

Preparations of Organoclay Using Cationic Surfactant and Characterization of PVC/ (Bentonite and Organoclay) Composite Prepared via Melt Blending Method

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Abstract

Calcium-Montmorillonite (bentonite) [Ca-MMT] has been prepared via cation exchange reaction using benzalkonium chloride [quaternary ammonium] as a surfactant to produce organoclay which is used to prepare polymer composites. Functionalization of this filler surface is very important factor for achieving good interaction between filler and polymer matrix. Basal spacing and functional groups identification of this organoclay were characterized using X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy respectively. The (XRD) results showed that the basal spacing of the treated clay (organoclay) with the benzalkonium chloride increased to 15.17213 \AA , this represents an increment of about 77.9% in the basal spacing. FTIR spectra illustrate that benzalkonium chloride compound was successfully intercalated in to clay layers. The results confirm the effectiveness of the synthesis of organoclay with similar characteristics compared to those ones observed in the bentonite. The features were obtained by a simple process and enable interaction with organic compounds (polymers and plastic). PVC/bentonite composite and PVC/organoclay composite were prepared by the melt intercalation method. The results have been analyzed and compared for PVC samples with (3wt%, 7wt% and 12wt %) bentonite and organoclay micro filler. Mechanical properties, thermal properties, flammability and water absorption percentage of prepared samples were tested. Mechanical characteristic such as tensile strength, elongation at break, hardness and impact strength (charpy type) were measured for all samples, where the tensile strength and elongation at break of PVC composites increased with increasing organoclay loading compared with unmodified bentonite. Also, the hardness and impact strength of the composites increase with increase in filler content. Thermal properties of PVC/ (bentonite, organoclay) composites were characterized using Differential Scanning Calorimeter (DSC) and thermal conductivity analyzer. The results showed T_g shifted toward higher temperature for all type of filler compared to neat PVC. Also, thermal conductivity measurement values illustrated that PVC/bentonite composites have a good thermal insulation at 12wt%, thermal conductivity was decreased from 0.222 W/m.K for neat PVC to 0.11 W/m.K at 12wt% PVC/bentonite composites. Organoclay give the best possible water absorbability of the PVC, with other word making it moisture resistant. The higher the filler content the higher burning time, the lower rate of burning and the lower height of the flame which are evident at 12wt% for all fillers.

Key words: PVC Composites, Bentonite, Organoclay, Benzalkonium Chloride, Cationic Surfactant , Cation exchange capacity and Melt blending method.

Introduction

The polymer is a word of a Greek origin where “poly” is a synonym of “many”, while “meres” stands for “parts”, so a polymer is a large molecules consisting of repeated smaller size chemical units. They can be made into types of final products as it is the case with the pure (new) form. Nonetheless, to make an effectively useful polymer, it is indispensable to modify it, particularly when the major limitations in the unmodified polymer are taken into account. Among those restrictions may be the low stiffness, low strength and the lack of stability when exposed to light rays, heat and radiation that can ionize. To make them vastly usable in different industrial fields nowadays, improved polymer composite productions are the right pathway to overcome the evident restrictions on one hand, and to insure the production of high quality polymers on the other.

A composite is defined as the combination at microscopic level between a couple (and more) of particular materials with a specific interference to link them together. The material could be of a metal, ceramic or polymer nature [1].

Nowadays, poly vinyl chloride occupies the third position in the list of the most commonly produced plastics, where the polyethylene comes at the top followed by polypropylene, by virtue of its valuable characteristics, wide applications, barrier properties, low cost and high chemical resistance. PVC is in the form of powders, slurries, liquids, and tablets. It has a wide range of properties of colors, solid , rigid, and stiff materials (with high viscosity) at room temperature, light weight with a good resistance to

bases & acids, alcohol, oils, compound hydrocarbon aliphatic. PVC has relatively low cost, biological and chemical resistance and workability and can be formed easily. For these reasons it is used for a wide range of applications, such as insulation on electrical cables, solid pipe manufacturing, window frames and doors, bottles, containers, furniture industry, etc. [2].

The thermal stability and processing of poly vinyl chloride, on the other hand, are unimportant in comparison with familiar polymers .These properties can be improved by making the poly vinyl chloride compound with some additives. The most commonly used additives in PVC are lubricants, heat stabilizers, plasticizers, fillers and pigments. Either polymerization or melt blending processes are used [3, 4].

Bentonite, which is predominantly montmorillonite clay, Montmorillonite is of a 2:1 layered structure pattern, a mono- aluminum-layer of octahedral plate inserted between two layers of silicon tetrahedral plates. The primary unit in the outer tetrahedral plates is the silicon oxide tetrahedron SiO_4 where the silicon atom is bonded to four oxygen atoms [5].

The isomorphous replacement of Al^{+3} for Si^{+4} in the tetrahedral layer and Mg^{+2} for Al^{+3} in the octahedral layer causes the charge of the clay surface to be a negative one. This lack of balance in the charge is caused by exchangeable cations, usually the clay surface Na^+ and Ca^{+2} [2]. The layered structure of the clay contributes to the expansion following hydration. Na^+ and Ca^{+2} ions with the existence of

water cause the clay surface to become hydrophilic medium [5, 6]. That is why, natural bentonite is considered to be a hydrophilic material. So, it is not compatible with organic materials such as polymers and plastics. By converting it to organoclay, it will, actually, be transformed into a hydrophobic material which- in this case- is more compatible with organic materials [7, 8].

It is the most familiar layered silicate in use because of its abundance in nature and useful properties (high surface area, high cation exchange capacity and large aspect ratio). It finds usage, as filler, for composites [9].

Due to the existence of the $-OH$ groups at the clay surface, it is important to modify it using the organic surfactant so as to make it compatible with polymer matrix [10].

The surface properties of natural bentonite can be greatly modified by simply ion-exchange reactions. Organoclay is normally made by replacing the alkali cations with alkylammonium [11]. This cation exchange widens the inter-gallery distance in addition to changing the surface polarity of the clay. The latter is extremely important for the wanted intercalation phenomena, as it becomes easier for the polymer chain to access the space of the organoclay inter-layers [12].

Quaternary ammonium salts are the most commonly used organic compounds to modify clays. They represent a form of an organic nitrogen compound, where a central nitrogen atom joined to four organic groups together with an acid radical included in the molecular structure [11, 13 and 14]. Also, they are all considered to be surface-active coordination compounds and tend to be adsorbed on surfaces; this is where their name (surfactants) comes from. By exchanging ions, the

surface properties variation from hydrophilic to hydrophobic [6].

This cation replacement alters not only the surface polarity of the bentonite but also widens the intergallery space. The latter is of paramount importance for the targeted intercalation phenomena, as the space between the layers of organoclay becomes more accessible for the polymer chain [12, 15]. The most widely used kinds of quaternary ammonium compounds to modify clays are dimethyl ammonium, methyl benzyl ammonium, and benzyl dimethyl ammonium and di benzyl methyl ammonium quaternary [16].

The nature of organoclay (OMMT) was affirmed by X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy. It can be used in the composite materials as the filler for PVC.

Dibasic lead stearates (DBLS), dibasic lead phosphate (DBLP) are used as the stabilizer; stearic acid is used as a lubricant. Dioctyl phthalate (DOP) is used as a plasticizer for compounding. It is noticed that raising the PVC temperature to more than $70^{\circ}C$ imposes some absurd changes on its properties. In practice, when temperatures of $(150-200^{\circ}C)$ are used, sufficient degradation may occur upon normal processing operation which makes the product useless [17, 18].

Xu et al. [19] gives a dioctyl phthalate (DOP) as intercalator for organoclay and poly vinyl chloride because they discovered alkylammonium salts in between the interlayers of organoclay, could trigger PVC degradation. DOP can impede the degradation of poly vinyl chloride.

On the other hand Yalcin & Cakmak [5] searched the influence of dioctyl phthalate on the penetration of organoclay in a poly vinyl chloride matrix. It was noticed that DOP

increases the penetration of organoclay in a polymer matrix.

The objective of this paper is to prepare a sample of organoclay by purifying bentonite and modifying it by quaternary ammonium salt and the produced bentonite was compared with the unmodified bentonite as filler for PVC. The effects of different modified bentonite (organoclay) (OMMT) and unmodified bentonite loading on the mechanical and thermal properties; flammability and water absorption of poly vinyl chloride (PVC)/ OMMT composites and poly vinyl chloride (PVC)/ unmodified bentonite composites respectively, were investigated.

Experimental Work

1. Materials

The PVC powder, a suspension polymer, supplied by Saudi Basic Industries Corporation and Kingdom of Saudi Arabia; The PVC used in this research has been analyzed by FTIR.

Iraqi bentonite powder ((Na, Ca)(Al, Mg)₆(Si₄O₁₀)₃(OH)₆nH₂O) was brought from an Iraqi Quarry around the area Suffra / the Ministry of Industry/the State Company of Geological Survey and Mining. The specifications of the bentonite are given in Table 1

Surfactant: Benzalkonium chloride (C₆H₅CH₂N(CH₃)₂R]Cl) (R: n -C₁₂H₂₅) (Quaternary Ammonium Chloride) was used to modify bentonite from hydrophilic nature to organophilic. Benzalkonium chloride is produced by Indian Company/ Sigma Ultra. A solution of 50% concentration was prepared.

Additives such as dibasic lead stearates (DBLS) (2PbO.Pb(C₁₇H₃₅COO)₂), dibasic lead phosphate (DBLP) (O₈P₂Pb₃) are used as the stabilizer; stearic acid

(C₁₈H₃₆O₂) is used as lubricant. These materials are from the Ministry of Industry/the State Company of Plastic Industries/ Baghdad Plastic Plant. Dioctyl phthalate (DOP) (C₆H₄-1, 2-[CO₂ CH₂ CH (C₂H₅) (CH₂)₃CH₃]₂) used in this study was used as a plasticizer by Indian Company/ Sigma Ultra.

Table 1: The characteristics of the Bentonite

Characteristics	value
Partical size	0.075 µm
Cation exchange capacity(CEC) meq/100g	80
Chemical composition (wt% dry basis)	
Silica(SiO ₂)	56.77
Alumina(Al ₂ O ₃)	26.2
Ferric Oxide(Fe ₂ O ₃)	8.12
Magnesium Oxide(MgO)	3.42
Calcium Oxide(CaO)	4.48
Sodium Oxide(Na ₂ O)	1.11
Potassium Oxide(K ₂ O)	0.6
Loss on ignition(L.O.I)	0.49
P2O5	0.65
So3	0.59

2. Methods

• Bentonite Washing (Rinsing)

Bentonite has been washed and used for the preparation of organoclay as follows [20]:

500 g of bentonite were weighted by using sensitive electric balance, to separate the insoluble salts, an amount of 500 g bentonite was dispersed in 10 liters of tap water using electrical mixer, for 10 min. The mixture was left for 30 min to stagnate.

The precipitate was rinsed with distilled water for several times to remove as much of the insoluble salts as possible using the same method. The mixture is filtered, dried in electrical oven at 80 °C, Milled and Sieved.

• Preparation of Organoclay

Organoclay was prepared by adding the required quantity of quaternary

ammonium chloride solution (benzalkonium chloride 50% solution) (alkyl benzyl dimethyl ammonium chloride) to the desired quantity of rinsed bentonite thoroughly by hand. The amount of consumed quaternary ammonium versus CEC% of mineral clay are given in Table 2. Cation dosages varied in range from 0 to 150% CEC. The suitable equation for brevity is: $A=0.30 B$, where B is CEC% and A is (g benzalkonium chloride/100g bentonite) [7, 21]. The produced paste was then introduced into the electrical mixer for (1hr) and collected in a container. All organoclay products were washed three times with deionized water to remove excess surfactants, filtered and dried at room temperature or in the electrical oven at 60-80 °C for two days, ground in agate mortar followed by screening to particle size 0.075µm [22].

Table 2: Amounts of quaternary ammonium used for preparation of organoclay

CEC %	100
g (benzalkonium chloride)/100g bentonite	30

• Sample Preparation

The following couple of steps summarize the production of poly vinyl chloride composite [23]:

In the first one, 1% by weight of the stabilizer (Dibasic Lead stearate, DBLS and Dibasic Lead phosphate, DBLP) were added to the PVC powder. 1% by weight of the stearic acid as a lubricant was also added. In addition to that, a mounts of 3%, 7% and 12% by weight of the filler were added. The filler used were bentonite and organoclay. The blend was mixed in a high_ speed mixer for 20min forming a dry mixture.

In the second step, the dry blend was blended with 20% by weight dioctyl phthalate (DOP). The details of additives percentage are given in Table 3. The blending took place in the

plastograph internal mixer (PLASTIC-CORDER), (Bra Bender .GmbH & CO. KG, Duisburg, Germany, 0-1000 °C) at (65-80°C) for 20 min and a 64-rpm mixing speed.

Table 3: PVC composite formulation with filler Composition (%)

Material	1	2	3	4
PVC	100	100	100	100
Stabilizer :DBLS	1	1	1	1
Stabilizer :DBLP	1	1	1	1
Lubricant: Stearic acid	1	1	1	1
Plasticizer :DOP	20	20	20	20
Bentonite	0	3	7	12
Organoclay	0	3	7	12

• Compression Molding (Hot Press)

A hydraulic press (made in ENGLAN, NOORE, BIRMINGHAM and SERIAL NUMBER /D369) was used to mold the sheets to be tested in this study. It consisted of lower and upper moving platens. A sample of the above mentioned mold was wrapped by an aluminum thin sheet [1]. Using the controlled hydraulic ram, the lower platen was pushed toward the upper platen causing the mold to close and putting it under pressure. The compression of the resulting film took place under the following conditions; a temperature of (170-185 °C), and a pressure of (10 bars) for (7 min). When the seven minutes passed, the pressure was removed letting the lower platen to fall down under the effect of gravity. The mold was dismantled rapidly and running water was used to cool it down. The aluminum foil paper was neatly un-wrapped to clear the produced film sample out of it. The compression-molded sheets of 90gm weight and 180 * 180 mm size with 5mm thickness were fabricated [24].

Measurements

1. Clay Measurements

The natural bentonite and prepared organoclay were analyzed by:

- **X-ray Diffraction (XRD)**

X-ray diffraction analysis was carried out to confirm the interspacing of the used bentonite and also to confirm whether the organoclay was formed or not. XRD performed by the powder method using a Shimadzu XRD-6000 diffractometer (with Cu-K α radiation, 40 K – 40 mA, the scan speed of 0.05 2 θ /s and 5 seconds per step).

- **Infrared Spectroscopy (FTIR)**

Fourier transformation infrared spectrophotometer (FTIR) was performed by the KBr method with a Shimadzu FTIR-8400 s spectrophotometer.

- **X-ray Fluorescence (XRF)**

The XRF performed by SPECTOR, Analytical Instruments, Boschstra Be 10, D_47533 Kleve /Model: XEPOS /type: 76004814, S/N: 4L0058.

2. Mechanical Properties

- **Tensile Strength and Elongation at Break**

Mechanical Properties of the polymer blends films were measured on a Shimadzu Autograph in air at room temperature. Tensile strength and elongation at break point were measured using a universal testing machine (tension_ compression to 5KN; manufactured by Tinius Olsen (UK).The compressed sheets were cut into dumbbell-shaped specimens according to ASTM D647-68.

- **Hardness**

The hardness of all specimens was read and recorded; using a Vickers diamond indenter (Digital Micro hardness Tester), HVS– 1000.Vickers indentation is a valid tool for evaluating the hardness of polymers. With a load of 0.4403 N. The load is applied for 20s (ASTM Standard “Test Method for Vickers Hardness”, 1997).

For every specimen, three readings were taken in accordance with Polymeric Matrix Composite (PVC) ASTM-02240-97 for Hardness test. The hardness value was determined by the penetration of the Durometer indenter foot into the specimen. The sample was placed on a flat surface on the pressure foot of the instrument. A calibrated spring in the Durometer applies a specific pressure to an indenter foot parallel to the surface of the specimen.

- **Impact Strength**

Impact test sample specimens were fabricated by the standard specification [ASTM-E23] and which are appropriate for testing by the impact device type Charpy (produced by (Tokyo Koki Seizosho, Ltd) company). The depth of the groove in the samples is 5mm with the groove base radius of 25mm and a groove angle 45⁰.For the purpose of identifying the extent of impact strength which the composite material is capable of withstanding; Equation 1 is used:

$$\text{Impact strength} = \frac{\text{Fraction Energy (KJ)}}{\text{Cross-Sectional Area (m}^2\text{)}} \dots(1)$$

- **Water Absorption of the Composites Samples**

Water absorption test was performed according to ASTM D570-99 (Standard Test Method for Water Absorption of Plastics, 1998) by conditioning and weighing the sample. Each sample was immersed in distilled water in a transparent thermoplastic container and covered with the lid for 24 hr at 27 ⁰C. Excess water on the sample surface was wiped off with a filter paper before reweighing [1]. From Equation 2 it was seen the percentage increase in mass during immersion was calculated using the equation:

$$\% \text{ Water Absorption} = [(\text{Wet weight} - \text{Dry weight}) / \text{Dry weight}] * 100 \quad \dots(2)$$

Wet weight: is the weight of sample after immersing in water for 24 h (g).

Dry weight: is the initial weight of sample (g).

3. Thermal Properties

- **Differential Scanning Calorimeter (DSC)**

The thermal properties of the composites were determined by Differential Scanning Calorimeter DSC measurements performed using a Shimadzu DSC-50, Japan, at a heating rate of 10 °C/min in the temperature range 25-250 °C under nitrogen purge. The glass transition temperature was taken as the midpoint of the transition.

- **Conductivity Measurement (k,ε and Cp)**

Thermal Conductivity measurements were done using SETARAM, Instrumentation, KEP Technologies-THERM TCi™, and Thermal Conductivity Analyzer/Made in France. The Mathis TC i is based on the modified transient plane source technique. It uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample. Both thermal conductivity and effusivity are measured directly and rapidly, providing a detailed overview of the thermal characteristics of the sample material. Sample material can be a solid, liquid, paste or powder [25, 26]. From equation 3 the heat capacity values of polymer composite [27] can be determined from the effusivity value equation by:

$$\epsilon, \text{effusivity} = \sqrt{k \cdot \rho \cdot Cp} \quad \dots(3)$$

Flammability

- **Burning Speed Measurement Test [To measure the time required for burning until a full self-extinguish take place using ¹⁶⁴(ASTM: D_635)]**

This method is considered as an internationally adopted one and is used to measure the flame dispersing speed in the different polymer material and to calculate the time duration needed for the burning. It is vastly used in polymer material convertible into plates, sheets or bars. Polymers testable in this method are categorized to be flammable and self-extinguishable after a certain time of burning according to ASTM: D_635.

- **Flame Height Measuring Using the Test ¹⁶⁵(ASTM: D-3014)**

This test is one of the lab methods used to measure the flame height a burning polymer can make. It is vastly used in polymer material convertible in to plates, sheets or bar.

Results and Discussion

1. Clay Measurement

- **X-ray Diffraction (XRD)**

Figures 1 and 2 shows the XRD analysis of natural Iraqi bentonite and prepared organoclay, respectively.

From the XRD, the interlayer spacing of the pristine of natural bentonite and prepared organoclay, as shown in Figures 1 and 2. The peak data lists of these figures are given in Table 4 and 5 respectively. The organoclay and natural bentonite were previously dried at 60-80 °C. The properties of organoclays were investigated by basal x-ray diffraction analysis. Considering there figures, it can be shown that the benzalkonium salt is introduced in the spaces of the silicate; and this is done via a reaction of an exchange of cations [9, 21 and 28]. The basal

spacing increased from 3.34264 to 15.17213 Å, with 77.9% increase [29]. The interlayer spaces are greater in the case of the organoclay, showing the formation of intercalated structure. This behavior was confirmed by

Valenzuela Diaz FR. [30] and Caroline et al. [31].

To increase these spaces, two factors are considered: (i) large hydrophobic groups are present; (ii) the bentonite surface energy is decreased [32].

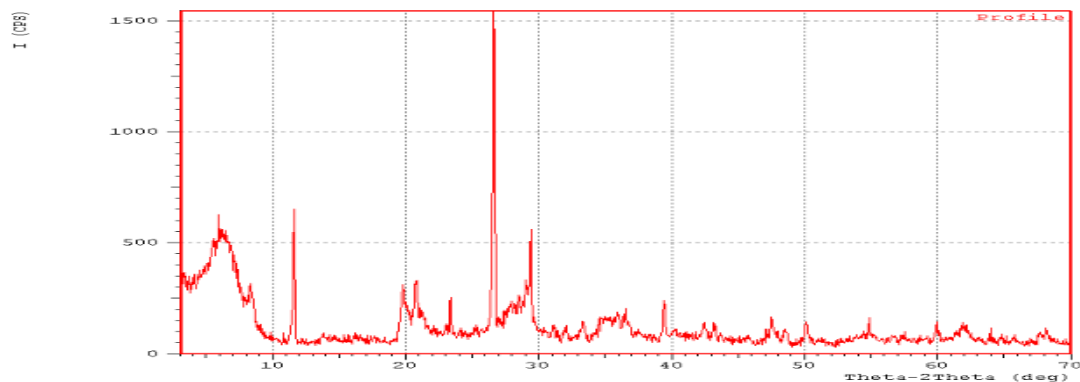


Fig. 1: XRD of natural Iraqi bentonite

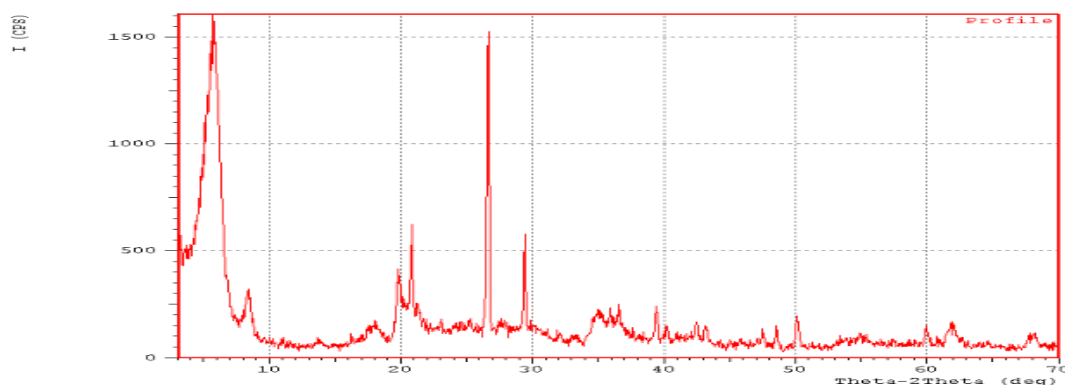


Fig. 2: XRD of prepared of organoclay

Table 4: Peak data list of natural Iraqi bentonite

No.	2Theta (deg)	d (°A)	I/I1	FWHM (deg)	Intensity (counts)	Integrated Int(counts)
1	26.6467	3.34264	100	0.15960	602	2138
2	11.6813	7.56961	38	0.15240	231	821
3	29.4167	3.03388	29	0.17870	174	763

Table 5: Peak data list of Organoclay

No.	2Theta (deg)	d (°A)	I/I1	FWHM (deg)	Intensity (counts)	Integrated Int(counts)
1	5.8204	15.17213	100	1.32500	454	13015
2	26.6421	3.34321	46	0.75450	207	2978
3	20.8105	4.26501	22	1.18000	101	2691

• **Fourier Transformation Infrared Spectrophotometer (FTIR) of Bentonite and Organoclay**

The range of 4000 to 400 cm⁻¹ shows the absorption of infrared radiation. The Fourier transformation infrared

spectrophotometer (FTIR) of natural Iraqi bentonite is shown in Figure 3.

Iraqi natural bentonite has vibration peaks at 470.60 and 1114 cm⁻¹. This clay has a stretching and bending structure of Si-O-Si and Si-O-Al. Si-O stretching peak at 1037.63 cm⁻¹ and Si-

O bending peak at 518.82 cm⁻¹ are also presented. This is shown by Gonzaga et al., [28]. The H-O-H bending region which corresponding to absorbed water is

1600-1700 cm⁻¹, while the stretching region of 3100-3700 cm⁻¹ represents the O-H symmetric and asymmetric, this is shown by the results of Bertagnolli & Silva [33].

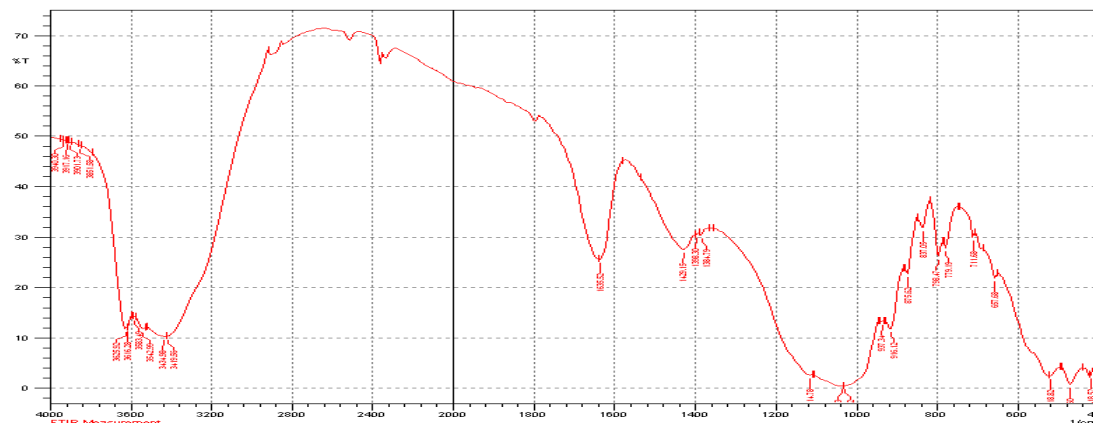
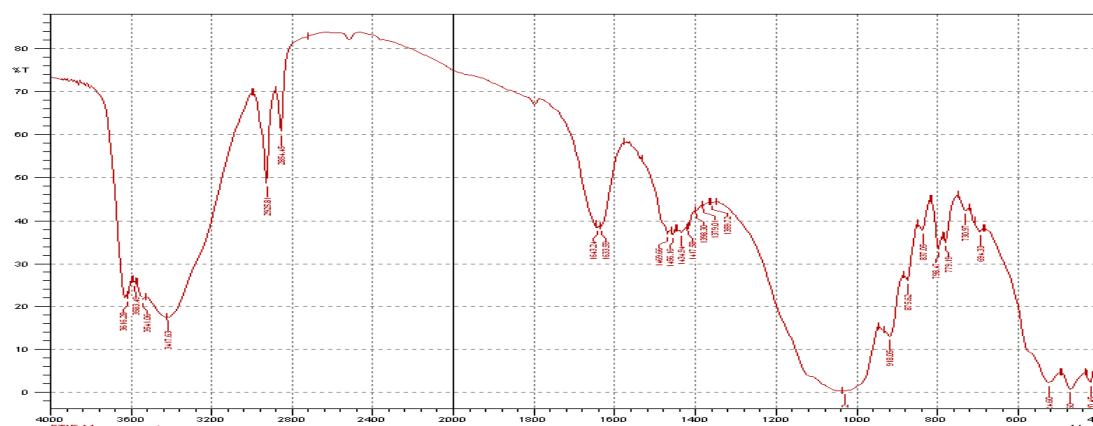


Fig. 3: Infrared curve of natural Iraqi bentonite

Figure 4 shows the Fourier transformation infrared spectrophotometer (FTIR) of organoclay. FT-IR spectra of organoclay shows the peaks at 2854.45 and 2925.8 cm⁻¹ which correspond to the organic matter. It also shows the presence of the additional band at 1434.94, 1456.16 and 1469.66 cm⁻¹ compared to bentonite. The stretching vibrations of the C-H bonds occurred in the 2800-2900 cm⁻¹

region. The symmetric and asymmetric stretching [-CH- [-CH₂ and -CH₃ stretching respectively] are shown by the absorption bands of 2854.45 and 2925.81 cm⁻¹ [32, 34].

The asymmetric angular deformation of the CH₃ groups occurs at about 1434.94 and 1379.01 cm⁻¹ and of the CH₂ groups occurs at about 1456.16 cm⁻¹ [33].



modifying organic matter, with no distortion of the clay structure. This is evident also from the results of Sulayman and Kshash [21], Bhattacharya and Aadhar [32].

The CH₃, CH₂, CH, N-H and C-N vibration bonds in the infrared spectra of organoclay are good evidence. Also, the intercalation of alkyl ammonium in the interlayer galleries of the clay is very clear [21, 28, and 36].

• Fourier Transformation Infrared Spectrophotometer (FTIR) of Poly Vinyl Chloride

The FTIR spectra for poly vinyl chloride are shown in Figure 5; poly vinyl chloride can be confirmed from the peak near 600 cm⁻¹, due to C-Cl stretching vibrations [37]. The characteristic vibration peak of poly vinyl chloride between 570-760 cm⁻¹ [35], so 599.82, 632.61, 684.88 and 692.40 cm⁻¹ corresponding to the C-Cl stretching vibrations.

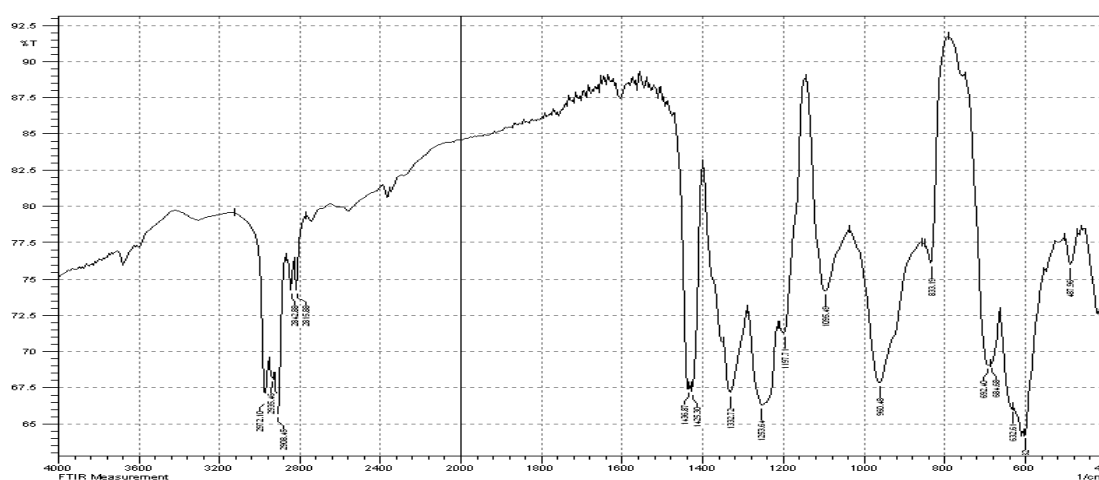


Fig. 5: Infrared curve of poly vinyl chloride

• X-ray Fluorosis Analysis of Bentonite and Organoclay

An XRF test was performed for bentonite, rinsed bentonite and organoclay. It was found that the Cl content is getting smaller (from 0.2740 to 0.1364) for the rinsed bentonite (compared to) raw bentonite (non-rinsed). It was also found that the Cl content increased in the organoclay (as compared to) the rinsed bentonite (from 0.1364 to 0.3084). This indicates that a reaction has taken place.

2. Mechanical Properties

• Tensile Strength and Elongation at Break

The effect of filler loading on mechanical properties of PVC composites is shown in Figures 6, 7 and Table 6. The tensile strength and

elongation at break of PVC composites based on organoclay as compared with unmodified bentonite were found to be increased with increasing organoclay loading. The enhancement in the tensile and elongation at break of PVC composites is very clear using organoclay compared to bentonite. This may be due to the functionality of the organoclay which activated the PVC matrix and the organoclay to be intercalated and it was due to the good distribution of organic filler in (PVC) polymer matrix [3]. Likewise, the increment in strength can also be attributed to the increasing in the ability of adhesion between the filler and the matrix leading to decrease the sliding between composite layers when applying stress in the composites [38, 39].

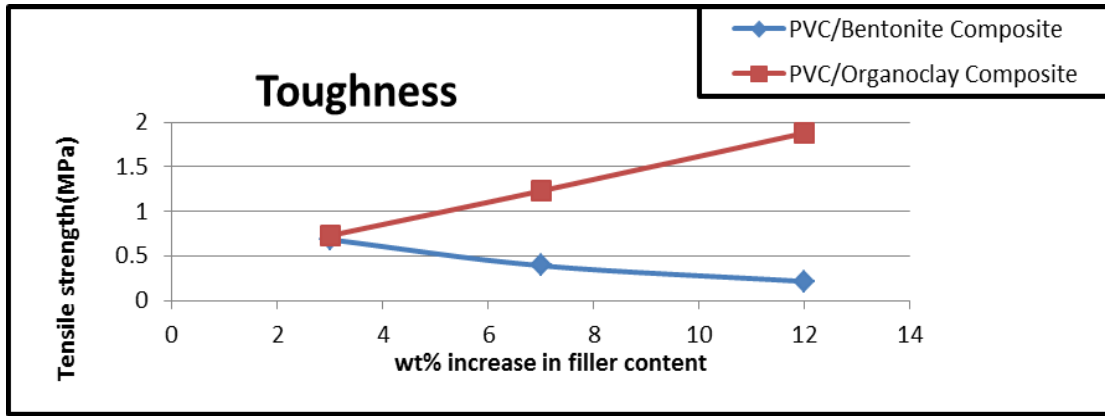


Fig. 6: Tensile strength curve of PVC/bentonite composite, PVC/organoclay composite

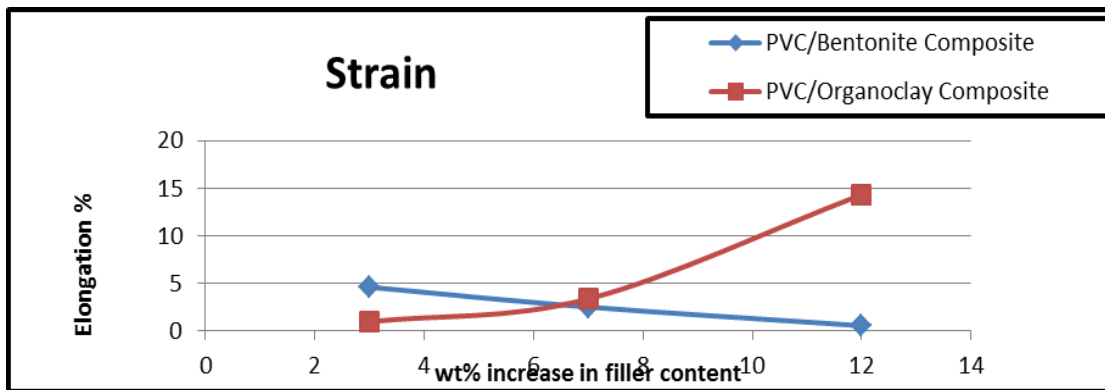


Fig. 7: Elongation curve of PVC/bentonite composite, PVC/organoclay composite

• **Hardness**

The test results for the hardness values for the basic PVC material reinforced with bentonite and organoclay as shown in Figure 8, and given in Table 6. The results show a significant improvement in the values of hardness for the different content of reinforcement. The 12% content showed the best hardness values. The difference in the result of hardness values for the reinforcing materials [bentonite, organoclay], is caused by the granular size of each of the

materials. The lowest hardness value shown was found belonging to the case of bentonite content. The reason is due to the semi globular shape of its grains. Similarly, the non-globular grain shape of the organoclay caused the hardness to be at the highest value [3]. This improvement in hardness was found to be more effective with organoclay as compared with bentonite and this is because the hardness of composite depends on the distribution of filler particles in the matrix [40].

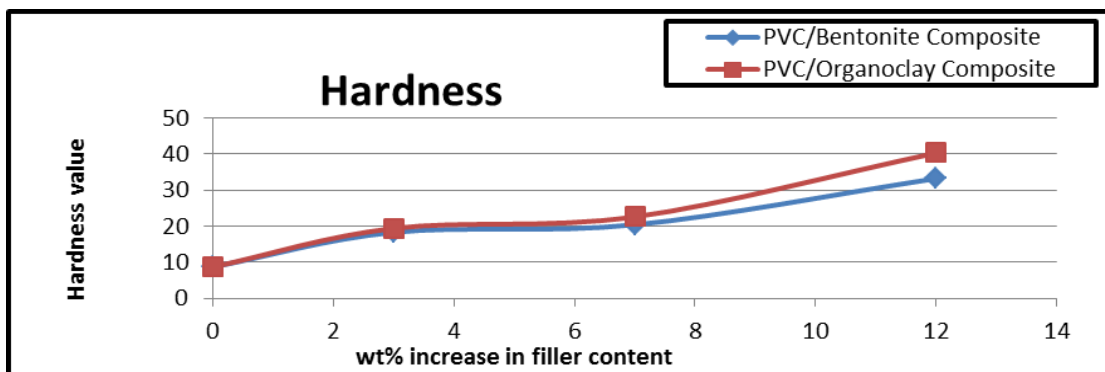


Fig. 8: Hardness (Shore A) of Unfilled PVC, PVC/ (bentonite and organoclay composite)

• **Impact Strength**

From Figure 9 and Table 6, it can be seen that the impact strength value changes with the change of the content added to (bentonite and organoclay). It is noticed that the impact strength value increased for all types of fillers when compared with the neat PVC for which the value of the impact strength is 4.57 kJ/m². The larger the filler content added, the higher the impact strength value. The reason is attributed to the fact that the filler particles would bear the major part of the impact energy which the composite material is subjected to. Thus the strength in

question is improved. The increase in the reinforcement and toughness of PVC is due to the high dispersion and interface interaction [41].

The dispersion and interfacial properties of the organoclay are improved when the organoclay surfaces graft long organic chains. With the small amount of organoclay, it can disperse uniformly in the PVC matrix and have a good interface interaction with PVC matrix [38]. It was found that the best content of the organoclay is 12%wt added to the PVC.

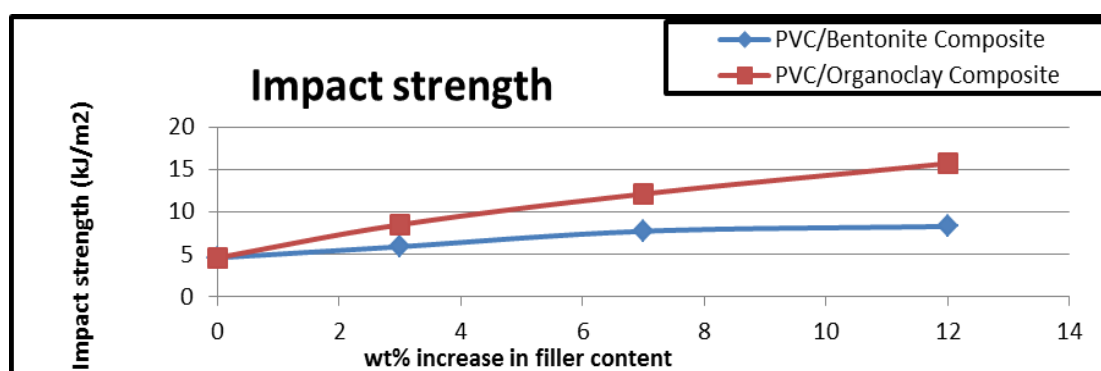


Fig. 9: Impact Strength curve of Unfilled PVC and PVC/ (bentonite and organoclay) composites

• **Water Absorption of the Composites Samples**

From Figure 10 and Table 6 it is noted that the organoclay was the best kind of fillers as it produced (for all its different content used; 3%, 7% and 12%wt) the best possible absorbability of the PVC .With other word making it

moisture resistant. Owing to its organic nature the organoclay is the best kind of clays as it is more compatible with the polymers which are already organic materials .In addition to the fact that the existence of the groups in question made the bentonite hydrophobic [1].

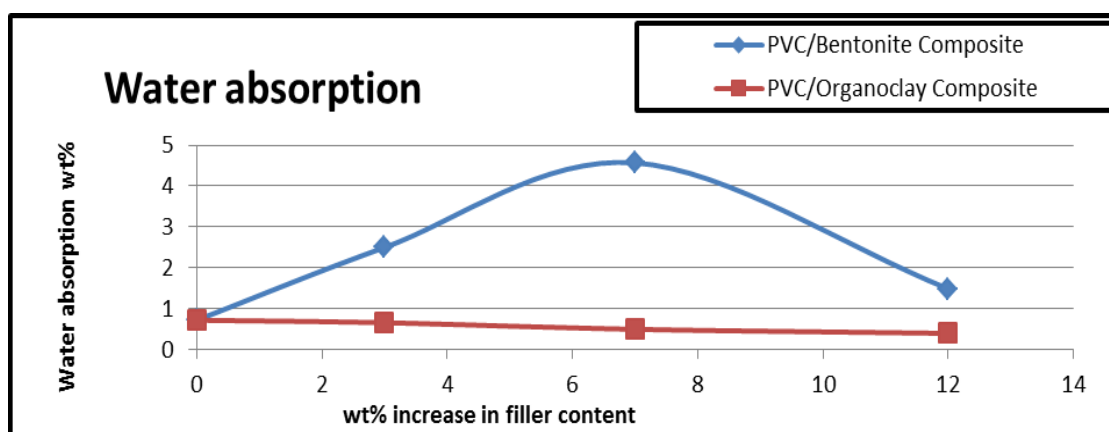


Fig. 10: Plots water content against percentage increase in filler

Table 6: Mechanical Properties of Unfilled PVC, PVC-bentonite composites and PVC-Organoclay composites

Sample Designation	Tensile Strength (MPa)	Elongation %	Shore A Hardness	Impact strength (kJ/m ²)	% water uptake (after 24 h of immersion at 25 C ⁰)
PVC neat	2.615	45.6	8.7	4.57	0.722
PVC-3% bentonite	0.683	4.613	18.3	5.877	2.50
PVC-7% bentonite	0.3904	2.533	20.4	7.7	4.57
PVC-12% bentonite	0.2137	0.567	33.2	8.27	1.49
PVC-3% Organoclay	0.728	0.995	19.4	8.47	0.66
PVC-7% Organoclay	1.23	3.385	22.6	12.1	0.5
PVC-12% Organoclay	1.879	14.35	40.3	15.7	0.4

3. Thermal Properties

• Differential Scanning Calorimeter (DSC)

Based on the data collected from the DSC thermo-gram as shown in Figure 11 and given in Table 7 the glass transition temperature was found out. Whereas the fillers do fill and (patch) the gaps or spaces between the polymers chains, those restricting the chains movement to improve their plastic properties. The results showed $T_{3\%}$, $T_{7\%}$, $T_{12\%}$ shifted toward higher temperatures for all type of filler

compared to neat PVC. This improvement in thermal stability was found to be more effective with organoclay as compared with bentonite because of the dispersed organoclay can restrict the segmental mobility of PVC molecules. As a consequence, the increase of long organic chains contents is proportional to the increase of organoclay content. So the long organic chains improve the interface adhesion of bentonite and PVC matrix [10, 38].

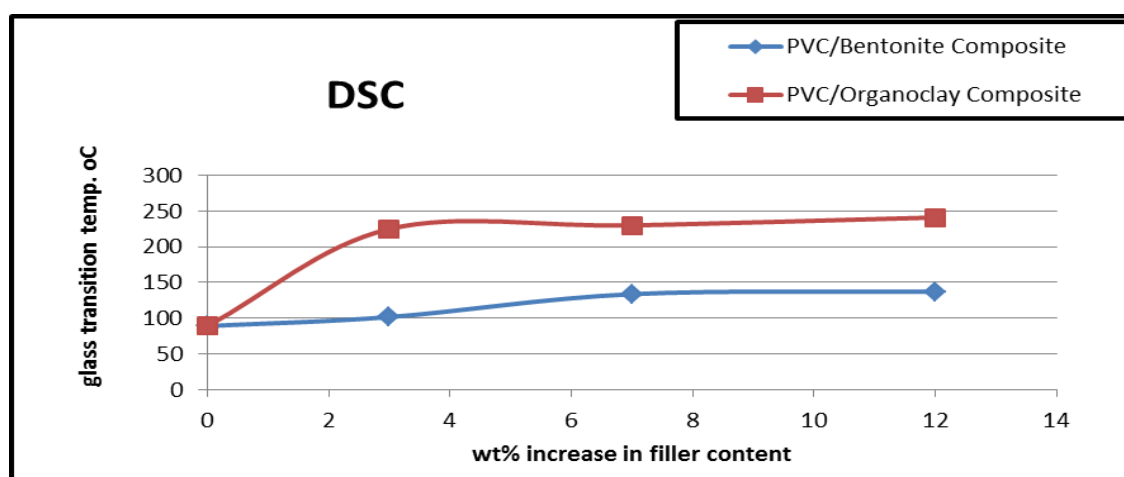


Fig. 11: Plots Glass Transition Temperature against percentage increase in filler

• Conductivity Measurement (k,ε and cp)

As the content of the organoclay filler increases so does the thermal

conductivity as shown in Figure 12, accompanied by the increase of thermal effusivity as shown in Figure 13 and a decrease in heat capacity as

shown in Figure 14 and given in Table 7. This is in agreement with the results of [27].

As for the bentonite, it is notice that with the increase in its content down the thermal conductivity decreases and the minimum value of thermal conductivity 0.11 w/m. k corresponds at the highest value (12% of bentonite

content). When compared with 0.222 w/m.k value of the thermal conductivity of neat PVC, the thermal insulation of the product is improved with a ratio of 50.4% [2, 42]. So the higher the bentonite contents the lower the thermal effusivity and the greater heat capacity.

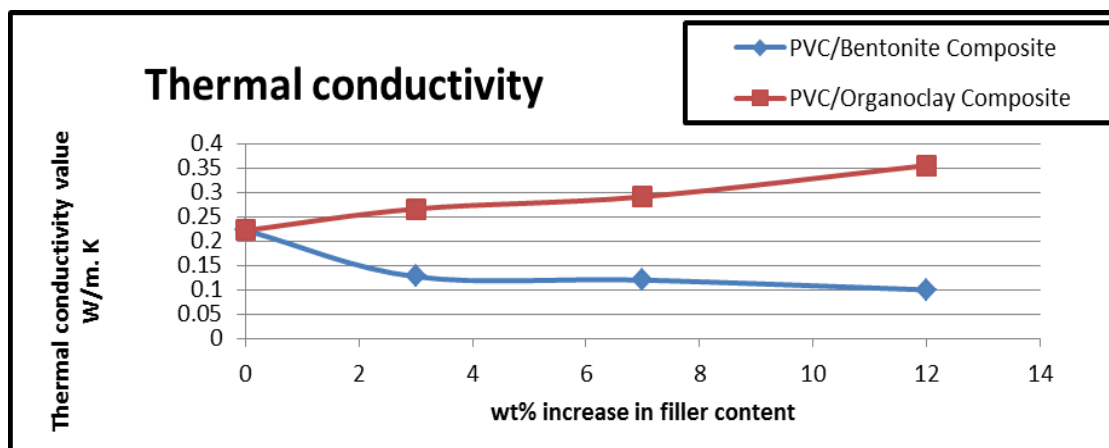


Fig. 12: Thermal conductivity against filler content

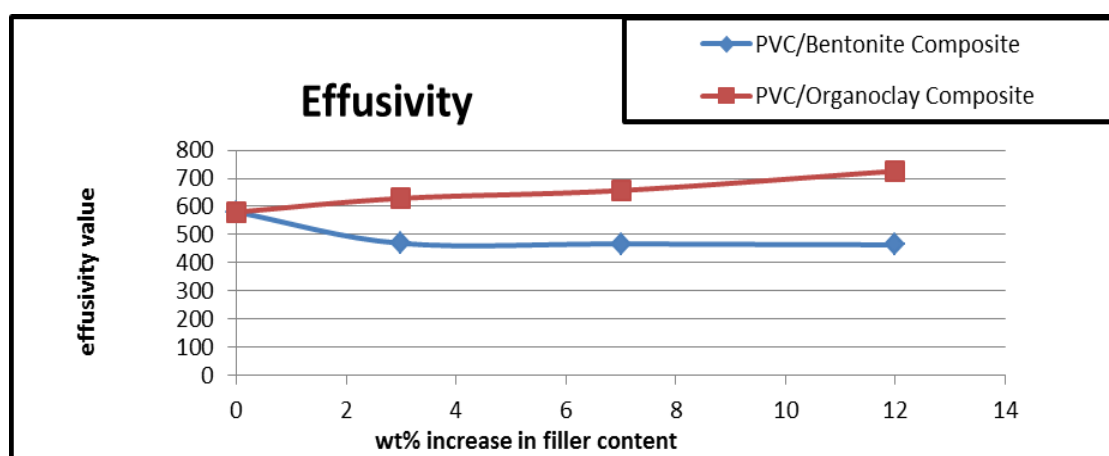


Fig. 13: Effusivity against filler content

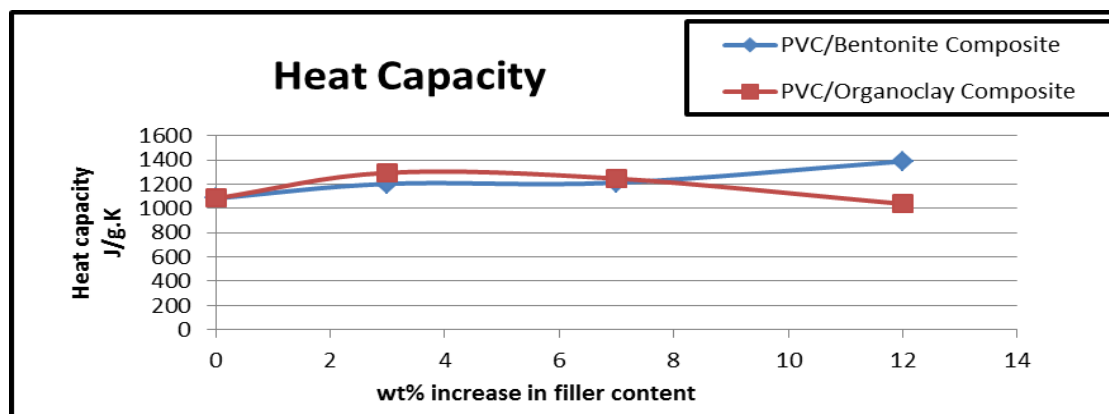


Fig. 14: Heat capacity against filler content

Table 7: Thermal Properties of Unfilled PVC, PVC-bentonite composites and PVC-Organoclay composites

Sample Designation	Glass Transition Temp. (T _g) (°C)	Thermal conductivity value (k) (W/m. K)	Effusivity (ε) (Ws ^{1/2} / m ² .K)	Heat capacity Results cp (J/g.K)
PVC neat	89.09	0.222	580.4	1083
PVC-3% bentonite	101.68	0.127	469.1	1203
PVC-7% bentonite	133.73	0.12	467.1	1212
PVC-12% bentonite	137.34	0.10	463.9	1388
PVC-3% Organoclay	224.86	0.266	629.2	1294
PVC-7% Organoclay	229.95	0.291	657.5	1246
PVC-12% Organoclay	240.98	0.355	726.1	1038

4. Flammability

• Burning Speed Measurement

The results of the measurement showed a large increase in the burning time. It also showed a large decrease in the rate of burning for PVC/filler composite, with other words the higher the filler content, the higher burning

time and the lower rate of burning which are evident in Figures 15 and 16 and given in Table 8. The best filler content was found to be 12% for all filler types where as the best filler among then found to be the 12% organoclay. This is agreement with the results of Faris, A.H. [43].

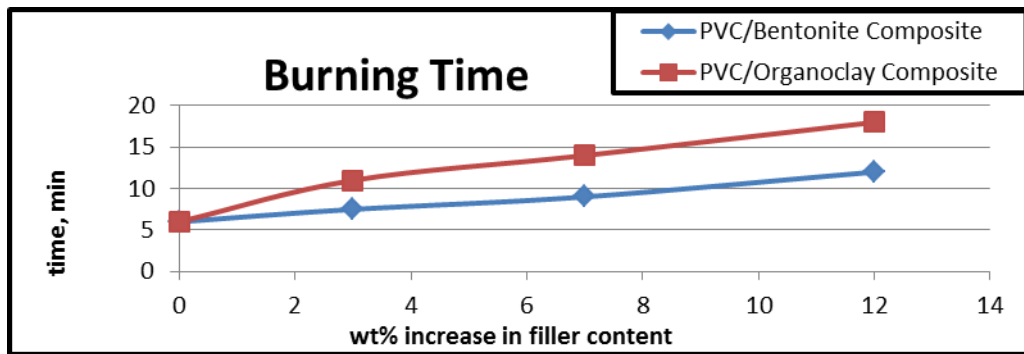


Fig. 15: The burning time against filler content

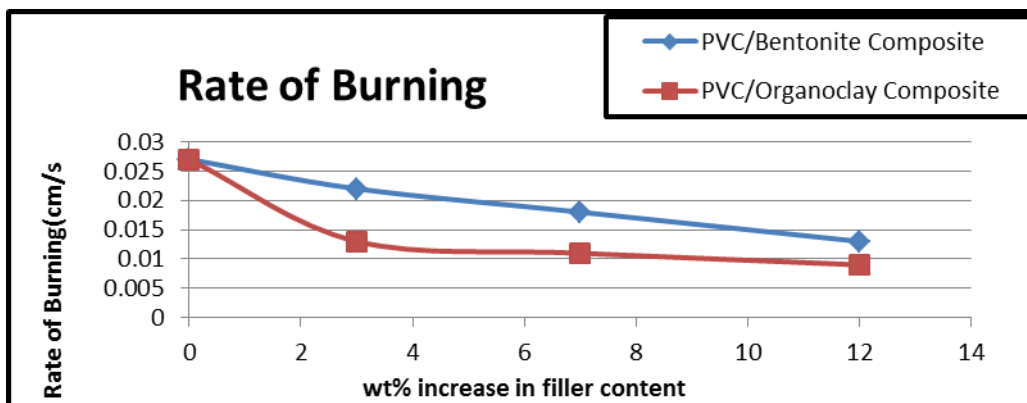


Fig. 16: Rate of Burning against filler content

• Flame Height measuring

The results of the measurement showed decrease in the flame height (H) for PVC/filler composite. This decrease in the flame height (H) is

inversely proportional with the filler content in the neat PVC .With other words the higher the filler content, the lower rate of the flame height (H) which is evident in Figure 17 and

given in Table 8. The best filler content was found to be 12% for all filler types where as the best filler

among them was found to be the 12% organoclay [44].

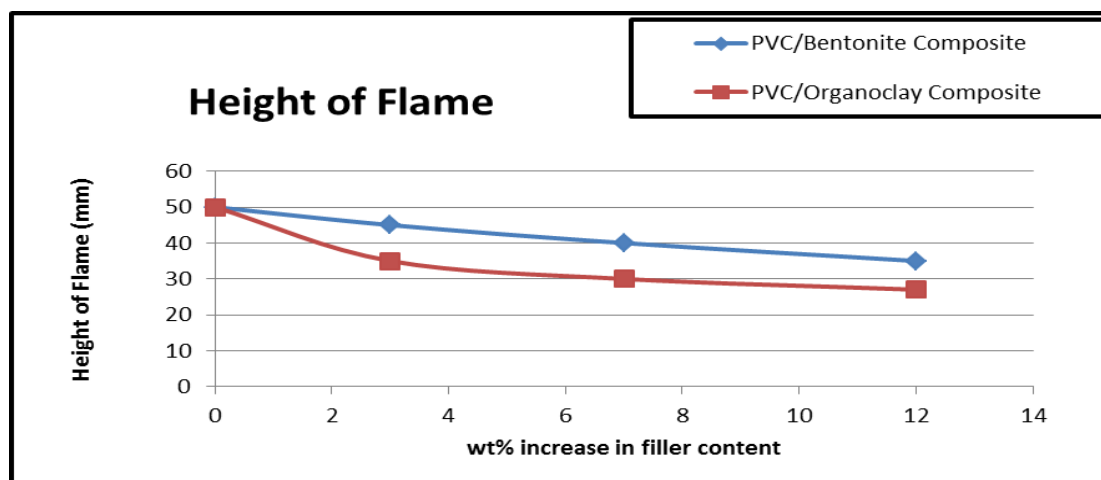


Fig. 17: Flame height against filler content

Table 8: Flammability Properties of Unfilled PVC, PVC-bentonite composites and PVC-Organoclay composites

Sample Designation	Burning Time (min)	Rate of Burning (cm/s)	Height of Flame (mm)
PVC neat	6	0.027	50
PVC-3% bentonite	7.5	0.022	45
PVC-7% bentonite	9	0.018	40
PVC-12% bentonite	12	0.013	35
PVC-3% Organoclay	12	0.013	25
PVC-7% Organoclay	15	0.011	22
PVC-12% Organoclay	18	0.009	20

Conclusion

By analyzing the results obtained in this work, the following conclusions can be drawn:

1. The benzalkonium chloride was used to modify bentonite in an attempt to create susceptible clay to polymers and it was successfully incorporated in the montmorillonite clay.
2. From XRD results, it could be concluded that the organoclay (modified bentonite) presented larger basal distance than unmodified bentonite, because of intercalation of the ammonium quaternary salt in the inter-lamellar spaces of the clay.
3. The basal spacing of the montmorillonite clay was increased

as a result of incorporating benzalkonium chloride and it was increased to 15.17213 $^{\circ}$ A by the incorporating of quaternary ammonium.

4. From infrared spectroscopy results, the presence of CH₂, CH₃, N-H and aromatic tert. amines (C-N) vibration (groups) could be detected in the samples that modified the efficiency of the organophilization process.
5. Considerable differences are noticed considering the XRD and FTIR diagram of the prepared organoclay and natural bentonite. This is because of the exchange of quaternary ammonium with Ca⁺⁺ ions at the surface of bentonite.

6. Increasing the organoclay loading increased the tensile strength and elongation at break of PVC composites compared with unmodified bentonite, which is attributed to the increasing in the ability of adhesion between the filler and PVC matrix.
7. The results showed a significant improvement on the values of hardness for the different content of reinforcements. The highest hardness value was found in the case of organoclay content.
8. Increase in impact strength was noticed in all fillers, when compared with the neat PVC for which the value of the impact strength is 4.57 KJ/m^2 . This may be due to the bearing the major part of the impact energy by the filler. The 12% content of the organoclay showed the best impact strength value.
9. The results showed T_g shifted toward higher temperature for all type of filler compared to neat PVC. Also, thermal conductivity measured values illustrated that PVC/bentonite composites have a good thermal insulation at 12wt%. Thermal conductivity was decreased from 0.222 W/m. K for neat PVC to 0.11 W/m. K at 12wt% PVC/bentonite composites. The thermal insulation of the product is improved with a ratio of 50.4%.
10. The higher the filler content the higher burning time, the lower rate of burning and the lower height of the flame which are evident at 12wt% for all fillers. It was found that the best content of the organoclay is 12wt% added to the PVC.
11. There are general increases in absorption rate with increase in bentonite content. This behavior might be due to the presence of void spaces in the matrix which could

have been formed during compounding of composites. The void space in the matrix accommodates the water absorbed, so the Organoclay give the best possible absorbability of the PVC. with other word making it moisture resistant.

Abbreviations

Impact strength	KJ/m^2
Fraction Energy	KJ
Cross-Sectional Area	m^2
Specific heat capacity	J/g. K
Density of sample	g / cm^3

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