



A REVIEW OF THE POLYMERIZATION PROCESSES AS WELL AS THE APPLICATIONS OF POLY (METHYL METHACRYLATE) AND GRAPHENE OXIDE NANOCOMPOSITES

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ABSTRACT: Graphene oxide (GO) nanocomposites of poly (methyl methacrylate) (PMMA) have shown a wide range of desirable mechanical, electrical, and physical properties. The fabrication of PMMA-GO nanocomposites and their potential use as multifunctional structural materials are interesting research directions. In order to create PMMA-GO polymeric nanostructured membranes, our research focuses on radical polymerization techniques, particularly bulk and liquid polymerization. This summary also discusses the influence of solvent polarity on the isomerization and the function of anionic, cationic, and nonionic surfactants in addition to the role of the initiator. Radical polymerization-based techniques for the production of PMMA-GO nanocomposites are a promising field of study due to the great growth potential and diverse range of emerging applications.

KEYWORDS: Polymerization processes, poly (methyl methacrylate), graphene oxide nanocomposites, etc.

INTRODUCTION

Often, a hybridization process is required to develop polymers with optimum performance and specialised properties. The design specifications of a given application dictate whether organic or inorganic additive ingredients are used by manufacturers when making hybrid polymer materials. While hybrid fillers and additives are sometimes employed in polymer composites, the term composite materials is typically reserved for materials that have undergone hybridization. Polymerization routes and interactions between substituents also have a role in determining the features and functionalities of the resulting polymer composite, in addition to the materials utilised. Methods for synthesising functionalized polymeric hybrids/composites vary according to the specific properties and applications sought for, solvents. Nanohybrid materials of the polymer nanocomposites kind are widely used (NHPs). Common areas where NHPs excel include drug delivery devices, polymer batteries, construction materials, and even architecture and wastewater treatment.

Poly (methyl methacrylate), or PMMA, is one kind of polymer that is often used to make polymer composites or NHPs by combining with nanoparticles. The performance and utility of PMMA may be enhanced by adding nanoparticles to the matrix. PMMA is produced using a straightforward and low-cost method using methyl methacrylate (MMA) monomer and a free radical initiator. MMA's volatile monomer is liberated after depolymerization of PMMA between 300 and 400 degrees Celsius. PMMA, which may be found in both solid and liquid resin forms, has extraordinary mechanical properties in addition to great optical and thermal stability. By increasing the system's elastic modulus, low shrinkage, impact modulus, fungal resistance, high UV absorption, and absorbance value, nanoparticles may enhance the system's overall performance. NHPs may be created by fusing together metal oxide nanoparticles, carbon nanotubes, graphene, or graphene derivatives with polymers. Table 1 summarises the nanoparticles used in the production of PMMA nanohybrids for functionalized applications.

Table 1. Specializations of PMMA Nanohybrids

polymerization/method	nanoparticle	specialization
free radical of MMA	oxide: SiO ₂ , ZnO, and TiO ₂	photoselective nanofilms
sol-gel of MMA + 3-(trimethoxysilyl)propyl methacrylate (MSMA)	TiO ₂	optoelectronic thin films
Pickering (oil-water) emulsion	rGO and carbon nanotubes	electrically conductive nanocomposites
solution casting	CdSe quantum dots	optical characters for LED

Recognizing the inclusion of nanoparticles and PMMA to enhance their characteristics and provide remarkable applications is an important step in this direction. It is the nanoparticles themselves that provide the final NHPs their desirable and adjustable optical, electrical, and mechanical characteristics. As a result of their large surface area, nanoparticles' surface activity with the polymer matrix is boosted not just by surface functional groups but also by the nanoparticles' surface size and structure. In particular, carbon-based nanoparticles have attracted a lot of attention for their functionalized high-end applications due to their exceptional strength, electrical characteristics, and modular biocompatibility. Because of the presence of OH, it may dissolve in water. Because of its high production, nontoxicity, safety, and time efficiency, the conventional Hummers' process has been frequently employed to manufacture GO nanoparticles. GO's dispersibility in polymeric solutions is facilitated by its functional groups. Hydrophobic polymer matrices make it difficult for GO to disperse, therefore an entropy loss is required to overcome the polarity discrepancy and allow the chain to spread.

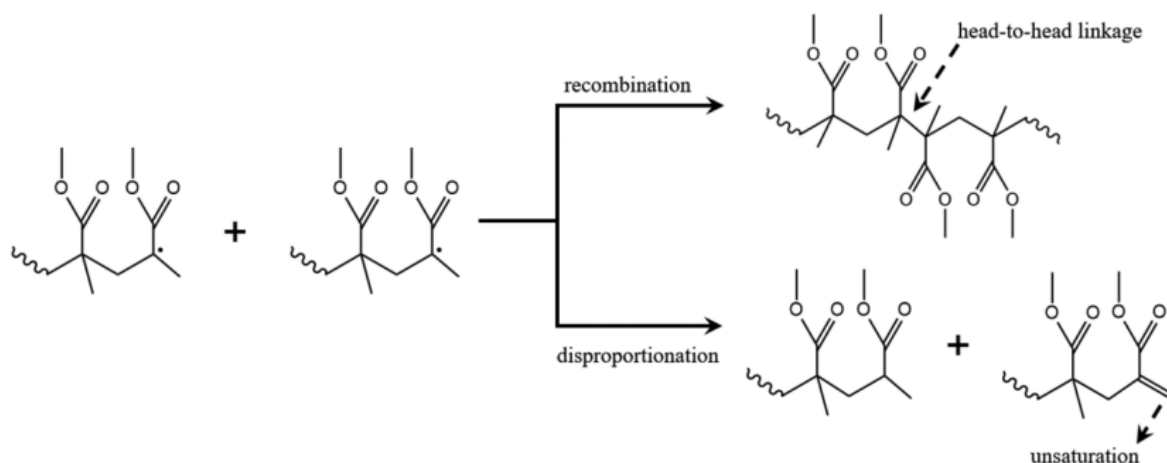


Figure 1. Schematic diagram of chain termination of PMMA radical polymerization via recombination and disproportionation .

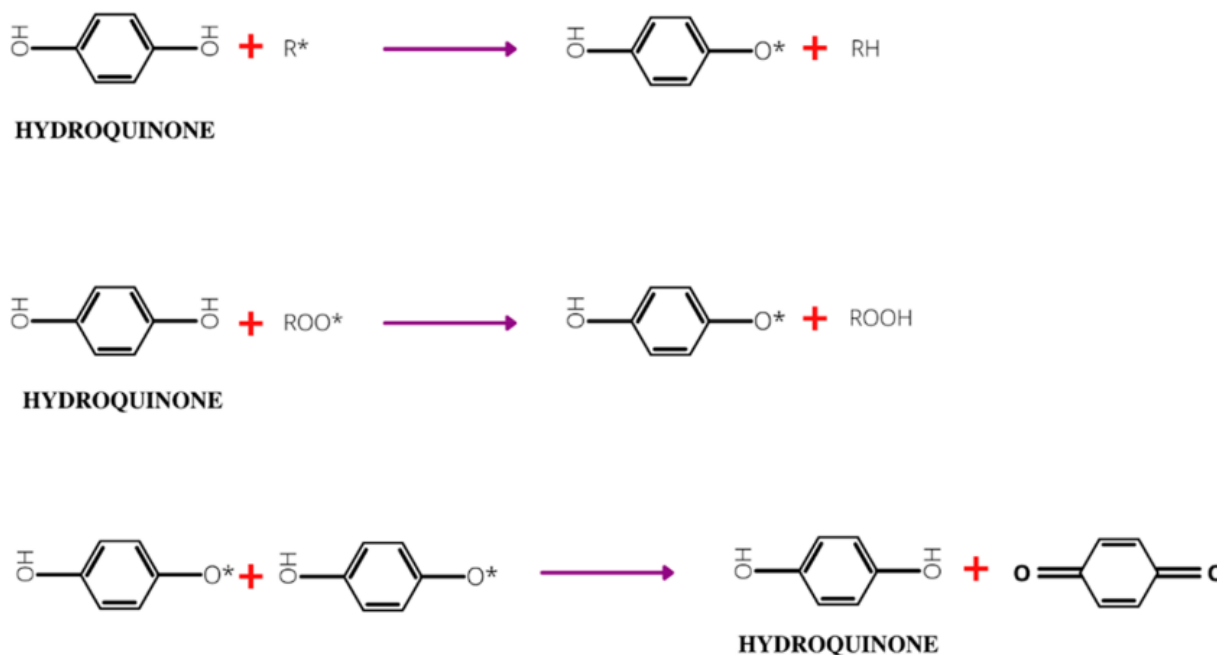


Figure 2. Illustration of the mechanism of hydroquinone as a polymerization inhibitor

Malachite green dye is toxic to aquatic life, yet PMMA-GO-based composites have been demonstrated to effectively filter it out of water systems, as documented in a recent study. More dye molecules were absorbed into the nanocomposite surfaces thanks to efficient collisions facilitated by the presence of iron(III) oxide. Here, we demonstrate that PMMA nanohybrids may be tailored to meet a variety of surface modification and performance requirements by using a variety of nanoparticles and additives. Using bulk and emulsion polymerization methods, we investigate the expanding field of large PMMA nanofillers of GO nanoparticles.

SYNTHESIS METHOD

Polymerization of PMMA

PMMA may be polymerized in emulsion, solvent, or bulk if MMA is the main monomer and a hydroxyl radical initiator is present. When subjected to energy, such as heat or light, the initiator dissolves into free radicals, the number of which depends on the chemical volatility of the component. Figure 1 shows free radicals, which we will refer to as $R\cdot$ for simplicity; after reacting with MMA, these radicals create a chain of oligoradicals or initiator radicals. The current phase of the process is called the chain start phase. In the next stage, when additional MMA monomers react with an R -MMA oligoradical to form a macroradical, the reaction becomes more exothermic. Each new monomer molecule receives the oligoradical's active core. In this process, the chain keeps expanding until no more monomers are available. The termination phase, which may occur by combination or deprotonation, signals the conclusion of polymerization.

Nevertheless, using an excess amount of hydroquinone can slow down the polymerization rate. Figure 3 depicts the mechanism via which HQ inhibits polymerization. Di- and polyhydroxy aromatic compounds are assumed to exert their effects primarily via their ability to donate hydrogen to free radicals. The reaction between the inhibitor and polymerization mixture will yield stable molecules if oxygen is present. As compared to other forms of inhibitors, hydroquinone's nontoxicity, effectiveness in both ambient and enhanced polymerization settings, and manageability throughout the process all make it a standout choice for the polymerization of acrylic polymers. Acrylic polymer inhibitors include not just hydroquinone, but also 2-methyl-2-nitrosopropane and nitrosobenzene.

Bulk Polymerization

Without a solvent, bulk polymerization may be performed with only a monomer and an initiator. Polymers with both step-growth and other forms of chain-growth are being synthesised using this straightforward technique. The bulk polymerization technique is flexible enough to be used with many different kinds of monomers and many different polymerization temperatures.

Table 2. Polymerization Procedure of Bulk Polymerization of PMMA-GO

1.1	method	1.2
graphite powder, ODA, hexane, acetone, anhydrous toluene, methacryloyl chloride, MMA, AIBN, THF	materials	graphite powder, DMF, BPO, hydroquinone, methanol, MMA
1. preparation of GO (Hummers' method)	stages	1. preparation of GO (Hummers' method)
2. reaction of methacryloyl chloride with GO-ODA		2. preparation of the initial monomer/GO mixtures
3. preparation of PMMA-graphene nanocomposites		3. synthesis of PMMA/GO nanocomposites
reaction in a round-bottom flask (magnetic stirrer inside); underwent two freeze-pump-thaw cycles	polymerization setup	ultrasonication for dispersion of GO in solution; nitrogen flow for the reaction of mixture with initiator (polymerization in small test tubes); place into temperature bath for preheated reaction
the products were mixed in THF as a solvent and precipitated in hexane, with drying in vacuum overnight and recovering the samples	procedure to retrieve the sample	stop the polymerization reaction with hydroquinone the products were mixed in dichloromethane as a solvent and precipitated in methanol

Table 3. Surface-Active Agents Used in Emulsion Polymerization of PMMA

surface-active agent	type
polyoxyethylene nonyl phenyl ether	nonionic
<i>N'</i> -hexadecyl- <i>N,N</i> -dimethylacetamidinium bicarbonate and <i>N'</i> -dodecyl- <i>N,N</i> -dimethylacetamidinium bicarbonate	cationic
<i>p</i> -(11-acrylamido)undecanoyloxyphenyl dimethylsulfonium methyl sulfate (AUPDS)	cationic
inulin lauryl carbamate (INUTEC SP1)	nonionic
sodium dodecyl sulfate (SDS)	anionic
sorbitan trioleate (Span 85)	nonionic

Using Table 3's technique 1.1, the GO was functionalized with octadecyl amine (ODA) before being reacted with methacryloyl chloride during the bulk polymerization process. The conductivity of polymer nanocomposites is enhanced when GO is functionalized with ODA, since the dispersion of nanofillers is much enhanced. This reaction is required so that the polymerizable C=C bonds may be incorporated into the nanoparticle surfaces, showing a 9.8-percentage-point decrease in the thermal degradation rate (%/°C) compared to pure PMMA. As shown in Table 3's Method 1.2, GO raised the minimum temperature required to initiate thermal degradation activity. The phenomenon occurs because the produced polymer has a very high molecular weight. The improvement in PMMA-thermal GO's behaviour was not correlated with the molecular weight analysis in method 1.1.

Considering Table 3, it is clear that ultrasonication improves GO dispersions in organic compounds, hydroquinone stops generally accepted that ultrasonication improves GO system-wide dispersion and homogeneity, and that surface damage may be kept to a minimum with careful sonication duration and management. The process of sonication employs the use of sound waves to agitate the dispersion particles inside a solution. When an electronic signal is turned into a mechanical vibration, it may cause materials to shatter. Because of this, solids dissolve more quickly into liquids when the solutions combine.

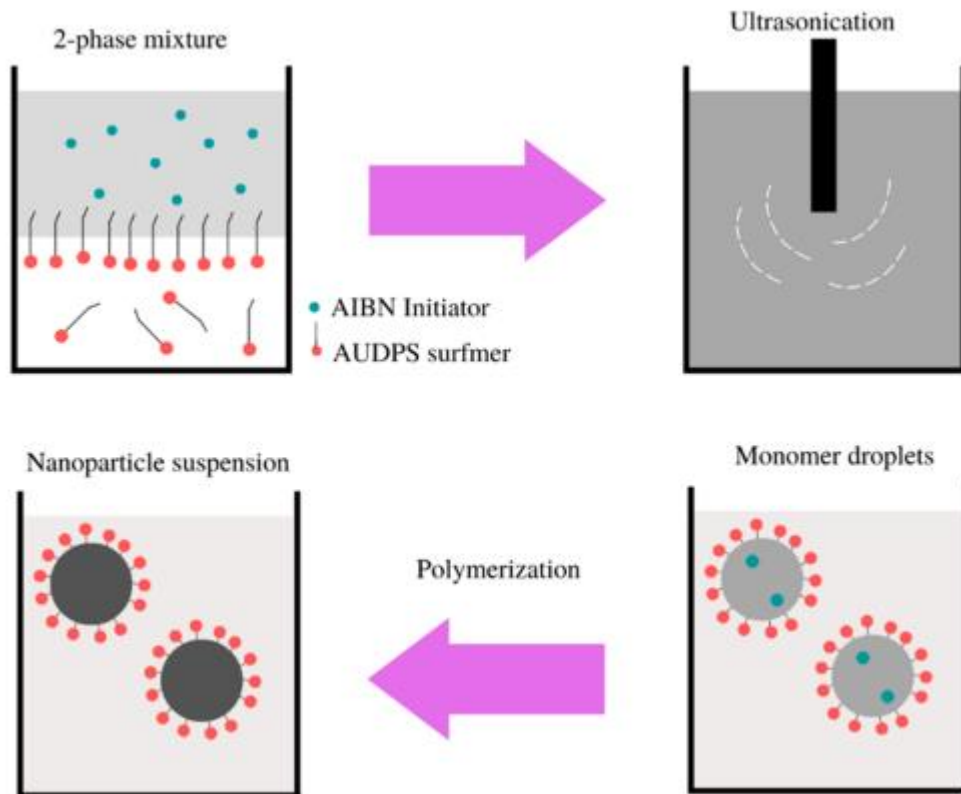


Figure 3. Representation of emulsion polymerization of PMMA using AIBN initiator and AUPDS surfmer (surface active agent) .

Figure 3 displays AIBN-initiated and AUPDS-surfactant-catalyzed PMMA emulsion polymerization (surface-active agent). It was observed that the zeta-potential of the produced NPs was reduced after using AUDPS as a cationic surfactant, most likely due to the AUDPS being internalised during the polymerization process. Sodium dodecyl sulphate (SDS) interacted electrostatically with a polymer, the anionic head groups of which were drawn to the partly positively charged oxygen atoms of the polymer. These surfactants combine with water to produce anions, which are charged negatively. With increasing SDS concentration, particle size may decrease dramatically even before the micelle reaction threshold is reached (CMC).

$$N = K \left(\frac{R_i}{\mu} \right)^{2/5} (a_s S)^{3/5} \tag{i}$$

where N refers to the amount of particles, Ri is the ratio of radical formation (in units of high interfacial area), S is the amount of surfactant, and the value represents the volume growth rate of the micelles. Hence, the kind of surfactant utilised and the quantities of such have substantial effects on particle size.

Earlier studies have shown that surfactants may alter the water phase and the monomer phase (SDBS). The difference between cationic surfactants like VBTAC and anionic surfactants like SDBS may be seen in their chemical structures. The VBTAC process transforms hydrophilic GO into organophilic GO. Therefore, due to the presence of reactive acrylic groups in MMA, it may react with GO during miniemulsion polymerization. In Table 3, you'll find a number of widely used emulsion polymerization creators including AIBN and KPS. One way to polymerize an emulsion is

via a Pickering emulsion. Crystals in this process act as a barrier by attaching to the interfacial of the surfactant molecules and preventing the droplets from merging.

Materials Polarity and Solubility in Polymerization

Polymerization solvents are selected based primarily on the chemical structure and polarity of the polymers. Solvents are optimal for polymers when their solubility characteristics are similar to those of the polymer. Hence, the solubility of the polymer is improved by interactions between molecules of various kinds that are almost at the same energy level. Chain transfer procedures may inhibit polymer development, therefore choosing the right solvent is crucial. Hence, the initiator, monomer, and final polymer must be compatible with the solvent or solvent combination being considered. There won't be any swelling or dissolving if the polymer and solvent have highly distinct molecular structures. Table 4 displays the results of using several solvents in PMMA-GO free radical polymerization. A solvent may be rated as excellent, theta, or poor. It is essential that a solvent encourages maximal monomer-solvent interaction for chain development to occur. In chemistry, the term theta solvent refers to a solvent that, via a series of interactions, produces a stable chain. If you're using a weak solvent, the interaction between your monomer and the solvent won't be too strong to precipitate and cluster, causing links in chains to shatter. Hildebrand's solubility parameter (H) is useful for estimating the degree to which a polymer will dissolve in an organic solvent.

Table 4. Types of Solvent and Initiator in Polymerization of PMMA-GO

polymerization technique	solvent	polarity of solvent	initiator	solubility of initiator
Pickering emulsion	water	polar	KPS	polar
Pickering emulsion	water	polar	KPS	polar
emulsion	water	polar	KPS	polar
in situ free radical	toluene	nonpolar	BPO	nonpolar
in situ free radical	toluene	nonpolar	BPO	nonpolar
in situ	DMF	polar		
	methanol	polar	AIBN	soluble in the most solvent, but insoluble in water
dispersion	methanol	polar	AIBN	
bulk radical	acetonitrile and methanol	polar	AIBN	

APPLICATION OF PMMA-GO

This is some serious Bone Cement. PMMA's exceptional compressive strength plus the fact that it is chemically inert make it a promising polymer for use in orthopaedics. PMMA is utilised as a filler in bone cement applications, where it is injected into fractured vertebrae as a liquid or powder. PMMA nanohybrids may be created by incorporating nanoparticles, which can improve the material's mechanical and biological performance. Extensive optimization of GO has been performed to broaden PMMA's functional scope. Using GO nanoparticles to improve PMMA's

performance, a team of researchers found that even at concentrations as low as 0.25 wt%, GO may have a notable impact on the composites' density, porosity, etc.

Table 5. Applications of PMMA-GO

application	optimum GO (wt %)	aids for application
(a) bone cements	0.10, 0.25	hydroquinone
(b) coating		ATRP (technique)
(c) pour point depressant	1.00	xylene
(d) malachite green dye adsorption	0.5	
(e) antimicrobial adhesion	2	orthocryl resin

When added to PMMA, GO may increase its bending strength by 13% and its Young's modulus by 10%, both compared to GO-free PMMA at a loading ratio of 0.25 wt%. Changes may be responsible for the enhanced bending features of GO. The outcome is an improvement in the matrix international engagement force, which in turn increases the load bearing capacity of polymer composites. As it measures how well a material resists bending displacements, flexural strength is closely related to bending characteristics. When the compression and flexural strengths improve together, the result is greater bending strength. The mechanical properties was 12.6% higher than in the control sample. According to Campose's findings, eq 3 shows a correlation between flexural as well as compressive strength;

$$f_r = a(f_c)^n$$

to the power of n, where f_r is the flexural strength, a is the regression coefficient, f_c is the compressive strength, and n is the power of regression coefficient. Values of f_r and f_c are used to determine the value of a , with f_r and f_c being completely correlated and a value of 1 defining this, and f_c and a value below 1 indicating a skewed interdependence between f_r and f_c . Both a and n have different values depending on the qualities of the material.

In this case, the GO nanopowder led to a shift in the crack front's propagation direction, which led to the emergence of a new fracture surface at an angle to the original crack. As an excessive amount of loading GO reduces fracture toughness, the research concluded that 0.1 wt% was the optimal value of load GO, yielding a 42.2% increase in fracture toughness relative to the control sample.

Fatigue is a leading cause of complete collapse in steels due to dynamic crack propagation in reply to cyclic stresses. Nanoparticle agglomeration is a common phenomenon, and it has a negative impact on the wear resistance of polymer nanohybrids. Including just the proper quantity of GO might be useful here by guaranteeing that the GO is uniformly distributed over the polymer matrix. A study of the energy loss mechanisms related with crack bridging explains how the pullout and breakage of nanomaterials near the deformation crack front slows the crack's rate of propagation.

Although polymethylmethacrylate (PMMA) bone cement has many desirable properties, heat bone necrosis may reduce its efficacy. Because of this, it is crucial that bone cement not melt or shatter when subjected to high temperatures. Research into this issue showed that when GO loading increased from 0.1 to 1.0 wt%, the amount of



heat generated during polymerization decreased. Carbon-based nanoparticles like GO may function as a radical scavenger during the polymerization process in cement, which is produced by heat events.

With high GO loading levels, air trapping and enhanced cement porosity may be the result of the spreading of the nanosized powder and the high cement viscosity. It is generally acknowledged that porosity in the cement microstructure comes from the postpolymerization release of an unreacted residual monomer. Characterization data shows that the porosity content (%) of PMMA is reduced when GO is loaded at a rate of 0.1 wt% compared to the control sample. Increased loading, here defined as 0.1 wt% GO, has an effect on the trend towards greater porosity, however.

Hydroquinone and other polymerization inhibitors are used in the manufacturing of nanocomposite polymer bone cement to mitigate the effects of heat and light on the material.

CONCLUSION

Functionalization of GO on the PMMA matrix yields PMMA-GO nanohybrid composites (NHPs), a new class of materials with excellent properties. For polymerizing PMMA-GO NHP, the choice of surfactant, dispersant, and solvent is important to obtaining the desired characteristics and performance. Integrating GO into PMMA enhances the material's adaptability as a consequence of GO's high specific area and outstanding mechanical, chemical, and thermal characteristics. GO and its composites are good therapeutic materials because their biocompatibility, bioactivity, and physicochemical qualities may be adjusted to fit individual demands. Yet, it is well known that using nanofillers like GO may result in the dispersion of a considerable number of aggregates owing to its surface activity, which may lead to the failure of the composite and a loss of its features. The completed NHP may yet be able to dazzle with the assistance of the suitable dispersion agents and surfactants. When GO is distributed in PMMA at the right concentration, the following applications are guaranteed:

- Bone cement: incorporating small amounts (0.25 wt%) of GO into a PMMA bone cement may improve its fatigue characteristics and fracture toughness.
- PMMA doped with 1 wt% GO drastically lowers viscosity and weakens the wax gelation network, making it an effective pour point depressant.
- Adsorption of Malachite green dye: PMMA with the most GO incorporation absorbs the dye most effectively.
- The antimicrobial adhesion effect was assured by the presence of 2 wt% nGO in PMMA.

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