A RCHAEOLOGICAL bones are exposed to various deterioration factors, so polymers are used to improve their properties and give more durability. Traditional pastes were applied and evaluated before. This study aims to evaluate some modified pastes in order to improve the properties of traditional pastes. Montmorillonite (MMT) was modified with amino acid and characterized in terms of Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction XRD and scanning electron microscope SEM. Nanocomposites of modified MMT with paraloid as acrylic polymer were evaluated using XRD to be used for gap filling and completion of archeological bones to give more resistance against surrounding environmental conditions.

Accelerated ageing were used for evaluation of modified pastes and estimated through change of color by UV spectrophotometer, FTIR, mechanical properties (tensile, elongation and compressive strength) and surface morphology by SEM.

The results confirmed that the modified pastes with modified mMMT nanocomposite showed good resistance against thermal ageing, and give high stability in terms of color change value, surface morphology and mechanical properties. As pastes with the mMMT gave negligible color difference as 0.98. In addition, the contact angles measurements reduced with smaller ratios as 12% and 7.5% than their corresponding pastes with no mMMT 22% and 11%, respectively. Moreover, pastes with mMMT showed higher density, lower porosity and lower water absorption and exhibit more resistance against thermal ageing.

Keywords: Archeological bone, Clay/polymer nanocomposite, Physico-mechanical properties

Introduction

Polymer nanocomposite is a composite material comprising a polymer matrix and an inorganic dispersive phase that is nanometric in scale (≤100 nm). Applying nanomaterial with nanoscale size permit to create high performance materials with novel properties and be compatible with other materials. So, these have gained tremendous attention to overcome the imitations of polymeric materials by preparing suitable nanocomposites with their superiority, excellent barrier properties, reinforcement of mechanical performance [1].

Nanoclay is one of silicon-based nanomaterials with a layer structure. The most common of which is montmorillonite MMT, hydrated Sodium Calcium Aluminum Magnesium Silicate Hydroxide (Na, Ca) (Al, Mg)\textsubscript{6} (Si\textsubscript{4}O\textsubscript{10})\textsubscript{3} (OH)\textsubscript{6} - nH\textsubscript{2}O [2-5].

Montmorillonite MMT was selected to be used with the polymers as nanocomposites and form interfacial bonding between polymer and nanoclay to improve the polymer performance in terms of rheological and physico-mechanical properties (elasticity, toughness) at high
temperature and control over ageing resistance. Due to the nanoscale dispersion and the high aspect ratios of the clays, polymer-layered silicate nanocomposites exhibit light weight, good dimensional stability, high heat resistance, high stiffness, high barrier properties, and improved fracture toughness and tensile strength [6-11].

The MMT/polymer nanocomposite can be synthesized through various preparation methods including in-situ template synthesis, solution intercalation, in-situ intercalative polymerization and melt intercalation. We used in this paper the solution intercalation method. Simply, it involves dissolving the polymer in a solvent and the clay is dispersed in the same solution by the aid of sonication and the polymer chains intercalate between the layers. The intercalated nanocomposite is obtained by solvent removal through vaporization or precipitation [12].

On the other hand, bone composition consists of organic material, collagen, non-collagenous protein, lipids and carbohydrates in addition to inorganic mineral as calcium hydroxyapatite Ca$_5$(PO$_4$)$_3$(OH)$_2$. Although its composition varies considerably with age and type of bone. Moreover, when bones are removed from the body they become unstable because they are moved from a relatively closed environment to an open one and can be broken down over time through physical breaking, decalcification and dissolution due to acidic soil and water [13-16].

The deterioration of the archaeological bone may occur as a result of weathering, fracturing, cracking, surface marks, microbial attack, abrasion, polishing and breakage and these factors occur in isolation or in combination [17, 18]. So the preservation of bone depends not on the length of time has been underground, but the type of bone and burial environment [19].

Examples of the polymer almost used in traditional pastes are polyvinyl acetate (PVA), paraloid B72 (ethyl methacrylate copolymer), polyvinyl acetate (PVA) emulsions, and in some cases Elmer’s Glue is suitable for the completion of missed parts in bones[20]. Stollman tested a mixture of glass micro-balloons and Paraloid B72 dissolved in acetone for filling the missing parts of blue whale skeleton [21].

The current article is concerned in modification of montmorillonite mMMT with amino acid and its using with paraloid B72, B82 as acrylic polymers to form MMT/paraloid nanocomposite. Then, studying the effect of applying these nanocomposites to improve the resistance of pastes that used in gap filling and completion the missing parts of archaeological bones against surrounding environmental conditions in terms of physico-chemical and optical properties.

**Materials & Methods**

**Materials**

Montmorillonite MMT (with CEC 92 mg.eq) was from southern clay products, inc., Gonzales, Texas. Paraloid B 72, paraloid B 82, calcium carbonate and glass micro-balloons were purchased from Rohm and Haas Co., USA. Hydrochloric acid was from Sigma-Aldrich-Germany. Xylene were from ADWIC- El Nasr pharmaceutical chemicals co-Egypt. L (+)-Asparagine amino acid AA was purchased from Pour biochimie-MERCK eurolab, made in CE.

**Preparation of MMT/polymer nanocomposites**

**Intercalated modification of MMT with amino acid:**

Montmorillonite MMT clay was modified with amino acid to organophilic clay. MMT (2.5 g) was dispersed in 250 ml distilled water for stirring for 1 h and then heated to 70 °C to obtain aqueous suspension of clay. The desired amount of L (+)-Asparagine amino acid AA (0.5 gm) (2x concentrations of the clay based on CEC) dissolved in 50 ml distilled water and 2 ml of hydrochloric acid was added into the mixture then stirring was continued for 4 h. The modified clay as a white precipitate was filtered and washed with distilled water. The obtained wet precipitate was dried in oven under vacuum at 80 °C for 24 h [22].

**Preparation of MMT/polymer nanocomposites by solution method:**

The weighed amount of modified MMT clay (1% of polymer) was suspended in 20 ml of xylene using ultrasonic apparatus. MMT suspension was mixed with solution of the polymer either paraloid 72 or paraloid 82 in xylene (with concentration of 15%) at a temperature of 80 °C and stirred for 2hr using magnetic stirrer at 500 rpm. MMT/polymer nanocomposites solution became ready to be applied [23].
Preparation of pastes

Pastes no. 1, 2: consist of nanocomposites modified montmorillonite mMMT/paraloid B72; which was used as adhesive; and filler as calcium carbonate CaCO₃ or glass microballoons was added to adhesive in ratio 1:1 and 1:3 in pastes 1 and 2, respectively.

Pastes no. 3, 4: consist of paraloid B 82 which was used as adhesive; and filler as calcium carbonate CaCO₃ or glass microballoons was added polymer in ratio 1:1 and 1:3 in pastes 3 and 4, respectively.

Pastes no. 5, 6: consist of nanocomposites mMMT/ paraloid B 82; as adhesive; and filler as calcium carbonate CaCO₃ or glass microballoons in ratio 1:1 and 1:3 in pastes 3 and 4, respectively.

Pastes were prepared at room temperature. A stainless template was made to mold pastes, and the size of samples were adjusted as 10 cm length × 2 cm width × 0.5 cm thickness. Pastes were left for a week to dry at room temperature.

Thermal ageing

The prepared pastes were placed in an oven (PID system, Type: M 120 - VN). Pastes were exposed to thermal ageing at 100°C for various ageing time from 1 day to 8 days [24, 25].

Investigation Methods

Change of color by spectrophotometer

Color changes of the studied samples were measured by spectrophotometer Optimatch 3100 model, from the SDL Company. The dimension of the measured area of each sample was (1x1) cm². The total color difference ΔE* between two color stimuli ΔE* = [(ΔL*)² + (Δa*)² + (Δb*)²]¹/² [26, 27]. Where the colors are given in CIE Lab coordinates, L* corresponding to the brightness (100 = white, 0 = black), a* to the red–green coordinate (positive sign = red, negative sign = green), and b* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue).

Fourier Transform Infrared Spectroscopy (FTIR)

The changes of pastes samples before and after ageing were determined by using FTIR spectrophotometer (JASCO-FT/IR-6100) in the range of 4000–400 cm⁻¹ using KBr powder.

Each sample was mixed with KBr and placed in a Drift cell [28]. FTIR Spectra were assigned for samples (standard (0 day) & after heat ageing (8 days)) from each paste.

Tensile and elongation measurements:

Tensile strength and elongation were determined by using an electronic tensile testing machine (Zwick 1425) and was calculated by using the following equation: Tensile strength (T.S) = (F/t.w) MPa, Where F= load applied to rupture, t= the thickness of the specimen and w= width of the specimen. Load cell: 500MPa and the Cross head speed: 100mm/min.

At the break, the elongation

n is expressed as the percent of the original bench mark length attained beyond rupture. Ultimate elongation E % = ((L-L0)/ L0) 100, Where: L = Length of the specimen at the moment of rupture and L0= the length between bench marks accordingly to ASTM, D 412-66 T [29, 30].

Compressive strength

Measurement of compressive strength was taken by the TINIUS OLSEN H5KT dynamometer, accordingly to ISO 2062 standard. Load cell: 250MPa and the Cross head speed: 200mm/min [31].

Investigation of the surface morphology by a scanning electron microscope SEM:

The surface morphology of the pastes samples studied were examined by scanning electron microscope (SEM) using a QUANTA FEG250 model- Japan. All samples were conditioned under the standard atmospheric conditions for 24 hours [32].

X-Ray Diffraction (XRD)

X-ray diffraction patterns of model (XPERT – PRO – PANalytical – Netherlands) using a diffract meter equipped with a rotating target X-ray tube and a wide-angle goniometer. The X-ray source was Ka radiation from a copper target with graphite monochromater. The X-ray tube was operated at a potential of 45 kV and a current of 40 mA. The range (2hr) of scans was performed.
from 10 °C to 80 °C at a speed of 4º per minute at increments of 0.05º [13].

Density, porosity and water absorption

The measurement of water absorption, porosity and density were attempted in accordance with Al-Dosari et al. [33, 34], the size of the samples was 2cm (length) × 2cm (width) × 0.5cm (thickness). Tests were carried out on samples before and after heat ageing. The samples were completely immersed in deionized water at room temperature. After 24h, the samples were taken out, wiped with tissue paper carefully and weighed immediately.

Density was measured as weight (g) over volume (cc) with volume determined by displacement according to the equation [35]:

\[ \text{Density} = \frac{W}{V} = \ldots \text{g/cm}^3 \]

where W is the sample weight and V is the sample volume.

Porosity was measured according to the equation [35]

\[ \text{Porosity} = \frac{W_2 - W_1}{V} \times 100 = \ldots \% \]

where, \( W_1 \) is the mass of the sample before immersion, \( W_2 \) is the mass of the sample after immersion in water for 24h and V is sample volume.

Water absorption measurements were carried out according to (UNI 10859, 2000) [36] according to the equation: [37]

\[ \text{Water absorption} = \frac{W_2 - W_1}{W_1} \times 100 = \ldots \% \]

where, \( W_1 \) is the mass of the sample before immersion and \( W_2 \) is the mass of the sample after immersion in water for 24h.

Contact angle measurement (wettability)

Contact angle of pastes samples was determined by SDL image analysis high resolution video camera microscope and the sample was put on a leveled stage. 5μl distilled water was applied on the sample. The image of the water droplet was captured. After the imaging process, the contour was applied to fit the water droplet. The tangent at the point of contact between the water droplet contour and surface of the sample was drawn and the inner angle of the tangent and the sample surface was measured manually using protractor [31].

Results and Discussions

Intercalated modification of MMT

To have a homogeneous dispersion in hydrophobic polymer matrix, the hydrophilicity of Montmorillonite MMT was decreased through ion-exchange reactions using L (+)-Asparagine amino acid, which, in turn, lower the hydrophilicity of the silicate surface and also increase the interlayer distance. The reaction process was carried out at a temperature of 70°C for 90 minutes in a batch reactor equipped with a magnetic stirrer rotating at a speed of 300 rpm. The amino acid treated MMT was collected as a white ppt and dried under vacuum. This intercalation could be confirmed by IR-spectra, X-ray diffraction and scanning electronic microscope SEM.

The FT-IR spectra for each of the L (+)-Asparagine amino acid, neat MMT and the modified MMT (AA treated MMT) is represented in Figure 1. The IR spectra for the neat MMT sample showed its absorbance at various wave numbers. At 3600 cm⁻¹ band, the peaks for both neat and modified MMT samples 2, 3 are the same. But within 1600 to 3000 cm⁻¹ band region, the peaks are well pronounced on the amino acid treated MMT while such peaks are not found in untreated MMT spectra.

The XRD patterns of neat MMT and modified MMT are illustrated in Figure 2 and it is observed that XRD of the neat MMT shows a diffraction peak at about 2θ = 6.5064, corresponding to a d-spacing of 13.5 nm. The data for d-spacing are listed in (Table 1) which shows that the diffraction peaks of the modified MMT sample are shifted to smaller angel and the d-spacing increased compared with the neat MMT. This indicates that mMMT was successfully intercalated homogeneously with L (+)-Asparagine amino acid [38].

The transformation in surface morphology of both of the neat MMT and modified MMT was examined by scanning electron microscope SEM and their images are represented in Figure 3. The SEM images showed an obvious surface morphology transformation and interlayer spacing that confirm the successful intercalation of MMT by the amino acid and increasing the space between layers.

MMT/polymer nanocomposite:

The weighed amount of modified MMT
Figure 1: FT-IR Spectra of Amino acid (1) neat MMT (2) and modified MMT (3).

Figure 2: XR diffraction patterns for the neat MMT clay (A) and modified MMT clay (B)

Figure 3: SEM of the neat MMT (A) and the modified MMT (B)

was suspended in solution of the polymer either Paraloid 72 or Paraloid 82 in xylene solvent at a temperature of 80 °C and stirred for 2 hour to form MMT/polymer nanocomposite. The nanocomposite formation was proved by X-ray diffraction in Figure 4 that shows XRD patterns for the MMT composites with both of Paraloid 72 and Paraloid 82. It could be observed the absence of any sharp crystalline peak that characterize the MMT indicating homogenous dispersion in the composite which refer the formation of amorphous complex [39]. From XRD results, it could be concluded that the inter-gallery spacing of MMT facilitates the entry of the polymer matrix molecules into the galleries, as the hydrophilic MMT surface changed to an organophilic surface.

Modified pastes

Change of color

Lightness (L*): The data obtained from color change measurements were listed in table 2 and 3. Generally, it was clear that lightness of all pastes decreased with increasing thermal aging time. In the case of paraloid 82, pastes with mMMT (pastes 5, 6) showed slightly lower lightness compared with the corresponding pastes without mMMT (no.3, 4), but lightness of pastes with mMMT decrease with lower percentage compared to others with no mMMT. Pastes with CaCO$_3$ as filler recorded higher lightness than that with microballones and decrease with higher percentage with thermal ageing time.

In the opposite, it was observed that for paraloid 72 pastes with CaCO$_3$ exhibit lower lightness than that with microballons. And that with clay recorded slightly higher lightness than others with no clay as measured in the previous search but still decrease with lower percentage [31].

Red – green color (a*): It was noted from Tables 2 & 3 that the values obtained were in green color for all pastes (the results were minus). And the value (green color) slightly decreased with increasing the ageing time for all pastes.

Yellow – blue color (b*): The data obtained shows that the yellow color slightly increased with increasing the ageing time with all pastes studied.

Total color difference (ΔE): Generally, it could be concluded from Tables 2 & 3 that the color changes with thermal ageing for all pastes [40-42]. Colors became highly variable with the time exposure to high temperatures that may be explained that the heat exposure causes chemical and mechanical changes to materials that result in discoloration [43, 44].

But pastes with MMT/polymer nanocomposite as adhesive either paraloid 72 or 82 were the highest resistant to colour change with thermal ageing in which the changes were with negligible values, by comparing pastes no. 3, 4 with pastes no. 5, 6. Also, comparing pastes no. 1, 2 with others obtained in our previous work without MMT [31], we find that the presence of MMT nanocomposite caused increasing the lightness and increase the color resistance against thermal ageing.

In addition, pastes with micro-ballons as filler no. 2, 4 ,6 are more resistant to colour change with thermal ageing compared with pastes with CaCO$_3$ filler pastes no. 1, 3, 5. So, it was noted that paste no. 3 was with the highest color changes and followed by pastes 1, 5, 4, 2 and the lowest change was obtained from the paste 6.

It was common that one of the most important guidelines for the material used in conservation must not alter so as to affect the object physically or chemically, and should have a long service life [45]. So, the addition of modified MMT as nanoclay could provide indirect protection against the deleterious effect of weathering, resulting in less lightening [46]. According to Horie and Eshraghi et al. [47, 48] paste no. 6 with MMT/paraloid 82 is the highest resistant followed by pastes 2, 4, 5, 1 and the highest changes was obtained from the paste no. 3.

Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra of the pastes before and after ageing were presented in Figure 5 to show the effect of thermal aging on the structure of pastes with and without MMT. For paste no. 1, it was noted that absorption of Calcium Carbonate after ageing was very close to that before ageing indicating the stability of Calcium Carbonate during ageing process. For paraloid 72, C-H stretching bands didn’t change at 2924.5 cm$^{-1}$. C=O stretching bands shifted to little high value from 1737.6 to 1739.5 cm$^{-1}$ and its intensity increased after thermal ageing due to oxidation effect. C-O stretching bands were shifted to lower value from 1129.1 to 1108.9 cm$^{-1}$. O-H and Si-O stretching bands in montmorillonite clay (MMT) didn’t change after ageing.
**TABLE 1: XRD Data Obtained for the neat MMT and the modified MMT**

<table>
<thead>
<tr>
<th></th>
<th>2θ</th>
<th>d-space nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat MMT</td>
<td>6.5064</td>
<td>13.5</td>
</tr>
<tr>
<td>Modified MMT</td>
<td>6.2465</td>
<td>14.5</td>
</tr>
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</table>

**TABLE 2: Color changes of pastes No. 1, 2 studied before and after heat ageing**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ageing days</th>
<th>Paste (1) Color changes</th>
<th>Paste (2) Color changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L*</td>
<td>a*</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>87.76</td>
<td>-0.3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>87.84</td>
<td>-0.3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>86.98</td>
<td>-0.29</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>86.25</td>
<td>-0.29</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>86.1</td>
<td>-0.29</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>86.08</td>
<td>-0.28</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>85.51</td>
<td>-0.28</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>85.32</td>
<td>-0.27</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>84.93</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

**TABLE 3: Color changes of pastes No. 3, 4, 5 and 6 studied before and after heat ageing**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ageing days</th>
<th>Paste (3) Color changes</th>
<th>Paste (4) Color changes</th>
<th>Paste (5) Color changes</th>
<th>Paste (6) Color changes</th>
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<tr>
<td></td>
<td></td>
<td>L*</td>
<td>a*</td>
<td>b*</td>
<td>ΔE</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>95.66</td>
<td>-0.21</td>
<td>1.47</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>95.32</td>
<td>-0.2</td>
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<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
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<td>0.48</td>
</tr>
<tr>
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<td>3</td>
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<td>1.22</td>
</tr>
<tr>
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<td>4</td>
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<tr>
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<td>7</td>
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<tr>
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<td>8</td>
<td>92.8</td>
<td>-0.17</td>
<td>1.85</td>
<td>2.89</td>
</tr>
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</table>

*Egypt. J. Chem. 63, No. 5 (2020)*
Figure 4: XRD patterns for MMT/Paraloid 72 (A) and MMT/Paraloid 82 (B) nanocomposites

Figure 5: FTIR spectra of pastes before (1) and after ageing (2): (A) paste no. 1; (B) paste no.2; (C) paste no. 3; (D) paste no. 4; (E) paste no.5; (F) paste no. 6
Paste no.2, Glass micro-balloon Si-O-Si stretching band shifted to lower value from 1093.4 to 1085.7 cm\(^{-1}\). Paraloid B–72, C-H stretching bands shifted to high value from 2924.5 to 2927.4 cm\(^{-1}\). C=O stretching bands shifted to little lower value from 1737.6 to 1736.6 cm\(^{-1}\). O-H stretching bands for MMT didn’t change, but its intensity decreased after thermal ageing due to loss of water.

Paste no.3, for paraloid B-82, C-H stretching band shifted to lower value after ageing from 2929.3 to 2925.5 cm\(^{-1}\). C=O stretching bands shifted to little high value from 1732.7 to 1735.6 cm\(^{-1}\). C-O stretching bands shifted to higher value from 1161.9 to 1172.5 cm\(^{-1}\) and a new band appeared after thermal ageing at 1627.6 cm\(^{-1}\) due to oxidation.

Paste no.4, for Glass micro-balloon Si-O-Si stretching band after ageing shifted to very high value from 1042.3 to 1081.9 cm\(^{-1}\). For paraloid B–82, C-H stretching bands didn’t change at 2925.5, C=O stretching bands shifted to high value from 1734.7 to 1737.6 cm\(^{-1}\) and its intensity increased after thermal ageing due to oxidation effect. C-H bending bands shifted to very high value from 1427.1 to 1447.3 cm\(^{-1}\) Peaks before ageing between 1182.2 to 1042.3 cm\(^{-1}\) broader than that after ageing

Paste (5): paraloid B-82, C-H stretching bands didn’t change at 2925.5, C=O stretching bands shifted to higher value from 1734.7 to 1737.6 cm\(^{-1}\), C-O stretching bands shifted to high value from 1169.6 to 1172.5 cm\(^{-1}\). Peaks before ageing between 1734.7 to 1169.6 cm\(^{-1}\) completely changed after ageing. For MMT, O-H stretching bands shifted from 3441.4 to 3437.5 cm\(^{-1}\) and its intensity increased after thermal ageing due to oxidation effect.

Paste (6): for glass micro-balloon Si-O-Si stretching band didn’t change after ageing at 1079.9 cm\(^{-1}\); it means that there is stability for glass micro balloons after modification by nano MMT clay. Paraloid B-82, C-H stretching bands shifted to high value from 2924.5 to 2929.3 cm\(^{-1}\), C=O stretching bands didn’t change value and its intensity decreased after thermal ageing due to loss of water. For MMT, O-H stretching bands after ageing were shifted to high value from 3434.7 to 3438.5 cm\(^{-1}\) and its intensity decreased after thermal ageing due to loss of water.[49,50].

**Tensile and Elongation measurements:**

**Tensile strength:**

Data obtained are represented in Figure (6 A) and it was observed that, generally, tensile strength decreased with increasing aging time for all pastes studied but with variable values and it could be attributed to that accelerated thermal aging processes produced weak molecules and increased brittleness [51, 52]. The data in details show that before ageing, tensile strength of pastes no. 1, 3, 5 are with higher value than pastes no. 2, 4, 6, respectively, while the tensile strength of the first group decrease with ageing faster than second group. Ex., at 100°C after 8 days of exposure, the tensile strength decreased in paste no.1 by 54% and in paste no. 2 by 45%. Also, the tensile strength decreased in paste no.3 by 52% and in paste no. 4 by 45%. The tensile strength decreased in paste no.5 by 44% and in paste no. 6 by 30% . It was observed that pastes with clay showed resistance to the decay of the tensile with ageing time.[53]

**Elongation:**

It was clear from the data obtained (Figure 6 B) that, generally, elongation decreased with aging time for all pastes studied. It was noted that before ageing, elongation of pastes no. 1, 3, 5 are with higher value than pastes no. 2, 4, 6, respectively. While elongation values of the first group those with CaCO\(_3\) decrease with ageing faster than second group those with microballons. Ex., at 100°C after 8 days of exposure, the elongation decreased in paste no.1 by 48% and in paste no. 2 by 37%, in paste no.3 by 57% , in paste no. 4 by 42% , in paste no.5 by 43% and in paste no. 6 by 29%. It was noted that pastes with modified MMT enhance the mechanical properties of pastes with respect to those with no mMMT. [53]

According to results above, the presence of montmorillonite as mMMT/polymer nanocomposite enhanced the physico-mechanical properties of polymer and resist their decay over thermal aging [54-58].

**Compressive strength**

The data obtained are represented in Figure (6 C) that show, generally, the decrease of compressive strength with increasing aging time for all pastes studied. Compressive strengths of pastes no. 1, 3, 5 are with higher value than pastes no. 2, 4, 6,
Figure 6: (A) Tensile strength, (B) Elongation and (C) Compressive Strength
The increase in gaps on the surface. While, paste 3 that doesn’t show the lowest coarse and little gaps were formed. It was noted shown in (B images) and the surface became of calcium carbonate and nanocomposite as structural reconfiguration and promote changes under impact conditions [61]. Also, leads to a deterioration of the mechanical properties responsible for the surface effect and contribute to the deterioration of the mechanical properties under impact conditions [61]. Also, leads to a structural reconfiguration and promote changes in surface morphology. The aging mechanism responsible for the deformation and loss of sample surface [62-64].

Investigation of the surface morphology by SEM:

Surface morphology of pastes were investigated using the scanning electron microscope to provide more details about the state of the surface before and after ageing process. It could be concluded that the representative SEM images (Figure 7) could show that high temperature aging relaxes the intrinsic molecular stresses also degradation of materials at elevated temperatures are predominantly responsible for the surface effect and contribute to the deterioration of the mechanical properties [56].

It could be concluded that generally there is a considerable reduction in compressive strength with ageing [56] that may be attributed to that long term exposure to elevated temperatures resulted in loss of water leading to a decrease in compressive strength resistance [59]. On the other hand, pastes involved mMMT/polymer nanocomposite suggested excellent compressive strength resistance specially paraloid 82 (paste 6 has the most compressive strength resistance) where pastes with low compressive strength are required for completion and filling cracks processes [60]. So, the addition of mMMT enhance the properties of pastes such as stiffness, hardness and aging resistance [7].

Contact angle (wettability)

The images and values of contact angles on pastes’ samples were tabulated (Table 4). Generally, it was shown that the contact angle values of the pastes were varied with ageing time where its value decreased with the time. This means that the wettability increased with increasing the ageing time. However, they varied by different ratio, it was shown that the increase in contact angle hence the hydrophobicity is mainly attributed to the difference in both the chemical properties of polymer surface and its surface morphology.

When comparing pastes no.1 and 2 with reduction in contact angle as 18.3% and 9.2% with their corresponding samples in the previous paper [31] 29% for paste 1 without mMMT and 12.2% for paste 2 without mMMT. And comparing pastes 5 and 6 with reduction in contact angle as 12% and 7.5% with their corresponding pastes without mMMT paste 3 (22%) and paste 4 (11%), respectively. It was observed that pastes that contain the modified MMT/paraloid nanocomposite (pastes 2, 6) are with, somewhat, time-independent contact angle in comparison to other pastes in absence of mMMT. Where the modified MMT is responsible for increasing the...
Figure 7: Scanning electron micrographs of pastes (1-6) used; (A) the paste before ageing and (B) the paste after ageing.
It was noted that pastes with micro-balloons as filler (pastes no. 2, 4, 6) showed much lower ratio of reduction than their corresponding pastes (1, 3, 5) that contain CaCO₃ filler. The reduction in the contact angle value after 8 days of heat ageing was calculated for each sample and they were 18.3%, 22% and 12% for pastes 1, 3 and 5 respectively. 9.2%, 11% and 7.5% for pastes 2, 4 and 6 respectively. Jose, A. J. and Alagar, M. [66] proved that the raise in contact angle value or the hydrophobicity is related with the surface roughness that can be resulted from the addition of modified clay or from the nature of microballone with respect to CaCO₃.

Density, porosity and water absorption

Density

It was clear from the data obtained from density measurement (Table 5) that the paste no. 5 recorded the highest density, followed by pastes no. 1, 3, 6, 4, 2 consequently. So, samples with clay and CaCO₃ component recorded highest value of density with respect to samples with microballons component. Generally, it was noticed that the density decreased with increasing thermal ageing time. The reduction in density of pastes after 8 days of thermal ageing was calculated as 3.3% for paste no. 1, 2.4% for paste 2 (the corresponding pastes without clay recorded a reduction as 8.6% and 2.6%, respectively) [31], 2.7% for paste 3, 2.2% for paste 4, 1.8% for paste 5, and 0.8% for paste 6. It could be noted that samples with clay enhance more resistant to decay of density with thermal ageing.[67]

Porosity

The data obtained from porosity measurement showed that paste no. 1 recorded the highest value of porosity, followed by paste 3, 5, 4, 2 and 6 consequently. Generally, the porosity increased with increasing the thermal ageing time. The increasing in the porosity of pastes used after 8 days of thermal ageing were calculated as 69.7% for paste no. 1, 53.3% for the paste No. 2 (the corresponding pastes without clay recorded an increase as106% and 62.8%, respectively), [31] 65% for paste no. 3, 56.3% for paste no. 4, 32% for paste no. 5, and 27.3% for paste no. 6. It could be concluded that samples with clay exhibit lower porosity values and more resistance against time of thermal ageing.

Water absorption

It was clear from Water absorption measurement that paste no. 1 recorded the highest water absorption followed by paste 3, 2, 4, 5 and 6 consequently. Generally, Water absorption increased with increasing the thermal ageing time. The percentage of increasing the water absorption of pastes after 8 days of thermal ageing was 93.4% for paste no. 1, 56% for paste 2, (corresponding to 125.5% and 67% for the same pastes with no clay, respectively) [31], 60.4% for paste 3, 42.3% for paste 4, 38.6% for paste 5, and 32% for paste 6. It was noted that the incorporation the modified MMT increase the hydrophobicity of pastes and hence could reduce the water absorption and increase its sustainability against the thermal ageing time. [67]

Conclusion

It can be concluded that employing modified MMT with paraloid 72 or 82 as nanocomposite and their using as adhesive in filling pastes with glass microballoon filler enhanced their chemical and physical properties and achieved high thermal ageing resistance. Where, the presence of mMMT exhibited a good resistance against thermal ageing with the negligible change of color and high stability, it has the lowest change value in mechanical properties and there is almost no change in the surface morphology before and after exposure to thermal ageing with respect to pastes with no mMMT. Moreover, samples with mMMT enhanced the highest value of contact angle and density and are more resist to the reduction with ageing time, however, are with the lowest porosity and water absorption values and are more resist for raising over ageing. These may be due to the interfacial layered bonding between polymer and mMMT improve thermal resistance and improve outstanding mechanical performance.
### TABLE 4: Values of contact angle (wettability) for studied pastes samples before and after accelerated heat ageing

<table>
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<th>Samples</th>
<th>Ageing time (days)</th>
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<th>Paste (4)</th>
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### TABLE 5: Density, porosity and water absorption of pastes studied before and after heat ageing

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<td>Water absorption (%)</td>
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Environmental Laboratory, Bechtel, BWXT Idaho, LLC, September (2004).


تتعرض العظام الأثرية للعديد من عوامل التلف. لذا تستخدم البوليمرات لزيادة تح신 خصائصها لتعطي ديمومة أعلى. وقد تم تطبيق وتقييم العجائن التقليدية من قبل. وتهدف هذه الدراسة إلى تقييم بعض العجائن التقليدية المعدلة من أجل تحسنتها. لذلك تم تحدي خواص طلقة المتمورولونيت باستخدام حامض أميني (وقد تم توصيف المتمورولونيت من خلال مطياف الأشعة تحت الحمراء (FTIR) وحيد الأشعة (XRD)، ودراسة المظهر السطحي باستخدام الميكروسكوب الإلكتروني الماسح (SEM). 

وقد تم عمل عجائن من المركبات النانوية من مادة المتمورولونيت المعدلة مع البارا بيد 72 (أكريلك بوليمر) وتقييمها من أجل استخدامها لمليء الفجوات واستكمال العظام الأثرية لإعطاء مقاومة أعلى ضد الظروف البيئية المحيطة.

وقد تم عمل تقديم صناعي باستخدام الحرارة لتقدير هذه العجائن، كما تم استخدام بعض أساليب الفحص والتحليل لتقييم بعض الخصائص لهذه العجائن مثل التغير اللوني. التحليل بمطياف الأشعة تحت الحمراء (FTIR)، قياس الخصائص الميكانيكية (قوة الشد ونسبة الاستطالة وقوة الانضغاط) ودراسة المظهر السطحي باستخدام الميكروسكوب الإلكتروني الماسح (SEM).

أكدت النتائج أن العجائن المعدلة مع المتمورولونيت النانوية أظهرت مقاومة أعلى للتدفق الحراري. وتعطي ثبات أعلى فيما يخص التغير اللوني (حيث أن الاختلاف في اللون الكلي كان طفيفا بمقدار 0.98) والمظهر السطحي والخواص الميكانيكية. ويشير انخفاض نتائج زاوية التلامس (CONTACT ANGLES) إلى زيادة صلابة السطح. بالإضافة إلى ذلك فقد أظهرت العجائن التي تحتوي على الطاقة في الصورة النانوية أعلى كفاءة. وأعطت مسامية وامتصاص مائي قليل، وأظهرت مقاومة عالية للتدفق الحراري.