

Preparation of PMMA/SiO₂ Composite Sheets for Tribological and Mechanical Tests

Mushtaq Abdul Kareem Hussein

Mechanical Engineering Department, Engineering College, Misan University, Misan, Iraq.
**Corresponding author E-mail: mushtaqkareem@uomisan.edu.iq*

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Abstract: This paper aims to prepare PMMA sheets (Polymethyl methacrylate sheets) reinforced with SiO₂ nanoparticles (Silicon oxide nanoparticles) to obtain samples for tribological and mechanical tests. PMMA reinforced sheets are prepared by three methods; dissolving, pressing, and casting. In the first method, the pure PMMA granules were dissolved with an organic solvent. The SiO₂ nanoparticles were dispersed using a magnetic stirrer. Then, the solution was poured into a glassy mold. In the second method, pure PMMA powder was used, and SiO₂ nanoparticles were dispersed using a nanoparticle disperser device; then, the mixture was placed in a metal mold and pressed by a thermo-hydraulic press. While in the third method, pure PMMA resin and hardener were used, and SiO₂ nanoparticles were dispersed using an ultrasonic probe machine, and then the mixture was poured into a glassy mold. The three preparation results showed that the obtained sheets were free of bubbles and that their surfaces were of excellent smoothness and could be cut using a laser to obtain the samples required for tribological and mechanical tests such as tensile test, impact test, wear test, surface hardness test, surface roughness test, and scratch resistance test and others.

Keywords: PMMA, SiO₂, Dissolving method, Pressing method, Casting method.

1. Introduction

At the beginning of the twentieth century, the industry's need for rubber increased dramatically, which prompted some German scientists to make several attempts through which they were able to produce synthetic rubber that is characterized by the same composition as natural rubber in terms of chain length [1]. From that date to the present day, the polymeric materials industry has grown and developed rapidly until it has become one of the largest industries, surpassing the aluminum, iron, copper, and other industries. Polymeric materials are used in all applications of human life, bypassing other types of materials. They have been used to manufacture textiles, composite materials, foam materials, industrial fibers, adhesive materials, packaging materials, paints, medical devices, optical devices, and many high-precision technical products [2]. The general classification of polymeric materials is based on the structure, source origin, molecular forces, and polymerization type. While the technical classification depends on the effect of temperature on polymers, it is classified into thermoset polymers and thermoplastic polymers [3]. Thermoplastic polymers are characterized by their transformation from a solid-state to a molten state when the temperature increases and back to the solid-state when the temperature decreases. On the contrary, thermoset polymers are subjected to chemical changes when the temperature rises, leading to their chains' entanglement and changing their chemical structure. They do not return to their original state after decreasing the temperature [4].

Polymethyl Methacrylate was manufactured in 1928 by Rohm and Haas. It is a thermoplastic transparent plastic put on the market in 1933 under many trade names such as PMMA, Optix, Plexiglass, and Acrylic [5]. The first use of PMMA was in World War II, where it was used in submarines, aircraft windows, turrets, and canopies. Nowadays, PMMA is used in many industries and engineering applications such as automotive, furniture, LCD screens, lenses, aircraft industry, construction, medical devices, and security barriers. The main reason for the widespread use of PMMA is its advantages such as cheap price, abundance, relatively good durability, low density, ease of cutting into required sizes and shapes, non-toxicity, moisture resistance, and non-electrical conductivity, and the possibility of recycling

[6,7]. PMMA sheets are prepared industrially using the polymerization method, which requires much complex equipment and great experience. A common method to prepare PMMA sheets in the laboratory for research is using a double extruder, which also has many difficulties in determining the melting point of PMMA with high accuracy. The resulting sheets conform to scientific specifications.

This paper aims to enable researchers to prepare PMMA sheets in easy and practical ways and to overcome the difficulties of other methods.

2. The Organic Solvent Used

An organic solvent is a liquid capable of dissolving organic and inorganic substances without changing the chemical properties of those substances. This property of organic solvents has led to their use in many important industries, such as the manufacture of polymeric composite materials. The well-known rule (like dissolves like) helps choose the appropriate solvents for organic compounds; applying this rule requires knowledge of some characteristics of solvents to choose the most appropriate. The most important characteristics required to be known for the organic solvent used are the boiling point, the evaporation temperature, the ability to isolate the solvent by distillation, and the safety conditions to be followed when using each solvent [1]. The solvents used in the current work are acetone, isopropanol, and tetrahydrofuran.

Dissolving PMMA in organic solvents is an important process for several reasons, including the ability of the solvent to dissolve the PMMA, the dissolution rate, temperature, the evaporation rate of the solvent, and the formation of bubbles after the evaporation of the solvent. Two solvents were used to dissolve the PMMA granules: acetone and tetrahydrofuran (T.H.F.); their specifications are listed in the table (1). During experiments in the current work, it was observed that tetrahydrofuran was faster than acetone in dissolving the PMMA granules, as well as the number of bubbles present in the sample after the evaporation of tetrahydrofuran, was less compared to acetone; this is completely identical to the result obtained by Evchuk et al. [8], as a result for that, tetrahydrofuran was adopted. The perfect amount of solvent used for dissolving the mixture of PMMA granules and filler was four times the weight of the mixture (i.e., for each 100 g of the mixture, 400 g of solvent was used).

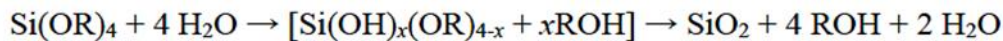
Table (1) Specifications of THF and Acetone [8].

| Property | THF | Acetone |
|--------------------------|---------------------------------|---------------------------------|
| Chemical Formula | C ₄ H ₈ O | C ₃ H ₆ O |
| Gas Number | 109-99-9 | 67-64-1 |
| Molecular Weight (g/mol) | 72.11 | 58.08 |
| Appearance | Colorless | Colorless |
| Physical State | Liquid | Clear liquid |
| Boiling Point (° C) | 66 | 56 |
| Freezing Point (° C) | -108 | -96 |
| Autoignition Temp. (° C) | 230 | 465 |
| Density (kg/l) | 0.89 | 0.786 |
| Vapor Pressure (Pa) | 19300 | 24700 |
| Purity % | 99.7 | 99.5 |

3. The Method Used to Disperse the Filler

As a result of the beneficial and exciting properties possessed by polymeric composites, such as thermal resistance, chemical resistance, mechanical properties, and surface properties, they have received great attention from researchers and manufacturers in recent years. Polymeric composite materials (polymer/filler) are manufactured by adding fillers of different types and percentages to the polymer substrate to improve the desired properties in the original polymeric materials. The difficulty of manufacturing polymeric composite materials lies in finding the appropriate method for dispersing the filler in the polymer substrate. Four methods are used to disperse SiO₂ in a PMMA substrate:

Interpolating method, in situ polymerization method, method of in situ formation for both the nano SiO₂ and polymerization, and method of direct mechanical mixing of PMMA and nano SiO₂ [9]. Some of these methods require modifications to the surface of the filler particles (SiO₂) and modifications to the polymerization reactions. Such modifications make using these methods to disperse filler particles (SiO₂) in a PMMA substrate unsuitable and difficult. The first method is based on reducing the size of the SiO₂ particles to the nanoscale by inserting an organic compound between the layers of the SiO₂ particles, which works to convert the filler to the nanoscale dimensions [10]. PMMA is then inserted into the silica layers that have undergone modification using chemical or mechanical methods, and chemical methods include in situ polymerization of monomers within the silica layers [11]. The second method, in addition to in situ interpolative polymerization method, depends on polymerization reactions [12]. Inorganic nanofillers are dispersed either inside the monomer or in the solution of the monomer. The resulting mixture after the dispersion process is polymerized using the standard methods of polymerization. The difficulty of this method is finding the appropriate method for dispersing the filler in the monomer; this requires a modified organically of the surface of the filler particles to enhance the wettability. The third method relies mainly on the solution-gel technique in its work. Many molecular hybrid materials (organic/inorganic) are produced in this method using metallic alkoxides reactions [13].



The equation above shows the reactions of polycondensation and hydrolysis of tetraalkoxysilane as a reaction to the solution-gel technique used to produce SiO₂/polymer molecular hybrid materials. Using the solution-gel technique, it became possible to disperse the filler with dimensions shorter than the length of the molecular chain of the polymer matrix. The fourth method is based on breaking the filler agglomerates resulting from the direct mixing process of both the nanofillers and polymer matrix. This method is more suitable for producing filler/polymer composites that contain nano or micron-scale fillers. In general, two ways are used to mix fillers and polymer. The first is without using any solvents, called (the powder mixing method) [14,15]. The second uses solvents to mix the fillers and polymer as a solution called (the solution mixing method) [16,17].

From the above, it is clear that the first three methods used to produce filler/polymer composites require the modification of nanofillers surfaces and/or complex polymerization reactions, making them unsuitable for the production of SiO₂/PMMA composites for the current work. The fourth method was adopted in the current work to produce the SiO₂ / PMMA composites, including the simplicity of this method, availability of required equipment, and SiO₂ used as a nano-filler. Silicon oxide nanoparticles (SiO₂) were used as reinforcing filler treated with a silane coupling agent. The specifications are the size of a particle 10-30 nm, purity of 99%, pH 5.5-6, and surface area of 400 m²/g. The most important reasons that led to the selection of this filler are abundance, cheapness, non-toxicity, high hardness, and high melting point; another important reason is that PMMA transparency is not significantly affected when adding small amounts of SiO₂.

4. Preparation of PMMA/SiO₂ Composite Sheets

4.1 Dissolving Method

In this method, pure and reinforced PMMA sheets are prepared using 3 mm diameter spherical granules of PMMA raw material, an organic solvent that is T.H.F., and a nano-filler that is SiO₂; all these materials are shown in the figure (1). The casting molds used are made of glass with dimensions of 140 mm in width, 210 mm in length, and 20 mm in height, which are placed on horizontal leveling platforms to obtain a uniform thickness of the resulting sheets. After the casting process, the glassy molds are

covered with containers to protect the resulting sheets from impurities, dust, and other undesirable external factors; all this equipment is shown in the figure (2). To prepare pure PMMA sheets, a mixture of 100 g of PMMA granules and 400 g of T.H.F. is placed in a closed flask, while to prepare the reinforced sheets, the amount of SiO₂ added is subtracted from 100 g of PMMA granules, table (2) shows the mixing ratios of PMMA granules with SiO₂ nanoparticles. The closed flask is placed on a magnetic stirrer for two hours at room temperature (23° C) and at a speed of 1500 rpm to complete the process of dissolving PMMA granules and dispersing SiO₂. The solution is poured after the dissolving process into the glassy molds placed on the horizontal leveling platforms and left under the sun for five days after covering the glassy containers to complete the evaporation process of the solvent, as shown in figure (3). After five days, the resulting sheets are removed by placing the glassy molds in a cold water tank for 30 minutes. The sheets are then placed in an electric thermal oven for 45 minutes at a temperature of 95 °C and then pressed using a hydraulic, thermal press for 2 minutes at a pressure of 0.5 MPa to obtain a smooth surface free of bubbles, figure (4) shows the sheets prepared in this method.

Table (2): Mixing ratios of SiO₂ nanoparticles and PMMA raw granules.

| Sheet code | PMMA granules (wt %) | SiO ₂ nanoparticles (wt %) |
|------------|------------------------|---|
| G0 | 100 | 0 |
| G1 | 99.9 | 0.1 |
| G2 | 99.8 | 0.2 |
| G3 | 99.7 | 0.3 |
| G4 | 99.6 | 0.4 |
| G5 | 99.5 | 0.5 |

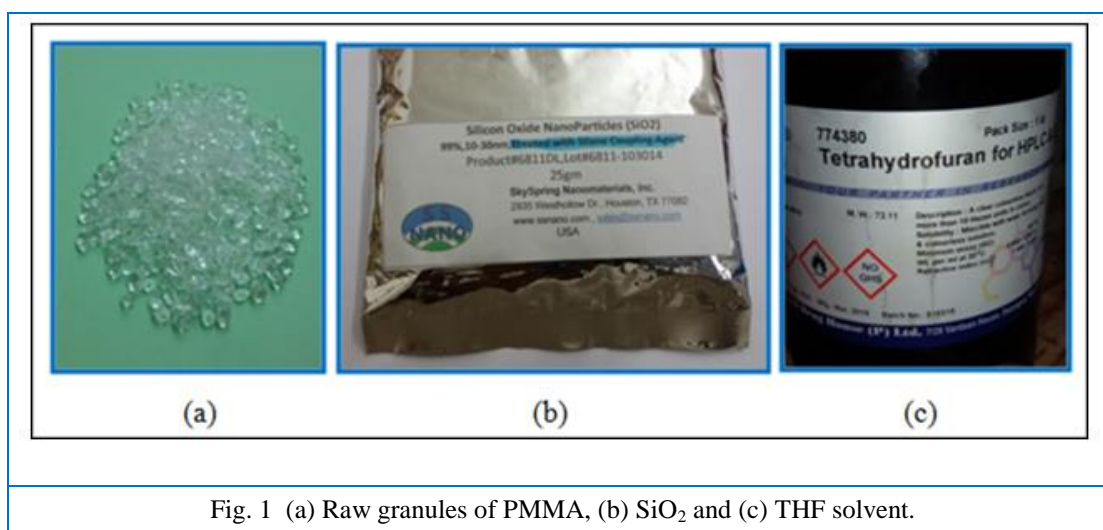


Fig. 1 (a) Raw granules of PMMA, (b) SiO₂ and (c) THF solvent.

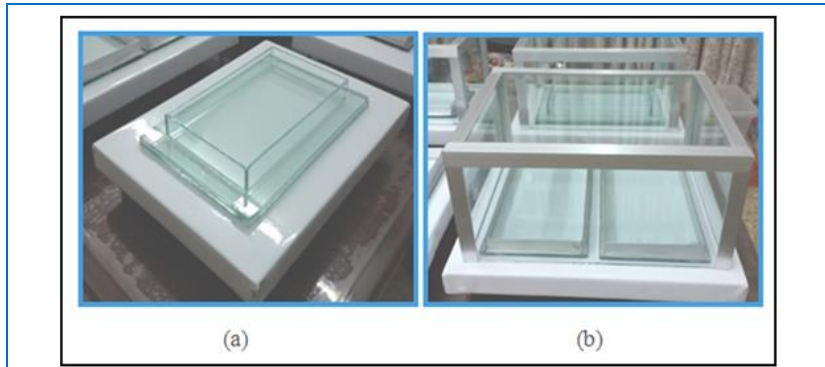
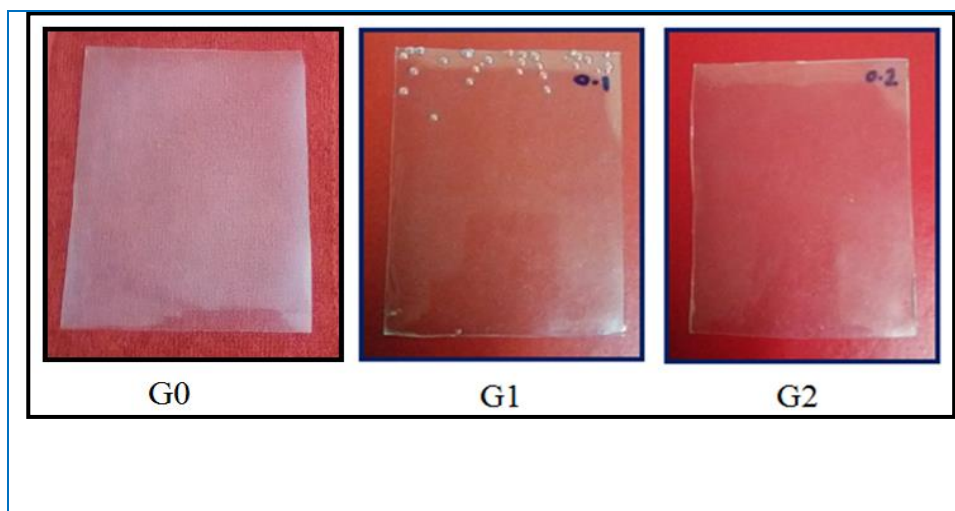


Fig. 2 (a) Leveling platforms and glassy molds and (b) Glassy containers.



Fig. 3 Preparation of PMMA/SiO₂ composite sheets.



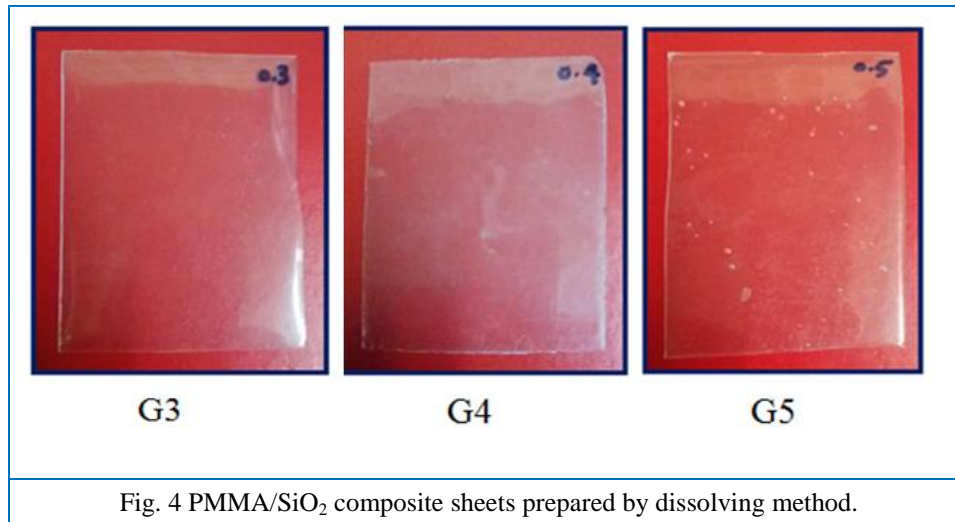


Fig. 4 PMMA/SiO₂ composite sheets prepared by dissolving method.

4.2 Pressing Method

The Polymethyl methacrylate used in this method is PMMA powder and has the following specifications: fine white powder, an average particle size: of 5.5 - 80.5 μm , P.H.: 5 -7.5, and hearing loss: 2.0% or less. SiO₂ is the same used in the first method; these materials are shown in figure (5). Equipment used: (a) a three-part iron mold; parts one and two are plates have dimensions (200 mm \times 140 mm \times 10 mm) and (145 mm \times 85 mm \times 6 mm). The third part is a ring that has dimensions (200 mm \times 140 mm \times 10 mm) for the outer rectangle and dimensions (150 mm \times 90 mm \times 10 mm) for the inner rectangle. (b) Nanoparticles are dispersing devices with three speeds of 750/600/450 rpm. (c) Electric thermal oven (d) Hydraulic, thermal press, all these equipment are shown in figure (6). The steps for preparing pure and reinforced PMMA sheets using this method are as follows, the required quantities of PMMA powder and SiO₂ nanoparticles are placed inside a closed plastic vessel containing three iron balls with a diameter of 5 mm on a nanoparticle dispersal device for 6 hours at a speed of 600 rpm. The mixture resulting from the mixing and dispersal of nanoparticles is placed in the iron mold and placed in an electric oven at temperatures from 165°C to 220°C for 90 minutes until the mixture is completely melted. After completely melting the mixture, the mold is pressed with a pressure of 5 MPa at temperatures from 165°C to 220°C for 3 minutes using a thermal-hydraulic press to expel bubbles to obtain composite sheets of the required thickness. Then a mold is left to cool down to extract the sheets from it. Table (3) displays mixing ratios of SiO₂ nanoparticles and PMMA powder, electric oven temperature, and thermal press temperature, figure (7) shows the resulting sheets for this method.

Table 3 Mixing ratios of SiO₂ nanoparticles and PMMA powder, electric oven temperature, and thermal press temperature.

| Sheet code | PMMA powder (wt %) | SiO ₂ nanoparticles (wt %) | Temperature of Oven & Press (°C) |
|------------|----------------------|---|----------------------------------|
| P0 | 100 | 0 | 165 |
| P1 | 99.9 | 0.1 | 176 |
| P2 | 99.8 | 0.2 | 188 |
| P3 | 99.7 | 0.3 | 197 |
| P4 | 99.6 | 0.4 | 209 |
| P5 | 99.5 | 0.5 | 220 |

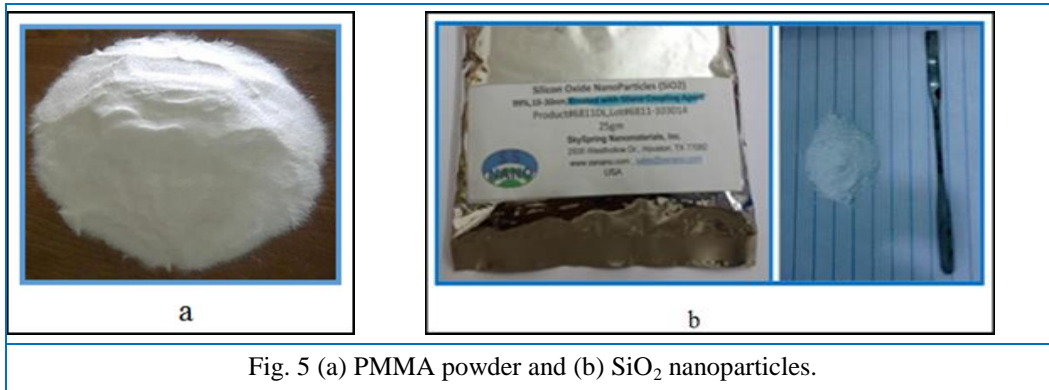


Fig. 5 (a) PMMA powder and (b) SiO₂ nanoparticles.

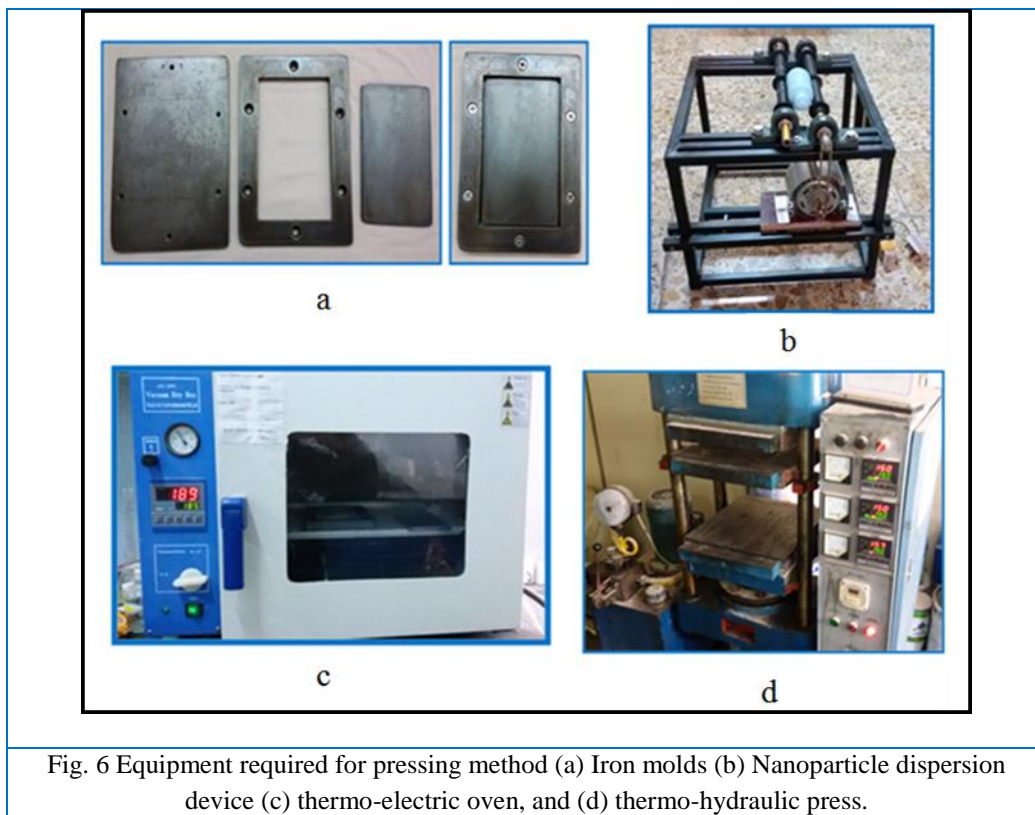


Fig. 6 Equipment required for pressing method (a) Iron molds (b) Nanoparticle dispersion device (c) thermo-electric oven, and (d) thermo-hydraulic press.

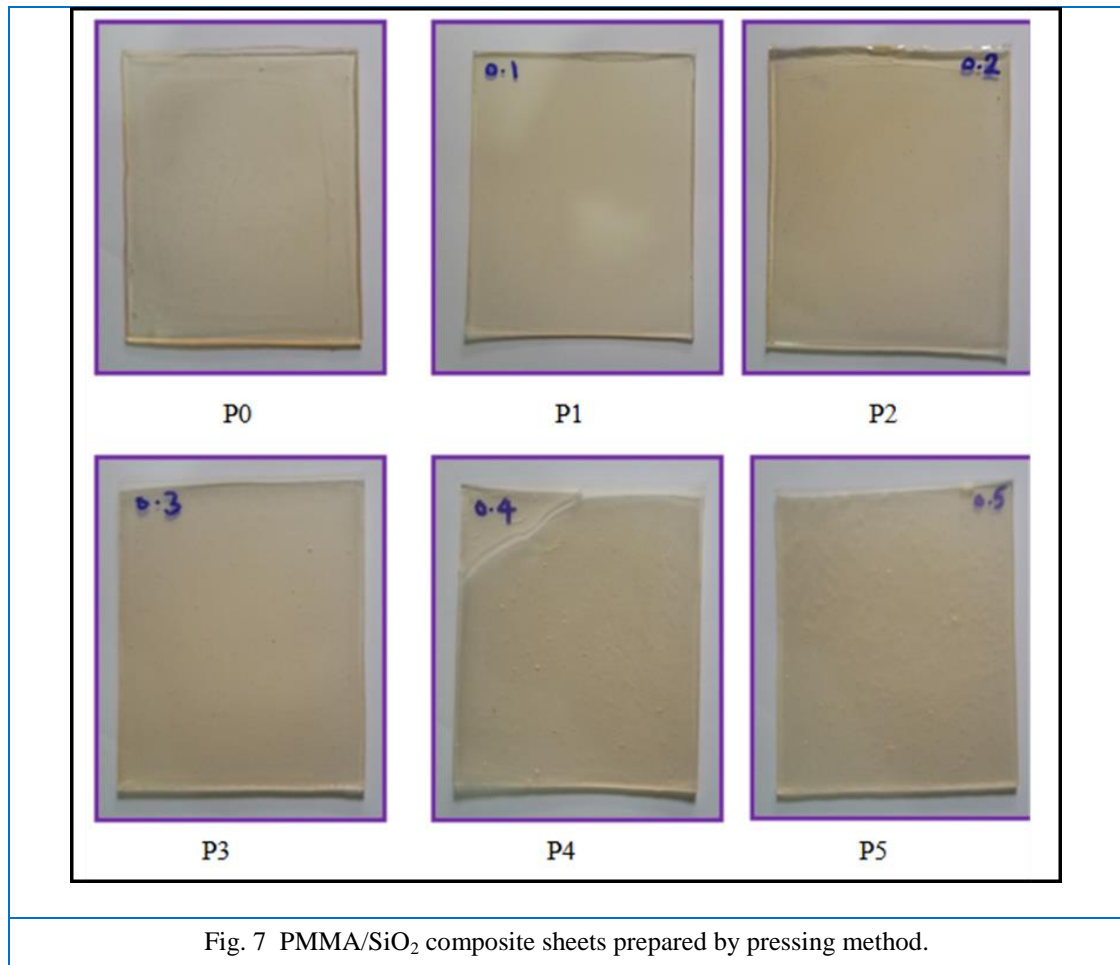


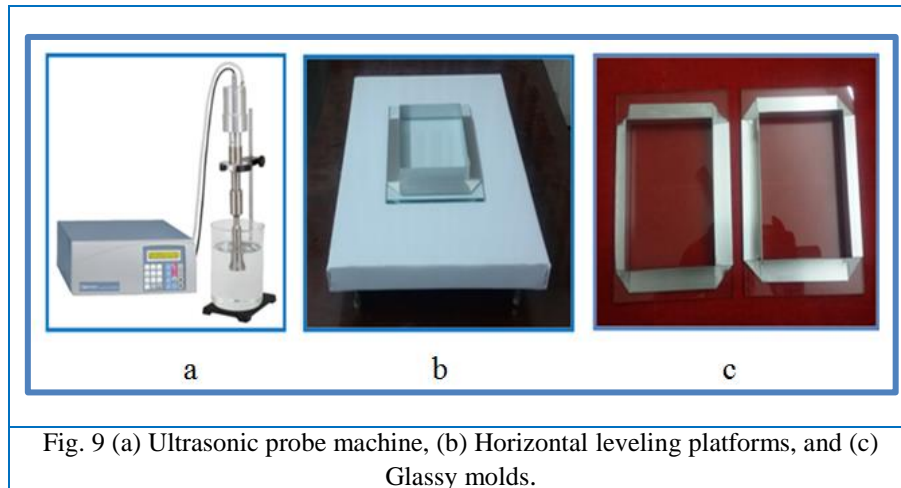
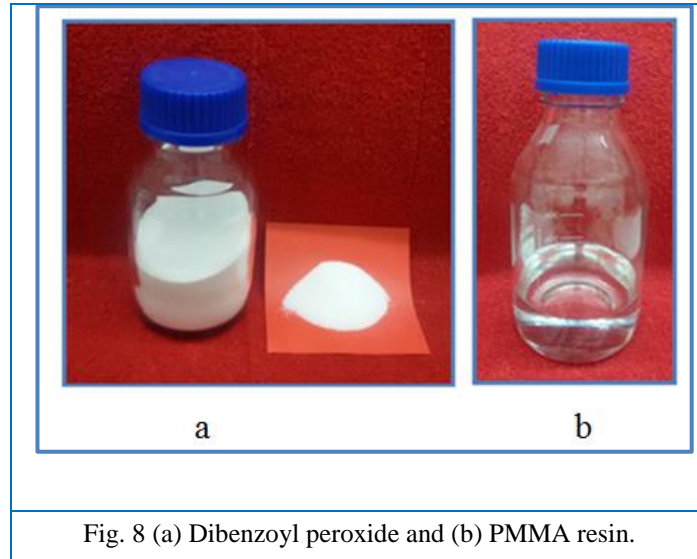
Fig. 7 PMMA/SiO₂ composite sheets prepared by pressing method.

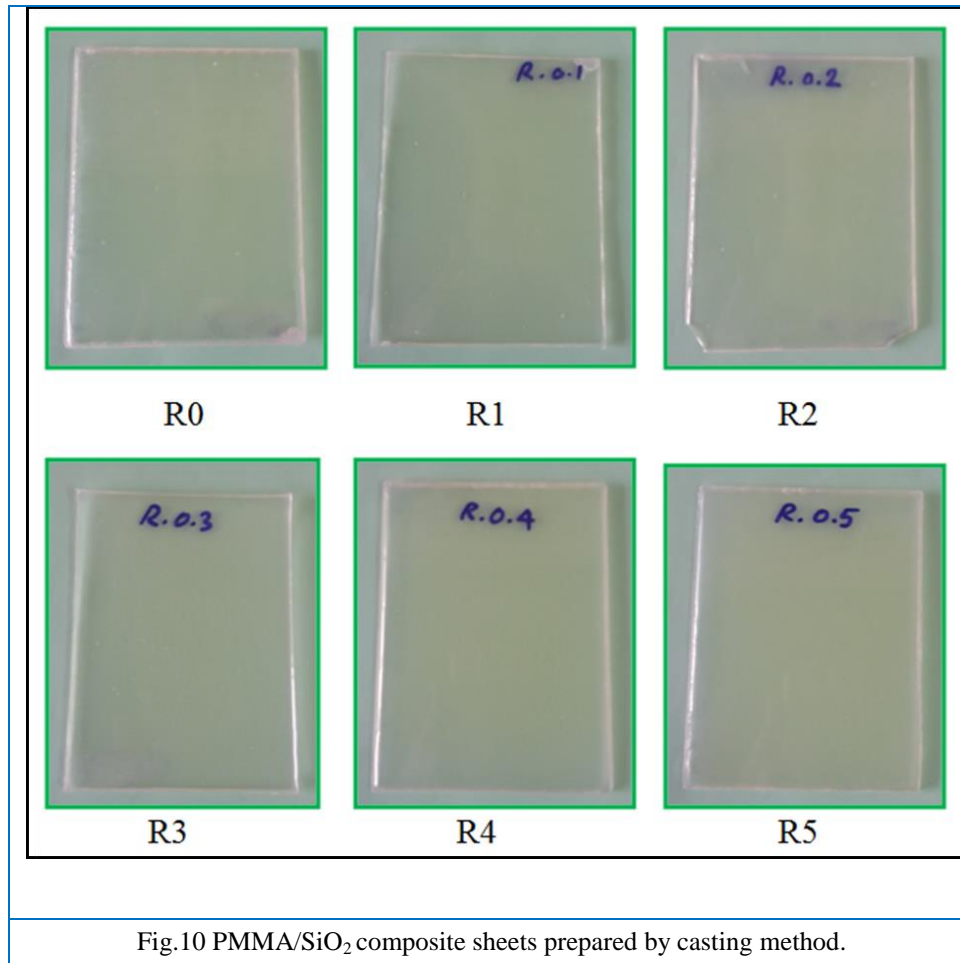
4.3 Casting Method

In this method, the PMMA resins were used with specifications: colorless transparent liquid, density ranging from 1.02 g/l to 1.05 g/l, P.H.: 8-9, size ranging from 0.2 μ m to 0.3 μ m, and T_g: 105 °C. While the hardener used was Dibenzoyl Peroxide with specifications: Chemical name Diphenylperoxyanhydride, molecular formula: C₁₄H₁₀O₄, white powder, solid at ambient temperature, melting temperature: 103-108°C and density: 1.33 g/cm³, as provided in figure (8). The equipment used are: (a) Glassy casting molds having dimensions of (140 mm \times 110 mm \times 20 mm) for the first group and (210 mm \times 140 mm \times 20 mm) for the second group, and (b) Horizontal leveling platforms to ensure uniform thickness for molded material inside the molds, (c) Ultrasonic probe machine to dispersal the SiO₂ nanoparticles having specifications power rating: 2000 Watts, voltage: 230V, 50/60Hz, frequency: 20 kHz, timer of programmable: 10 Hours, and adjustable pulses On/Off: 1 second to 1 minute, figure (9) shows all of this equipment. To prepare pure and reinforced PMMA sheets using this method, required amounts of PMMA and SiO₂ are placed inside a glass vessel; an ultrasonic probe machine was used for 1 hour to disperse SiO₂ nanoparticles; after that, the hardener with the ratio of 1wt % is added to the mixture and mixes well. Then the mixture is poured into glassy molds placed on horizontal leveling platforms, which are left to solidify. Table (4) shows the mixing ratios of the PMMA resin and SiO₂ nanoparticles. The molds are placed in a cold water tank for 30 minutes to extract the resulting sheets; the sheets prepared by this method are shown in figure (10).

Table 4 Mixing ratios of SiO₂ nanoparticles and PMMA resin.

| Sheet code | PMMA resin (wt %) | SiO ₂ nanoparticles (wt %) |
|------------|---------------------|---|
| R0 | 100 | 0 |
| R1 | 99.9 | 0.1 |
| R2 | 99.8 | 0.2 |
| R3 | 99.7 | 0.3 |
| R4 | 99.6 | 0.4 |
| R5 | 99.5 | 0.5 |





5. Conclusions

The three methods used in the current work to prepare pure and reinforced PMMA sheets proved their success, ease of work, and short time, as the resulting sheets were characterized by a smooth surface and were free from bubbles. The methods used also proved the possibility of preparing sheets of large sizes, enabling researchers to obtain the samples required for tribological and mechanical tests according to the approved standards for each test from the same sheet.

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