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Studying the Effect of Adding Aleppo Pylon to the Properties of Insulating and Accumulation of Polyvinyl Chloride Films

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Abstract: This research presents a study of the effect of adding natural and modified Aleppo Pylon (Syrian clay) in different proportions to the properties of polymeric films prepared from poly vinyl chlorid (PVC) polymer and dried at three different drying degrees (60ºC, 100ºC, 150ºC). The clay surface was changed from hydrophilic to hydrophobic by treating the surface with quaternary alkyl ammonium salts. Both types of Aleppo Pylone were added to the polymer by weight (0%, 2.5%, 5%, 7.5%, 10%), and the polymeric films were prepared by way of mixing well of PVC polymer and clay. The mixing technique used hexanol as a solvent. The clay was mixed with the polymer at 150 Cº temperature using a magnetic stirrer.

The effect of adding natural and modified Aleppo Pylon to the properties of water absorption ratio, moisture content, migration of components in moderate, acidic and alkaline aqueous solutions, thermal stability and air permeability of polymeric films prepared from PVC polymer and clay with different drying degrees was studied and compared with them, in order to reach an improved PVC that can be used in the field of packaging.

Keywords: Clay, polymer, water absorption, moisture, thermal stability, air permeability

1 Introduction

Technical progress and technological development have prompted engineers and scientists alike to develop new engineering materials with unique and distinctive properties called composite materials. This term is given to materials that consist of two or more different types of materials producing new homogeneous materials so that one of them surrounds and is known as the base material with the other material, known as the reinforced material in the form of fibers, particles, or granules, such as carbon fibers, fiberglass, calcium carbonate, or clay granules. It is required that the reinforced (supporting) materials have the ability to adhere to the base material, and that no chemical reaction should occur between them. The properties of the resulting compounds depend largely on the following factors: the proportion of the filler, the size of the particles, and the good dispersion of the fillers within the structure of the base material [1-3].

Polymeric composite materials have a set of properties that cannot be obtained together from basic polymeric materials, such as high resistance, good impermeability and insulation, high mechanical resistance and modulus of elasticity, thermal stability, ease of formation and flexibility of design [4].

Polyvinyl chloride (PVC) is one of the most widely used polymeric materials in the world, and its multiple uses are in many important fields due to its distinctive properties. To expand the range of PVC applications, it was necessary to develop polymeric compounds composed of polyvinyl chloride and various supporting materials [5,6].

Most of the research is currently concerned with the use of clay as a reinforcing material for polymeric composite materials since it has great endurance , and it possesses good properties, is available and cheap, and in addition, it is environment and nature-friendly [7]. Polymeric composite materials supported by granules are the most important engineering materials used in industrial applications today, due to the possibility of their use in various fields and uses.

Casba et al (2013), in Hungary, selected a group of different polymers, then added Zeolite to these polymers to prepareed a packaging material with good properties. According to this study, the water absorption was very slow in PVC and HDPE but very fast in PC [8].

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Lucas prepared and studied the properties of PVC/Silica-Lignin compounds, and the results showed that the mechanical and thermal properties of PVC/Silica-Lignin compounds are good, and better than basic PVC [9].

Sadgate and Ghamami prepared compounds of polyvinyl chloride (PVC) and montmorillonite (MMT) by melting mixed Technique and in different proportions of ingredients. The results showed that the new PVC/OMMT compounds have enhanced mechanical, thermal and physical properties and better than the basic PVC [10].

Maria Carrera enhanced high-density polyethylene with montmorillonite modified with polyvinyl alcohol, The results showed a decrease in the permeability of carbon dioxide in the films prepared from the mentioned mixture, The films showed good mechanical and thermal stability properties [11].

In previous studies, researchers and engineers were interested in developing and producing polymeric composite materials by adding montmorillonite, bentonite or kaolin clay into the structure of polymers such as polyethylene, polypropylene and polyvinyl chloride resins. While the aim in this research was to add a type of Syrian clay of a brown color that is available in the Aleppo lands called the Aleppo Pylon. The surface of Aleppo Pylon clay has been treated to change its chemical nature from hydrophilic to hydrophobic, add the modified and natural Aleppo Pylon clay to the polyvinyl chloride polymer, then study the properties of insulation and impermeability of polymeric films produced from polymer and clay against moisture, water absorption, air permeability, migration of components in aqueous solutions and thermal stability.

The actual importance of the current study is in the production and development of a material with better resistant to moisture and water absorption than the basic polymer, by adding materials available in the environment and affordable, which will reflect positively on industries that depend on polymer in terms of product quality and cost reduction.

2 Materials and methods:

2.1-Materials:

Table (1) shows the specifications of the PVC used in the present work. The natural clay used in the present work, Aleppo Pylone, comes from Aleppo lands of Syria.The natural brown clay was washed, dried and ground to a degree of smoothness of 75µm, the natural clay was analyzed by OXFORD Instruments Analytical X-RAY. Table (2) shows The chemical composition of the clay according to XRF apparatus. The surface of the clay was treated with quaternary alkyl ammonium salts to transform it from hydrophilic to hydrophobic [7], in order to obtain modified Syrian clay. Medical glycerin was used as a plasticizer and zinc oxide as a stabilizer.

Table(1): specifications of the polyvinyl chloride

Density	1.4 g/cm^3
Molecular weight	30000-40000 g/mol
Appearance	White to beige
K-value	42±1
Chlorine (Cl)	48.8 % ± 0.6 %
Volatile parts	< 1.0%
Viscosity (20% in MEK)	28 ±5 mpa s

Table(2): The chemical composition of the clay by XRF

Color	$CaCO_3$	SO_3	SiO_2	K_2O	Na_2O	MgO	CaO	Fe_2O_3	Al_2O_3
brown	%0.00	%0.00	%49.40	%0.57	%0.45	%10.23	%4.64	%10.47	%13.76

2.2-Preparation of the films:

The films were prepared by solution mixing technique.[10] This method depends on choosing a suitable inert solvent to dissolve the polymer, as hexanol. The components (polymer, clay, glycerin, zinc oxide, hexanol) were placed according to the proportions mentioned later in flask and mixed using a magnetic stirrer at a temperature of 150Cº. The mixture was then poured into clean, dry glass dishes. the resulting films were dried at three different drying degrees (60Cº, 100Cº, 150Cº). The thickness of the resulting films was about 0.3mm.

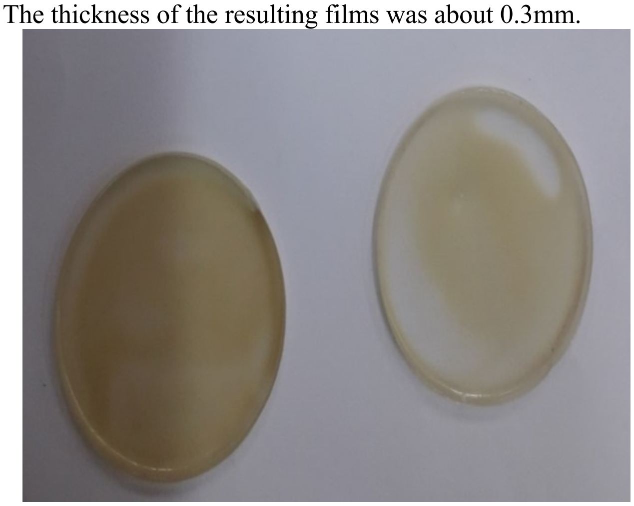

Fig (1): *A sample of the films prepared in this research*

2.3- Moisture content test:

The polymeric films prepared in this work were weighed to obtain their first weight, then dried at a temperature of 105Cº until the weight was stable to obtain their second weight after drying. From these values, the moisture content was determined according to the following relationship:

Moisture (%) = ((First weight – Second weight) / (First weight))x100

This method is applied according to the Syrian Standard Specification No. (21) for the year 1971 used in the laboratories of the Ministry of Industry to measure the amount of moisture for polymeric materials and plastics.

2.4- Migration test:

The films were weighed to get their original weight, then the films were placed in three glass bottles. 100ml of distilled water was added to the first bottle, and 100ml of acidic solution of hydrochloric acid with pH=1 was added to the second bottle, 100 ml of an alkaline solution of sodium carbonate with pH = 12 was added to the third bottle. The three containers were tightly closed for six weeks at a laboratory temperature of 25Cº. After six weeks, the films were removed from the aqueous solutions, then they were placed in glass desiccators containing anhydrous calcium sulfate for a week in order to obtain their dry weight. From these values, the weight loss was determined according to the following equation [12] :

Weight Loss (%) = ((Original weight – Dry weight) / (Original weight))x100

2.5-Water absorption test:

The films were weighed to obtain their original weight, then they were placed in a glass container, immersed in distilled water, and closed tightly for six weeks at a laboratory temperature of 25Cº. The films were removed from the water and dried with filter paper to remove the suspended droplets on their surface, then weighed to obtain the wet weight. The water absorption values were determined according to the following relationship [13,14]:

Water absorption (%) = ((Wet weight – Original weight) / Original weight)x100

2.6- Thermal stability test:

The films were weighed to obtain their original weight, then they were placed in an oven at 20°C, then the temperature was raised 10°C every hour, up to 180°C, and the weight of the films was determined at each temperature [10].

2.7- Air permeability test:

Air permeability: It is a measure of the ability of air to pass through the polymeric film (Specification No.: ISO5636-52003), It expresses the volume of air passing at a certain time through the polymeric film installed in the device in front of the air. The unit is SECONDS GURLEY. To perform the air permeability test, the device GENUINE GURLEY from rycobelgroup was used [11].

3 Results and Discussion:

3.1-Moisture content test:

Figures (2, 3, 4) show the results of the moisture content measurement test for polymeric films prepared from polyvinyl chloride and glycerin at a fixed percentage for all samples 5%, zinc oxide with a fixed percentage of 0.01%, and natural and modified Aleppo Pylone clay in different proportions, where the components were added as percentage of the weight of the PVC polymer. The prepared films were dried at three different drying degrees (150Cº, 100Cº, 60Cº).

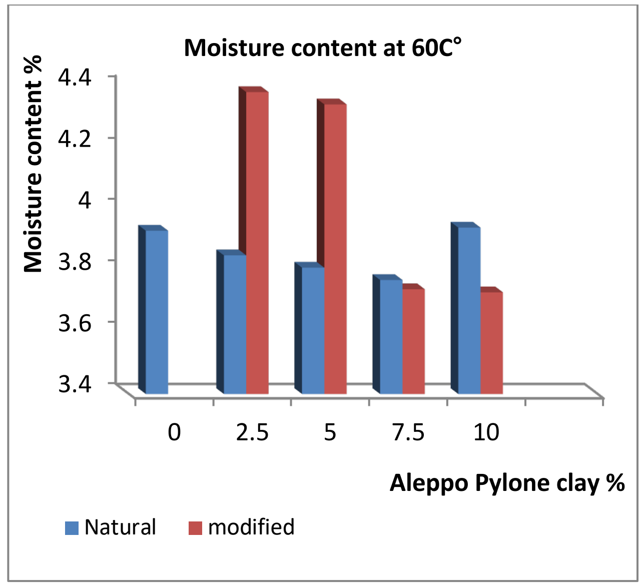

Fig. (2): Moisture test results for polymeric films dried at 60C

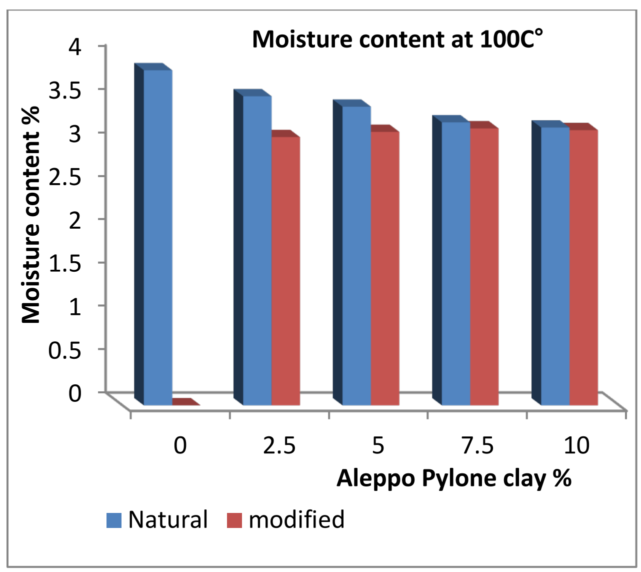

Fig. (3): Moisture test results of polymeric films dried at 100℃

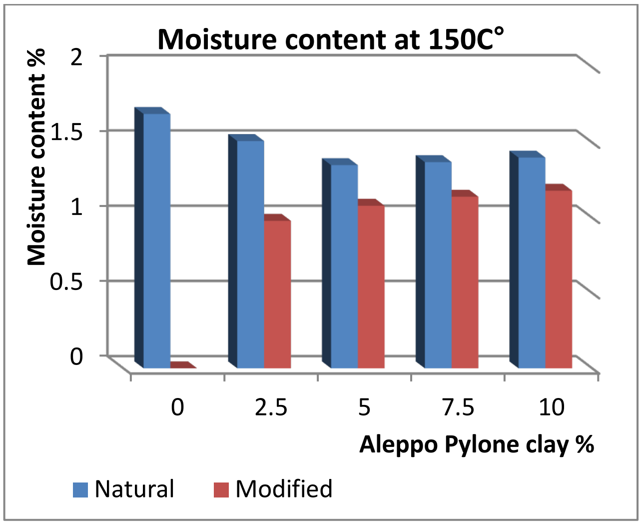

Fig. (4): Moisture test results of polymeric films dried at 150ºC

The results are shown in Figures (2, 3, 4): a decrease in the moisture content of the polymeric film, when adding granules of natural and modified Aleppo Pylon clay within the polymer structure more than pure polymer. Examples: In Figure (3), the results show a decrease in the moisture content (about 7.7%) when adding natural clay, and (about 20%) when adding modified clay at a clay rate of 2.5%. There is also a decrease when adding natural clay (about 10%), and (about 18%) when adding modified clay by 5% within the polymer structure. The results in Figure (4) show a decrease in the amount of moisture (about 10%) when adding natural clay and (about 42%) when adding modified clay by 2.5%, and a decrease (about 20%) when adding natural clay, and (about 36%) when adding modified clay by 5% within the polymer structure.

It is observed from the three forms that by increasing the drying degree of the films prepared in this research, the decrease in the amount of moisture content of the films in general increased, and the lowest amount of moisture content was for the polymeric film containing modified Aleppo pylone by 2.5% at the drying temperature of 150ºC. This is due to because of the placement and overlapping of the clay granules between the polymeric chains within the polymer structure, which reinforces the polymer structure and forms a barrier to prevent the penetration of moisture and give a more impermeable and moisture-insulating material. This crosslinking also increased by increasing the drying temperature of the films.

3.2- Migration test:

Forms (5, 6, 7) show the results of the migration test in distilled water for polymer films prepared from polyvinyl chloride polymer and glycerin at a fixed percentage for all samples (5%, zinc oxide) at a fixed rate of 0.01%, and the natural and modified Pylon clay in different proportions, where the ingredients were added as percentage by weight of the PVC polymer, dried at three different drying temperatures (60ºC, 100ºC,150ºC).

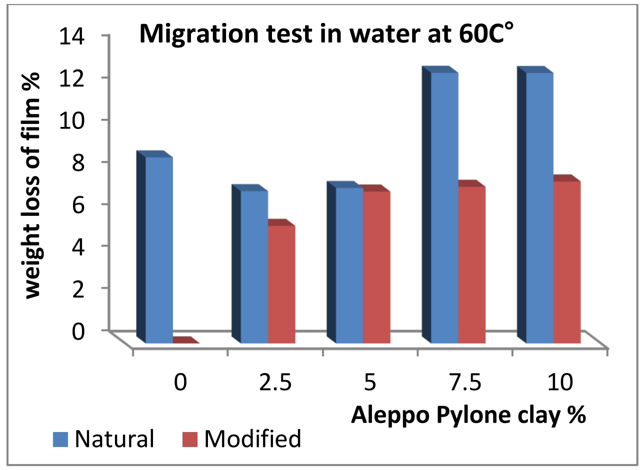

Fig. (5): Migration test results in distilled water for polymeric films dried at 60ºC.

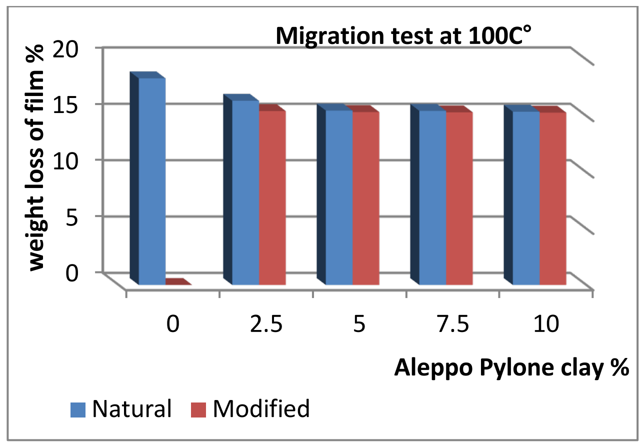

Fig. (6): Results of migration test in distilled water for polymeric films dried at 100ºC.

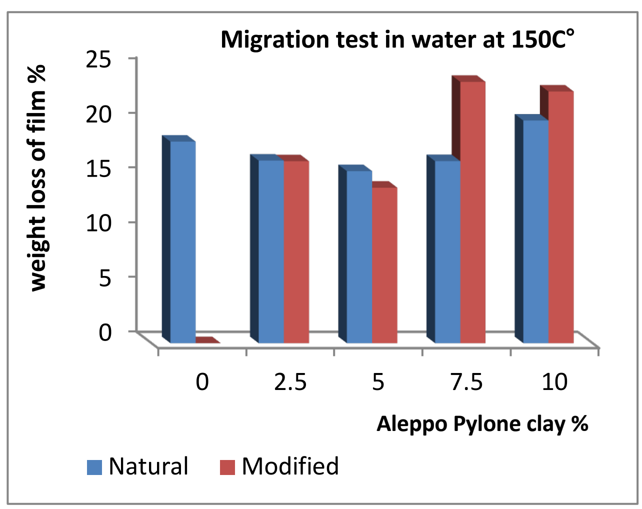

Fig. (7): Migration test results in distilled water for polymeric films dried at 150ºC.

Figures (5,6,7) show a decrease in the migration of components of the polymeric film in aqueous solutions when adding clay granules within the polymer structure more than the clay-free polymer. Figure (5) shows a decrease in the migration of components (about 18%) in distilled water when adding natural Aleppo Pylone clay by 2.5% and (about 36%) when adding modified Aleppo Pylone clay by 2.5% compared to the basic polymer (free of clay). Figure (6) shows a decrease in the percentage of migration of components in distilled water (about 10%) when adding natural clay at a rate of 2.5% and (about 15%) when adding modified clay at a rate of 2.5% compared to the basic polymer. Figure (7) shows a decrease in the percentage of migration of components (about 9%) when adding natural and modified clay at a rate of 2.5%.

Figure (8) shows the results of the migration test in an acidic solution of hydrochloric acid, where pH = 1. Figure (9) shows the results of the migration test in an alkaline solution of sodium carbonate, where pH = 12. Polymeric films were prepared from polyvinyl chloride polymer and glycerin at a fixed ratio of 5% for all samples, zinc oxide with a fixed percentage of 0.01%, and natural and modified Aleppo Pylon clay in different proportions, where the components were added as percentage of the weight of the PVC polymer, and dried at the drying temperature of 60ºC.

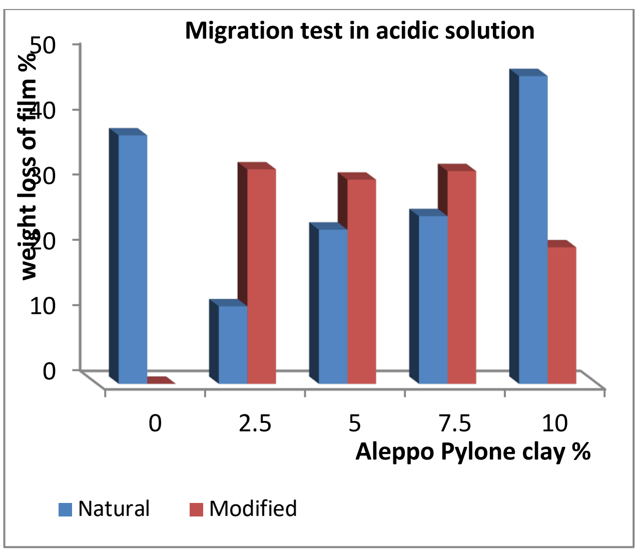

Fig. (8) *Migration test results in acidic solution of polymeric films dried at 60°C.*

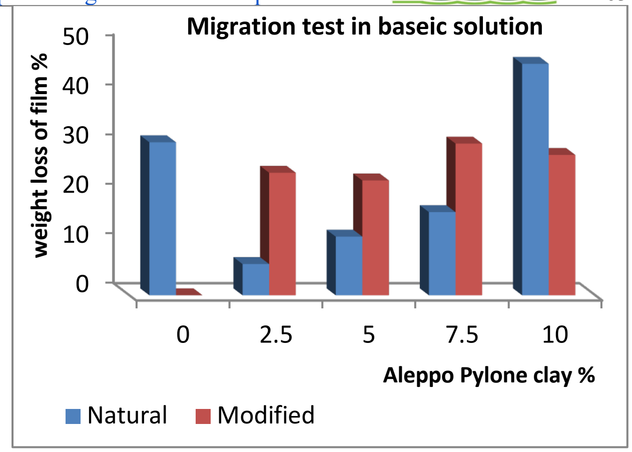

Fig. (9): *Migration test results in an alkaline solution of polymeric films dried at 60°c.*

It was observed from Figure (8) that in general, a decrease in the component migration ratio of the polymeric film prepared and dried at 60°C in acidic solution was observed when the clay granules were added within the polymer structure than the original polymer. A decrease in the migration of components from the polymeric film in an acidic solution was also observed (about 68%), by adding granules of natural clay by 2.5%, and (about 13%) by adding modified clay granules by 2.5%. Figure (9) also shows a decrease in the percentage of component migration of the polymeric film prepared and dried at 60°C in an alkaline solution when the clay granules are added within the polymer structure more than the original polymer. A decrease of (about 80%) is observed when adding natural clay granules by 2.5%, and (about 20%) by adding modified clay by 2.5%, compared to the basic polymer. thus, it can be said that the addition of clay granules reduced the migration rate of polymeric film components in Acidic and alkaline media. The reason is that clay particles are placed in the interspaces between the polymer chains giving a better cohesive and resistant structure. Consequently, a decrease in the percentage of migration of components from the polymeric film is observed while it is in acidic and alkaline aqueous media.

3.3-Water absorption test:

Figures (10,11,12) show the results of the water absorption test for polymer films prepared from polyvinyl chloride polymer and medical glycerin with a fixed percentage for all samples 5%, zinc oxide with a fixed percentage of 0.01%, and natural and modified Aleppo Pylon clay in different proportions. The components were added as percentage by weight of a PVC polymer, and dried at three different drying degrees (60ºC, 100ºC, 150ºC).

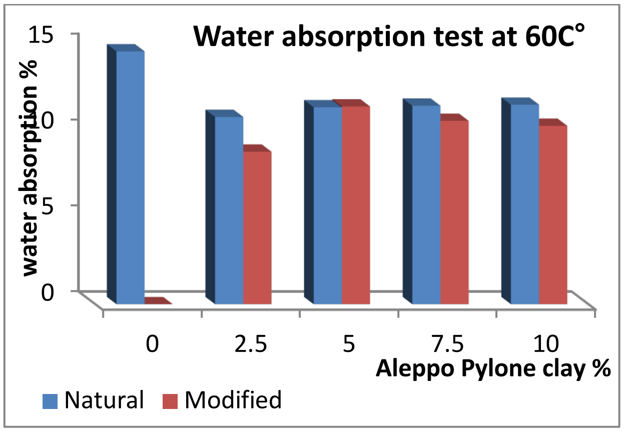

Fig. (10): Results of the water absorption test for polymeric films at 60C°

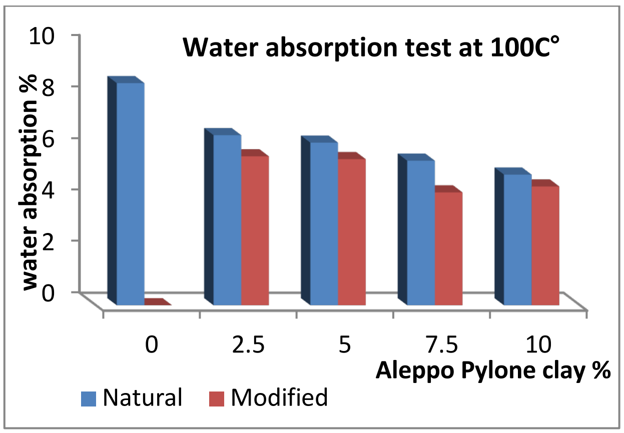

Fig. (11): Water absorption test results for polymeric films at 100ºC

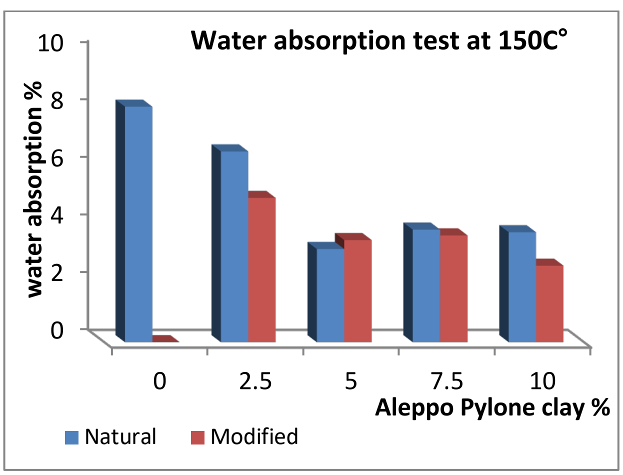

Fig. (12): Results of the water absorption test for polymeric films at 150C°

The results are shown in Figures (10,11,12): In general, a decrease in the water absorption ratios of the polymeric film when adding clay granules within the polymer structure is more than the base polymer. A decrease in the absorbance rates was also observed by raising the drying temperature of the polymeric films. (Examples of the figures): Figure (10) shows a decrease in the water absorption rate of (about 25%) when adding natural clay granules by 2.5% and (about 39%) when adding modified clay by 2.5%, compared to the basic polymer. Figure (11) shows a decrease in the water absorption rate of (about 23%) when adding natural clay by 2.5% and (about 32%) by adding modified clay by 2.5% compared to the original polymer. We notice from Figure (12) a decrease in the water absorption rate of (about 18%) by adding natural clay by 2.5% and (about 38%) when adding granules of modified clay by 2.5%, and (about 60%) when adding natural clay by 5%, and (about 56%) when adding modified clay by 5% compared to pure polymer. It is also shown from the forms that the lowest water absorption rate of the film containing natural clay is adjusted by 5% and the drying degree is 150ºC. Therefore, the addition of clay granules has improved the polymer material and reduced the polymeric film's absorption rate of water during long contact with aqueous solutions. This is because of the placement of clay granules in the interspaces within the polymer chains, where the clay granules act as a barrier that prevents the passage of water molecules while it is in aqueous solutions, hence increasing its impermeability and reducing its permeability to water molecules.

3.4-Thermal *stability test:*

Figures (13,14) show the thermal stability test results for the polymeric films prepared from polyvinyl chloride polymer and medical glycerin at a fixed percentage for all samples 5%, zinc oxide at a fixed rate of 0.01%, and natural and modified Aleppo Pylon clay in different proportions. The components were added as percentage of PVC polymer weight. The films were placed in an oven and the temperature was raised to 10Cº every hour. The weights of the films were recorded at each temperature.

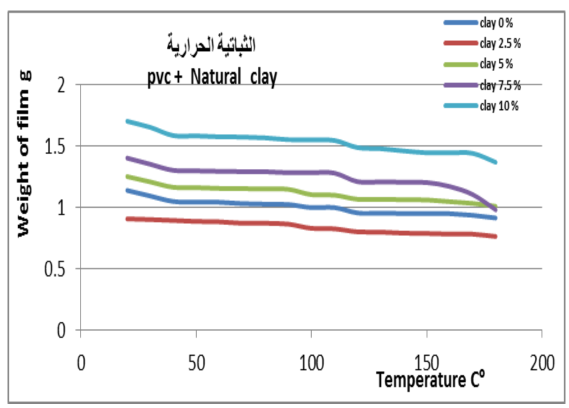

Fig (13): Thermal stability test results for polymeric films with natural clay

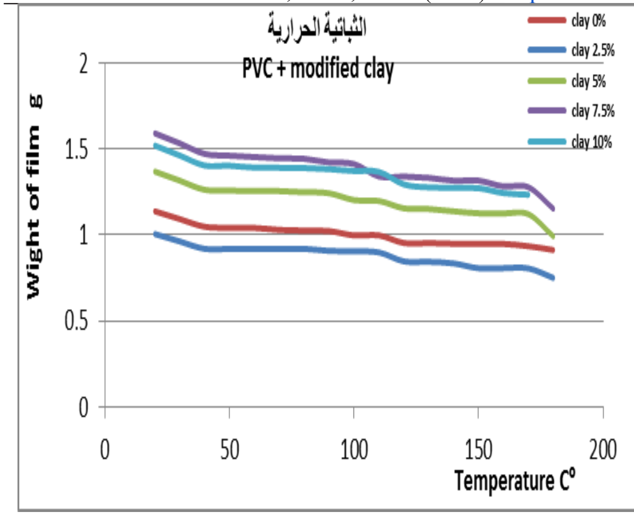

Fig. (14): *Thermal stability test results for polymeric films with modified clay*

Figures (13,14) show the decomposition curves of the polymer containing the different percentages of natural and modified clay with increasing temperature. All graphs lines show good thermal stability with increasing temperature, but the graph line of the 2.5% natural clay-containing polymeric film appears to be the most thermally stable among the graphs lines representative of the polymeric films containing natural and modified Aleppo Pylone clay.

Figures (15,16,17,18) show the thermal stability results of polymeric films with different ratios of natural and average Syrian clay, by calculating the weight loss of polymeric film at each temperature, from 20°C to 180°C, to obtain the weight loss for polymeric films according to the following equation:

Weight Loss (%) = ((Original weight – Dry weight) / (Original weight))×100

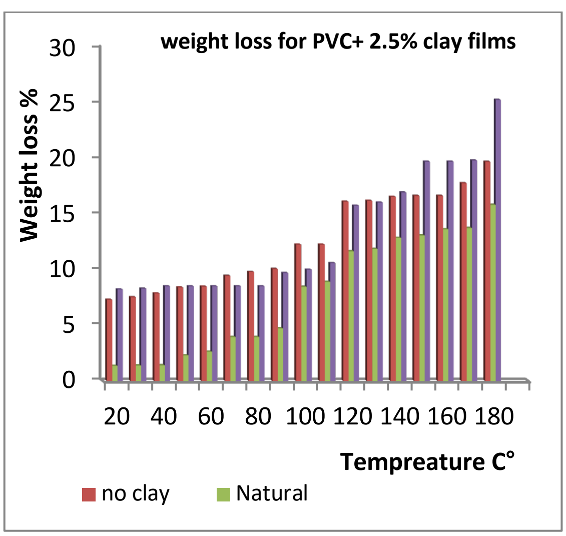

Fig (15): *Weight loss results of polymeric PVC films containing 2.5% clay*

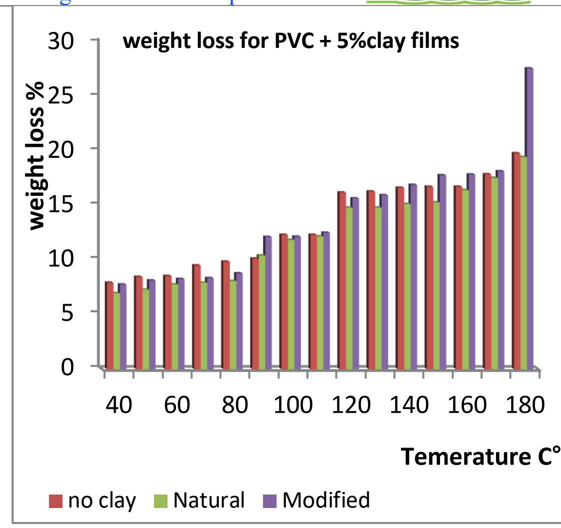

Fig. (16): *weight loss results of polymeric PVC films containing 5% clay*

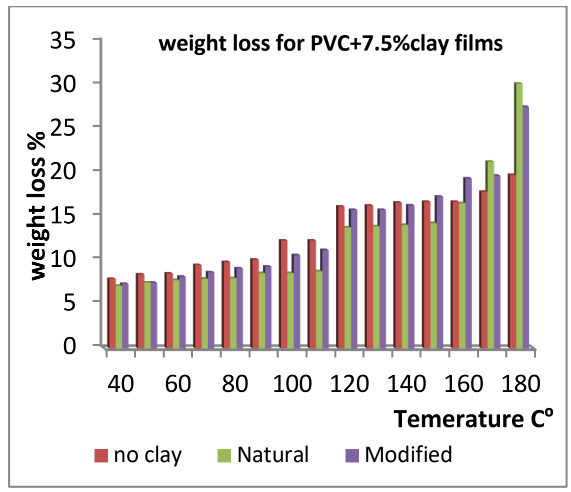

Fig (17): *Weight loss results of polymeric films containing 7.5% clay*

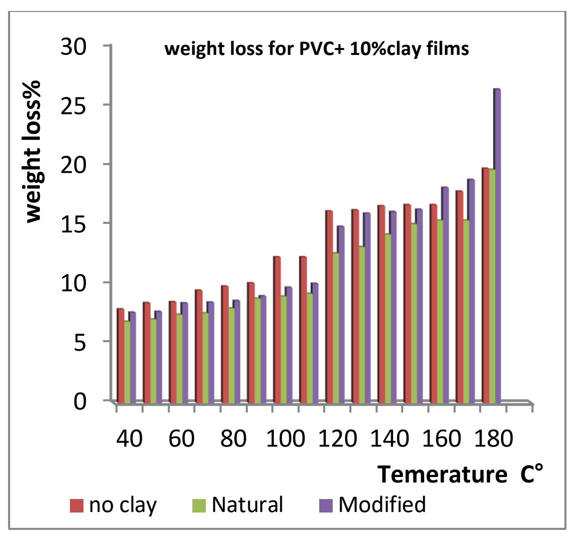

Fig. (18): *weight loss results of polymeric films containing 10% clay*

Fig (15,16,17,18) show an increase in the weight loss percentage of the polymeric film with an increase in temperature. The graphs also show a decrease in the weight loss of the polymeric film when adding clay granules within the polymer structure, especially with the addition of natural clay by 2.5% compared to the pure polymer with the temperature rises. This is because of the placement of the clay granules in the interspaces of the polymer chains, which bear a large part of the heat applied to the composite polymeric material, and thus the clay granules enhance the polymer's resistance to temperatures.

3.5-Air permeability test:
Figure (19) shows the results of the air permeability test for polymeric films prepared from polyvinyl chloride polymer and medical glycerin at a fixed percentage for all films 5%, zinc oxide at a fixed rate of 0.01%, and natural and modified Aleppo Pylon clay in different proportions. The components were added as percentage by weight of the polymer PVC, and the device gave air permeability results of the unit second Gurley within a time of three minutes, and the numbers appearing on the screen of the device indicate that the higher the value of the number, the more insulating and impermeable the sample against air permeability [11].

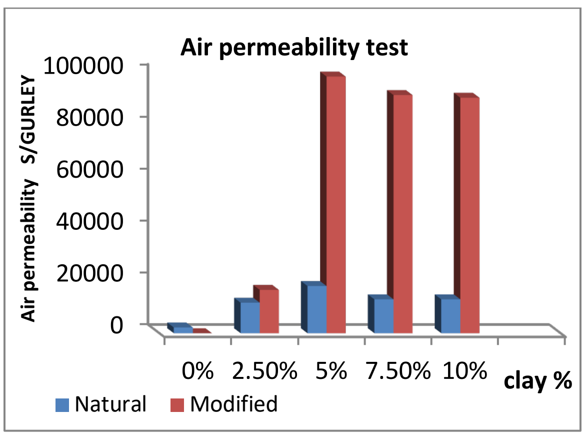

***Fig**. (19): Results of the air permeability test for PVC polymeric films and clay*

Figure (19) shows, in general, the increase in the percentage of impermeability and insulation against air permeability of the polymeric film when adding clay granules within the polymer structure more than the pure polymer. It was also observed that the percentage of air insulation increased significantly when adding modified clay granules by 5% within the polymer structure compared to the original polymer. This is because of the placement of clay granules in the interspaces within the polymer structure, and thus these granules form a barrier to change the air permeability pathways and prevent them from penetration, thus increasing the polymer's impermeability and air isolation.

4 The Results:

4.1-The results showed a good decrease in the amount of moisture content, the percentage of migration of components in aqueous solutions, the water absorption rate and the amount of air permeability of the polymeric film by adding natural and modified Aleppo Pylone clay. The best results were for the polymeric films dried at 150ºC compared to the basic polymer, in addition to good thermal stability.

4.2- The polymeric film containing natural Aleppo Pylone clay with a percentage of 2.5% gave the best results in the moisture content test, migration test in acid and alkali solution and thermal stability test. As for the polymeric film containing natural Aleppo pylone clay at 5%, it was the best in the water absorption test. The modified clay-containing polymeric film was presented at 5%, which was the best in the air permeability and Migration in the distilled water tests.

4.3-The insulating and impermeability properties of the PVC polymeric film are improved more than the original polymer by adding clay. Thus, the improved PVC can be used in the field of packaging.

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