

## Fire retardant properties of HDPE composite based on modification of Na-MMT treated with phenol formaldehyde resin modified by some silane reagents

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**Key Word:** HDPE; Phenol formaldehyde silane resin; FTIR; Cone Calorimeter; Time to ignition.

### Abstract

*In the present study, the attempts have been made to modify a phenol formaldehyde resin (PF) with N-[(3-trimethoxysilylpropyl)] ethylene diamine (NTMSPFEA) and 3-triethoxysilylpropyl amine (TESPA) to produce the corresponding phenol formaldehyde silane resin derivatives (PFS1) and (PFS2) respectively. The prepared phenol formaldehyde silane resin derivatives were used to modify the Na-MMT to produce the corresponding modified clay (O-MMTPFS1) and (O-MMTPFS2) respectively. Then the prepared materials were compounded with HDPE in the 3, 5 and 7 wt % to study the fire behavior of HDPE composites. The prepared composites was characterized by thermo gravimetric analysis (TGA) and Fourier transform infra red (FTIR). The fire behavior of prepared composites was characterized by UL-94 and Cone Calorimeter. It was proved by FTIR that the amino group had been successfully introduced to the structure of HDPE. The Cone Calorimeter results shows that the heat release rate of composites decrease and the time to ignition is increase in the comparison with the pure HDPE.*

### 1. Introduction

Flame – retarding polymers have been developed for many applications including airplanes, cars, textile and electrical devices. Flame – retarding polymers traditionally can be prepared by blending polymers with flame retardant additives such as halogenated or phosphorus compounds, but, this approach often generates toxic, corrosive or halogenated gases during combustion. Therefore, polymer nanocomposites have been an attractive area of organic – inorganic materials and not only for their obvious potential as technological materials, but also for providing convenient microscopic system to study fundamental scientific issues concerning confined polymers [1-4]. So it is very important to find a new materials used in the area of fire retardant and the most popular is via modification of layered silicate nanocomposites polymers [5, 6] In the last few years many coworker try to find a new thermally stable flame retardant polymer nanocomposites through development of organic treatment for montmorillonite with improved processing stability [7-15] and this usually accomplished by an ion exchange process [16]. It is known that montmorillonite clay has extraordinary intercalation and retention properties; these properties are even better in case of metal exchanged clay minerals particularly in respect of substances that form coordination compounds with those exchanged metal ions. As such, high thermal stability of intercalated compounds can be exploited in industrial applications and normal behavior of the intercalated

coordination compounds is remarkable [2, 7, 13, 14, 16, 17]. Modification of the clay surface is necessary to improve its interaction with most polymers [18]. Polyethylene (PE) is one of the most widely used polyolefin polymer but it can easily catch fire [19]. In order to solve this problem and improve the quality of polyethylene for high temperature, modification is necessary [20, 21]. The common method used to modify polyethylene is through cross linking, but recently the incorporation of fillers has been used to improve or modify some properties of the neat polymers. The phenol formaldehyde (PF) polymers, the first synthetic ion exchange resins according to the pioneer work of Baekeland [22]. Novolac (typically with a molar excess of phenols with formaldehyde, commonly 1.25: 1) is phenol formaldehyde in which phenols are linked together by alkylidene bridges without functional groups apart from phenolic hydroxyl groups and cannot on their own. Many modifications of (PF) resins are used as ion exchanger to remove heavy metals [23-25]. Several authors investigated the use of silane crosslinked / grafting as a method to improve the interaction between HDPE and LDPE and clay [26-29]. Organo silane polymers are preferred for their excellent thermal and thermo oxidative stabilities, moisture resistance, low stress, partial ionic nature to surface energy, low toxicity and enhanced the mechanical and thermal properties of the composites [30, 31]. In the present study, we report the investigation of fire retardancy HDPE composites with two organo modified clays (O-MMTPFS1) and (O-MMTPFS2) based on phenol formaldehyde silane resin derivatives (PFS1) and (PFS2) of modified phenol formaldehyde resin (PF) with N-[(3-trimethoxysilylpropyl)] ethylene diamine (NTMSPFEA) and 3-triethoxysilylpropyl amine (TESPA) respectively.

## **2. Materials and Methods**

### **2.1. Materials**

All chemicals are of analytical grade otherwise stated. PFS1 and PFS2 were synthesized according to the literature [24]. Phenol (Aldrich, 99 %), Formaldehyde aqueous solution (commercial, 37 %), Oxalic and sodium hydroxide (98 %) were used as received. N-[(3-trimethoxysilylpropyl)] ethylene diamine (NTMSPFEA) and 3-triethoxysilylpropyl amine (TESPA) were purchased from Diamond Advanced Materials of Chemicals Inc. Sodium montmorillonite (Na-MMT) was provided from fluka Chemika Company. The polymer used for preparation of composites was high density polyethylene (HDPE) with melt flow index 27 was obtained from Viba Laborchemie, APOLDA, Germany.

### **2.2. Synthesis**

#### **2.2.1 Preparation of PFS1 and PFS2 modified PF novolac [32]**

188 g of phenol, 138 g of 37% by weight formaldehyde, 3.7 g of oxalic acid were added to a boiling flask equipped with a stirrer, backflow condensed, and a thermometer. When oxalic acid was completely dissolved at room temperature, the solution was heated to 100 °C in an hour and kept boiled for 3 h under reflux, and then 0.094 g of sodium hydroxide was added. Subsequently the reaction mixture was dehydrated under reduced pressure for 60 min, thereafter, the temperature was stepwise raised from 100 to 150 °C. Then a calculated volume of N-[(3-trimethoxysilylpropyl)] ethylene diamine (NTMSPFEA) or 3-triethoxysilylpropyl amine (TESPA) was added in an hour and the mixture was stirred until the temperature reduced to 120 °C. The by-product alcohol; was removed under a reduced pressure for 30 min until the system was stepwise heated to 150 °C. An amber opaque corresponding resin PFS1 or PFS2 and about 7-9 g of alcohol were obtained.

### 2.2.2. Preparation of modified clays (O-MMTPFS1) and (O-MMTPFS2)

The Na-MMT was added during the preparation of PFS1 or PFS2 as describe above at the step after addition of (NTMSPFEA) or (TESPA) respectively.

### 2.2.3. Preparation of HDPE composites

All HDPE composites were prepared by melt blending method using Newplast twin screw extruder (India) at 185 – 190 °C. The twin screw speed was 30 rpm. The samples obtained from extruder were preheated using Morgan press injection unit (USA) at 190 – 195 °C to produce 7.5 X 7.5 X 0.4 cm and 10 X 0.9 X 0.4 cm mold. The samples codes and preparation conditions are listed in table (1).

### 2.3. Methods

Cone calorimeters tested were performed using Fire Testing Technology LDT equipment according to ASTM 1354-95. Samples, with dimensions of 7.5 x 7.5 x 0.4 mm<sup>3</sup>, were tested horizontally under an incident flux of 35 kW/m<sup>2</sup>. UL94 classification according to ASTM D635 (IEC606905) in horizontal position. Thermo gravimetric measurements were performed on a TGA-50 Shimadzu instrument. All measurements were conducted under nitrogen flow, with a sample weight of about 10+ 0.5 mg; for each test the heating rate was 10 °C / min from ambient to 750 °C. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 2000 as KBr pellets and as Nujol mulls in the 4000-370 cm<sup>-1</sup> spectral range.

Sample Code	HDPE %	PFS1 %	PFS2 %	O-MMTPFS1 %	O-MMTPFS2 %
ER1	100	---	---	---	---
ER2	97	3	---	---	---
ER3	95	5	---	---	---
ER4	93	7	---	---	---
ER5	97	---	---	3	---
ER6	95	---	---	5	---
ER7	93	---	---	7	---
ER8	97	---	3	---	---
ER9	95	---	5	---	---
ER10	93	---	7	---	---
ER11	97	---	---	---	3
ER12	95	---	---	---	5
ER13	93	---	---	---	7

Table1. The samples codes and preparation conditions for all HDPE – formulations

## 3. Results and discussion

### 3.1. FTIR analysis

The FTIR spectrum of novolac resin (PF), modified silane resins (PFS1 and PFS2) and modified clay (O-MMTPFS1 and O-MMTPFS2) are shown in Fig. (1). The C-H stretching vibration bands are observed at 2923 and 3000 cm<sup>-1</sup>. The strong band around 1250 cm<sup>-1</sup> is characteristic of V<sub>ph-O</sub>. The bands at 912 cm<sup>-1</sup> (asymmetric ring stretching in which C-C

stretches during contraction of C-O bond),  $819\text{ cm}^{-1}$  and  $752\text{ cm}^{-1}$  (out of plane bending of ring C-H bonds of aromatic ring) are typical of the novolac group [33]. The bands at  $3100$ ,  $3650$ ,  $1644$ ,  $1610$ ,  $1511$  and  $1106\text{ cm}^{-1}$  are assignable to stretching of OH, bending of molecule  $\text{H}_2\text{O}$ , C-C stretching in  $\text{C}_6$  ring (double) and the ph-O vibrations, respectively. The FTIR absorption spectrum of PFS1 and PFS2 shows new bands at  $3772$ ,  $1610$ ,  $1358$ ,  $1165$ ,  $990$ ,  $931$ ,  $819$ ,  $592$  and  $500\text{ cm}^{-1}$ , which are assignable to isolated  $\text{V}_{\text{OH}}$  (SiOH), free  $\text{NH}_2$  scissoring, C-N,  $\text{V}_{\text{as}}$  (Si-O-Si),  $\text{V}_{\text{Si-O}}$  (Si-O-C),  $\text{V}$  (SiOH),  $\delta$ (Si-O) [33–35], asymmetric stretching of Si-C and  $\delta$  (Si-O-Si) respectively. These results provide a substantial evidence reaction of (NTMSPFEA), (TESPA) and (PF) novolac. Water was not completely removed from PF, so some of trimethoxy silane and triethoxy silane was transformed into silsesquioxane mixture with formation of Si-OSi bonds under the broad peak about  $1200 - 1000\text{ cm}^{-1}$  [32]. The absorption bands observed in range between  $2830 - 3000\text{ cm}^{-1}$  is assignable to different C-H symmetric ( $\text{V}_s$ ) and asymmetric stretching ( $\text{V}_{\text{as}}$ ) vibration [36]. There are three bands at about at  $3630$ ,  $1100$  and  $523\text{ cm}^{-1}$  indicating that the chemical loading of PFS1 and PFS2 on montmorillonite [37].

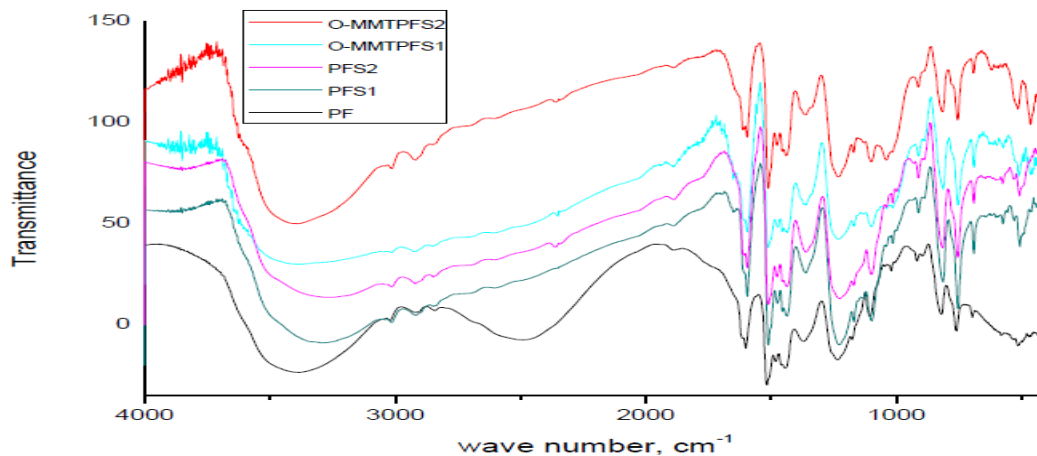


Figure1. FTIR for PF, PFS1, PFS2, O-MMTPFS1 and O-MMTPFS2

### 3.2. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) represents a quantitative methodology useful to analyze the stability of materials. TGA scans were performed on all composites samples for each concentration. The results of TGA reported that the onset, mid point and maximum degradation temperature for all HDPE- compositions when compared with the neat HDPE (sample ER1). It can be noticed that there are an appreciable increase of both temperature levels are found. It can be concluded that the addition of PFS1 or PFS2 and O-MMTPFS1 and O-MMTPFS2 retards the degradation behavior of HDPE - compositions and enhancing the flame retardancy of HDPE – composites.

### 3.3. Cone calorimeter test

Cone calorimeter represents a small – scale testing configuration which provides important correlating parameters with real fire scenario. The values provided by cone calorimeter are mainly: time to ignition (TTI), which corresponding to the period that a combustible materials can withstand when exposure to a constant radiant heat flux before igniting and undergoing sustained flaming combustion; Heat release rate Peak (pHRR) and average (HRR average) are a quantitative measures of thermal energy released by a materials per unit area when exposed to a fire radiating at constant heat flux (or temperature) usually at  $35\text{ kW/m}^2$ . The cone

calorimeter data reported in Table (2) are average of three replicate experiments. The HRR value considered the single most important fire reaction property as it represented the most valuable indicator of the fire hazard for a combustible material.

Table (2) reported that the peak heat release of pure HDPE is 1635.53 kW/m<sup>2</sup> (sample ER1) and when 3 wt % of PFS1 was added to pure PE (sample ER2); the peak heat release (pHRR) was 1421.40 kW/m<sup>2</sup> with 13.1% reduction in pHRR. When the 5 wt % and 7 wt% of PFS1 were added to pure HDPE (sample ER3 and ER4), the curves shows that the pHRR were 1151.08 kW/m<sup>2</sup> and 1167.56 kW/m<sup>2</sup> for samples ER3 and ER4 by 29.62% and 28.61 % reduction in pHRR respectively. It was noticed that when 3 wt % of modified clay (O-MMTPFS1) was added to pure HDPE (sample ER5); the peak heat release (pHRR) was 1139.00 kW/m<sup>2</sup> with 28.61% reduction in pHRR. When the 5 wt % and 7 wt% of O-MMTPFS1 were added to pure HDPE (sample ER6 and ER7), the curves shows that the pHRR were 1035.35 kW/m<sup>2</sup> and 1026.86 kW/m<sup>2</sup> for samples ER6 and ER7 by 30.35 % and 37.22 % reduction in pHRR respectively. Similarly the average heat release HRR has the same trend in reduction of their values as collect in Table (2).

Samples	Time to Ignition (s)	Maximum HRR (kW/m <sup>2</sup> )	Average HRR (kW/m <sup>2</sup> )	FIGRA (kW/m <sup>2</sup> s)	Total Heat Release THR (MJ/m <sup>2</sup> )	Time To end (s)	FPI (sm <sup>2</sup> /kW)	Residue Yield %
R1	53	1635.53	368.37	7.72	106.8	228	0.03240	0.11
R2	82	1421.40 (13.1%)	370.11	7.68	104.5	242	0.05768	0.24
R3	81	1151.08 (29.62%)	389.10	4.89	118.7	272	0.07034	0.44
R4	73	1167.56 (28.61)	313.71	5.19	105	285	0.06252	0.22
<b>R5</b>	66	<b>1139.00</b> <b>(30.35%)</b>	292.59	<b>5.99</b>	95.1	275	0.05794	0.15
<b>R6</b>	54	<b>1035.35</b> <b>(36.7%)</b>	250.21	<b>5.45</b>	76.3	251	0.05216	0.16
<b>R7</b>	44	<b>1026.86</b> <b>(37.22%)</b>	280.15	<b>6.42</b>	81.2	215	0.04284	0.18
R8	66	1384.15 (15.37%)	100.74	3.79	91.4	275	0.04768	0.19
R9	58	1353.48 (17.25%)	334.59	6.60	95.4	229	0.04285	0.23
R10	67	1346.72 (17.65%)	270.49	6.12	96.1	290	0.04975	0.22
R11	79	<b>972.57</b> <b>(40.53%)</b>	402.50	<b>3.41</b>	88.6	330	<b>0.08122</b>	0.18
R12	76	<b>653.33</b> <b>(60.05%)</b>	172.43	<b>2.33</b>	60	305	<b>0.11632</b>	0.23
R13	73	<b>614.76</b> <b>(62.41%)</b>	230.25	<b>4.18</b>	67	246	<b>0.11874</b>	0.34

Table 2. Main cone calorimeter parameters evaluated for HDPE - composites at different concentrations

Also table (2) reported that the peak heat release of pure HDPE is 1635.53 kW/m<sup>2</sup> (sample ER1) and when 3 wt % of PFS2 was added to pure HDPE (sample ER8); the peak heat release (pHRR) was 1384.15 kW/m<sup>2</sup> with 15.37 % reduction in pHRR. When the 5 wt % and 7 wt% of PFS2 were added to pure HDPE (sample ER9 and ER10), the curves shows that the pHRR

were 1353.48 kW/m<sup>2</sup> and 1346.72 kW/m<sup>2</sup> for samples ER9 and ER10 by 17.25 % and 17.65 % reduction in pHRR respectively. Also, it was noticed that when 3 wt % of modified clay (O-MMTPFS2) was added to pure HDPE (sample ER11); the peak heat release (pHRR) was 972.57 kW/m<sup>2</sup> with 40.53 % reduction in pHRR. When the 5 wt % and 7 wt% of O-MMTPFS2 were added to pure HDPE (sample ER12 and ER13), the curves shows that the pHRR were 653.33 kW/m<sup>2</sup> and 614.76 kW/m<sup>2</sup> for samples ER6 and ER7 by 60.05 % and 62.41 % reduction in pHRR respectively. Similarly the average heat release HRR has the same trend in reduction of their values as collect in Table (2).

Ignition data are reported as time to substance ignition, which is defined as ignition with the assistance of a spark igniter. The time to ignition for the HDPE -compositions (ER2, ER3, ER5, ER8, ER10, ER11, ER12 and ER13) is higher than pure high density polyethylene sample ER1 except samples ER7 is shorter than ER11, while samples ER6, ER7 and ER9 is slightly or similar to sample ER1 as reported in table (2).

The fire performance index (FPI) was calculated as the ratio between the time to ignition (TTI) and peak of heat release (pHRR):

$$FPI = TTI/pHRR \quad (1)$$

This FPI value gives useful information about all HDPE – composition used in this study in reference of the degree of fire hazard [38, 39]. Table (3) contains the data of final masses of the samples under investigated. The highest final masses corresponded to the HDPE – compositions showing the highest FPI values. All HDPE – compositions are completely effective.

### 3.4. UL-94 test

The burning out behavior of HDPE compositions was characterized in response to a small flame chamber UL94 (Horizontal Flame Test, ASTM D 635). This behavior was found to fit the category FH-3, where the linear burning rate dos not exceed 40 mm / min (ASTM D635). Some improvements are observed flammability in most HDPE composites samples and all data are collected in table (3).

Samples	ER1	ER2	ER3	ER4	ER5	ER6	ER7	ER8	ER9	ER10	ER11	ER12	ER13
T (s)	2.05	2.32	2.08	1.56	1.53	2.08	2.03	1.58	2.30	2.30	2.19	2.48	2.20
Burning rate (mm/min)	31.2	25.6	30.46	33.6	34.5	30.46	31.71	33.05	26.0	26.0	28.0	24.1	27.8

Table 3. Results of the flame characterizing ASTM D 635 Test

## 4. Conclusion

Flame retardant high density polyethylene composites were prepared by melt blend depending on the phenol formaldehyde silane derivatives as a key intermediate for clay modification. The fire behavior of prepared HDPE composites showed that by adding 3, 5 and 7 wt. % of each PFS1 or PFS1 and their O-MMTPFS1 and O-MMTPFS2, the reduction in peak heat release are about 13 – 62%. Moreover the FPI was increase.

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