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Effect of Silicon Oxide Nan Particles (SIO2) on Mechanical and Tribological Properties of Polymethyl Methacrylate (PMMA)

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Abstract:
The urban planning policy that has been applied in the city of Constantine has contributed to the creation of an urban dynamic towards its periphery and satellite cities. The policy sought to solve the problem of urban growth, in the face of concern about the preservation of agricultural land and the spread of areas of natural hazards such as landslides and floods. In this context, satellite cities appear as a strategic option to solve this problem according to the direction of successive urban development plans. Satellite cities are supposed to contain urban growth; in Constantine, this is achieved through the redirection of surplus population and the provision of extensive land for urbanization. These opportunities offer significant possibilities for extension and the realization of different residential and equipment projects. The aim of this paper is to highlight the variety of relationships as well as their intensity with the mother city, without forgetting to appreciate the degree of dependence on Constantine.This paper studies the effect of adding silicon oxide nanoparticles (SiO_2) with ratios (1wt%, 2wt%, 3wt%, and 4wt %) and an average particle size of 10-30 nm on the mechanical and tribological properties of polymethyl methacrylate. The dissolving and casting method in glass molds was used to prepare samples of neat and reinforced PMMA. The influence of the addition of silicon oxide nanoparticles on hardness and ultimate tensile strength of polymethyl methacrylate was studied using shore D hardness test and tensile test, respectively. The behavior of scratch resistance and friction coefficient of neat and reinforced polymethyl methacrylatewas studied using scratch test was performed by a new automated scratch device designed in this work. The results show that the ultimate tensile strength of reinforced polymethyl methacrylate is improved compared with neat polymethyl methacrylate. The hardness of polymethyl methacrylate increases with increasing the nanoparticles ratio. The scratch resistance of reinforced PMMA improved significantly compared to neat PMMA and increases with increasing nanoparticles ratio. The friction coefficient of the reinforced polymethyl methacrylate is lower than of neat polymethyl methacrylate and decreases with increasing SiO_2 ratio. The friction coefficient values calculated from the input and output of the device for all samples against filler ratio are 0.554 for neat PMMA, 0.488 for 1wt %, 0.436 for 2 wt%, 0.385 for 3 wt% and 0.3401 for 4 wt% of SiO_2.

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Keywords:*Urban growth, urban planning, urbanization, mother city, satellite city, city of Constantine, Algeria ,PMMA/SiO_2, tensile strength, hardness, scratch resistance, friction.*

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I INTRODUCTION

Advantages such as abundance, cheap price, low density, relatively good durability and ease of cutting to desired shapes and sizes are reasons for increasing the use of polymethyl methacrylate)PMMA(, especially transparent ones, in the medical, construction, automotive and aircraft industries[1, 2]. The most important disadvantages of polymethyl methacrylate are abrasion and poor scratch resistance [3, 4]. Scratches on the surface of polymethyl methacrylate reduce their use in the optical industry and many engineering applications, as the presence of scratches leads to increase stress during tensile, impact and fatigue loading that undermines the longevity of PMMA during use.

Scratch resistance test for polymers depends on some parameters such as indenter geometry, applied load, and sliding velocity. Height of the accumulation on both sides of the scratching and the strain hardening are increased with increasing the indenter attack angle. [5]. The value of applied normal load required to start scratching on the surface of the polymeric material is greatly influenced by the geometry of the indenter, this value does not mean anything without accurate description of the tip used [6]. The wear volume resulting from the scratching is proportional to the applied load [5, 7]. The true contact radius decreases and the mean strain in the contact region increase with increasing sliding speed [8]. The scratching resulting from various contact conditions provides an appropriate and reliable method for studying the mechanical properties of polymers [3, 9, 18].

Scratching occurs as a result of friction between the polymeric material surface and the hard bodies in contact with it. The ratio between the tangential force that causes the movement of the scratching tip and the vertical force due to the load applied on the scratching tip is called the apparent friction coefficient which includes two friction coefficients types, one of which is the result of separation at the region between scratched surface and tip is called coefficient of true local friction, the other is a result of plowing the material formed in front of the moving tip is called geometrical friction coefficient. The apparent friction can be divided into adhesive friction and plowing friction and the second term may include two terms, one for viscosity and the other for plasticity. Factors such as sliding speed, material kind, indenter geometry, and lubrication have a significant impact on the coefficient of total friction of polymers when performing a scratch test. [10]. The level of the strain in contact region and the senility of polymer are factors on which the true local friction depends [11, 12]. The gradient of plastic strain under the moving tip heavily dependent on the coefficient of true friction and the surface smoothness of PMMA [13]

Several published papers focused on improving the scratch resistance of PMMA by adding nanoparticles fillers, also, study the correlation of scratching with other properties of PMMA, the researches also dealt with the method of dispersing the nanoparticles fillers and the method of preparing the composite specimens. Fracture strain during scratch test can be associated with the fracture strain during tensile test, and polymeric material begins fracturing when the value of tensile stress generated behind the indenter reaches the value of ultimate tensile strength [3].The PMMA hardness improved significantly when added filler system of (ZrO2 - Al2O3 - SiO2) [16]. The factors affecting the preparation of nanocomposite particles (PMMA/SiO2) by using the free radical addition polymerization of methyl methacrylate (MMA) was studied by Min Chen et al. The researchers concluded that the increase in temperature of reaction leads to decrease the silica content and a slight increase in the average size of particle [15].

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This work aims to study the effect of adding silica oxide nanoparticles (SiO2) at the percentages of (1 wt%, 2 wt%, 3 wt%, 4 wt%) on the surface hardness, tensile strength, scratch resistance , and friction coefficient for polymethyl methacrylate, in addition, use a new automated device to perform PMMA scratch tests.

II EXPERIMENTAL WORK

2.1 Materials

Polymethyl methacrylate used is a spherical granule with a diameter of 3 mm purchased from Xinxiang Chuangmei Technology Co., Ltd in China. The filler is a silicon oxide nanoparticles (SiO2) treated with silane coupling agent purchased from SkySpring Nanomaterials, Inc. Houston, TX. 77082. USA. The solvent used is tetrahydrofuran (C4H8O) with minimum assay (GC) 99.7% purchased from Central Drug House (P) Ltd - CDH Company, New Delhi, India, as shown in figure (1). All these materials were supplied by Areej Al Furat Company, Baghdad, Iraq. Silicon oxide (SiO2) is classified as a very hard material used as filler in many materials such as adhesive, paint, plastic, coatings and rubber to improve the hardness and scratch resistance for these materials. A well-known scientific fact is that covalent systems are always more hard, so the reason for the hardness of silica is that it forms a covalent bond with oxygen. The specifications of nanoparticles SiO2 used in this work are purity: 99%, APS: 10-30 nm, PH: 5.5~6.0, and SSA: ~400m2/g.

(a) (b) (c)

Fig.1. (a) PMMA granules, (b) Silicon oxide nanoparticles (SiO_2) and (c) Tetrahydrofuran solvent

2.2 Casting Equipment

Casting molds are glass molds with dimensions of 220 mm length, 130 mm wide and 20 mm high. These molds were placed on horizontal adjustment tables to ensure uniform thickness of the cast material. The molds are covered by glass containers to protect them from unwanted external factors such as dust and wind as well as to ensure a saturated perimeter around the casting mold, as in figure (2).

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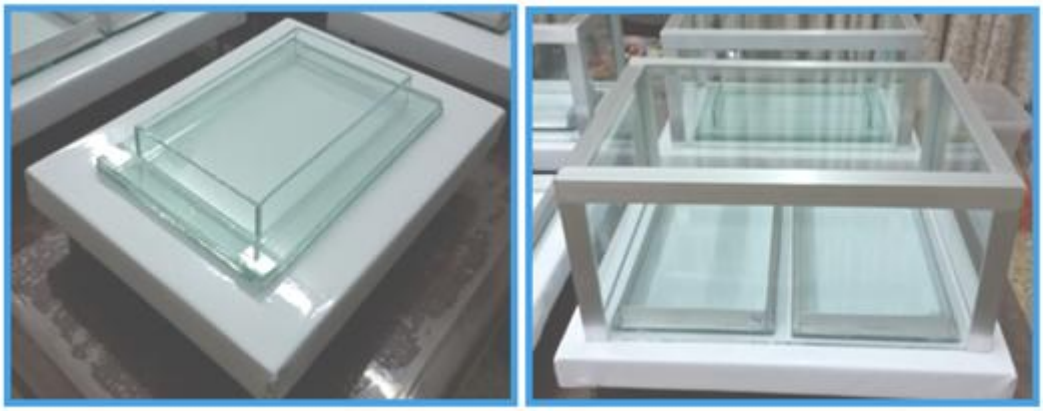

(a) (b)

Fig. 2. (a) Glass molds with (b) Glass containers and leveling platforms

2.3 Specimens Preparation

The method used to prepare the specimens and disperse nanoparticles was based on the technique of dissolving PMMA granules using a solvent placed inside a closed flask with the addition of filler and mixing the mixture using stirrer at room temperature (20°C) for two hours with a speed of 1500 rpm. Table (1) shows the ratios of mixing nanoparticles (SiO2) with PMMA. The resulting solution was then poured into glass molds placed on the leveling platform and covered with a glass container and left to dry under the sun for 5 days to ensure complete evaporation of the solvent, as shown in figure (3). The specimens were then removed from the mold by placing them in a cold water tank for 30 minutes. The final stage of preparation is to compress the specimens at a pressure of 0.5 MPa and temperature of 95°C for 2 minutes using a hydraulic thermal press to ensure a smooth surface and free of bubbles, as shown in figure (4). The specimens required for each test were cut using a laser cutting device.

Fig. 3. Preparation of PMMA/SiO_2 composites

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Table 1
The mixing ratios between PMMA and SiO2

Sample code	PMMA wt %	SiO_2 wt %
S0	100	0
S1	99	1
S2	98	2
S3	97	3
S4	96	4

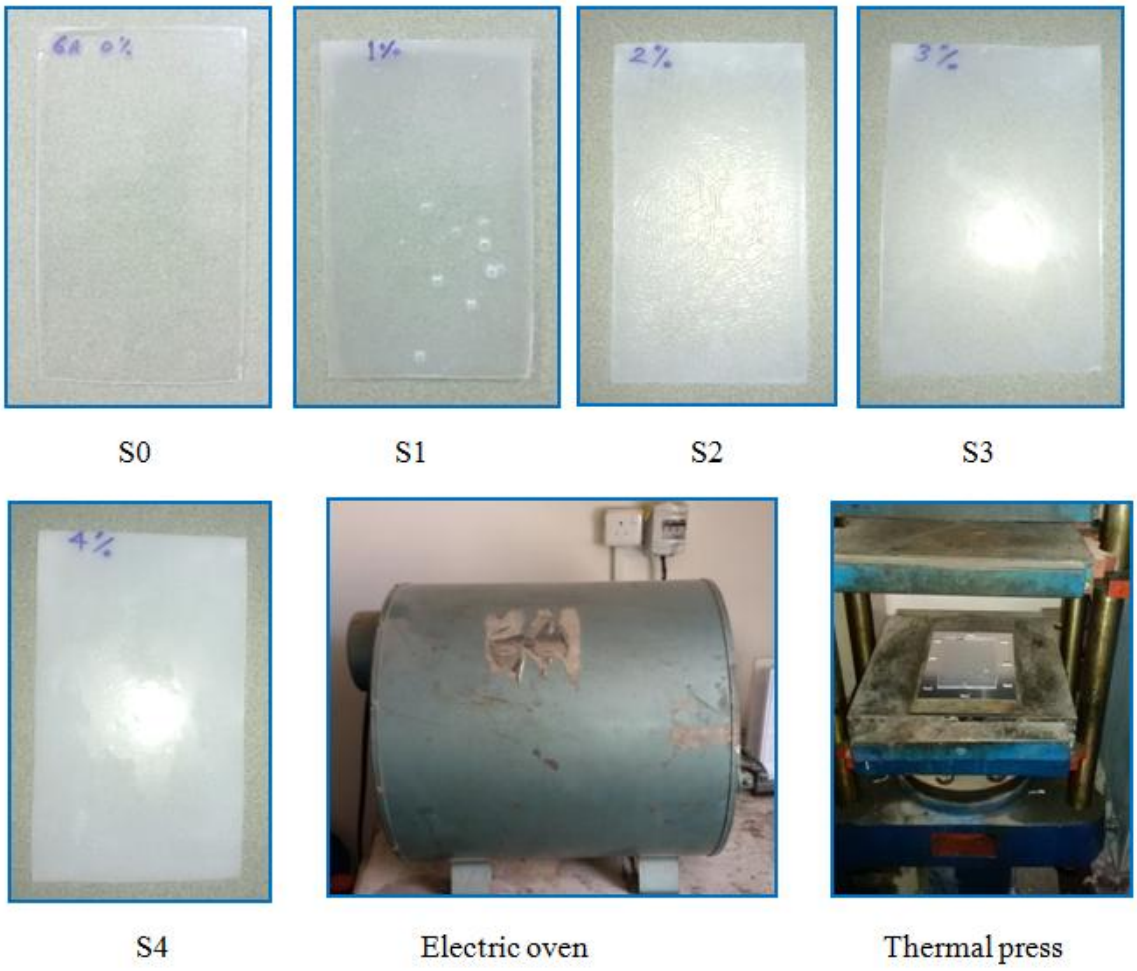

Fig. 4. Pressing process of samples

2.4 Tensile Test

Samples used in the tensile test were cut according to (ASTM) D-638; the dimensions and shape of test sample are shown in figure (5). Tensile tests were conducted at room temperature (20°C) with rate of displacement of 5 mm/min using a universal test machine, as shown in figure (6). Tensile tests were conducted in laboratories of Materials Engineering College, Babylon University. The curve of stress and strain of the samples tested is plotted by the device itself on graph paper.

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ASTM D638-10 Type IV	Dimensions (mm)
W – Width of narrow section	6
L – Length of narrow section	33
WO – Width overall, min	19
LO – Length overall, min	115
G – Gage length	25
D – Distance between grips	65
R – Radius of fillet	14
RO – Outer radius	25
T – Thickness	4

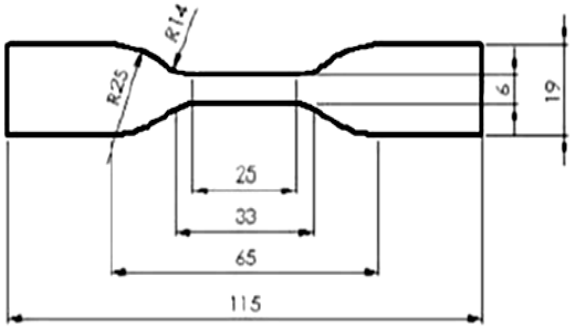

Fig. 5. Dimensions and shape of the tensile test sample

Fig. 6. Tensile test machine

2. 5 Shore D Hardness Test

Shore D hardness tests were performed at room temperature (20°C) using Chinese hardness device (type TH 200) in laboratories of Materials Engineering College, Babylon University. Test samples were cut based on (ASTM) D-2240, the dimensions and shape of test sample and device used are shown in figure (7). The interphase region, which is the area between the inorganic filler (SiO2) and organic polymer (PMMA), mainly affects the improvement of the properties of the resulting PMMA / SiO2 composite, it depends on the type of coupling agent used. The silane coupling agent acts as a bonding agent to improve the adhesion between PMMA and SiO2. Many desired changes can be obtained as a result of modification of the interphase region such as improve the SiO2 distracting in PMMA, reduce viscosity and improve hardness and scratch resistance by formation of overlapping polymer networks.

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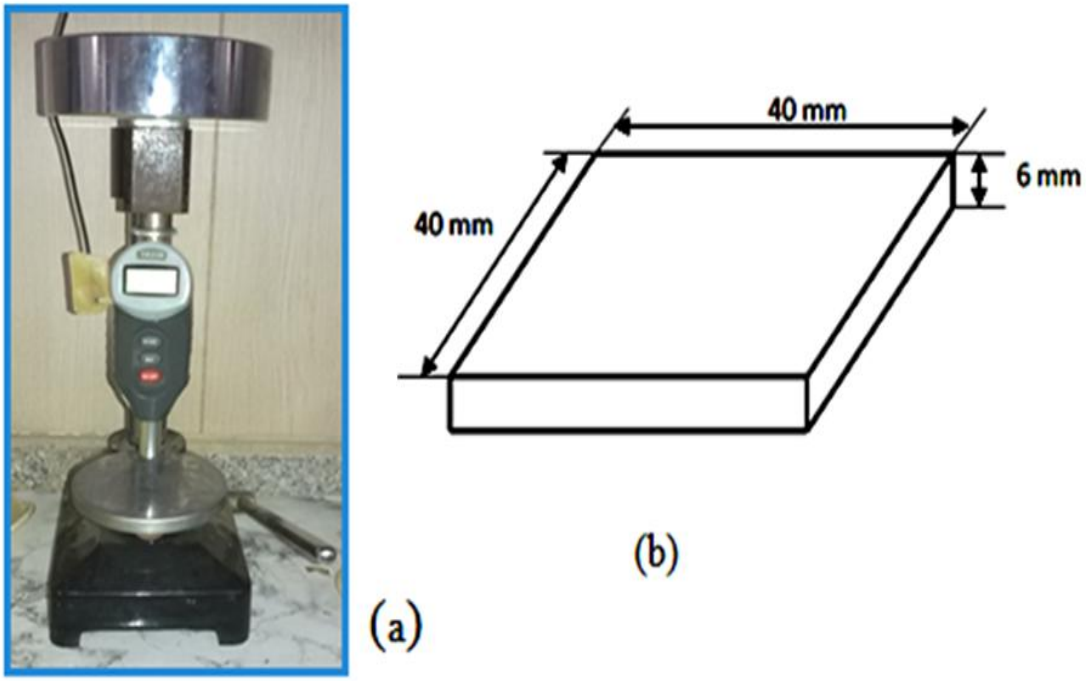

Fig. 7. (a) Shore D hardness machine (b) Dimensions and shape of the hardness test sample

2. 6 Scratch Test

Scratch resistance tests were conducted with sliding velocity of 20 mm/s, the applied load from 1 N to 10 N and the scratch path length of 40 mm at room temperature (20°C) using a new automated scratch device designed in this work. A stainless steel indenter with a conical tip with a radius of 0.2 mm and apex angle of 60° was used to scratch all samples. The dimensions of the scratch test sample were 60 mm width, 100 mm length and 4 mm thickness which allow repeating the scratch test more than three times in several locations of the sample. A new automated scratch device consists of a metal box with dimensions of 260 mm width, 260 mm height, 420 mm length and 3 mm thickness of all plates. The control panel and electrical circuit are installed inside the box; the moving platform with dimensions of (210 mm×180 mm) is mounted on the top surface of the box and is used to install the sample. The platform is driven by a stepper motor through a serrated shaft connecting to the platform via a load cell used to measure tangential force. The scratching mechanism consists of two iron pillars in L-shaped attached to one end of the box in addition to a set of serrated and non-serrated bars are used to install the indenter holder, dead weights and counterweight, figure (8) show the photograph of the scratch device. The program is designed using Visual Basic programming language to control the sliding speed, scratch path length and displays the results of the test via the computer, figure (9) presents the program windows of apparatus operation.

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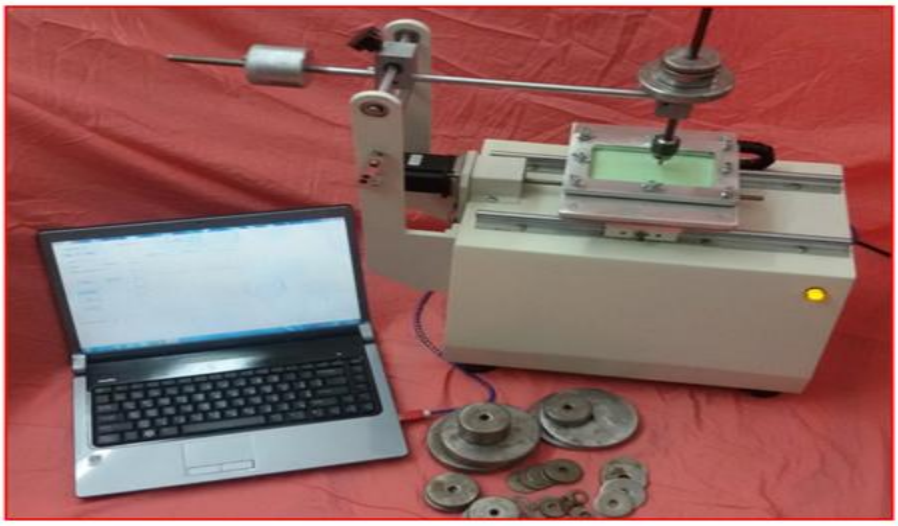

Fig. 8. Automated scratch device

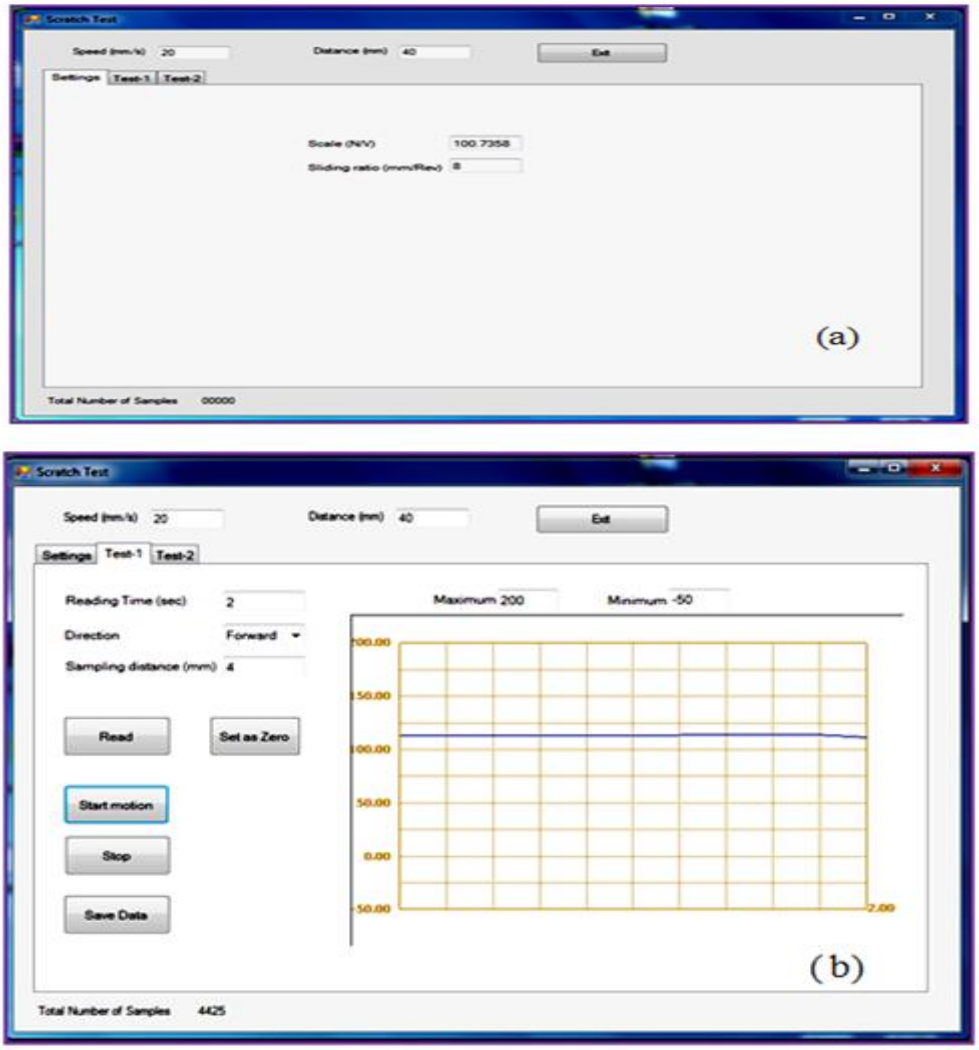

Fig. 9.The program windows of apparatus operation (a) the main interface and (b) The settings interface

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The scratch test in all researches related to the study of scratch resistance of polymeric materials was performed using various devices with different specifications. For example, Ezio Amerio et al. used a CSM scratch device (Micro-Combi Tester) with specifications: normal load (0.05N-30N), sliding speed (0.4- 600 mm/min) and maximum scratch length of 120 mm [17]. A new device depended on the moving head of tensile machine with specifications: normal load (0.05N - 5N) and sliding speed (1 µm/s to104 µm/s) was used by C. Gauthier and R. Schirrer [19]. Christopher M. et al. used a CSM nano-scratch tester with specifications: normal load (10µN-1N), sliding speed (0.4 - 600 mm/min), the tangential force measured by load cell (6 µN - 1 N) and dimensions of the sample (20mm × 120mm) [20]. The specifications of the device designed in this work can be summarized as follows: applied load (0.1 N - 325 N), sliding velocity (1 mm/s - 35 mm/s), tangential force measured by the load cell (0.1 N to 294 N), the samples dimensions (length: 10 - 140 mm, width: 10 - 80 mm, and thickness: 0.25 - 50 mm), maximum length of scratch path of 135 mm, and the height of the indenter from the platform surface (0.25 mm to 50 mm)

III RESULTS AND DISCUSSION

3.1 Tensile Strength

Figures (10 - 15) represent the tensile test behavior of neat and reinforced PMMA with ratios (1wt%, 2wt%, 3 wt%, and 4 wt% of nanoparticles SiO2). The results showed an improvement of the tensile strength for PMMA/SiO2 composites compared to neat PMMA. This behavior is caused by the effect of nanoparticles scattered between free spaces within the chain on restricting the movement of molecular chains in the PMMA matrix. A significant increase in ultimate tensile strength can be observed for reinforced PMMA by 1wt% compared with the other ratios of SiO2. Any other increase in SiO2 nanoparticles content above 3wt% imposes an adverse effect by reducing the ultimate tensile strength as shown in figure (15). The reason for this behavior is that the increase in SiO2 ratio leads to the agglomerate of nanoparticles with each other. Aggregated nanoparticles act as centers of stress concentration within PMMA and impose a negative effect by reducing the ultimate tensile strength. Figure (16) represents the elongation of PMMA as a function of nanoparticles (SiO2) ratio, the results showed a decrease in elongation for reinforced PMMA by 1 wt% and 3wt%, this behavior is due to the distribution of stress on both the base material and the reinforcement filler, while an increase in elongation is observed for reinforced PMMA by 2 wt% and 4wt%, the reason is that at a certain stress, the interface between the base material and the stiffening filler fails, which leads to its withdrawal, which makes it work as gaps and areas to focus the stresses.

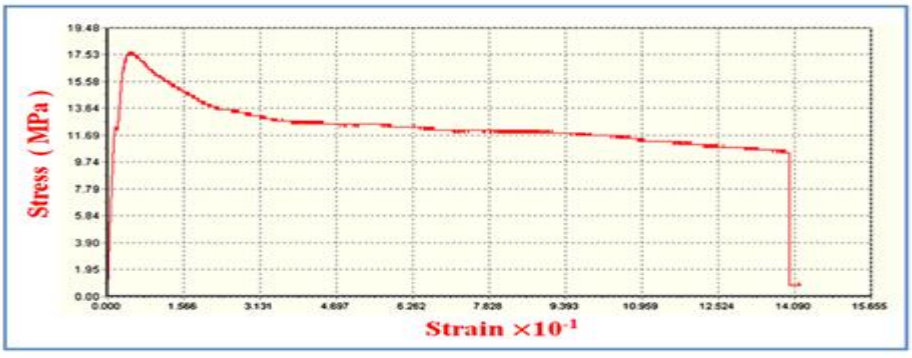

Fig. 10. Stress-strain scheme of neat PMMA

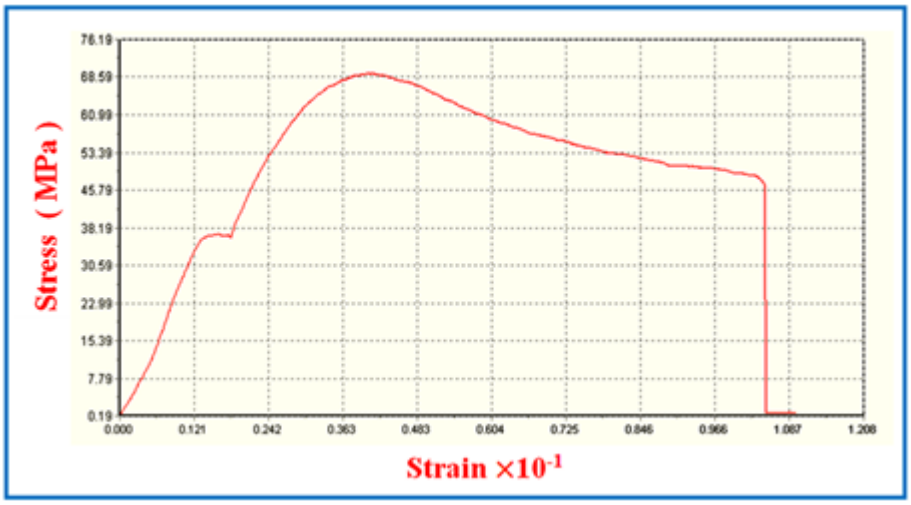

Fig. 11. Stress-strain scheme of PMMA with 1wt% SiO_2

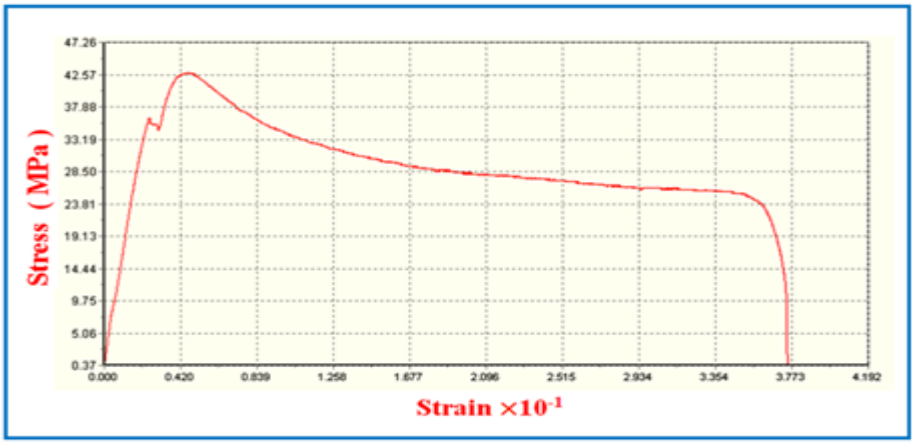

Fig. 12. Stress-strain scheme of PMMA with 2wt% SiO2

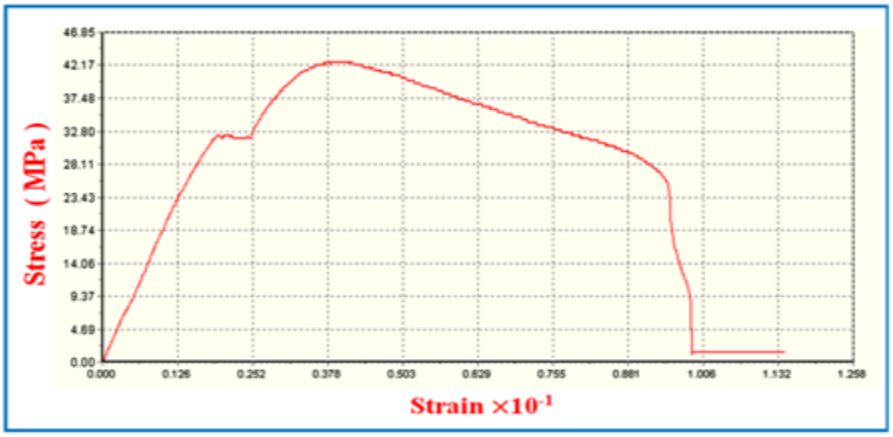

Fig. 13. Stress-strain scheme of PMMA with 3wt% SiO_2

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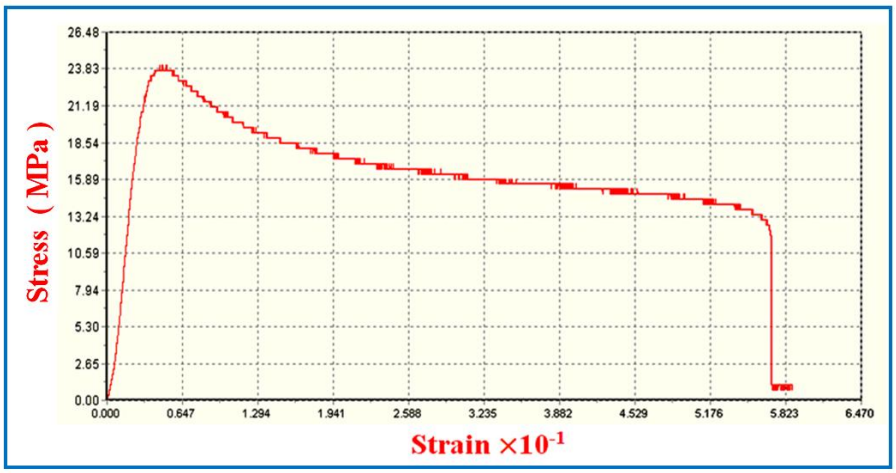

Fig. 14. Stress-strain scheme of PMMA with 4wt% SiO_2

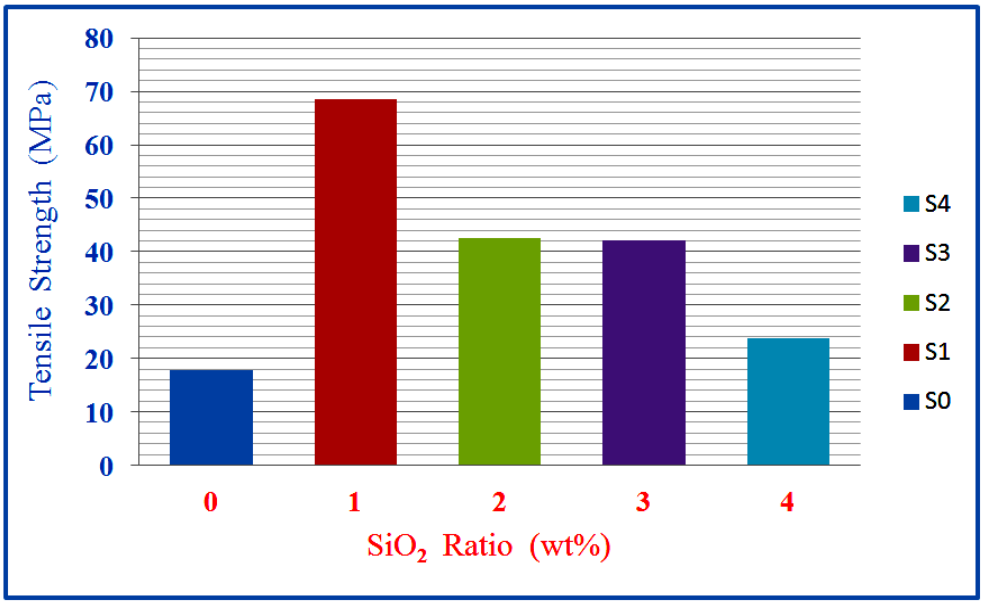

Fig. 15.Ultimate tensile strength of PMMA as a function of nanoparticles (SiO_2) ratio

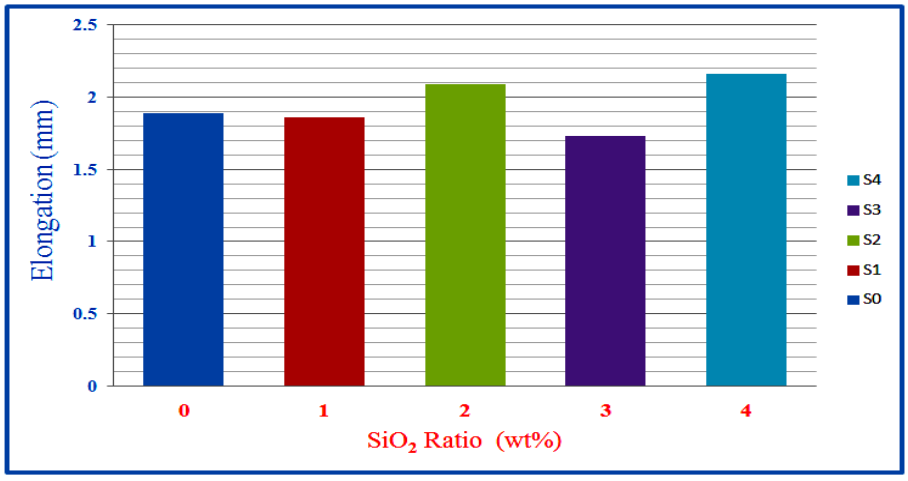

Fig. 16.Elongation of PMMA as a function of nanoparticles (SiO_2) ratio

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3.2 Surface Hardness

Figure (17) illustrates the evolution of PMMA hardness as a functionof nanoparticles (SiO2) ratio. The hardness of PMMA increases with increasing the ratio of nanoparticles (SiO2), this is due to the effect of silicon oxide nanoparticles where this material was characterized by high hardness and their diffusion between the molecular chains of PMMA improves penetration resistance and thus improves the hardness. Hasanen A. and Mohammed M. studied the effect of adding nano SiO2 powder on impact, transverse strength and hardness of heat-cured PMMA resin. The results showed increased significantly in hardness at the percentages of 3 wt%, 5 wt% and 7 wt%, and significant decrease in impact and transverse strength at 7 wt% [14].

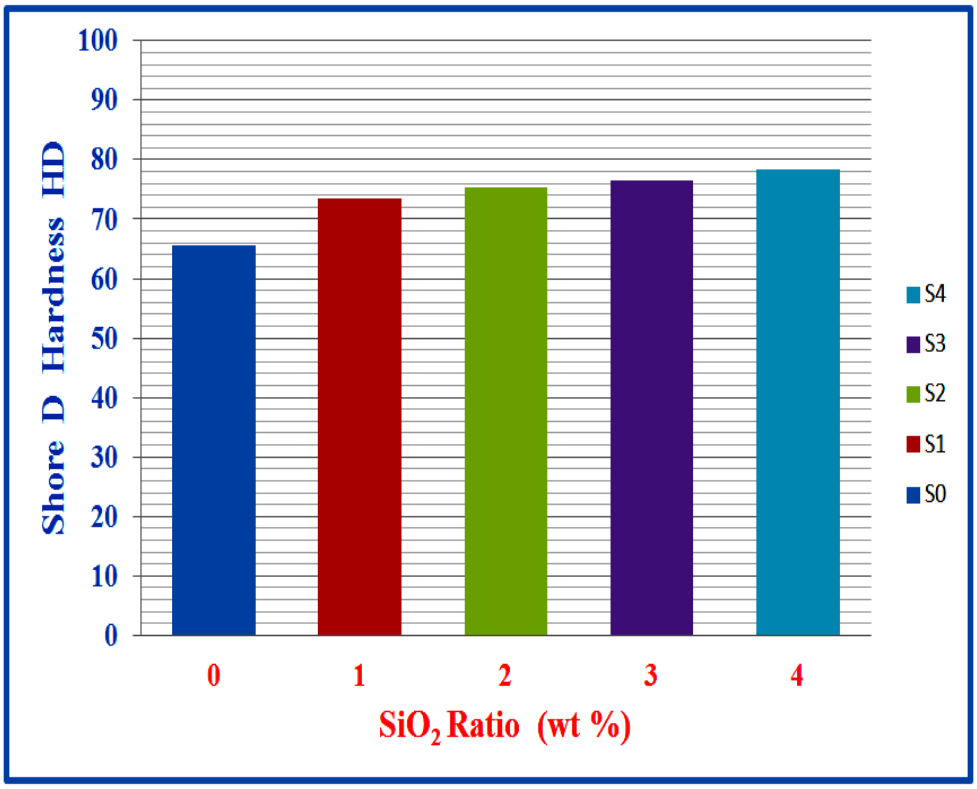

Fig. 17. Hardness of PMMA as a function of nanoparticles (SiO2) ratio

3.3 Scratch Resistance

The normal load applied to start scratching, measured tangential force, and friction coefficient for all samples was recorded in Table (2). The applied load required to start scratching for each sample was obtained using small dead weights gradually during the scratch test until the minimum load required to start scratching was reached. Figure (18) presents the distribution of tangential force (Ft) against the scratch path length (40 mm) for each sample of the PMMA. It should be noted that the values of tangential force (Ft) are approximately equal at all points along the scratch path and this is good evidence of the uniform distribution of nanoparticles (SiO2) within the PMMA matrix. Figure (19) shows the applied load (Fn) required to start scratching for each PMMA sample against the nanoparticles (SiO2) ratio. It should be noted that the applied load increases with increasing nanoparticles (SiO2) ratio due to increasing scratch resistance as a resulting of increased hardness due to the addition of nanoparticles which are characterized by high hardness.

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Ezio Amerio et al. carried out a comparison of scratch resistant behavior between PMMA coating films obtained through double-processing with those of PMMA coating films containing pre-formed Nano SiO2 Particles. The pre-formed nano SiO2 particles (Aerosil TT600 silica nanoparticles) at the percentages of 5 wt% and 10 wt% were dispersed by ultrasonication device for 30 minutes. The results showed high scratch resistance for coatings obtained by double-processing while low scratch resistance for coatings obtained by dissipated pre-formed nano-silica within the PMMA resin [17].

Table 2
Applied load (Fn) required for scratching, measured tangential force (Ft) and the friction coefficient of PMMA/SiO2 composites

Sample code	Normal Load required for Scratching F_n (N)	Measured Tangential Force F_t (N)	Friction Coefficient μ $\mu = F_t / F_n$
S0	3.581	1.987	0.554
S1	4.493	2.192	0.488
S2	5.268	2.297	0.436
S3	6.112	2.353	0.385
S4	7.122	2.421	0.340

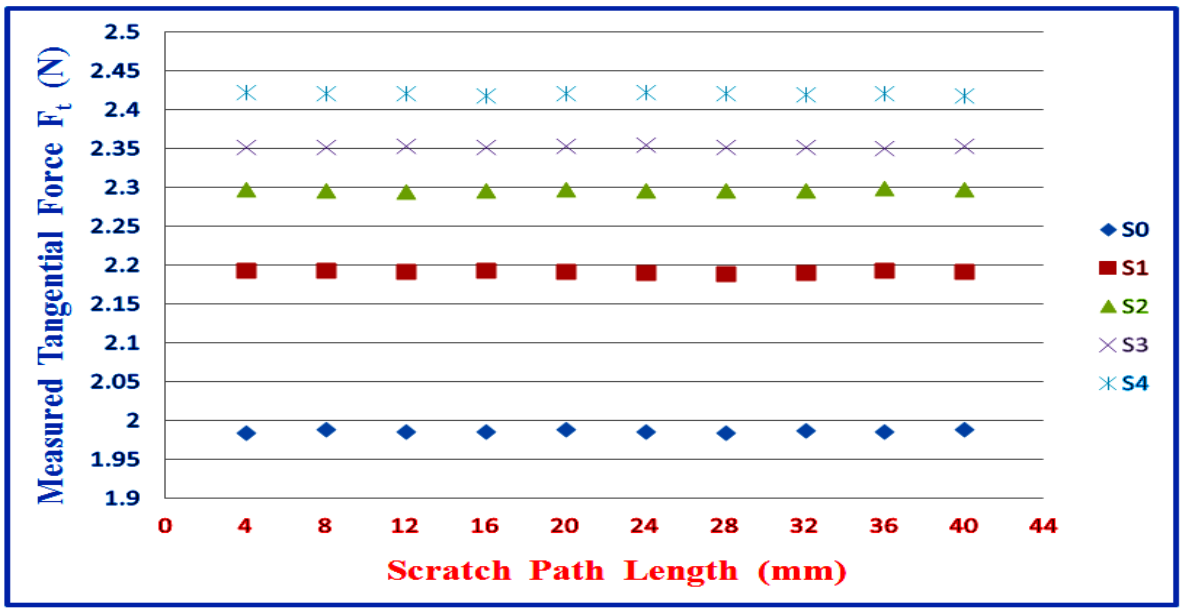

Fig. 18. Measured Ft against the scratch path length for each PMMA sample

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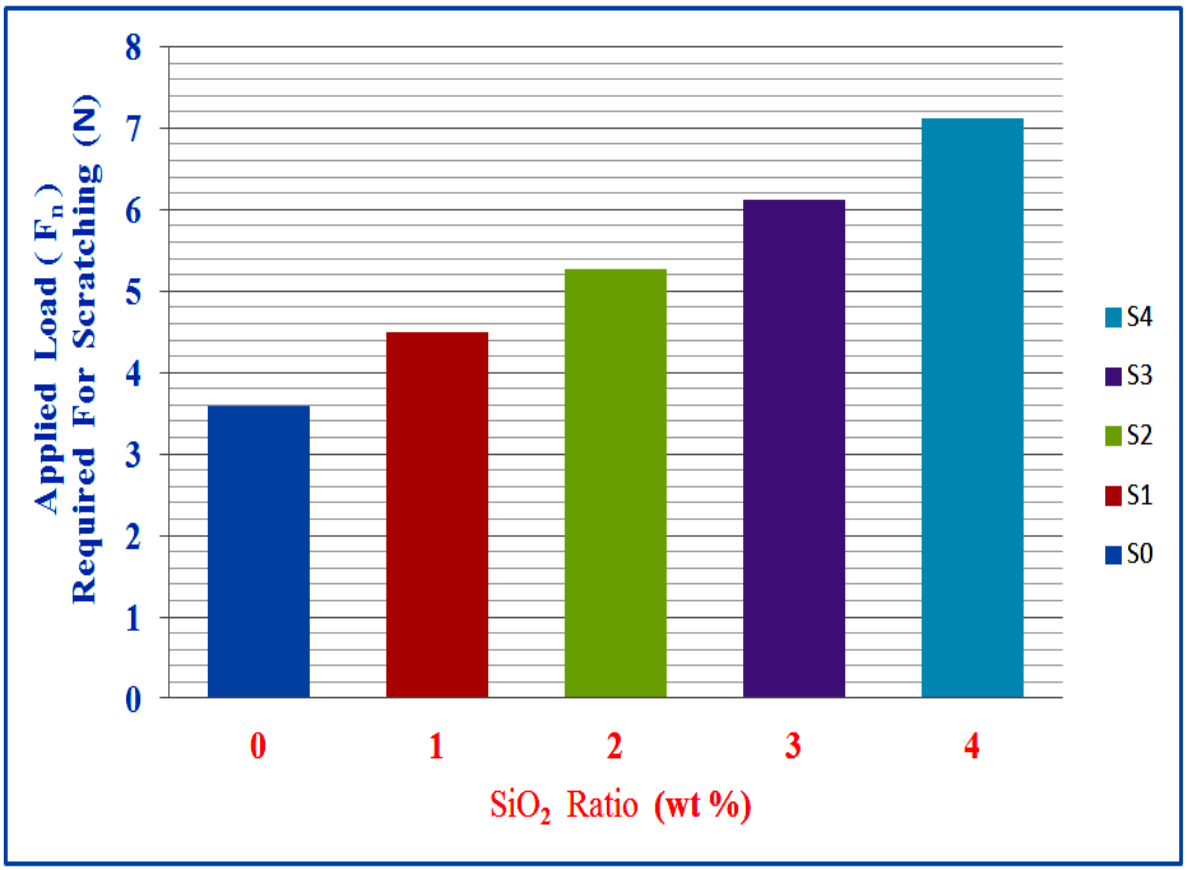

Fig. 19. Applied load required for scratching (Fn) as a function of nanoparticles (SiO2) ratio

3. 4 Coefficient of Friction

The friction coefficient μ for each PMMA sample can be calculated by dividing the measured force (Ft) which represents device output on the applied load (Fn) which represents device input. Figure (20) shows the friction coefficients of neat and reinforced PMMA against the scratch path length (40mm); the values of the friction coefficient μ for each sample were approximately equal along the path of scratch, this is evidence of homogeneity of properties along the scratch path at all points of the sample due to the uniform distribution of nanoparticles. Figure (21) shows the friction coefficients of neat and reinforced PMMA against the nanoparticles (SiO2) ratio along length of the scratch path of 40 mm, it can be noted that the friction coefficients of the reinforced PMMA are lower compared to neat PMMA. A decrease in the friction coefficient of reinforced polymethyl methacrylate is also observed when the ratio of nanoparticles increases and the lowest value at 4 wt% of SiO2. Decreasing in friction coefficient refers to increase in the hardness and scratch-resistance of the PMMA due to the addition of high hardness silicon oxide nanoparticles.

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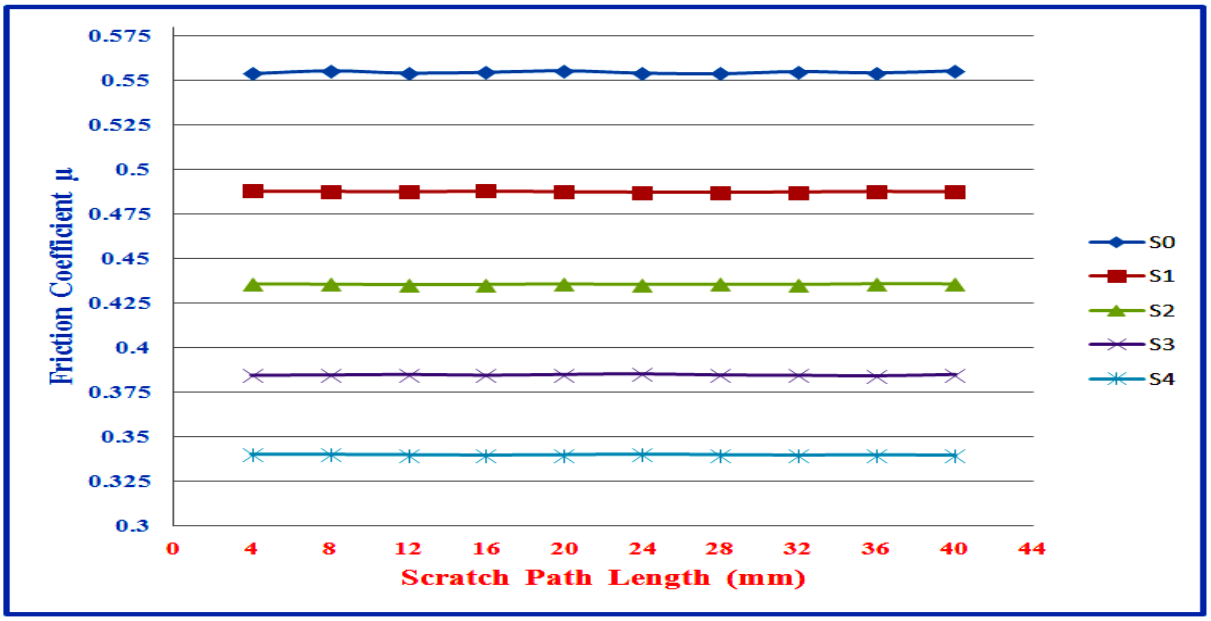

Fig.20. Friction coefficient μ for PMMA/SiO_2 composites against the scratch path length

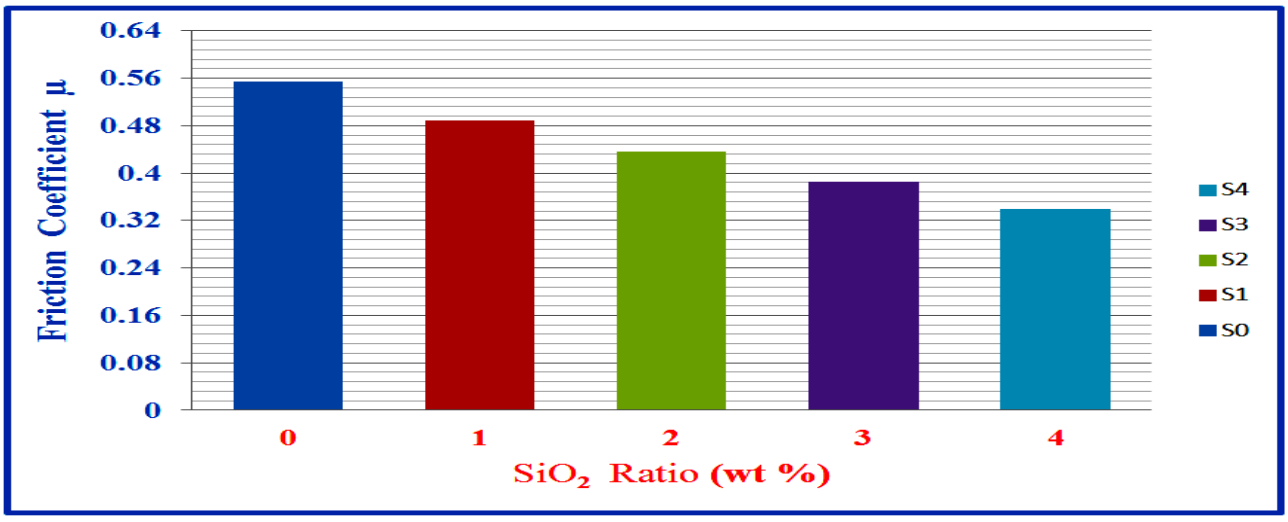

Fig.21.Friction coefficient μ for PMMA/SiO_2 composites as a function of SiO_2 ratio

IV CONCLUSIONS

The most important points in this work can be included as follows:

1. An improvement of the ultimate tensile strength for PMMA/SiO2 composites compared to neat PMMA.
2. The ultimate tensile strength for reinforced PMMA with 1wt% SiO2 was significantly increased compared to other ratios.
3. Any other increase in SiO2 nanoparticles content above 3wt% imposes an adverse effect by reducing the ultimate tensile strength.
4. Scratch resistance and hardness of PMMA increase with increasing the nanoparticles (SiO2) ratio.
5. Friction coefficient of PMMA decreases with increasing the SiO2 ratio and the lowest value at 4 wt% SiO2.

6. The study proved the ability of the designed device to measure the tangential force required for scratching accurately and quickly and in simple steps as well as the possibility of calculating the friction coefficient directly from the inputs and outputs of the device.

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