Graphene oxide and TiO$_2$ based PMMA nanocomposites for dental applications: A comprehensive study of the mechanical properties

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Abstract. This work reports synthesis of PMMA/TiO$_2$ blend nanocomposite for its application as dental materials. Two different amount of TiO$_2$ nano particles 1% (wt.) was mixed homogeneously through melt compounding with constant ratio of PMMA to obtain desired properties. The properties of these two blend nanocomposites were compared GO (0.001% wt.) reinforced PMMA nanocomposite for the same purpose. As prepared blend nanocomposites were characterized by Field Emission Scanning Electron Microscopy (FESEM), depth indentation, and scratch analysis. Moreover, this work also showing effect of different amount of TiO$_2$ on open ring hole structures and matrix droplet morphology. So, that this work may open up an opportunities to produce new compatibilized blend that are of great interest in the industrial applications using specific amount of TiO$_2$.

Keywords: Dental Materials, Depth Indentation, Scratch Analysis, FESEM, Mechanical Properties, etc.

Introduction

The application of polymer in daily life of human being is increasing day by day which led to the demand for improving their properties and performance. They are required to have very good mechanical properties, stability at extreme conditions and possibilities of self healing[1-2]. Polymer is an important material for dentistry because it can be used in various clinical applications, which is not possible with other types of materials. It is widely used for applications such as denture bases, artificial teeth, cements, dyes, provisional crowns, endodontic fillings, tissue conditioners etc [3]. Out of all the available polymers, PMMA is one of the suitable polymer for the use in dental applications, which is the field of the present research work. PMMA has been used in dental applications since 1937 [4]. A denture material is required to withstand the masticator load for a long term along with minimum irritation effects. The material should not react with the aqueous environment of the mouth. It is required to withstand the craze formation caused by solvents present in food, drinks, or medicines. The sensitivity of the polymers related to change in atmospheric condition is also required[5]. These days PMMA has been widely used because of its excellent combination of optical properties, mechanical properties, thermal strength, electrical properties conditions resistance and easy shaping[6-7]. Also PMMA is widely used in the field of medical science (Orthopedics). However, this material is not ideal in every aspect, such as failure due to fatigue and chemical degradation[8]. In order to improve the properties of polymer, different methods can be used, one of them being the application of suitable fillers. The resulting composite materials will find use in different applications. The polymer matrices have been introduced with different shape and morphology nanofillers[9]. Fillers are used to improve the properties of the polymers, in the present research work Graphene
Oxide (GO) and Titanium Oxide (TiO₂) have been used as fillers. In twentieth century Titanium Dioxide (TiO₂) has been widely used as a pigment in paints, ointments, toothpaste etc[10]. Many researchers have worked in the field of addition of TiO₂ to some host materials which led to the improvement in the properties of the resulting material as a whole.

Now a days, graphene based polymer composites have been extensively studied to improve the electrical and mechanical properties of a polymer. The extraordinary electrical and mechanical properties of graphene along with its high specific surface area led to its use in a variety of engineering applications and as fillers in a polymer. Since graphene is quite expensive Graphene Oxide is used as fillers for polymer based material to improve the properties of the polymers also it has good electrical conductivity[11-12].

**In present work,** We have been used PMMA as a base material for two different filler TiO₂ powder and GO. The mixture of first sample PMMA and GO (PMMA/GO) in the turning round of 50 gm by 0.001 g. The second sample consist of PMMA/GO/TiO₂ in the ratio of (50g/0.001g/0.5g) by weight. After mixing and characterization we have been found PMMA/GO/TiO₂ has shown better hardness and elastic properties which is good for dental application.

**Experimental**

**Materials**

All the chemical reagents used for synthesis, reduction and purification of graphite powder, potassium permagnate(KMnO₄), sulfuric acid (H₂SO₄, 98%), orthophosphoric acid (H₃PO₄, 88%), hydrogen peroxide(H₂O₂, 30%), selenium powder (particle size: 100 mesh), and hydrochloric acid (HCl, 10%), were procured from Sigma Aldrich (India) with purity level of >99.9%.

**Synthesis of Graphene Oxide**

For the synthesis of Graphene Oxide (GO) authors have adopted procedure developed by Marcano et al. In brief, graphite powder (6.0 g, 1 wt equiv) were oxidized using a mixture of concentrated H₂SO₄/H₃PO₄ in 9:1 ratio (720:80 mL) along with very slow addition of KMnO₄ powder (36 g, 6 wt equiv). Addition of KMnO₄ is a slight exothermic (around 40 °C) step. After the completion of KMnO₄ addition reaction was heated up to 60 °C and stirred continuously for 15 h. Then reaction mixture was cooled to room temperature and transferred to ice bath (500 mL) with drop wise slow addition of 30% H₂O₂ (6 mL) in a dark chamber. For workup, reaction mixture was neutralized (pH around 6.5 slightly acidic) by multiple washing with distilled water and then centrifuged @ 3000 rpm for 2 h, and then supernatant materials was decanted away. Now the residual material was washed in a sequence with 400 mL of dist. H₂O three times, 400 mL of 30% HCl, and 400 mL of ethanol two times; after the each wash, finally solution was filtered over a PTFE membrane with a pore size of 0.45 m. The product obtained on the PTFE membrane (Graphene Oxide nearly 10 g) was dried in vacuum for 48 hours at 45°C.

**Preparation of PMMA/GO/ and PMMA/GO/TiO₂ blend Nanocomposites**

| S.N. | Sample code | Composition and mixing order | Processing Conditions |
|------|-------------|-----------------------------|----------------------|
| 1    | PMMA/GO     | PMMA(50g)+ GO(0.001g)       | Temp.270°C, rmp. 10 |
| 2    | PMMA/GO/TiO₂| PMMA(50g)+ GO(0.001g) +TiO₂(0.5g) | Same                |
Characterization of prepared PMMA

Scratch hardness and depth indentation Analysis: We have used micro-Hardness Tester instrument to investigate scratch hardness and depth indentation of prepared PNCs. This instrument is fully automatic and commands can be preloaded through a software Tribotester. On pushing the Start Button of the instrument its head moves down to reach the test surface from distance in multiples of 50 mm and automatically starts the hardness test cycle in automatic succession without breaching a phase. The indentation experiment was carried out at the room temperature and at a relative humidity of 40 %.

Results and Discussion

1. Simple indentation, Multi cycling and Scratch hardness Analysis:

1.1 Scratch hardness Analysis:

Hardness is a mechanical property of the materials and it is an ability of material to resist diffusion by other materials under the applied force[13-14]. Scratch analysis is a fundamental parameter to obtain material’s hardness and nowadays it is normally used to measure hardness of polymeric materials. This analysis is simply based on an idea that harder materials can obviously scratch another material under a constant applied force, but not contrarily. To measure micro-scratch hardness of prepared samples we have used compressed and polished strip of samples. Proper polishing is very necessary because even a very minute disturbance on the surface might cause noticeable disorder in both force and depth measurement based on following fundamental equation[14].

\[ HS = \frac{F_i}{W \times D} \] ..........2

\[ HS = 2C \frac{\cos \phi (1 - \sin^2 \theta)}{1 - \sin \theta \cos \phi \sqrt{1 + (\tan \phi \sin \phi)^2 - \sin \phi \cos^2 \theta}} \] ..........3

Where \( F_i \) is horizontal applied force, \( D \) is width of scratch surface and \( D \) is depth of scratch surface, \( \phi \) is angle of internal friction, \( \theta \) is back-rake angle, \( C \) is cohesion; an important part of unconfined compressive strength (UCS) of material and all these parameters of equation 2 and 3 further depends on friction coefficient \( (F_i/F_v = \tan \phi) \) which is the basic principle behind scratch hardness testing[15]. Nanocomposites PMMA/GO and PMMA/GO/TiO\(_2\) shows maximum scratch resistance under the applied progressive scratch load. The tangential force curves of PMMA/GO and PMMA/GO/TiO\(_2\) shows very little fluctuations from the beginning to end of the test. Such little fluctuations for PMMA/GO and PMMA/GO/TiO\(_2\) is due to the prominent inertial effects and compact crystalline arrangement which strongly different progressive force applied by the indenter tip on the surface of PMMA/GO and PMMA/GO/TiO\(_2\).
1.2 Simple indentation, Multi cycling Analysis:

The simple-indentation test has been used as an established method in which an indenter tip is pressed into specific sites of the material to be tested by applying an improved normal load. The multi-cycling testing is an important method for the evaluation of material’s mechanical response to applied load. This technique has been used for applied force resulting depth of the penetration of an indenter during the whole loading and unloading cycle, when applied force has been controlled [16]. These techniques have been allowed for the purpose of the conventional values of hardness without the need to measure the residual size of an indentation produced by an applied force. Whereas it has been first referred to as micro hardness testing or nano-indentation testing because of the force and length scales involved, today instrumented indentation testing has been used to encompass a much broader range of force of up to 50 KN and resulting depths. The indentation technique which is usually used to examine the mechanical properties of materials can also be utilized to measure residual stresses by controlling the indentation load or indentation depth. In order to determine hardness of prepared PMMA/GO and PMMA/GO/TiO$_2$ in term of depth indentation, we have used depth sensing nano indentation technique. The indentation response allows hardness and elastic modulus to be assessed. As the indenter is driven onto the surface of material, an impression conforming to the shape of the indenter to some contact depth $h_c$ appears. Parameter contact depth ($h_c$) is an important parameter and it may be defined by equation (1)

$$h_c = h - \frac{\varepsilon P}{S}$$

Where $h$ is resulting penetration during the analysis, $P$ is the load applied to the surface of sample, $\varepsilon$ is equal to 0.75 for Vickers type indenter. In the present work we have focused on the lower end of the applicable vary of instrumented indentation testing. In this work, indentation load-displacement curve obtained at the stressed position was compared with that measured at the non-stressed position, and then residual stress variation at the stressed position was calculated [15].
Fig. 2. Simple indentation analysis for PMMA/GO and PMMA/GO/TiO₂.

Fig. 3. Multi cycling analysis for PMMA/GO and PMMA/GO/TiO₂.
2. FESEM Analysis:

The surface morphology and fractured surfaces of the prepared blends were analyzed using FESEM instrument (model No. Supra 55 Carl Zeiss, Germany) by breaking the samples in liquid nitrogen and then coating by platinum to make samples conducting under an accelerating voltage of 5-7 kV. FESEM instrument have been used for organic/inorganic hybrid materials, dispersion of inorganic dopant in organic materials have very important to study the properties of composite materials\cite{16}. So, microscopic study have been used on cross section of composite sample conducted FESEM. Figure 4 and Figure 5 shows FESEM micrographs of PMMA/GO and PMMA/GO/TiO$_2$. In FESEM analysis we have prepared different weight percentages of PMMA/GO and PMMA/GO/TiO$_2$. In FESEM images for PMMA/GO smooth and uniform surface with some strap obtained. The PMMA/GO/TiO$_2$ have been uniform and well-suited without any phase separation occurring when a 0.001 g Go and 0.5 g TiO$_2$ fillers has been added in 50g PMMA polymer matrix. In first case we have used 0.001 g Go filler added in 50g PMMA polymer matrix, the surface morphology of the composite polymer sample shows many clusters or chunks randomly distributed\cite{32}. So PMMA/GO/TiO$_2$ have good mechanical and thermal properties compared to PMMA/GO. Figure 4 and Figure 5 represents the FESEM images of the fractured surface for PMMA/GO and PMMA/GO/TiO$_2$ nanocomposites\cite{17}. Micrograph exhibits the surface morphology of PMMA/GO and PMMA/GO TiO$_2$ respectively. The smooth and fine layered morphology of PMMA/GO showing fibrous nature of PMMA/GO rough & fractured morphology is characteristics of PMMA/GO/TiO$_2$ which is quite scratch sensitive as shown in micro hardness section. This was due to the significant incompatibility between PMMA/GO and PMMA/GO/TiO$_2$ which imports the feeble interfacial adhesion at the interface. This morphology investigation also supports the rheological behavior of PMMA/GO and PMMA/GO/TiO$_2$. Because of weak interfacial interaction of PMMA/GO and PMMA/GO/TiO$_2$ there operates an interlayer slippage between the two blend partners under the applied sheer force.

Fig.4. FESEM micrograph of PMMA/GO Nanocomposites.
3. Conclusion
In this work we have reported synthesis of PMMA/GO and PMMA/GO/TiO$_2$ based blend nanocomposites for the dental application. Both composites were fabricated using PMMA as matrix and TiO$_2$ and GO as nanofiller. The properties of the both blend nanocomposites were analyzed using Field Emission Scanning Electron Microscopy (FESEM), depth indentation, and scratch analysis. FESEM analysis shows that among the two prepared blend nanocomposites, GO containing composites shows maximum improvement and seems very efficient for the dental application.

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