



Synthesis and Characterization of Organo- Montmorillonite Clay and its Metal complexes for Polypropylene Clay Nano composites Applications



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Abstract

1-acetylpyridinium Chloride-salicylhydrazone (H_2ACSH) was prepared from *Salicylaldehyde* and 1-acetylpyridinium chloride hydrazide for using in modification of sodium montmorillonite clay in order to prepare organo - montmorillonite clay (OMC) and its Zinc (OMC-Zn) and Zirconium (OMC-Zr) complexes in two different weight percentage (3 and 7 wt %). Polypropylene /clay nanocomposites were prepared by melt intercalation technique using the prepared organo - montmorillonite clay and its metal complexes. The obtained nanocomposites were characterized by infrared absorption spectroscopy (FTIR) and atomic force microscopy (AFM) to determine the morphology of obtained materials. The thermal behavior was evaluated from thermo gravimetric analysis (TGA). The combustion behavior of these intercalated ratios was studied using cone calorimeter measurement to assess the PP/clay nanocomposites behavior during combustion. The obtained results indicate decreased flammability properties of PP/clay nanocomposites due to better char enhancement. **The new clay provides an occasion for polymer / clay melt intercalation** to obtain composites materials with important properties.

Key words: 1-acetylpyridinium Chloride salicylhydrazone ; Organic modified clay; Polypropylene; Nanocomposites

Introduction

Polymer layered silicate nanocomposites based on thermoplastic polymers usually displayed significant improvement in enhancement at relatively low levels of clay content (2-10 wt. %) [1]. Polypropylene (PP) is one of the most widely used polyolefin polymers, due to its non polar properties, it is difficult to make nanocomposites of polyethylene by melt intercalation with organically modified clay. In most cases, maleic anhydride grafted polypropylene is used as a compatibilizer [2, 3] to permit the formation of the nanocomposites [4, 5]. However, much attention has been focused on the modification of clay surface to facilitate the silicate layers interaction with polymer [6-10]. Although, the modified clay is miscible with polar polymers [11 – 13], the organically modified clay does not disperse well in the non polar polymer, which is still hydrophobic [14]. So, the incorporation of a modified oligomer or surfactant during melt blending is an important way to mediate the polarity between the clay surface and polymer [15]. It is very useful to synthesize non polar polymer / clay nanocomposites with an improvement in mechanical, thermal and provides enhanced barrier properties and reduces flammability of the resultant polymer

composites [16]. In this work we report the use of zinc or zirconium complexes of this new modified clay to form composites by blending with polypropylene. The formed composites were characterized by Infrared (FTIR) and Thermo gravimetric (TGA). The cone calorimeter was used to evaluate the fire properties of these PP / clay composites containing zinc or zirconium complexes.

Experimental

The polymer used for preparation of polymer layer silicate composites was polypropylene, supplied by RAM TECH Overseas, Inc, USA. The sodium montmorillonite was provided by Southern clay products, Inc. 1- acetylpyridinium chloride hydrazide, *Salicylaldehyde*, zinc chloride, zirconium chloride, anhydrous calcium chloride were acquired from Aldrich and ethanol and toluene were supplied from Across - Germany.

Synthesis of 1-acetylpyridinium Chloride-salicylhydrazone(H_2ACSH) [17].

By refluxing 5 g of 1-acetylpyridinium chloride hydrazide (Girard-P) with 4 mL *Salicylaldehyde* in

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50 mL of absolute ethanol over water bath for 4 hours. The reaction mixture was left to cool till white crystals were separated out. These were filtered off, re-crystallized from ethanol and finally dried in vacuum desiccators over anhydrous calcium chloride. Yield: 6.5g (74%) of (H₂ACSH). Found: C, 51.1; H, 4.25; N, 15.85. Calc. for C₁₂H₁₁ClN₄O₂ (278.58): C, 51.35; H, 4.31; N, 15.97 %.

Synthesis of organo - modified montmorillonite (OMC) [17].

10 g from montmorillonite was added to 200 ml ethanolic solution (95%) containing 2 g of (H₂ACSH) and refluxed over hot plate with vigorous stirring for 24 hours. The yellowish yielded montmorillonite was filtered off using vacuum pump and washed with ethanol followed by water. Modified montmorillonite was dried in a vacuum oven at 80 °C for 6 hour. Elemental analysis for carbon and nitrogen percent indicated that 8% (H₂ACSH) is loaded with C and N.

Synthesis of zinc and zirconium complex of modified montmorillonite (OMC-Zn and OMC-Zr) [18].

By refluxing modified montmorillonite (OMC) with zinc chloride and zirconium chloride (1.0 mol) in 30 ml of ethanol for 2-3 h to form the corresponding Zn and Zr complex of modified montmorillonite. The formed complex was filtered while hot, washed with ethanol followed by water and dried in vacuum over CaCl₂.

Preparation of the polypropylene composites [19].

The polypropylene composite formulations were prepared by compounding of polypropylene with organo modified montmorillonite (OMC) and its complexes in the presence of maleic anhydride grafted polypropylene using a Brabender (plasti – corder) at about 200 - 210 °C for 10 min. This was flowed by compression molding at 195 – 200 °C at 10 bars to obtain specimens for cone calorimeter and other characterization experiments. Samples codes and the preparation conditions are listed in Table I.

Table (1): The prepared polypropylene formulation codes and preparative conditions

Sample Code	PP wt. %	PPg-MA wt. %	OMC wt. %	Zn-OMC wt. %	Zr-OMC wt. %
SW01	95	5	---	---	---
SW02	92	5	3	---	---
SW03	88	5	7	---	---
SW04	92	5	---	3	---
SW05	88	5	---	7	---
SW06	92	5	---	---	3
SW07	88	5	---	---	7

Instrumentation

Elements analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Series II Analyzer. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 2000 in the range 4000-370 cm⁻¹. Thermo gravimetric measurements were performed on a DTG-50 Shimadzu instrument. The morphology of polypropylene composites was investigated by atomic force microscopy (AFM) (CP-II, Veeco, USA). Combustion properties were characterized using Cone Calorimeter (Fire Testing Technology) according to ISO-5660-1:2002 [20].

Results and Discussion

Characterization of organically modified clay:

FTIR spectra

Infrared spectra of OMC, OMC-Zn and OMC-Zr are shown in Figure 1. The characteristic bands of montmorillonite appear at 3630, 1043 and 523 cm⁻¹. The bands at 3236, 3123 and 3078 cm⁻¹ are assigned to NH (4), NH (1) and NH (2) modes, respectively. The two strong bands at 1710 and 1640cm⁻¹ were attributed to (C=O) and (C=N), respectively. Also, two bands at 1595 and 1620 cm⁻¹ are assigned to pyridine and phenyl rings, respectively. The medium intensity band at 970 cm⁻¹ is attributed to the (N–N) vibration. The bands at 3500 cm⁻¹ and the band at 2550 cm⁻¹ were assigned to (OH) stretching. Comparison of montmorillonite and OMC-Zn or OMC-Zr spectra (Figure 1) indicates that no change occurs in NH band, the bands of C=O and OH shifted to lower values (10 cm⁻¹) and the band of C=O disappeared. These results indicate that the sorption mechanism is mainly through the chelating of metal ions *via* phenolic OH and keto/enol groups.

TGA analysis

TGA curves of pristine MMT and three organically modified clays, OMC, OMC-Zn and OMC-Zr are shown in Figure 2. The decomposition peaks of montmorillonite at 95 °C and 650 °C are attributed to the loss of water molecules. The first peak

corresponds to the loss of adsorbed water, whereas the second peak is due to dehydroxylation of MMT. TGA curve of OMC shown in Figure 2 has three degradation stages. The weight loss (8 %) attributed to the organic part in the temperature range (200 – 500 °C) is in good agreement with the results obtained by elemental analysis which predicted a weight loss of (7.05%) giving rise to a grafting capacity. TGA curve shows that OMC is thermally stable up to 200 °C. The TGA curve of OMC-Zn and OMC-Zr complex has three main stages. The water loss occurs at 100 °C (4.0%), whereas the second and third peaks correspond to the organic degradation which ends up at 750 °C (10.14%).

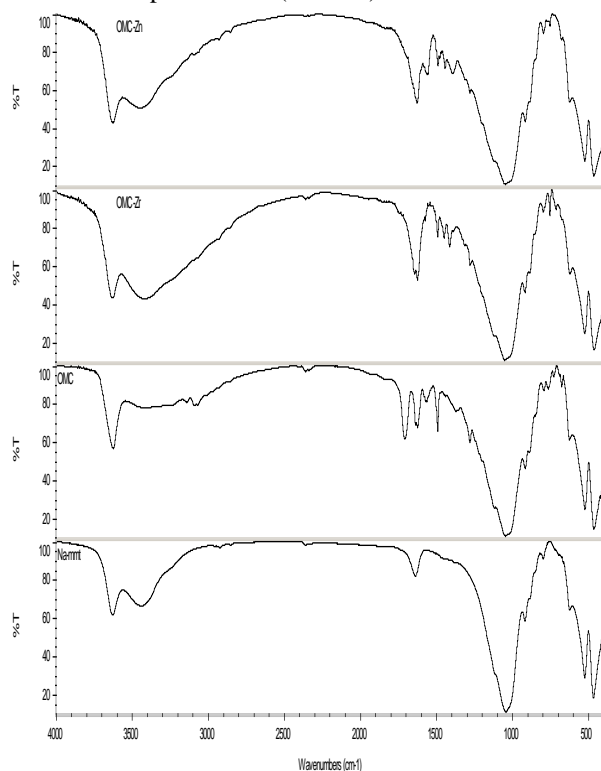


Figure (1): IR spectra of sodium montmorillonite (Na-MMT) modified Montmorillonite (OMC) and its Zinc and Zirconium complex (Zn-OMC and Zr-OMC).

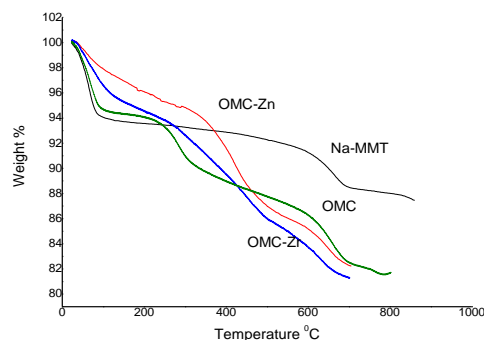
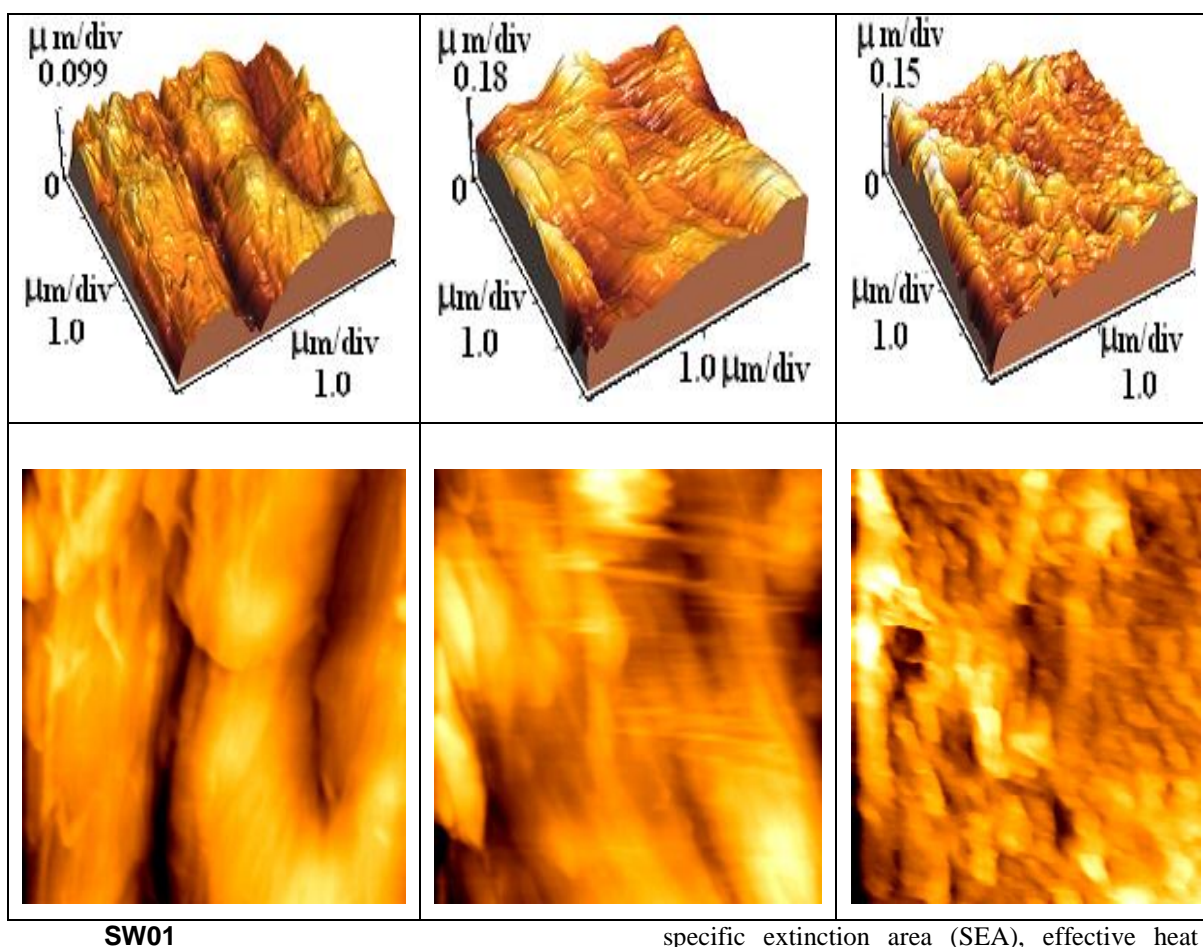


Figure (2): TGA curves of sodium montmorillonite (Na-MMT), modified Montmorillonite (OMC) and its Zinc and Zirconium complex (Zn-OMC and Zr-OMC).

Characterization of Polypropylene Composites: Atomic Force Microscope (AFM)

The morphology of polypropylene composites was investigated by AFM. The surface profile was scanned by AFM in contact mode and the related topography images captured are shown in Figure 3. The great difference in the topography from the results of microscopic images reflects the effect of OMC and its metals indicates a good dispersion of clay into polypropylene matrix and the particles was in range of nano particle size. In contrast, in the case of SW03 composite, the microscopic images indicate that some irregularities appear on the polymeric surface increase in the case of SW07 composite, demonstrating that the incorporation of metal complex of modified clay strongly influence the morphology of the polymer. It was also noticed that the distributions and the dimensions of the particles are homogeneous, indicating a good dispersion of both modified clay and its metal complexes in the polymer matrix (intercalation).



SW01
SW03
SW07

Figure (3): AFM surface topography (contact mode) of PP (SW01), PP/clay (SW03) and PP/clay (SW07).

specific extinction area (SEA), effective heat of combustion (HC), carbon monoxide yield (CO), and heat release rate, especially its maximum value (pKHRR). The heat release rate is an important parameter for studying the fire safety where it determines the fire extent and its rate of propagation.

Evaluation of combustion by cone calorimetry

Cone calorimetric data is listed in Tables 2, 3. The data includes the studied evaluated parameters as time to ignition (s), the total heat release (THR), the

Table (2): Summary of ignition, time to end, maximum HRR, average HRR and total heat release HR of prepared PP – compositions

Samples Code	Time to Ignition (s)	Maximum HRR (kW/m ²)	Average HRR (kW/m ²)	Total Heat Release THR (MJ/m ²)	Time To end (s)
SW01	55	2238.51	688.74	176.4	312
SW02	34	1755.82 (21.56 %)	586.52 (14.84 %)	156.0	300
SW03	37	1894.35 (15.37 %)	600.83 (12.76 %)	164.7	312
SW04	36	1984.52 (11.34 %)	533.89 (22.48 %)	147.4	312
SW05	30	2060.94 (7.93 %)	670.18 (2.64 %)	155.5	262
SW06	36	1905.78 (14.86 %)	519.62 (24.55 %)	151.8	168
SW07	27	2077.34 (7.19 %)	634.74 (7.84 %)	152.8	215

Table (3): Summary of other cone calorimeter data at 35 kW/ m².

Sample Code	Average smoke extinction area (SEA) (M ² /Kg)	Average heat of combustion (HC) (MJ/Kg)	Average CO (Kg/Kg)	Average CO ₂ (Kg/Kg)	Residue Yield (%)
SW01	1128.02	41.03	0.2220	1.95	1.60
SW02	1018.47	40.85	0.1938	1.86	3.73
SW03	1168.71	41.72	0.2149	2.04	6.40
SW04	1253.98	41.91	0.2200	1.96	4.19
SW05	1045.76	41.25	0.2130	2.04	6.58
SW06	955.57	39.95	0.2309	2.02	3.52
SW07	976.75	41.06	0.2057	1.98	6.07

The combustion behavior shows differences depending on the loading ratios of OMC and its Zn and Zr complex. The time to ignition for all samples is shorter than that of pure PP sample (SW01). This reduction in ignition time may be due to the presence of nanoparticles of modified clay and its metal complexes, which induce layer

mobility of the polymer, melt by particles alignment with the flow to combustion zone [21, 22]. This could promote the initiation of combustion in shorter time. The heat release rate results of PP composition are shown in Figures (4, 5 and 6). The pKHRR is reduced by 21 % and 15 % with respect to that of 3 wt % and 7 wt % blending of OMC (SW02 and SW03)

with PP. The pKHRR is reduced by 11 % and 7 % for sample SW04 and SW05 respectively, which contains 3 wt % and 7 wt % of Zn-OMC. Also it was reduced by 14 % and 7 % for samples SW06 and Sw07, which contain 3 wt % and 7 wt % of Zr-OMC. It can be clearly noticed that the reduction in pKHRR for all samples containing 3 wt % of OMC or its metal complexes was reduced more than samples containing 7 wt %, which, showed low decrease in peak heat release.

The reduction in peak heat release rate is due to the formation of char layer at the surface of the melt under combustion. This layer acts as a barrier insulator and hence retards energy transfer and mass loss [23]. The char yield (≈ 3 to ≈ 6.5 %) is close to the clay concentration in the samples. This layer is weak at the decomposition temperature. Therefore, samples were burned during the combustion process especially in all samples containing Zn and Zr metal; this may be due to the broken of metal bond with OMC at this temperature as it can be seen from the shape of the curve. It shows two slope changes on line behavior [24].

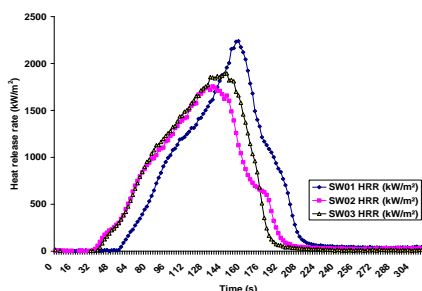


Figure (4): Heat release rate versus time for the PP/clay composites (SW02 and SW03) and pure Polypropylene (SW01).

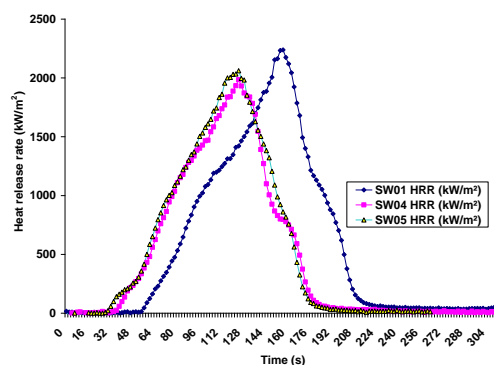


Figure (5): Heat release rate versus time for the PP/clay composites (SW04 and SW05) and pure Polypropylene (SW01).

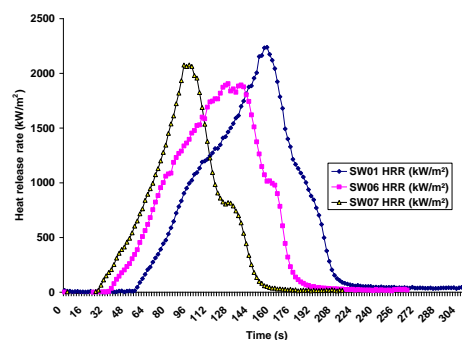


Figure (6): Heat release rate versus time for the PP/clay composites (SW06 and SW07) and pure Polypropylene (SW01).

The total heat values evolved are shown in Figure 7. It is clearly noticed that the addition of modified clay and its Zn and Zr complex to the pure polypropylene has a remarkable effect in decreasing the total heat evolved. The total heat evolved from the pure polypropylene sample (SW01) is 176.4 MJ/m². The decrease in THR is as follows: SW04, SW06, SW07, SW05, SW02 and SW03, respectively.

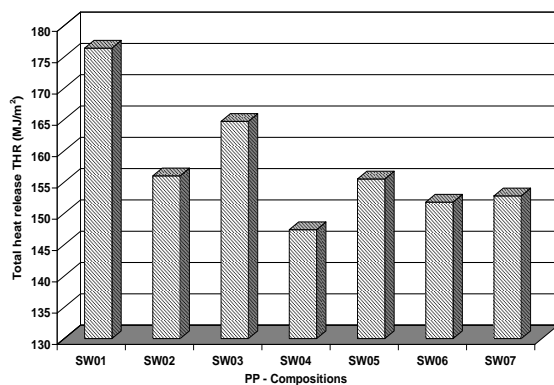


Figure (7): Total heat release of different PP – compositions

Meanwhile, the smoke production (SEA) was reduced for samples, SW02, SW05, SW06 and SW07 by 9.7 %, 7.29 %, 15.28 % and 13.14 % respectively as shown in Figure 8. The effect of an organically – modified montmorillonite (OMC) and its metal complexes on smoke production is rather interest. The smoke reduction is observed for all polypropylene composites as compared to pure polypropylene sample (SW01). The smoke production (SEA) was increased only for samples SW03 and SW04 by 3.6 % and 11.16 % respectively. This provides more environmental advantage for Zn and Zr complexes of OMC.

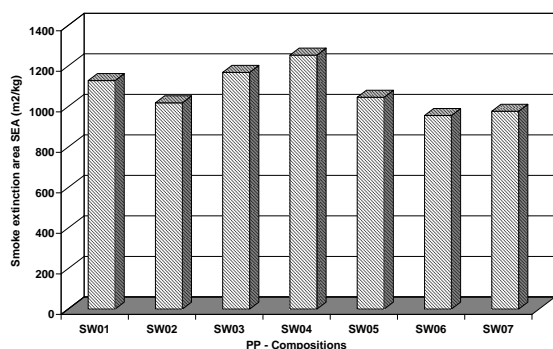


Figure (8): Specific extinction area (SEA) of different PP – compositions.

In addition the effective heat of combustion (HC) as shown in Figure 9 was reduced for samples (SW02 and SW06) and increased for samples SW03, SW04 and SW05. Meanwhile, sample SW07 has the same value as sample SW01 which is due to the formation

of an effective char layer at the surface of burning sample.

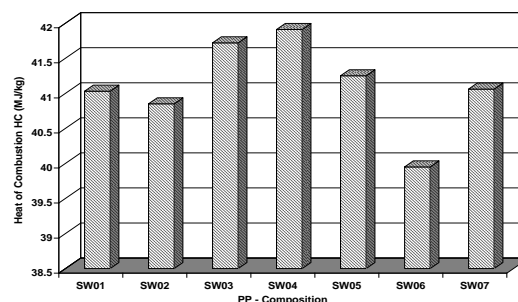


Figure (9): Heat of combustion (HC) of different PP – compositions.

At the same time the CO yield increased by 4 % for sample SW06 only, but it decreased by 12.7 %, 3.19 %, 0.90 %, 4.05 % and 7.34 % for all other samples SW02, SW03, SW04, SW05 and SW07 as shown in Figure 10.

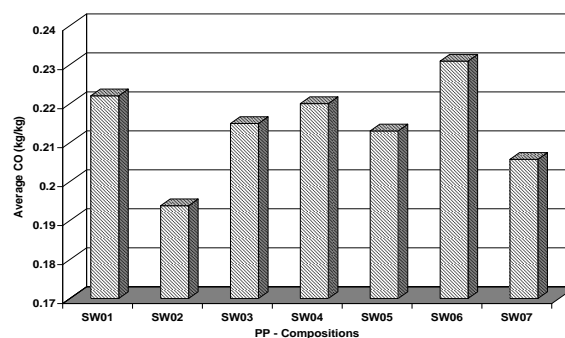


Figure (10): Carbon monoxide (CO) yield (kg/kg) of different PP–compositions.

Flame Chamber UL 94 - H Test (ISO 1210):

The burning out behavior of SW01, SW02 and SW03 samples was characterized in response to a small flame chamber UL 94-H (Horizontal Flame Test) [25]. This behavior was found to fit the category FH-2 for SW02, SW04 and SW06, and the category FH-3 for SW03, SW05 and SW07, where the linear burning rate does not exceed 40 mm / min. Thus, some improvement has been observed in UL flammability (Horizontal Test).

Thermal Stability

TGA under nitrogen atmosphere with a heating rate of 10 °C / min was used to assess the thermal stability of the PP/clay compositions. The results are reported in Table 4 and in Figure 11. The initial degradation temperature (Onset, the main degradation temperature (Peak) and the percentage of residues remaining at 700 °C was shown in Table 4. The higher the main degradation the better thermal stabilities.

Table 4. Decomposition temperature of different PP - composition samples.

Samples Code	Onset - T _{dec} °C	Peack - T _{dec} °C	Weight Loss % at 700 °C (Char Yield)
SW01	353.88	418.07	0.25
SW02	330.66	402.69	2.37
SW03	350.95	418.30	5.65
SW04	412.31	447.29	2.93
SW05	416.87	449.32	5.82
SW06	368.60	425.62	3.15
SW07	406.04	448.14	5.26

Figure 11 shows the mass loss versus temperature and it reveals that the samples SW02 and SW03 present lower initial degradation temperature. It also showed low main degradation temperature (– 16 °C) for sample SW02, while it shows the same main degradation temperature for sample SW03. For all other samples the initial and main degradation temperature is higher than that of pure sample SW01. It is clear that the thermal stability is enhanced in the case of metal complexes of OMC than OMC itself.

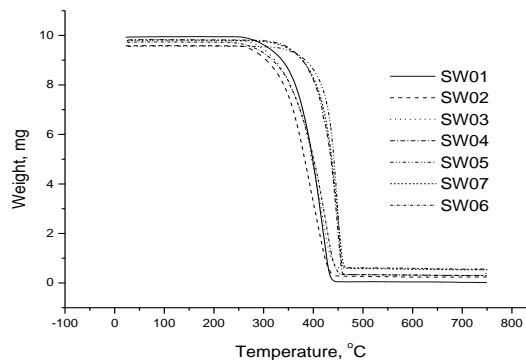


Figure (11): TGA Curves of Different PP – Compositions.

Conclusion

MMT clay was successfully modified by 1-acetylpyridinium Chloride-salicyolhydrazone which prepared from Salicylaldehyde and 1-acetylpyridinium chloride hydrazide. OMC-Zn and OMC-Zr were prepared from the obtained modified clay with different weight percentage. Polypropylene /clay nanocomposites were prepared by melt intercalation technique using the prepared organo - montmorillonite clay and its metal complexes. The obtained nanocomposites were characterized by infrared absorption spectroscopy (FTIR) and atomic force microscopy (AFM) and thermo gravimetric analysis (TGA).

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