46,*** 10085–10091.

[8]. Viviana P. Cyras, Liliana B. Manfredi, Minh-Tan Ton-That and Analia Vazquez (2008). Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films, *Carbohydrate Polymers* ***73***, 55–

Corresponding Author: zainalat@science.upm.edu.my

63.
[9]. Ji Woo Kim, Feng Liu and Hyoung Jin Choi (2002). Polypyrrole/Clay Nanocomposite and its Electrorheoligical Characteristics, *J. Ind.Eng. Chem., Vol.**8**. No.4,* 399-403.
[10]. Hong et al., 2001 S.H. Hong, B.H. Kim, J. Joo, J.W. Kim and Hyung J. Choi (2001). Polypyrrole–montmorillonite nanocomposites synthesized by emulsion polymerization, *Current Applied Physics **1***, 447–450.
[11]. D.R. Lewis, Ion exchange reactions of clays, *Publication No. 26, Exploration and Prodviction Research Division, Shell Development Co.,* Houston, Texas.
[12]. Ray et al Suprakas Sinha Ray and Masami Okamoto (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog. Polym. Sci. **28**,* 1539–1641.
[13]. Owen P. Bricker (1999). An Overview of the Factors Involved in Evaluating the Geochemical Effects of Highway Runoff on the Environment, *U.S Department of Transportation,* Northborough, Massachusetts.
[14]. S. Chandra, S.B. Rai, Pramod K. Singh, Kaushal Kumar and Amreesh Chandra (2006) Thermal diffusivity and electrical conductivity in fast ion conducting composites: A correlation, *Solid State Ionics* **177**, 1613–1617
[15]. T.G. Gopakumar, J.A. Lee, M. Kontopoulou and J.S. Parent (2002). Influence of clay exfoliation on the physical properties montmorillonite/polyethylene composites, *Polymer **43***, 5483–5491.
[16]. Awalendra K. Thakur, Dillip K. Pradhan, B.K. Samantaray and R.N.P. Choudhary (2006). Studies on an ionically conducting polymer nanocomposite, *Journal of Power Sources **159***, 272–276
[17]. Miroslava Mravakova, Kada Boukerma, Maria Omastova and Mohamed M. Chehimi (2006). Montmorillonite/polypyrrole nanocomposites. The effect of organic modification of clay on the chemical and electrical properties, *Materials Science and Engineering C **26**,* 306 – 313.
[18]. Binay K. Dutta (2006). Heat transfer principles and applications, *Prentice-Hall of India Private Limited,* New Delhi.

Corresponding Author: zainalat@science.upm.edu.my