

Full Length Research Paper

A study on thermal and electrical properties of high density polyethylene/high density polyethylene grafted maleic anhydride/montmorillonite/polypyrrole blend

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Conducting polypyrrole (PPy) was synthesized by chemical polymerization method. The synthesized PPy was characterized by Fourier transform infrared spectrometer (FTIR) and its conductivity was measured by a resistometer. Then, PPy was incorporated into high density polyethylene/montmorillonite nanocomposites. PPy concentration varied in the range of 5 to 20% by weight in nanocomposites using melt mixing follow by compression molding. The effect of PPy concentration on thermal and electrical properties of nanocomposites was investigated. The results of thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) show that incorporation of PPy in nanocomposite improves the thermal stability. Two probe conductivity measurements have indicated that raising the amount of PPy increases the conductivity of nanocomposites.

Key words: Conducting polymer, polypyrrole, high density polyethylene, montmorillonite.

INTRODUCTION

High density poly ethylene (HDPE) is one of the most popular polymers due to its availability and competitive cost. Furthermore, it is a thermoplastic with noticeable mechanical properties. Although, it uses a lot in daily life but its thermal stability is poor and also it is an insulating polymer. The approach to the enhancement of thermal stability based on the use of polymer nanocomposite has been developed in the last years (Lomakin et al., 2007; Adamecc et al., 1981).

Polymer nanocomposites are moderately new group of materials that poses a wide range of properties. The combination of nano sized particle and big interfacial area can strongly influence the nanocomposites behavior (Zhu et al., 2004). The use of reinforcing agents like layered silicates in composites enables us to design nanocomposites with a wide range of properties.

Montmorillonite (MMT) is one of the commonly used

nanofiller. Significant enhancements in optical, electric, mechanical, thermal, flammability, dimensional and barrier properties are because of the large nanoscale contact area between the clay and the polymer (Araújo et al., 2007). Zhou et al. (2005) concluded that polyethylene and inorganic MMT have different characterization and cause of this difference, two stages should were taken using MMT and also modifying PE with MAH by grafting. Grafting polyethylene has polar groups in its backbone and this helps to improve the compatibility between PE and MMT. Nanocomposites of MMT/PE/PE-g-MAH could have better intercalation by utilizing HDPE as matrix. This may be the cause of more branched segments in LDPE than HDPE, which resist intercalation. By addition of MMT to HDPE, thermal stability improves and the mechanical properties can be increased but there was no enhancement in electrical conductivity of nanocomposite. The attribution of PPy as regarding to its high conductivity is to form a conductive nanocomposite.

There is dramatic interest in conductive polymers as a material that has magnetic and electrical properties.

During the last decade, the study on inherently

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Table 1. Blends composition and their designations.

| samples | HDPE (%) | PPy (%) | HDPE-g-MAH (%) | MMT (phr) |
|---------|----------|---------|----------------|-----------|
| 1 | 95 | 0 | 5 | 1.2 |
| 2 | 90 | 5 | 5 | 1.2 |
| 3 | 85 | 10 | 5 | 1.2 |
| 4 | 80 | 15 | 5 | 1.2 |
| 5 | 75 | 20 | 5 | 1.2 |

conductive polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) have been increased intensively due to their special properties (Schulza et al., 2010). Intrinsically conductive polymers have advantageous morphological and structural properties. (Hatchett et al., 2008). Among intrinsically conductive polymers, polypyrrole (PPy) has many special properties such as easy synthesizing, high flexibility in the process and also good mechanical properties and stability (Schulza et al., 2010). Different methods can be used for synthesizing polypyrrole such as chemical, electrochemical, vapor phase and enzymatic routes (Pina et al., 2009). One of the key problems relating to the potential applications of electroactive polymers is their poor processability and inadequate mechanical properties; some of them (for example, polypyrrole) are not capable of film formation. The most promising approach to the solution of this problem is to prepare composite. Materials such as blends, filled polymers, and multilayer materials using conventional thermoplastic polymers (Elyashevich et al., 2003).

Boukerma et al. (2005) concluded that PPy/MMT nanocomposites are suitable fillers for improving the conducting and mechanical properties of insulating polymer matrices. Elyashevich et al. (2003) found that HDPE/PPy composites have high thermal stability. PPy layer can increase all mechanical characteristics of PE/PPy at PPy content less than 20%. They reported that at further increase of PPy, the breaking strength and break elongation starts to decrease.

EXPERIMENT

Materials

Pyrrole monomer with a density of 0.97g/cm^3 at 20°C and a melting point of -24°C was purchased from Merck Company. Montmorillonite (MMT) which was used as organoclay filler has a grade of 1.30p from a nano clay Company. High density polyethylene (HDPE) and High density polyethylene grafted maleic anhydride (HDPE-g-MAH) used in this study were purchased from Petrochemicals (Malaysia). Iron (III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) which was used as an oxidant was purchased from Qrec Company. Sodium dodecylbenzene sulfonate (DBSNa) which was used as surfactant in this study has a grade of 88% from Acros Organic Company.

Synthesis of polypyrrole

(0.1 mol) 27.03 gr $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 cc H_2O and 3.48 g DBSNa also dissolved in 100 cc water. After 15 min stirring in 0°C , 0.15 mol (10.4 cc) pyrrole monomer was dissolved in 50 cc of H_2O with water added dropwise within 20 min to the mixture. The black powder of polypyrrole was filtered off and washed with water and after that dried for 8 hours in an oven at 60°C temperature. The conductivity of synthesized PPy was around 3.18 S/cm.

Blending

HDPE/MMT/HDPE-g-MAH/PPy nanocomposites were prepared according to Table 1 by internal mixer at temperature of 170°C and screw revolution of 15 rpm. After blending the materials, compression molding was used to prepare samples with a temperature at 170°C .

Characterization

To evaluate the samples, different methods were used. FTIR analysis was carried out on a Perkin Elmer spectrum 2000 explorer FTIR Spectrometer. The samples were prepared by using a thin pellet of KBr. The thermal gravimetric analysis of samples was done using Perkin Elmer thermo gravimetric analyzer TGA7. XRD was conducted to study the intercalation of MMT in the matrix. It was performed with the Siemens 500 X-ray diffractometer by using Cu-WL anode in 2-Theta range between 1.5° to 10° and the voltage used was 40 kv. Electrical conductivity of synthesized PPy was measured by using two probe tests. The current is supplied from Tektronix PS280 DC Power Supply. The spectra of synthesized PPy are shown in Figure 1.

RESULTS

Fourier transforms infrared spectroscopy (FTIR)

The strong peak observed at 3405 cm^{-1} is related to N-H stretching. The peak at 2915 cm^{-1} is related to CH_2 and the peak observed at 1536 cm^{-1} is due to C-C and C=C stretching in the ring. The peak of C-N stretching can be found at 1462 cm^{-1} . The peak 1169 cm^{-1} refers to C-C PPy ring while the peaks of 786 cm^{-1} and 1036 cm^{-1} can be related to C-H out of plane bending and in plane deformation, respectively. Table 2, presents the absorption FTIR peaks for PPy from previous studies (Kharat et al., 2007; Geng et al., 2007; Trchova et al., 2003) and PPy synthesized in the laboratory. Based on

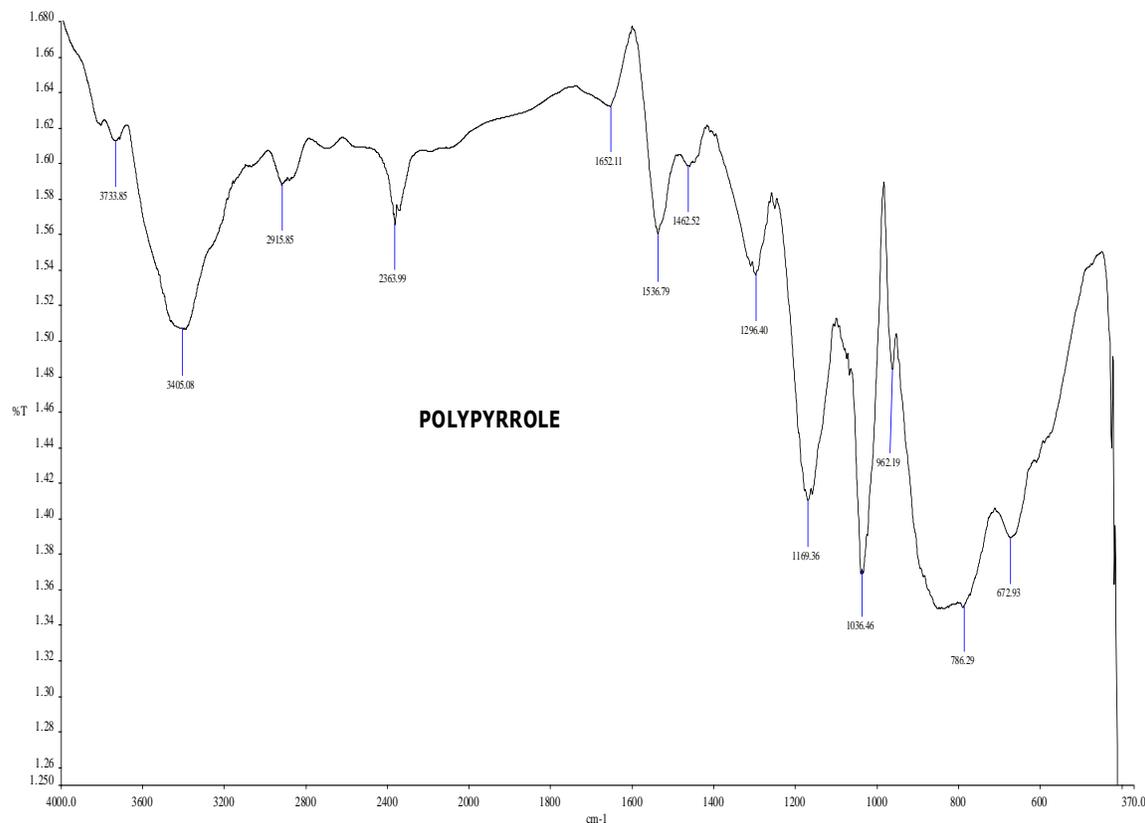


Figure 1. FTIR spectrum of synthesized PPy.

Table 2. Comparison of absorption peaks in the synthesized PPy with literature (Kharat et al., 2007; Geng et al., 2007; Trchova et al., 2003).

| Functional group | Peaks of synthesized PPy (cm ⁻¹) | Peaks of PPy according to literature(cm ⁻¹) |
|--|--|---|
| N-H (stretching) | 3405 | 3436 |
| Counter ion -CH ₂ | 2915 | 2910 |
| C-C (stretching) | 1536 | 1554 |
| C-N (stretching) | 1462 and 1169 | 1474 and 1189 |
| assigned to the doped bands | 1296 | 1297 |
| C-N in plane deformation | 1296 | 1308 |
| Breathing vibration of the pyrrole ring. | 1169 | 1166 |
| C-H in plane deformation | 1036 | 1050 |
| C-C out of plane ring deformation | 962 | 967 |
| C-H out-of-plane bending | 786 | 786 |

the comparison of peaks and high similarity between them, the formation of PPy can be confirmed.

Figure 2 represents FTIR spectra of HDPE/PPy/MMT blends with various amount of PPy. In the absence of PPy (0% PPy), the peak of 1642 cm⁻¹ is related to vibration of carbonyl group. This peak indicated that maleic anhydride (MAH) has been successfully grafted to the backbone of PE. Similar result was reported by Zhang et al. (1992). The vibration band observed at 717

cm⁻¹ is due to CH₂ rocking vibration of PE. The vibration bands of 2915 cm⁻¹ and 2848 cm⁻¹ are related to asymmetric and symmetric stretching vibration of CH₂ respectively (Elyashevich et al., 2004). Table 3 represents the comparison of absorption peaks in nanocomposites with a different amount of PPy. The peak at 3424 cm⁻¹ is for N-H stretching of MMT which shifted to lower wave numbers in the other nanocomposites. Rizvi et al. (2009) reported that these

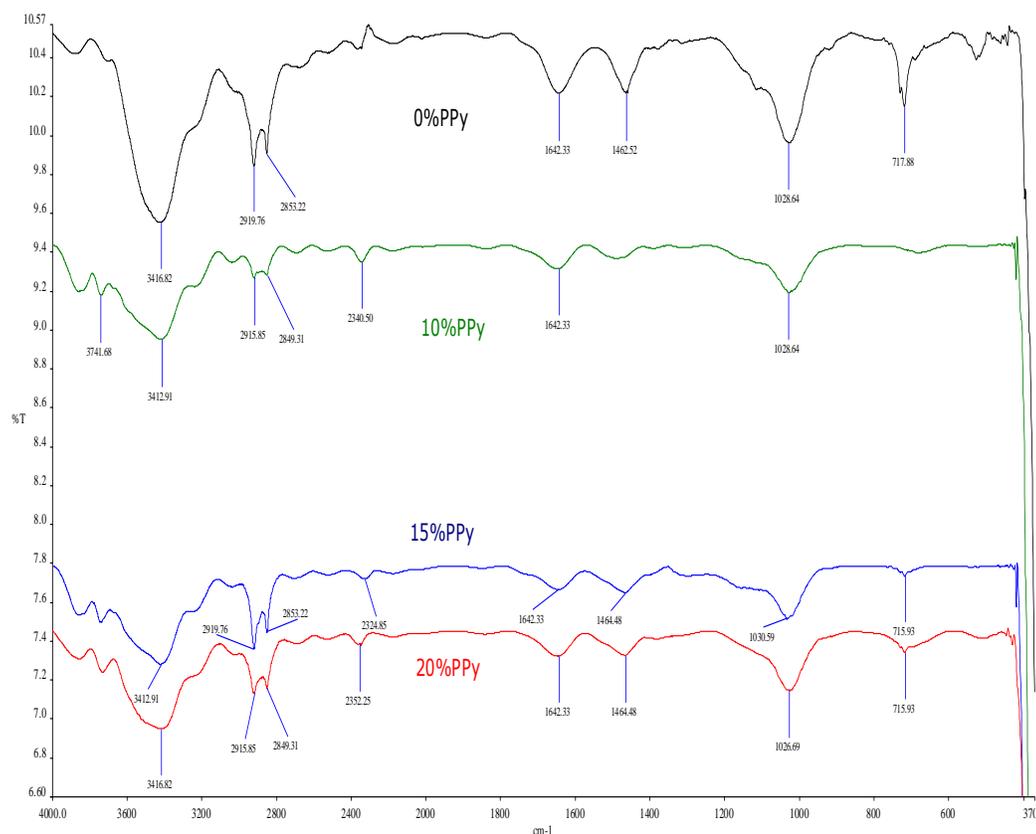


Figure 2. FTIR spectra of HDPE/MMT blends with different PPy content.

Table 3. Absorption peaks of HDPE/HDPE-g-MAH/MMT blends with different contents of PPy.

| Variable | HDPE/HDPE-g-MAH/MMT/PPY (cm ⁻¹) | | | | |
|--|---|----------------------------|-----------------------------|----------------------------|----------------------------|
| | 28.5/1.5/1.2/0 (0% PPy) | 27/1.5/1.2/1.5 (5% PPy) | 25.5/1.5/1.2/3 (10% PPy) | 24/1.5/1.2/4.5 (15%PPy) | 22.5/1.5/1.2/6 (20%PPy) |
| Assignment | | | | | |
| (PE)Scissoring bending CH ₂ | 1462 | 1462 | 1466 | 1485 | 1464 |
| (PE)rocking CH ₂ | 717 | 717 | 717 | 678 | 717 |
| (PE)stretching CH ₂ | 2923-2853 | 2919-2853 | 2919-2849 | 2915-2853 | 2919-2849 |
| Breathing vibration of PPy ring | - | 1026 | 1026 | 1030 | 1032 |
| N-H stretching of MMT | 3416 | 3412 | 3412 | 3412 | 3416 |
| C-H vibration of MMT | 2340 | 2344 | 2344 | 2344 | 2328 |
| PPy-MMT-HDPE aromatic substitution | 1024 | 1026 | 1026 | 1030 | 1032 |
| Carbonyl vibration | 1642 | 1636 | 1646 | 1648 | 1644 |

shifts in the peaks can be used to indicate good interfacial interaction between components.

According to Table 4, it can be said that the band of C–N stretching vibration in the ring of PPy which it observed at 1462 cm⁻¹ is overlapped by the doublet of the C–H bending of PE. There is also another overlap between asymmetric stretching vibration of CH₂ at 2923 cm⁻¹ in PE and the vibration band of 2915 cm⁻¹ from the counter ion

CH₂ of PPy.

X-Ray diffraction (XRD)

XRD patterns of MMT and HDPE/PPy/MMT nanocomposites are shown in Figures 3 and 4 respectively. The diffraction in MMT was registered at 2θ ≈ 4.1° which

Table 4. The 2θ angle and d -spacing of MMT for HDPE/HDPE-g-MAH/PPy/MMT nanocomposites with different content of PPy.

| Samples | HDPE (wt %) | HDPE-g-MAH (wt %) | PPy (wt %) | MMT (phr) | 2θ | d -spacing (nm) |
|---------|-------------|-------------------|------------|-----------|-----------|-------------------|
| PPy | 0 | 0 | 100 | 0 | 22 | 0.5 |
| MMT | 0 | 0 | 0 | 100 | 4.1 | 2.1530 |
| 0%PPy | 95 | 5 | 0 | 4 | 3.96 | 2.2284 |
| 5%PPy | 90 | 5 | 5 | 4 | 3.43 | 2.5726 |
| 10%PPy | 85 | 5 | 10 | 4 | 3.43 | 2.5726 |
| 15%PPy | 80 | 5 | 15 | 4 | 2.79 | 3.1562 |
| 20%PPy | 75 | 5 | 20 | 4 | 2.60 | 3.3944 |

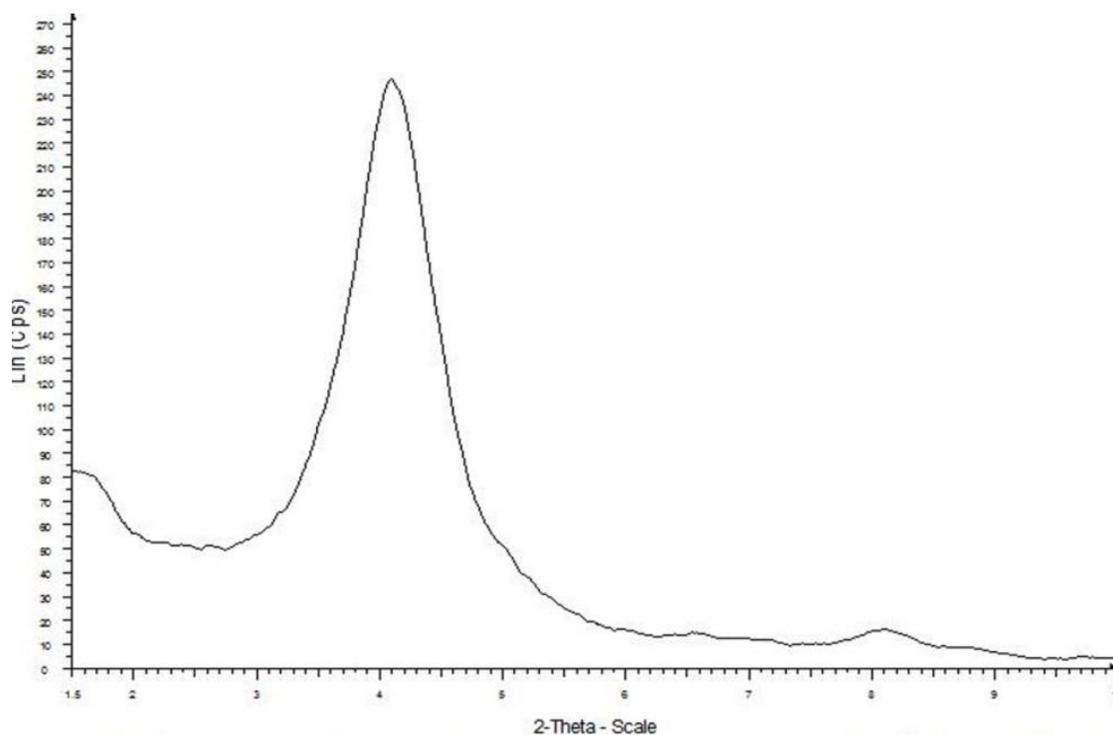


Figure 3. XRD pattern of pure MMT.

corresponded to a d -spacing of 2.153 nm.

It can be observed in HDPE/MMT and HDPE/PPy/MMT nanocomposites with different percentage of PPy, the diffraction peak was shifted from 4.1° to a lower angle (4° and became broader. All the MMT diffraction peaks in nanocomposites became weaker than MMT. The calculated d -spacings of MMT in HDPE/MMT and HDPE/PPy/MMT nanocomposites are shown in Table 4.

Conductivity

The change in electrical conductivity of blends by incorporation of PPy was investigated. The resistivity values of HDPE/HDPE-g-MAH/MMT with various amount

of PPy are shown in Table 5. The resistivity of nanocomposites without PPy was around 15.58 GΩ and upon the addition of 5% PPy to nanocomposites the resistivity decreased to 9.504 GΩ. Although it is clear that the addition of higher amount of PPy decreases the resistivity of nanocomposites, further addition up to 20% does not change the resistivity. The blend with 20% PPy presents the lowest resistivity (880 MΩ) with a large difference compared to other nanocomposites. Elyasherich et al. (2004) and Ong et al. (2008) also stated that the presence of small amounts of PPy can increase the conductivity of HDPE/MMT/PPy blend. The conductivity of PE is around 10^{-16} s/cm, so the low conductivity of the composite is due to a very small amount of conductivity in the matrix.

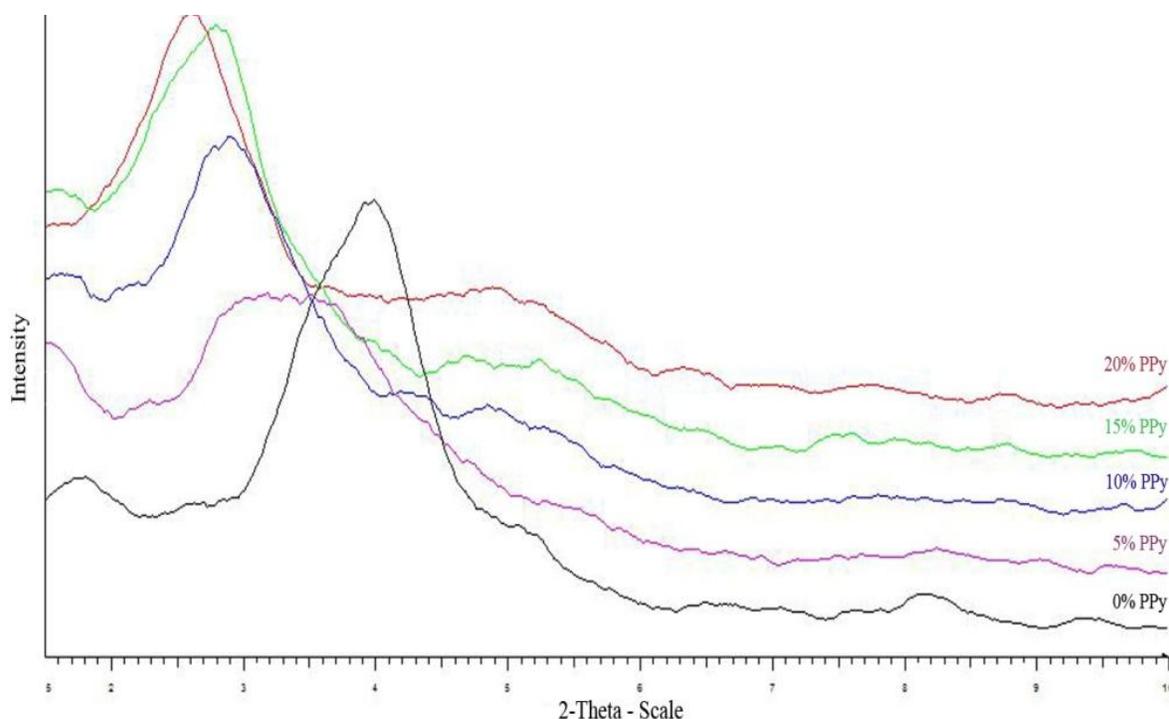


Figure 4. XRD pattern of HDPE/MMT/PPy with different amount of PPy.

Table 5. Resistivity and conductivity of different HDPE/HDPE-g-MAH/MMT/PPy blends.

| HDPE/HDPE g MAH/MMT/PPy | PPy (%) | Resistivity (GΩ) | Conductivity (S/cm) |
|-------------------------|---------|------------------|-------------------------|
| 28.5/1.5/1.2/0 | 0 | 15.58 | 6.41×10^{-11} |
| 27/1.5/1.2/1.5 | 5 | 9.504 | 1.052×10^{-10} |
| 25.5/1.5/1.2/3 | 10 | 5.784 | 1.728×10^{-10} |
| 24/1.5/1.2/4.5 | 15 | 2.120 | 4.716×10^{-10} |
| 22.5/1.5/1.2/6 | 20 | 0.880 | 1.136×10^{-9} |

Thermal gravimetric analysis (TGA)

Thermal stability of nanocomposites was studied by TGA. The stability of nanocomposites changed with concentration of PPy. Figure 5 represents the TGA curves of HDPE/MMT with different PPy content.

According to Figure 5, it can be observed that TGA results for HDPE/MMT and its blend with different amount of PPy did not exhibit a significant difference in maximum decomposition temperature. The degradation onset temperature in the first blend, without PPy was around 440°C. With the addition of PPy to HDPE/MMT, there is a slight change in the melting point of the nanocomposite and a shift to a higher region. However, no significant change in decomposition temperature of nanocomposites was observed with further increase of PPy. By increasing the concentration of PPy in nanocomposites the weight loss of blends during tests

was decreased. The weight of samples was 100% at 250°C and after that all of the samples started to decompose. Around 450°C the weight of samples with PPy decreased dramatically, similar to the case without PPy earlier at around 440°C. At 900°C the remained weight of the first sample was around 4% and in the samples with a higher amount of PPy this amount has been raised, for example the weight loss of samples with 20% PPy and 10% PPy was around 90% and 95% respectively.

DISCUSSION

According to IR spectroscopy, results achieved in this study showed that chemical structure of the material was unchanged as there are small changes in some peaks. X-Ray diffraction analysis shows that the shift of MMT

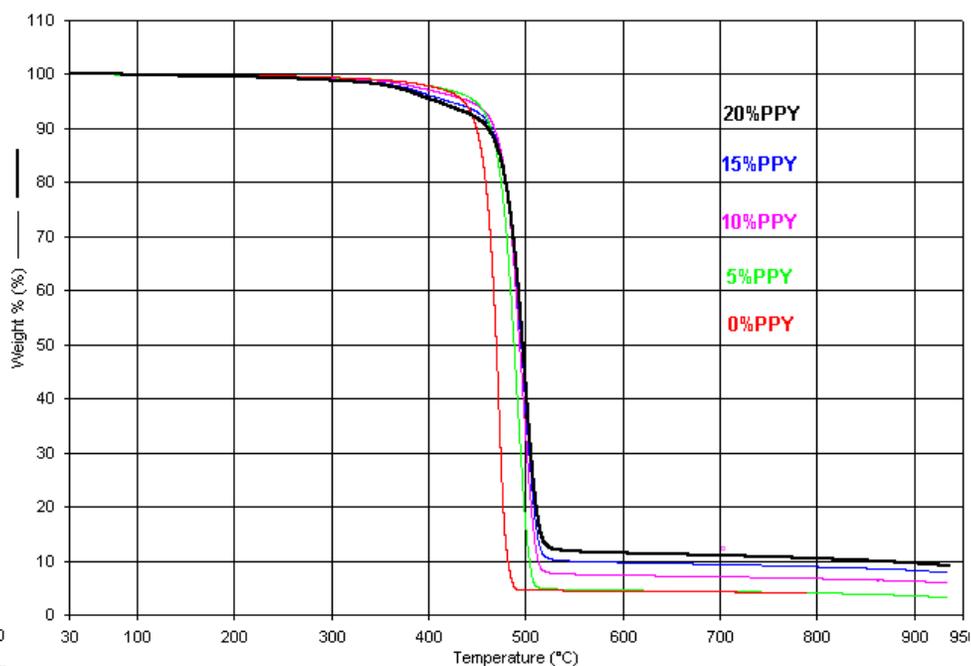


Figure 5. TGA plots of HDPE/MMT blends with different amount of PPY.

angles to lower amount is attributed to the presence of maleated HDPE and PPY which intercalated between the layers of MMT, thus the interlayer distance was enlarged. Therefore, it can be said that HDPE-g-MAH is compatible with MMT and also the rigid PPY chains as it can diffuse into MMT layers. Rizvi et al. (2009) also reported a similar result and stated that the growth of d -spacing show the MMT layers are further intercalated by PPY. These results indicated the formation of HDPE/MMT/PPY nanocomposites. The decrease of intensities on MMT peaks can be due to low percentage of MMT in the composite, and also is due to the chains of HDPE which were intercalated in MMT layers (Zhou et al., 1992).

According to an investigation by Aydinli et al. (1998) and Chen et al. (1994) the resistivity of filled polymer composite increases with temperature and this phenomenon is referred to as a positive temperature coefficient (PTC) and it occurs below a transition temperature. Above this temperature, a network with more conductivity may be formed and a lower resistivity can be observed. It is referred to as a negative temperature coefficient (NTC). The PTC and NTC phenomena are both observed during the process of the PE/PPy composite. The electrical conductivity decreases first with increasing temperature in blending and compression. On cooling, the electrical conductivity increases and the NTC phenomenon is observed. The intensity of the PTC and NTC effects of PE/PPy composite is different for different polypyrrole contents.

When a composite is heated due to the difference in thermal expansion between the charge and the polymer matrix, there is an interruption of the percolation path. This process is dynamic: with the interruption of the percolation path, other new percolation paths can be formed at the same time on PE/PPy composite. The thermal expansion induces the interruption of percolation paths, and the PTC phenomenon is observed. The intensity of PTC for the samples with higher amount of PPY is much lower than for the samples with lower content of PPY. At high concentrations of PPY the conductive particles are very close to each other and it is easy to form new percolation paths when the interruption of any percolation path occurs. But at low PPY concentrations, the distance between the conductive particles compared to the particle mobility is relatively large, so the possibility of forming new percolation paths is relatively low.

The TGA results show that by increasing the amount of PPY, the thermal stability of nanocomposites is improved. It should be also considered that the thermal stability of HDPE/MMT was also improved due to the presence of MMT in the matrix. Thus, it is believed that the effect of PPY in thermal stability of nanocomposite was not significant. Lomakin et al. (2007) stated that thermal stability of polymer nanocomposites is higher than that of pristine polymers, and this is explained by the presence of clay layers hindering diffusion of volatile products through the nanocomposite material. Dhawan et al.

(1993) who studied on composites of PPy and PE, reported that the composites were stable up to 150 °C and after there was weight loss. This implies that the breakdown of the host polymer matrix. Ong et al. (2008) also stated that PPy increases the thermal stability of PE composites.

Conclusion

Polypyrrole was prepared by chemical synthesis using FeCl₃ as an oxidant and DBSNa as the surfactant. The FTIR spectra of PPy synthesized is similar to that PPy from the previous studies. The electrical conductivity measurement has shown that electrical conductivity of PPy is 3.18 S/cm. PPy improves thermal and electrical properties of HDPE/MMT nanocomposites. Based on TGA results PPy improved thermal stability of HDPE/MMT nanocomposites and exhibited around 20 °C increase in Tg. The electrical conductivity measurements have shown that incorporation of PPy increases the conductivity of the nanocomposites up to orders of 5 Scm⁻¹.

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