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# A STUDY ON THE DIELECTRIC PROPERTIES OF POLYPYRROLE-BENTONITE COMPOSITES

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## Abstract

The main aim of the research work is to study the dielectric properties of the prepared polypyrrole-bentonite composites. Firstly, polypyrrole was prepared by chemical oxidative polymerization of pyrrole in aqueous medium using ferric chloride as an oxidant. Bentonite clay as filler was collected from Ta Da U Township, Mandalay Region. The polypyrrole-bentonite composites were prepared by various w/v ratios of pure bentonite/pyrrole (1:3, 2:3, 3:3 g/mL) and designated as PPy-B 1, PPy-B 2 and PPy-B 3, respectively. The prepared polypyrrole was characterized by FT IR, XRD and TG-DTA. Polypyrrole-bentonite composites were also characterized by FT IR, XRD, TG-DTA, and SEM. Dielectric behaviour of polymer composites were investigated in the 1-10 MHz frequency range and at different voltages (6 V and 10 V) by LCR measurements. According to XRD, the sharp peak of bentonite in PPy-B composites was shifted toward lower angle with low intensity. SEM micrographs show that the prepared polymer composites have denser and more compact surface morphology with increasing amount of bentonite clay. It was also found that thermal stability of polypyrrole-bentonite composite was enhanced with an increase amount of bentonite clay. From FT IR, polymer-clay composites have the characteristics peaks of both polypyrrole and bentonite's functional groups. Dielectric permittivities decreased with increase in frequency for all composites due to the typical behaviour of dielectric properties. It was observed that, as the amount of bentonite in the composites increased, dielectric permittivities decreased while the dielectric conductivity of composites increased.

**Keywords:** Bentonite clay, polypyrrole, polypyrrole-bentonite composites, dielectric properties

## Introduction

Conducting polymers (CPs) have drawn significant interest of research for more than 30 years because of their economical importance, superior stability, light weight, resistance to corrosion and satisfactory electrical conductivity. Some of the applications of CPs include: rechargeable batteries,

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electrochromic display devices, light reflecting or light emitting diodes (LEDs), transistors and printed electronic circuits (Kumar *et al*., 2015).

Polymers are the insulating materials. For example, metallic cables are covered in plastic to shield them. However, there are four major classes of semiconducting polymers. They include (1) conjugated conducting polymers, (2) charge transfer polymers, (3) ionically conducting polymers and (4) conductively filled polymers (Marquis *et al*., 2011).

Instrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials in recent years. The standard conducting polymers (CPs; i.e., Polypyrrole (PPy), Polythiophene (PTh), Polyaniline (PANI)) can be polymerized both chemically and electrochemically. Among the conducting polymers, PPy is one of the most frequently studied polymers because of high electric conductivity, ion exchange property, environmental stability as regards oxygen and water, and ease of synthesis (Wang *et al*., 2001; Bouabdallah and Djelali, 2014).

In general, PPys are brittle, insoluble, poor thermal stability, poor mechanical properties and infusible, hence not possible to process. When organic and inorganic components are mixed at molecular level, the resulting composites may exhibit unique properties for superior to those of the individual components. When polypyrrole chains are intercalated in interlayers of clay, PPys with an ordered chain structure and better properties can be obtained. Moreover, polymer-clay composites exhibit improved thermal and mechanical properties, reduced flammability and better barrier properties than unfilled polymers (Anuar *et al*., 2004; and Raiz and Ashraf, 2014).

Although there have been several reports on the preparation, characterization and properties of PPy/Na-montmorillonite, only a few studies investigate the dielectric properties of PPy/Na-montmorillonite composites. This study differs from most of the previous works in its use of bentonite clay that are available in Myanmar. A further difference is that it investigates ac conductivity and dielectric properties of the composites.

The aim of this study was to investigate ac conductivity and dielectric properties of PPy-B composites. Bentonite clay was used as filler in conductive composites because it is naturally abundant in Myanmar, low cost, ion exchange properties and has high thermal resistance and shell-shaped crystalline structure with nanometric thickness. PPy-bentonite composites were prepared by chemical oxidative polymerization of pyrrole in the presence of bentonite clay from Myanmar.

## Materials and Methods

### Sample collection

Pyrrole monomer was purchased from Aladdin Industrial Corporation, Shanghai and used without further purification. Ferric chloride was purchased from BDH Chemicals Ltd. Poole England and used as an oxidizing agent. Purified bentonite clay was collected from Saga Inn village, Ta Da U Township. Distilled water was used as the solvent in all analyses.

### Synthesis of Polypyrrole and Polypyrrole-Bentonite Composites

First, 3.4 mL of pyrrole monomer was added to 25 mL of ethanol under constant stirring at 5-10 °C. Next, 25 mL of 0.1 M $FeCl_3.6H_2O$ dissolved in 25 mL of water was added to the monomer drop wise. The reaction mixture was stirred at 5-10 °C for 1 h. The resulting black precipitate was filtered and washed with distilled water to remove unreacted monomer and excess ferric chloride. The black precipitate was dried at 60-70 °C in the incubator.

Polypyrole-bentonite composites were prepared by adding different amounts of bentonite clay (1 g, 2 g and 3 g) to pyrrole monomer. First, bentonite clay was dispersed in 25 mL of water under constant stirring. Pyrrole monomer was added drop by drop to bentonite clay suspension by constant stirring at 5-10 °C and then an oxidizing agent was mixed with bentonite-pyrrole solution dropwise. The purification step was performed as described above. The resulting composites were denoted as PPy-B X, where PPy-B means Polypyrrole-Bentonite composite and X refers to the mass of bentonite clay. For example, PPy-B 1 means that the used mass of bentonite is 1 g. So, the compsites were designated as PPy-B 1, PPy-B 2 and PPy-B 3, respectively (Celik and Onal, 2011).

## Preparation of Pellets

The obtained black powders (PPy and PPy-B composites) were pressed into pellets with diameter 1.5 cm and thickness 0.16 cm using MAEKAWA Testing machine.

## Characterization of the Prepared Samples

The chemical composition of bentonite in mass percentage was determined by Flame spectroscopy and Wet analysis.

The physicochemical properties (moisture, pH, bulk density, cation exchange capacity and swelling power) of bentonite samples were determined.

The structural characterization of polypyrrole-bentonite composites was analysed using FT IR. The interaction of polymer-bentonite composites was investigated by XRD analysis. Thermal properties of the composites were evaluated by TG-DTA. The morphological structure of the prepared composites was characterized by SEM. The dielectric properties and frequency dependent electrical conductivity were also determined by LCR meter in the frequency range of 1-10 MHz.

X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat. No 9240 J 101, Japan. Copper tube with nickel filter was used. The diffraction pattern was recorded in terms of $2\theta$ in the range of 10-70 °.

FT IR spectrum was recorded in the range of 4000-400 $cm^{-1}$ by using 8400 SHIMADZU, Japan FT IR spectrophotometer.

The scanning electron microscopy (SEM) images were obtained using JSM-5610 Model SEM, JEOL-Ltd., Japan.

Thermogravimetric analyses of samples were performed using TG-DTA apparatus, (Hi-TGA 2950 model). The temperature ranged between 0 °C and 600 °C under nitrogen gas (at a rate of 50 mL/min).

For the electrical conductivity measurements, the obtained samples were pressed in the form of pellet using MAEKAWA Testing machine. The dielectric permittivities such as D, K and tangent loss of composites were determined using LCR-B110G meter (DC 20-10 MHz) in the frequency ranged of 1-10 MHz at ambient temperature. Frequency dependent electrical conductivity was evaluated by using dielectric equation;

$$C = \frac{K\,\varepsilon_0 A}{d}$$

$$\tan\delta = \frac{D}{K}$$

$$\omega = 2\pi f$$

$$\sigma_{ac} = \omega \tan\delta\, K\, \varepsilon_0$$

where, C is capacitance (pF), K is dielectric constant, $\varepsilon_0$ is electrical permittivity in vacuum ($8.85\times10^{-14}$ F $cm^{-1}$), d is sample thickness (cm), ω is circular frequency (MHz), D is dielectric loss factor (D), tan δ is dielectric loss tangent and $\sigma_{ac}$ is electrical conductivity (μS $cm^{-1}$)

## Results and Discussion

### Physicochemical Analysis of Bentonite Clay

Table 1 shows the physicochemical properties of benotnite samples. The chemical composition of bentonite clay is shown in Table 2. The alumina/silica ratio of bentonite clay was found to be 0.36.

**Table 1:Physicochemical Properties of Collected Bentonite Clay**

| Physicochemical properties | Content |
|---|---|
| Moisture (%) | 8.19 |
| pH | 8.30 |
| Bulk density (g $cm^{-3}$) | 67.30 |
| Swelling power (mL/2 g/24 h) | 15 |
| CEC (meq/100 g) | 101.98 |

Cation Exchange Capacity

**Table 2: Chemical Composition of Collected Bentonite Clay**

| Constituents | Content (%) |
|---|---|
| $SiO_2$ | 53.41 |
| $Al_2O_3$ | 19.43 |
| $Fe_2O_3$ | 4.34 |
| CaO | 1.03 |
| MgO | 0.30 |
| $Na_2O+K_2O$ | 0.89 |
| Loss on Ignition | 19.98 |

## XRD Analysis

The interaction of PPy-B composites was investigated by XRD. Figures 1 (a-e) represent the XRD patterns of polypyrrole, bentonite and a series of PPy-B composites with different bentonite content, respectively. In Figure 1, the X-ray diffractions of bentonite and all composites show sharp peaks at 2θ (28 °) and at 2θ ~ 26 ° respectively. The crystalline peaks of bentonite in composites were shifted toward lower position due to the interaction of PPy and the bentonite. The characteristics XRD peak of polypyrrole was found to be amorphous nature at 2θ value between 20° and 30°. The average crystallite sizes of pure bentonite (B) and polypyrrole-bentonite composites were shown in Table 3. From the data in table 3, it was found that the crystallite size of the prepared PPy-B 3 composite has the smallest average crystallite size (12.85 nm) with lowest peak intensity among the three composites.

## FT IR Analysis

Figure 2 shows the FT IR spectrum of polypyrrole. The assignment data is summarized in Table 4. In the spectrum of polypyrrole, the peak observed at 3232 cm$^{-1}$ corresponds to N-H stretching vibration and the peak at 1529 cm$^{-1}$ corresponds to N-H bending vibration. The peak at 1031 cm$^{-1}$ can be attributed to C-H deformation of polypyrrole. A C-N stretching absorption band was detected at 1145 cm$^{-1}$. In the spectrum of bentonite, the bands observed at 3696 cm$^{-1}$ and 1641 cm$^{-1}$ can be attributed to O-H stretching and O-H bending vibrations. The peaks observed at 1045 cm$^{-1}$ is due to Si-O bond stretching vibrations, while the band at around 918 cm$^{-1}$ corresponds to Al-O stretching vibration. The peaks at 1033 cm$^{-1}$ and 1383 cm$^{-1}$ in all the spectra of all composites can be attributed to Si-O stretching vibration and C-H deformation in polypyrrole (Figure 3 and Table 5). The characteristics peaks of PPy and bentonite in the composites indicate the interaction of PPy in bentonite clay (Silverstein *et al*., 2003).

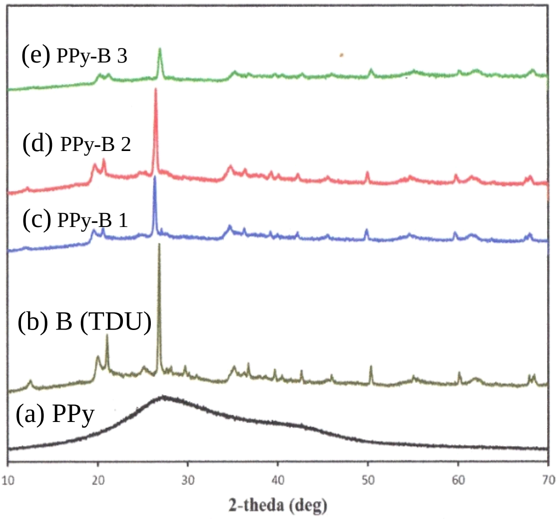


**Figure 1:** XRD diffraction patterns of (a) PPy, (b) pure B, (c) PPy-B 1, (d) PPy-B 2 and (e) PPy-B 3 composites

**Table 3: Average Crystallite Sizes of Pure bentonite (B) and PPy-B Composites**

| **Sample** | **Average Crystallite Sizes (nm)** |
|---|---|
| Pure B | 38.55 |
| PPy-B 1 | 31.24 |
| PPy-B 2 | 20.83 |
| PPy-B 3 | 12.85 |

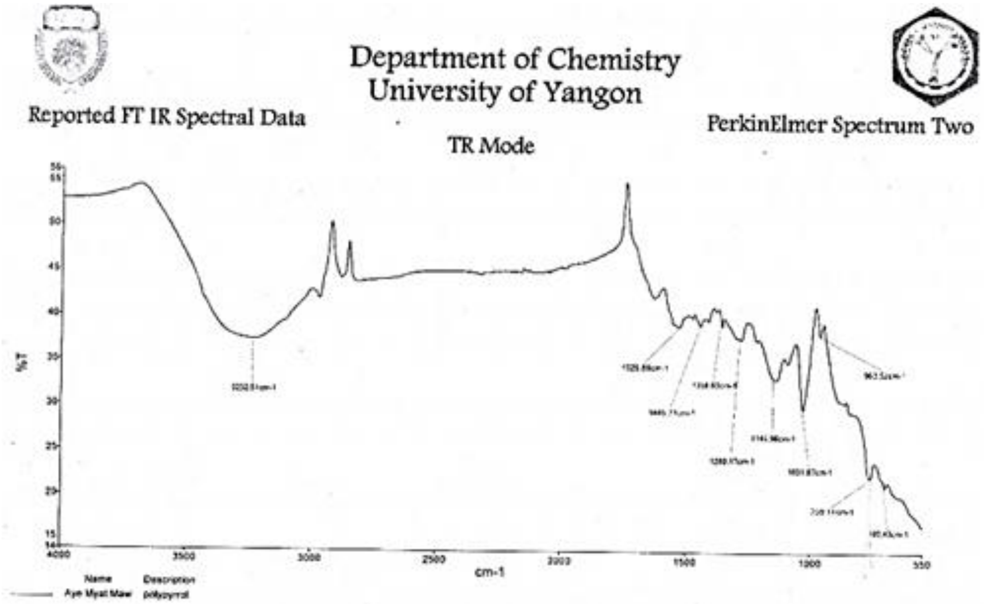


**Figure 2:** FT IR spectrum of the prepared polypyrrole

**Table 4: FT IR Band Assignments of the Prepared Polypyrrole**

| Observed wave number ($cm^{-1}$) | *Literature wave number ($cm^{-1}$) | Band Assignment |
|---|---|---|
| 3232 | 3460-3280 | N-H stretching vibration of polypyrrole |
| 3107 | 3100-3000 | = C-H stretching in aromatic ring |
| 2970<br>2881 | 2970-2850 | C-H stretching (asym) and (sym) |
| 1529 | 2565-1475 | N-H bending |
| 1445 | 1460-1440 | C-C ring stretching |
| 1280 | 1440-1260 | C-OH bending |
| 1145 | 1190-1130 | C-N stretching |
| 1031 | 1050-1030 | C-H deformation in polypyrrole |
| 963 | 980-960 | C-H bending |
| 759 | 770-690 | C-H out of plane bending |

* Silverstein *et al*., 2003

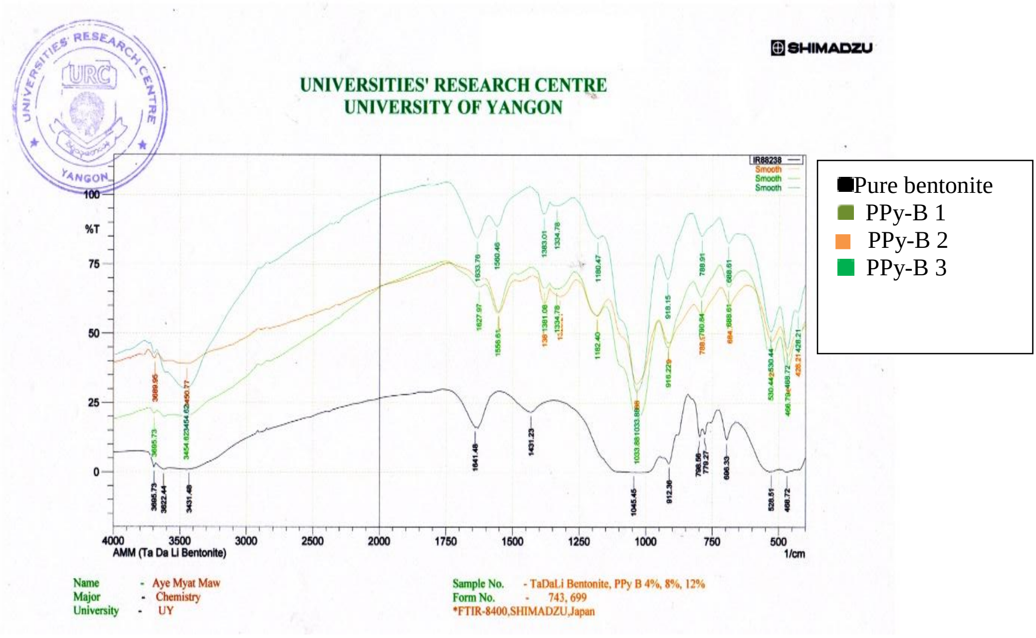


**Figure 3:** FT IR spectra of pure bentonite and polypyrrole-bentonite composites

**Table 5: FT IR Band Assignments of Pure Bentonite and PPy-B Composites**

| Observed wavenumber (cm$^{-1}$) | | | | * Literature wavenumber (cm$^{-1}$) | Band Assignment |
|---|---|---|---|---|---|
| **Pure B** | **PPy-B 1** | **PPy-B 2** | **PPy-B 3** | | |
| 3695 | 3689 | 3696 | 3696 | 3600-3400 | O-H stretching (and) N-H stretching |
| 3622 | - | - | - | | |
| 3431 | 3450 | 3455 | 3454 | | |
| 1641 | - | 1627 | 1633 | 1630-1655 | H-O-H bending (or) O-H bending |
| - | 1553 | 1557 | 1560 | 1580-1620 | C=C stretching |
| - | 1381 | 1381 | 1383 | 1450-1200 | C-H deformation of polypyrrole |
| 1045 | 1033 | 1033 | 1033 | 1045-1030 | Si-O stretching |
| 912 | 914 | 916 | 918 | 950-900 | C-H bending (or) Al-OH bending |
| - | 788 | 791 | 788 | 790-750 | C-H bending out of plane |
| 468 | 465 | 467 | 469 | 700-450 | Mg-OH stretching |

* Silverstein *et al*., 2003

## SEM Analysis

Figures 4 (a-d) show the morphological differences between the bentonite clay and PPy-B composites. The surface morphology of bentonite clay is sheet-like plate as shown in Figure 4 (a). After polymerization, the composites show significant changes in morphology as shown in Figures 4 (b-d). The surface morphology of PPy-B 1 and PPy-B 2 are as agglomerates. They are not much difference in their morphology. It may be due to inhomogeneous distribution of bentonite and polypyrrole. The morphological structure of PPy-B 3 looks like flake. It is distributed by interaction of bentonite clay and polypyrrole. The structures of composites exhibit more ordered and denser structure with an increasing amount of bentonite clay.

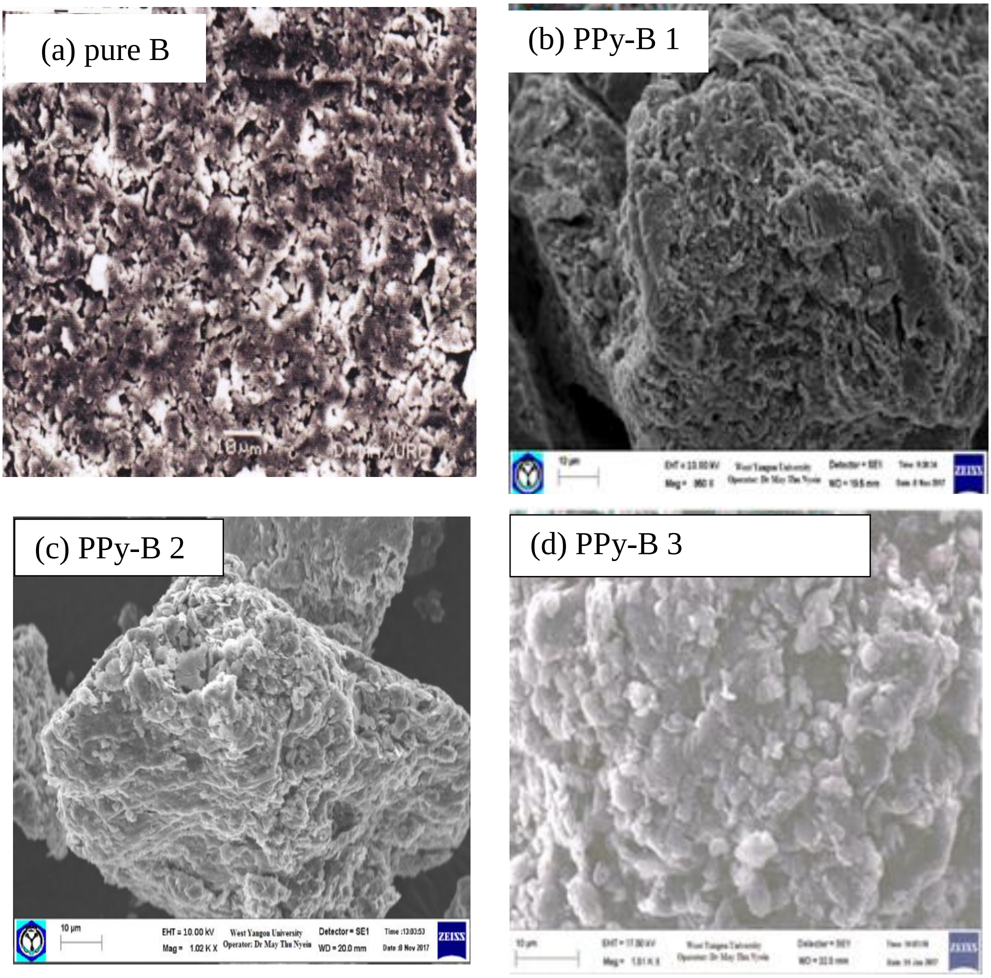


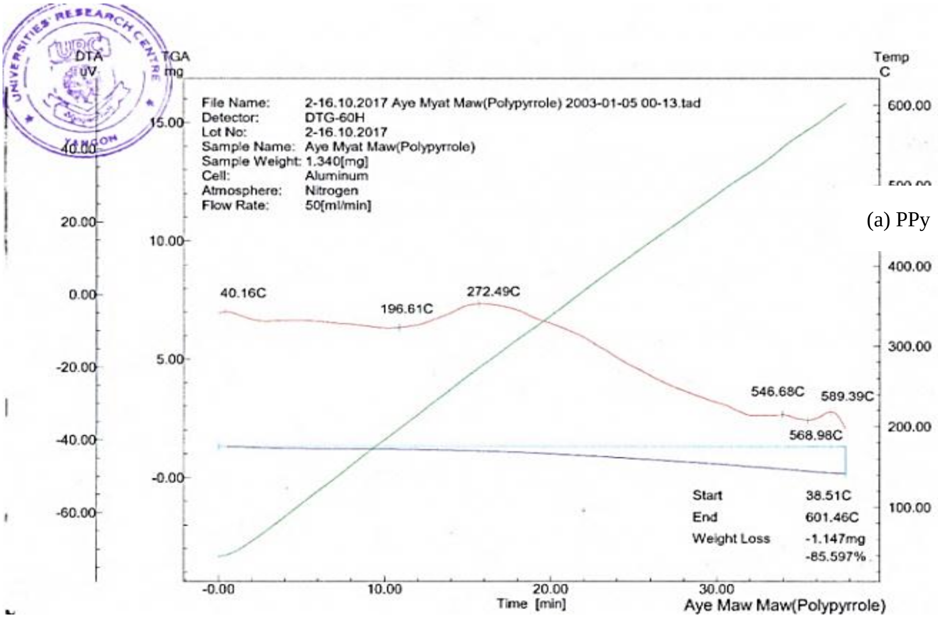
**Figure 4:** SEM micrographs of pure bentonite and PPy-B composites

## Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) thermograms of prepared polypyrrole, pure bentonite sample, and prepared polypyrrole-bentonite composites are shown in Figure 5. Weight loss percent of pure polypyrrole, bentonite, and PPy-B composites are listed in Table 6. TGA curve of prepared PPy indicates that there are two stages of decomposition in Figure 5 (a). Exothermic peak observed at 40 °C with 10.08 % weight loss is due to the loss of volatile materials of PPy. Exothermic peaks observed at 272 °C and 589 °C with the 75.51 % weight loss is due to the thermal decomposition of polymer chain. It was observed that prepared PPy shows a poor thermal stability.

As shown in Figure 5 (b), thermal decomposition of pure bentonite, two stages of weight loss are observed, endothermic peak observed at 74 °C with 6.89 % weight loss is due to the removal of absorbed water. In the temperature range between 400 and 600 °C, endothermic peak observed at 487 °C with 4.75 % weight loss is due to the dehydroxylation of bentonite.

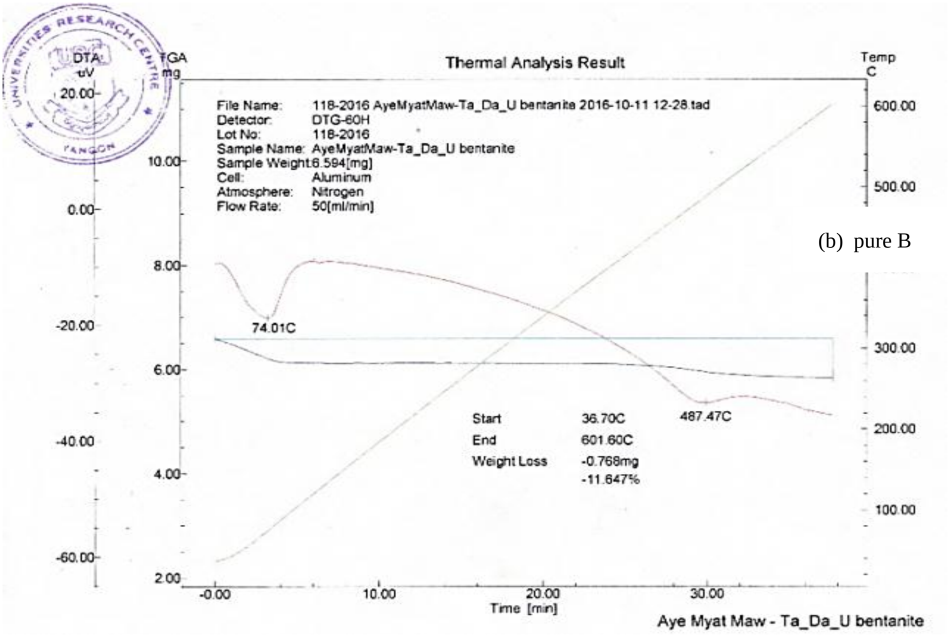
For PPy-B composites, two stages of weight loss are also observed. First weight loss in the temperature range between 37-180 °C is due to the dehydration of absorbed water and moisture. The final weight loss in the temperature range between 180-600 °C is due to the loss of volatile materials of polypyrrple and dehydroxylation of bentonite samples. It can be seen that the incorporation of PPy with bentonite increases the thermal stability of PPy-B composites relative to that of PPy. This enhancement in thermal stability is due to the fact that the introduction of well-dispersed bentonite can prevent the heat to transmit quickly and then improve the thermal stability of composites. Therefore, polypyrrole-bentonite composites exhibit higher thermal stability than pure polypyrrole. According to data in Table 6, it was found that more increase bentonite content in composites, higher thermal stability in them. When compare to other polymer composites (PPy-B 1 and PPy-B 2), PPy B 3 has 13.34 % of weight loss at 180-300 °C.



File Name: 2-16.10.2017 Aye Myat Maw(Polypyrrole) 2003-01-05 00-13.tad
Detector: DTG-60H
Lot No: 2-16.10.2017
Sample Name: Aye Myat Maw(Polypyrrole)
Sample Weight: 1.340[mg]
Cell: Aluminum
Atmosphere: Nitrogen
Flow Rate: 50[ml/min]

Start 38.51C
End 601.46C
Weight Loss -1.147mg
-85.597%

(a) PPy

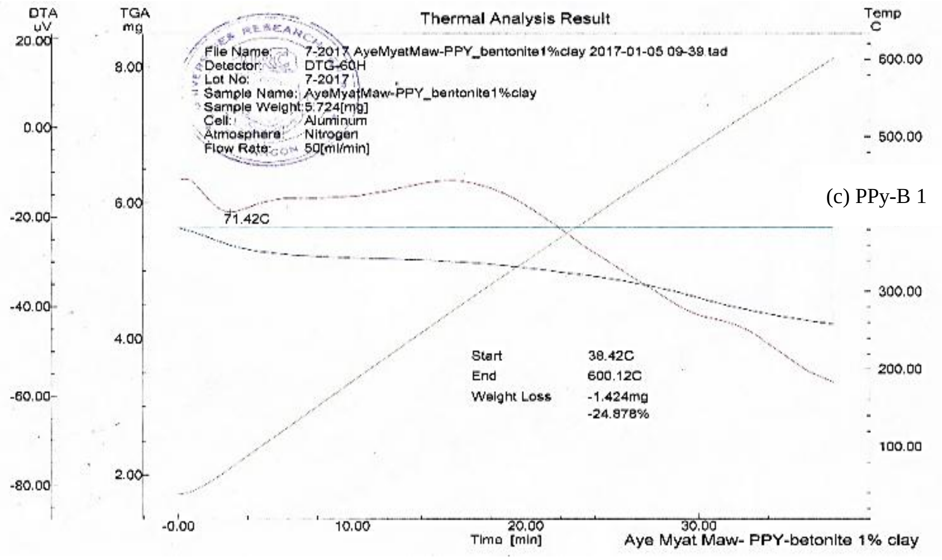


Thermal Analysis Result

File Name: 118-2016 AyeMyatMaw-Ta_Da_U bentanite 2016-10-11 12-28.tad
Detector: DTG-60H
Lot No: 118-2016
Sample Name: AyeMyatMaw-Ta_Da_U bentanite
Sample Weight:6.594[mg]
Cell: Aluminum
Atmosphere: Nitrogen
Flow Rate: 50[ml/min]

Start 36.70C
End 601.60C
Weight Loss -0.768mg
-11.647%

(b) pure B

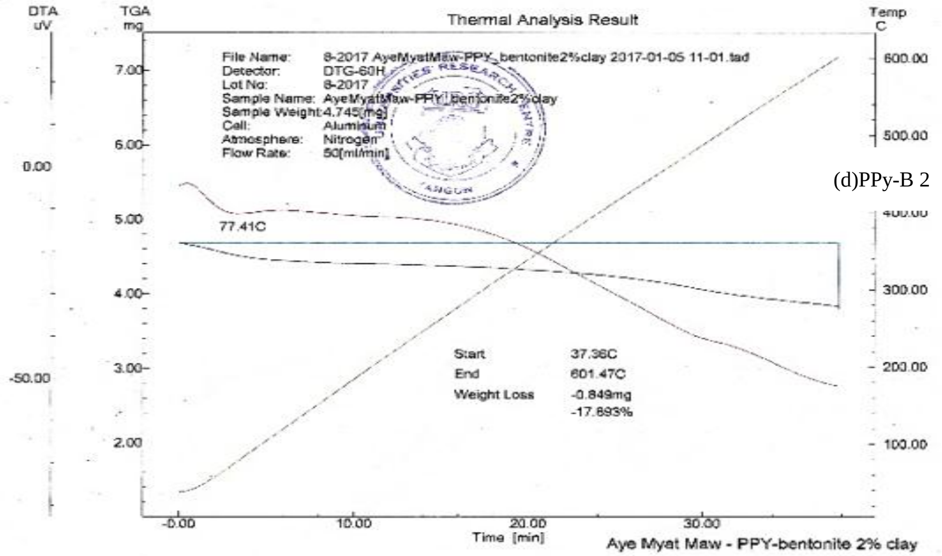


Thermal Analysis Result

File Name: 7-2017 AyeMyatMaw-PPY_bentonite1%clay 2017-01-05 09-39.tad
Detector: DTG-60H
Lot No: 7-2017
Sample Name: AyeMyatMaw-PPY_bentonite1%clay
Sample Weight: 5.724[mg]
Cell: Aluminum
Atmosphere: Nitrogen
Flow Rate: 50[ml/min]

Start 38.42C
End 600.12C
Weight Loss -1.424mg
-24.878%

(c) PPy-B 1



Thermal Analysis Result

File Name: 8-2017 AyeMyatMaw-PPY_bentonite2%clay 2017-01-05 11-01.tad
Detector: DTG-60H
Lot No: 8-2017
Sample Name: AyeMyatMaw-PPY_bentonite2%clay
Sample Weight: 4.745[mg]
Cell: Aluminum
Atmosphere: Nitrogen
Flow Rate: 50[ml/min]

Start 37.36C
End 601.47C
Weight Loss -0.849mg
-17.893%

(d)PPy-B 2

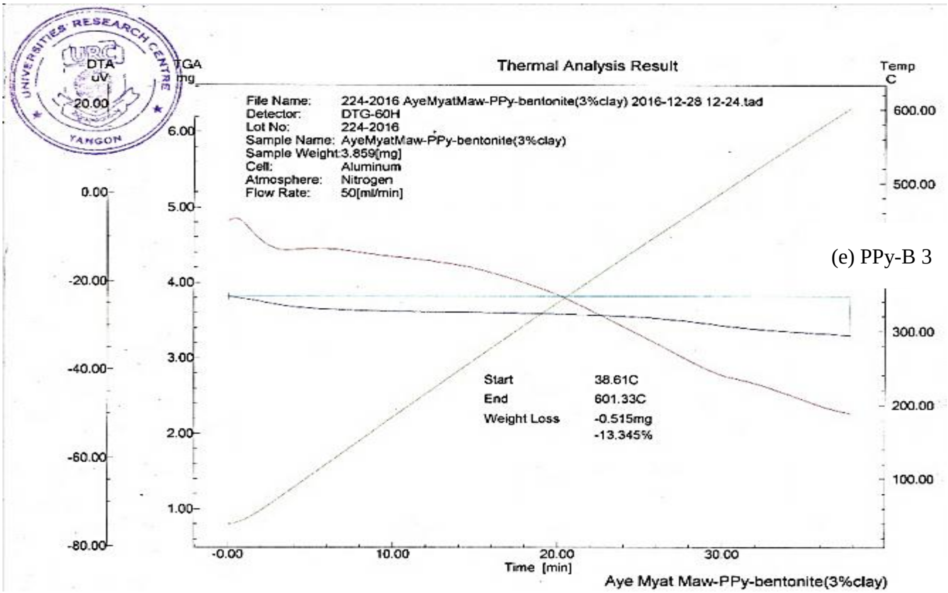


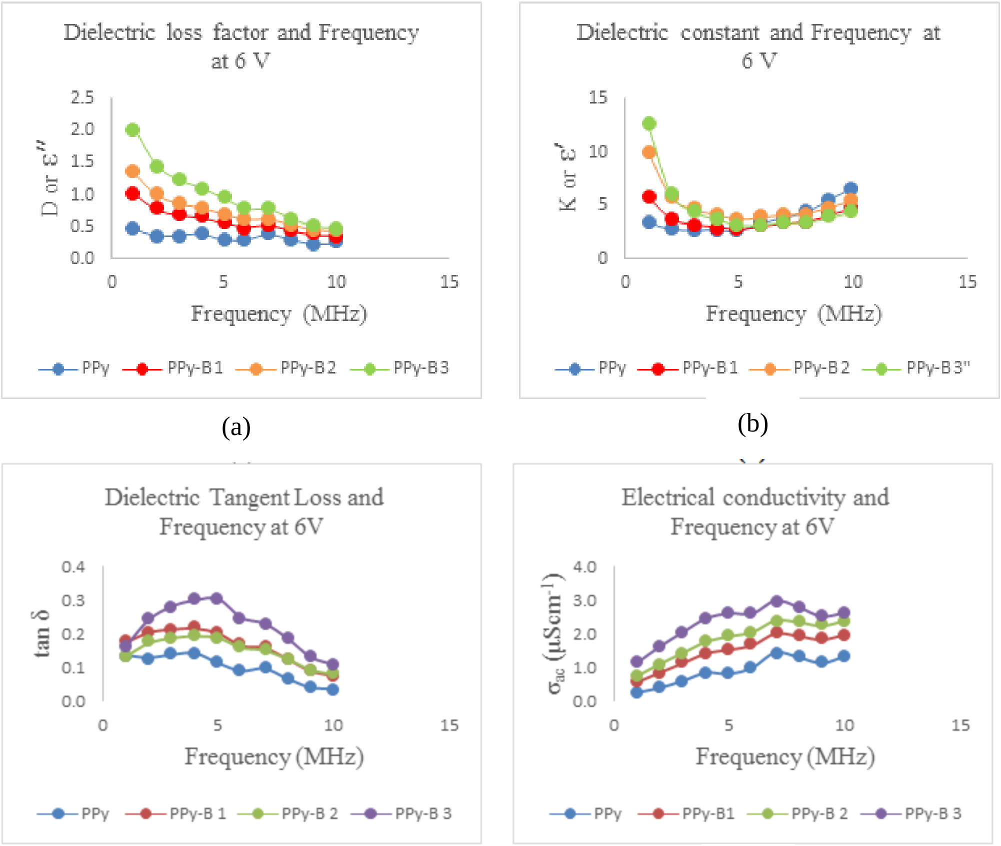
**Figure 5:** TG-DTA thermograms of (a) prepared polypyrrole (b) pure bentonite (c) PPy-B 1 composite, (d) PPy-B 2 composite and (e) PPy-B 3 composite

**Table 6: Total Weight Loss Percent of Pure Bentonite and Polypyrrole-Bentonite Composites from TG-DTA Analyses**

| Sample | Total Weight Loss (%) |
|---|---|
| (a) PPy | 85.59 |
| (b) Bentonite | 11.64 |
| (c) PPy-B 1 | 24.87 |
| (d) PPy-B 2 | 17.89 |
| (e) PPy-B 3 | 13.34 |

## Dielectric Properties

The frequency dependent dielectric permittivities such as D, K and tangent loss and ac conductivity of prepared PPy and PPy-B composities are presented in Figures 6 and 7. As shown in Figures 6 (a, b) and 7 (a, b) the dielectric permittivities decreases as the amount of bentonite in the composites increases, while dielectric conductivity increases. It is seen that the relative permittivity decreases with increasing frequency. Both $\varepsilon'$ and $\varepsilon''$ exhibit typical dielectric behavior especially at high frequencies. This can be interpreted that the maximum interaction occurs at low frequency. 3 g of bentonite containing sample (PPy-B 3) has a higher dielectric conductivity than samples containing 1 g and 2 g of bentonite clay (PPy-B 1 and PPy-B 2). It may be interpreted that as the amount of clay increases, the interactions with hydroxyl groups on the surface of bentonite increases and dielectric conductivity is enhanced. Thus, dielectric tangent loss also increases with an increase in amount of clay. The change in dielectric permittivity with respect to bentonite clay percentage and high dielectric permittivity values can be attributed to the absorbed moisture in interlayer of bentonite clay.



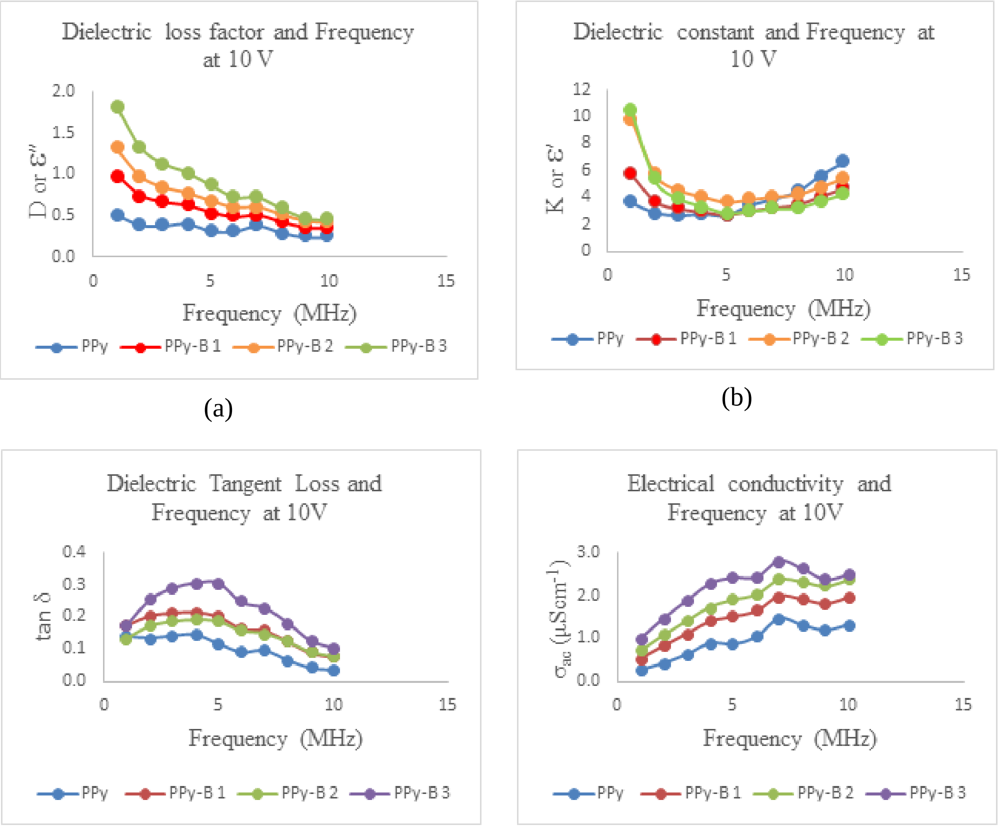
(a)

(b)

(c)

(d)

**Figure 6:** Frequency dependent (a) ε″ (b) ε′ (c) tan δ and (d) $\sigma_{ac}$ of PPy and PPy-B composites at 6 V potential



(a) (b)

(c) (d)

**Figure 7:** Frequency dependent (a) ε″ (b) ε′ (c) tan δ and (d) $\sigma_{ac}$ of PPy and PPy-B composites at 10 V potential

## Conclusion

In this study, polypyrrole and PPy-B composites were performed by chemical oxidative polymerization in aqueous medium. The polymerization mechanism and chemical structures of composite materials are investigated by means of XRD and FT IR. XRD results confirmed the insertion of PPy between the interlayers of bentonite clays. It was observed that the crystallite peak was shifted toward lower position in the PPy intercalated composites. The morphological study showed that polypyrrole polymerization occurred within bentonite interlayers. It is shown that the denser and more compact morphology of PPy-B composites with the increase in amount of bentonite clay. Intercalated composites are found to be more thermally stable than pure polypyrrole. The overall thermal stability trends are pure bentonite > polypyrrole-bentonite composite > polypyrrole in the TG-DTA thermograms. FT IR analysis shows the incorporation of PPy in the clay structure. It was observed that as the amount of bentonite clay increased in the composites, the dielectric permittivity decreased while the dielectric conductivity of the composite materials increased. The prepared PPy-B 3 can be used as a promising material for the variety of electronic applications within these frequency range of 1-10 MHz at 6 and 10 V potentials because it exhibits improved thermal properties, reduced flammability and better dielectric barrier properties than unfilled polymer. Therefore, cheap filler-like bentonite can be effectively used as a good reinforcement for PPy matrix.

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