Fire retardancy assessment of polypropylene composite filed with nano clay prepared from Iraqi bentonite

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Abstract: Fire retardants have an extraordinary importance because of their role in saving the people, property and reducing the damages and minimizing the dangers resulting from fires and burning of polymeric composites which are used in different civil and industrial fields. The work in this paper can be divided into two main stages. In first one nano-clay was manufactured from Iraqi bentonite and it was characterized using AFM, XRD, XRF, SEM, and BET. The AFM test showed the particle size of prepared nano clay was about 99.25 nm. In the second stage, polypropylene/nano clay composites at three low loading percents (0%,2%,4%,6%) were formulated via twin screw extruder. The fire retardancy tests included burning rate according to ASTM:D-635 and maximum flame height of flame according to ASTM:D-3014. Besides, the mechanical tests and thermal behavior of prepared samples were investigated. The results showed that (4%) of nano-clay had the maximum fire retardancy and while at (2%) loading, the maximum value of tensile strength and Yong modulus were obtained. The maximum heat of fusion was recorded for 6% nano clay sample. The final results assessment confirmed on the possibility of using low loadings of prepared nano clay to improve the fire retardancy, mechanical and thermal properties successfully.

Keywords: nano clay, Iraqi Bentonite, polypropylene, fire retardancy, burning rate, polymer composite

1. Introduction
No one could imagine the world without polymeric products. This important sector occupies very outstanding ranking in all industrial, civil and domestic fields. The world demand increases annually. In general, polymers are divided into two main categories thermoplast and thermoset. The polymeric compounds are characterized by a macromolecular structure which is either amorphous or semi-crystalline. Polypropylene (PP) is one of the most important semi-crystalline thermoplast types which is used extensively in many fields for different applications. The annual global need of polypropylene was about 83 million metric tons in 2013 and the expectations of experts
indicate that the expected global demand will increase rapidly to reach 126 million metric tons in 2023[1].

Polypropylene (PP) is a downstream petrochemical product that is derived from the olefin monomer propylene. The polymer is produced through a process of monomer connection called addition polymerization. Polypropylene is a vinyl polymer in which every carbon atom is attached to a methyl group and can be expressed as shown in 'figure 1' [2].

![Figure 1 Structure of polypropylene](image)

Polypropylene (PP) is a commodity polymer which offers a combination of outstanding physical, chemical, mechanical, thermal and electrical properties not found in any other thermoplastic [4]. Besides, polypropylene is easy to formulate using extruding or molding methods. In spite of these characteristics, PP like other polymers, its resistance against flame and fire is very weak and it is classified as sever flammable one. This drawback of PP limited its role in some products and that provokes the researchers and scientists to improve the flame retardancy of polymer for several decades. In the twentieth century, they used the micro size of different materials, metal oxides, hydroxides, halogens and phosphate-based retardants and the efforts continued in this field. But to achieve a good retardant performance, it must be used high loading of these materials. Typically filler levels required are between 20% - 60% by weight, but lower levels may be acceptable in combination with more effective alternative fire retardants or where the purpose of their inclusion in a formulation is principally to aid smoke suppression [5]. The high loadings of micromaterials have negative effects on other properties like mechanical, optical and thermals ones. So, the efforts were focused on finding high-performance fire retardants which their crucial role in saving the people souls and properties using small amounts.

With appearing nanomaterials and the huge developments in synthesis methods and applications, the fire retardants come in a new era. The scientists do their best to develop and to manufacture new polymeric composites filled with nanofillers of different substances which were used previously in micro size. One of the famous nanomaterials using extensively is the nano-clay.

The possibility of manufacturing nano-composites materials with tailored properties at low cost has gained much interest. In fact, there is already more than two decades of research on those materials. Particular interest has been paid to clay nano-platelets and their composites with non-polar thermoplastic polyolefin matrixes, namely polypropylene (PP)[6]

Nano clay is belonged in most cases to Montmorillonite type of clay. Montmorillonite is a 2:1 type consisting of two silicon-oxygen sheets held together by intervening cations with water molecules in the interlayer spaces1. Two outer tetrahedral layers which contain Si and O atoms are fused with an inner octahedral layer containing Al and Mg atoms which are bonded to oxygen or hydroxyl group. Individual clay particle has “platey” structure with a lateral dimension of 200 to 600 nanometers and thickness of only 0.96 nm. These layers organize themselves to form stalks by Vander walls force of attraction between them. The attraction force between layers is relatively weak so polymer molecules can be
intercalated between them so in pristine form, clay is hydrophilic (platelets contain Na⁺ or k⁺ ions) [7], [8], [9]. The structure of bentonite clarifies in figure 2. Using this type of clay in synthesis nano clay can be attributed to its characteristic properties. The methods of preparation nano-clay are varied.

Figure 2 Structure of bentonite clay [10]

1.1 Polymer combustion process mechanism:
Natural and synthetic polymers, when exposed to a source of sufficient heat, will decompose or ‘pyrolysis’ evolving flammable volatiles. These mix with the air and, if the temperature is high enough, ignite [11]. The polymer combustion is characterized by a complex combination of condensed and gas phase phenomena. Every phase consists of sets of complex reactions with heat and mass transfer processes [12], [13]. The complex reactions of polymer combustion process in both phases are shown in 'figure3'.

Figure 3 Polymer combustion process mechanism [14]

1.2 Mechanisms of nano-clay fire retardants:
In general, the mechanisms of fire retardants materials either micro conventional retardant or nanomaterials are still unsolved issues in spite there is a huge number of scientific papers dealing with this subject. Thus, what is suitable for specific polymer group it may not effective with other kinds. There are different explanations and opinions but there is no fully understood or complete mechanism valid for all polymers till now.

In previous, the general mechanisms of fire retardants are explained in details [15]. But nanomaterials mechanisms need to interpret depending on their characteristics which particle size of nanomaterials plays a very crucial role besides other properties. But, the proposed mechanisms of nano-clay retardancy performance will be explained.
1. Migration mechanism. It is hypothesized that migration of clay particles to the surface of the matrix polymer occurs during burning [16]. It is believed that the clay is pushed by the numerous rising bubbles of degradation products and the associated convective flow in the melt from the interior of the sample toward the sample surface, while the matrix polymer because of the pyrolysis with dewetted clay particles are left behind. Further, aggregation of clay layers occurs after the degradation of the organic treatment on the clay interlayers, which makes the clay more hydrophilic and less compatible with the matrix polymer, and thus leads to a clay-rich barrier that slows the rate of mass loss [17].

2. Barrier mechanism: it is a well-accepted mechanism in the condensed phase during burning. It suggested that, under pyrolysis conditions, the clay forms a char-like material that acts as both a barrier to the mass transport of the degradation products to the surface of the degrading polymer and a thermal barrier as in figure 4, preventing additional exposure of the polymer matrix to the heat and oxygen. The barrier function of the clay platelets can provide thermal insulation for the condensed phase and thus increase the thermal stability of the matrix polymer [17],[18].

3. Paramagnetic radical trapping mechanism: It assumes that the structural metals in the clay (especially iron) trap the radicals that form during the polymer degradation, thus slowing down the degradation reaction. This mechanism has an important role with the low loading of nano-clay.[19],[20]

![Image](image_url)

Figure 4 the nano-clay barrier mechanism [17]

Nano clay as fire retardant has been used extensively with different polymers types. Table 1 shows the published papers in recent years:

| Polymer matrix                        | References | Notes          |
|--------------------------------------|------------|----------------|
| Poly (methyl methacrylate) PMMA      | [21]       |                |
| Boron - Phenolic resins              | [22]       |                |
| EVA and LDPE                         | [23]       |                |
| Epoxy                                | [24]       |                |
| Polypropylene                        | [25]       | Till 20% loadings |
| Polystyrene                          | [26]       |                |
| Polyurethane/polypropylene           | [27]       |                |
| vinyl ester                          | [28]       |                |
| High-density polyethylene and wood flour composites | [29]       |                |

The aim of present work is to prepare and to characterize a nanoclay from Iraqi bentonite using acid activation method. Besides, nanoclay/polypropylene composite with different loadings are synthesized and the mechanical, thermal and fire retardancy properties are assessed.

2. Experimental Work

2.1 Chemicals & machines:
2.1.1 Iraqi raw bentonite: the chemical composition of this clay as in table 2:

| Composition | %mass |
|-------------|-------|
| SiO₂        | 57.4  |
| Al₂O₃       | 17.9  |
| TiO₂        | 1.6   |
| Fe₂O₃       | 8.9   |
| CaO         | 5.5   |
| MgO         | 3.5   |
| K₂O         | 1.57  |
| Na₂O        | 1.5   |
| Others      | 2.13  |

2.1.2 Hydrochloric acid: (36.4) conc. (BHD company), England

2.1.3 Polypropylene: the PP was used in this work was provided by Sabic company (KSA). Its density is 0.902 g/cc and melting flow is 3g/10 min at 216 kg load at 230°C. The process temperature is 235-250 °C.

2.1.4 Twin screw extruder (RD11-100 – 0254) was used to mold the samples. It is Chinese type with 20/25 L/D and motor speed 0-100 RPM. It has three thermal processing 180, 220, 250°C.

2.1.5 Assistant apparatuses: magnetic stirrer (Chinese), Dry oven (England), tubular furnace (Chinese) thermal press (Chinese).

2.1.6 Glassware with different measurements and shapes and filter papers

2.2 Nano clay preparation:
The Iraqi bentonite had been crashed and milled by using mill till fine powder had been obtained. Then clay powder was sieved and 53 microns had been chosen. The 2M hydrochloric solution was prepared and bentonite was added gradually to the solution and mixing for 2 hours using magnetic stirrer. After mixing duration, the solution was filtrated using vacuum filtration. The obtained precipitation was left for 72 hours to dry at room temperature. Then it was calcinated in a tubular furnace for 2 hours at 600 °C. The calcinated powder was milled and stored in a sealed desiccator for testing and characterization.

2.3 Nanocomposite synthesis:
Firstly, prepared nanoclay was mixed with polypropylene granules with the different clay loadings(0%,2%,4% and 6% wt.) with sample code (PNC0, PNC2, PNC3, and PNC4) respectively. The nanoclay/PP mixture was extruded using twin screw extruder (180-250°C). The molten has molded in the template with dimensions (20 cm x 10 cm x 4 cm) and thermally compressed (10 bar for 10 min). The sheets left for 24 hours at room temperature to dry. Then, the samples were cured in drying oven at 75 °C for 2 hours. Then the nanocomposite samples formulated in different shapes and dimensions according to the requirement of every test.

3. Tests and characterization:

3.1 Structural & phase characterization:
The X-ray diffraction (XRD) measurements of the clay samples were recorded with XRD-6000, Shimadzu, Japan equipped with Ni-filtered CuKα radiation (λ = 1.5418 Å) and operated at 40 kV and 30 mA. The diffractograms were recorded in the range of 20 from 3° to 20° at a speed rate of 5 degrees/min. While elemental analysis was conducted using X-ray Fluorescence (XRF), S2 PUMA Single model, Bruker, USA.
3.2 Thermal analysis:
Differential Scanning Calorimetry (DSC) of samples (0%, 2%, 4%, 6%) were performed using DSC TA60, Shimadzu, Japan, with a scanning rate of 10 °C/min. in air atmosphere with temperature range 20 -250 °C to assess their thermal behaviour and morphology.

3.3 Mechanical performance:
tensile properties of composite samples were investigated using mechanical testing machine (H50KT model, Tinius-Olsen, UK).

Particle size estimation:
Particle size measurements id done using (AA3000 Scanning Probe Microscope Angstrom Advanced Inc, USA) to specify the nano size of prepared nano clay.

3.5 Morphology:
the topography of nanoclay and micro bentonite was investigated using scanning electronic microscopy (SEM) (Vega3 model, Tuscan, Czech Republic).

3.6 Specific surface area:
the specific surface area and tests of nanoclay & bentonite were calculated using BET method. The test was conducted using surface area analyzer (SA-9600, Horiba company, USA).

3.7 Hardness:
microhardness (Vicker method): composite samples were tested using Microhardness tester (MODEL HV-1000A, JINAN Co., China). The applied force was 0.5N for 20 seconds.

3.8 Limited oxygen index (L.O.I):
defined is the minimum Oxygen amount required to combustion of the polymer or composite. It is expressed as a percentage of O2 concentration. The test is done according to ASTM D2863.

3.9 The rate of Burning (RB):
the burning rate was measured according (ASTM-D 635-03). The test was conducted for three specimens for each sample. The specimen dimension was (100 mm L*13 mm W*4 mm Thick).

3.10 Maximum flame height test (H):
the test is done according to (ASTM D 4804) using metal ruler. The test was conducted for two specimens for each sample. Specimen dimension was (100 mm L*10 mm W*4 mm Thick).

4. Results & Discussion:

4.1 Nano clay characterization:

4.1.1 Phase & structure characterization:
figure 5 shows the effect of acid treatment on the structure of prepared nanoclay. The comparison between Xray patterns of pristine bentonite without treatment and prepared nanoclay shows that there was a shift in angle occurred between both patterns. Pristine bentonite has a characteristic peak at (2θ=6.7° & d001=13.111°A) whilst nanoclay has characteristic one at (2θ=3.54° & d001=24.83°A). This shift to smaller angle with increasing in d-spacing between interlayers revealed that the distances between clay interlayers...
(galleries) of the bentonite were expanded due to the acid and thermal treatments. It is indicated that intercalated structure is formed. This expansion helps the polymer to exfoliate completely or partially with clay. This is in agreement with results obtained by [7], [9], [10], [30]. While the elemental analysis of prepared nano clay showed some oxides were disappeared as shown in table 3.

![Figure 5 XRD patterns A. Prestine bentonite B. Prepared nano-clay](image)

Table 3 chemical composition of prepared nano clay

| Composition | SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O  | Others |
|-------------|------|-------|------|-------|------|------|------|-------|--------|
| %mass       | 67.78| 16.48 | 1.336| 7.483 | 2.034| 3.485| 0.5485| 0.227 | 0.627  |

4.1.2 Particle size measurement:

The results of particle size (AFM) test showed that the size of prepared clay particle is in the range 70-130 nm and mean diameter is 99.29 nm as shown in figure 6.

![Figure 6 particle size & morphology of prepared nanoclay](image)
4.1.3 Surface area:
Surface area results showed the strong effect of synthesis process on surface area values. There is a big difference in surface area between pristine bentonite and prepared nanoclay where the surface area of clay changed from $11 \text{ m}^2/\text{g}$ to $60 \text{ m}^2/\text{g}$ for pristine bentonite and nanoclay respectively the improvement is about 450%.

4.1.4 Morphology investigation: The SEM images are listed in figure 7 for both types:

![SEM images of pristine Bentonite (left) and nanoclay (right)](image)

The SEM image showed the differences in particle size of pristine (Left) and nano clay (right) at two magnifications (5 kx, 10 kx). The shapes of both types are disorder structural shapes with different sizes which is can be attributed to milling effect in the final step of the preparation process. The disorder of shapes as a result of milling was indicated by Adham et al. [31].

4.2 Polypropylene/ nano clay Composite characterization

4.2.1 Thermal analysis:
the results of thermograms of composite samples showed that change in melting point is not big. The changes were about 5 °C from 160 to 165 but the clear changes were detected in heat of fusion for different loading samples. The nanoclay contributed to improving the crystallinity leading to increasing the heat of fusion. The results are shown in 'figure 8'.
4.2.2. Mechanical behavior:

the results of the tensile test were conducted for composite samples. The results showed that the mechanical properties (Tensile stress & modulus) improved at 2% loading. But with increasing clay loadings, these properties reduced as shown in 'figure 9'.

| Test               | Sample code | PCN0 (0%) | PCN2 (2%) | PCN4 (4%) | PCN (6%) |
|--------------------|-------------|-----------|-----------|-----------|----------|
| Tensile stress (MPa) | 2196        | 28.41     | 24.16     | 23.71     |
| Tensile modulus (Mpa) | 307         | 398       | 376       | 334       |

Figure 8 Heat fusion of composite samples

Figure 9 Mechanical tests Left – Tensile test Right- E-modulus

The improvement in mechanical properties (tensile stress & modulus) of nano-clay/PP composite samples compared with virgin PP, can be explained depending on two main factors. Firstly, the extended basal spacing of nano-clay layers (as shown in XRD tests), high aspect ratio and surface area help the intercalation between clay particles and polymer matrix leading to good interfacial connections and to completely or partially exfoliation. Secondly, nano-clay particles have good stuffiness property and when these particles
existed in polymer-particle interface enhance the resistance of composite against external stresses and preventing the sliding and movement of the polymer matrix as a result of a mechanical load applied.

The reducing in tensile stress and modulus with increasing nano-clay concentration can be attributed to two factors. First of all, the agglomeration of nanoparticles which contributes to reducing surface area so the exfoliation and interaction between clay interlayers and polymer chains become weak and poor. Second, the decreasing in the mechanical properties is because of the increasing nano-clay particulate-particulate interfaces instead of polymer-particle interfaces. This is compatible with the interpretations and results of many researchers who they assured on these facts in their published papers[32],[33],[34],[35]

4.2.3 Microhardness (Vickers method):
the results of microhardness tests showed the improvement effect of nanoclay additions on hardness values. The results are listed in table 4.

| Nanoclay loading | 0% | 2% | 4% | 6% |
|------------------|----|----|----|----|
| Hardness (hv)    | 33 | 46 | 62.3 | 76.8 |
| % Improvement    | -  | 39.39% | 88.78 | 132.7 |

The values of hardness increased with nanocaly concentration increasing. The maximum value was recorded for 6% wt. which was 76.8 hv and the improvement percent is about 132.327%.This means polymeric composite resistance to deformation increases with loading increasing because of nanoparticles which working on restraining the movement of polymer chain during the deformation process.

4.3. Fire retardancy tests & assessment:
4.3.1 Limited Oxygen Index (L.O.I): this test is a good indication about composite flammability. The results are shown in table 5. It is shown that all samples with different loadings needed Oxygen higher than what virgin PP sample (PCN0) needed. This means that nanoclay additions contributed to sustaining the flammability of polymer.

| Sample code Test | PNC0 | PNC2 | PNC4 | PNC4 |
|------------------|------|------|------|------|
| L.O.I            | 17.67| 18.75| 20.85| 19.28 |
| % improvement    | -    | 6.1% | 17.99% | 9.1% |

4.3.2. Rate of Burning (RB): it is measured mm/min using to Eq. according to ASTM: D635

\[ RB=60 \frac{X}{t} \quad (1) \]

Where: \( X = \) burned length of specimen and \( t = \) burning time (S)

Depending on the results of the test which are listed in figure 10, the burning rate (RB) of prepared samples were varied with nano clay loadings but it is noticed that all loadings
contributed to reducing the rate of burning compared with the pure sample. But the maximum reducing of RB is recorded for PCN4 (4% wt. loading) where the improvement is about 41% compared with pure PP (PCN0). It was noticed that burning was slow on contrary to the burning of the pure sample which was fast and strong. The efficiency is followed the next order:

\[ \text{PNC0} > \text{PNC2} > \text{PNC6} > \text{PNC4} \]

Reducing in RB

Figure 10 Rate of burning

4.3.3. The ignition time or flame exposure time:
is defined that time required to initiate burning process of the polymer sample. The results are clarified in table 6. The longest time was recorded for PNC4 is about (51s) compared with the time required to initiate burning process of virgin PP (PNC0) was (23 s). The improvement was about 121.7%

| Sample code | PNC0 | PMC2 | PNC4 | PNC6 |
|-------------|------|------|------|------|
| Exposure time | 21 | 23 | 25 | 35 |
| Mean exposure time | 23 | 35 | 51 | 41.3 |
| % delay improvement | - | 52% | 121.5 | 79.6 |

Table 6 Ignition time results

4.3.4. Maximum flame height (H):
The results showed the positive role of nanoclay loading on minimizing flame height. Different responses were recorded for different loadings but minimum height was recorded for PCN4 (4%) which was about 8.5 cm compared with the flame height of pure PP which was about 16 cm. Samples efficiency is following the next order and the results are shown in figure 11:

\[ \text{PNC0} > \text{PNC2} > \text{PNC6} > \text{PNC4} \]

Minimizing in flame height
4.3.5. First melt drip time:

It defined as the time required falling down the first drip of the polymeric composite after the glowing process. The results are shown in figure 12 for horizontal and vertical burning tests. The values showed that nano clay loading contributed to increasing the time required for first melt drip. All loadings have a positive effect on delay falling down of drips compared with the pure sample without additions. The PNC4 (4%) recorded the longest time compared to others according to following order:

\[ \text{PNC0} < \text{PNC2} < \text{PNC6} < \text{PNC4} \]

First melt drip time increasing

The polymers with low glass transition temperature melt in time shorter than those polymers with high Tg. The PP has very low Tg (-26 °C) (Josef 2015). When pure PP is subjected to flame, it will decompose and producing short chains with low viscosity because of random cleavage chain of PP structure. The nano clay additions to PP sustain the dripping via changing the viscosity of molten and it becomes more viscous and this leading to increase the time required for falling down first melt drip.

![Flame height results](image1)

![First melt drip time](image2)

**Figure 11** Flame height results  
**Figure 12** first melt drip time

Depending on the results of thermal and fire retardancy tests in above, it is noticed that nanoclay additions to PP composite have a positive impact on improving the flame retardancy performance compared with virgin PP. The improvements in thermal and fire properties can be attributed to more than a cause. First of all, migration mechanism with barrier played an important role to enhanced retardancy property of the PP/nanoclay composite especially the char formation mechanism do not work well with olefinic polymers which their degradation process depending on scission chains and volatilization processes.

The effect of insulating layer and effect of nanoclay particles is clear from results of L.O.I test and other tests which are mentioned above especially the time of burning increased with increasing clay loadings and the high of flame is shorter than in virgin PP because the clay particles sustained on scission and volatilization processes and making the degradation to be slower. Secondly, the chemical composition of used bentonite contained
on iron metal (7.483%) as shown in table 3. The iron existence led to pragmatic radical reactions which worked to make mass transfer slower. The deterioration in fire retardancy when the nanoclay loading is more than 6% can be attributed to the agglomeration of particles during manufacturing process.

4. Conclusions:

The assessment of results in this work shows that the possibility of synthesis nanoclay from Iraqi bentonite and using it as a fire retardant for polypropylene composites. The results clarified that mechanical properties (tensile stress & modulus) are improved and the maximum value at 2% loading. The thermal & fire test showed the positive role of nanoclay additions on these properties. The results of limited oxygen index, flame rate, height of flame, ignition time and first drip tests indicated to the role of nanoclay in the improvement. The result of 4% loading was the best among all samples relating to fire retardancy. Thermal properties are improved and heat of fusion increased with nanoclay increased.

6. Recommendation:

1- Testing nano-clay loadings more than 6% to assess their fire retardancy
2- Testing the effect of using different surfactants on nanoclay particle size and on fire retardant properties

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