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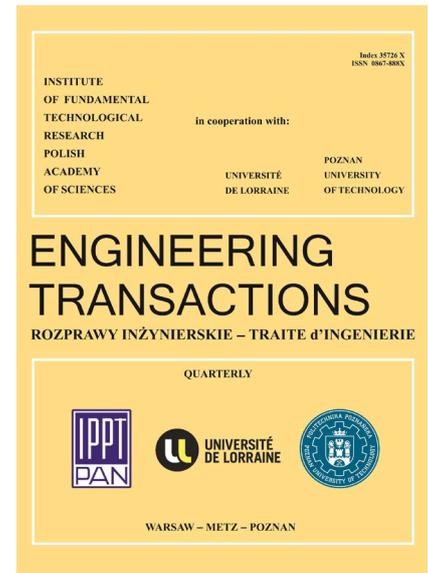
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# Exploring the Synergistic Influences of Clay Nanoplatelets and Waste Eggshell Particles on PMMA-Based Hybrid Nanocomposites

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## ABSTRACT

This study investigates the impact of incorporating clay nanoplatelets and waste eggshell particles into polymethyl methacrylate (PMMA) to develop hybrid nanocomposites with improved mechanical and structural properties. Waste eggshells, rich in biogenic calcium carbonate, were utilized as a sustainable, low-cost filler, while clay nanoplatelets provided nanoscale reinforcement and improved interfacial bonding. Hybrid nanocomposites were prepared with 5 wt. % of filler contents using the solution casting method. Scanning electron microscopy (SEM) was employed to examine the dispersion and morphology of the fillers within the structure of the PMMA matrix. At the same time, Fourier-transform infrared spectroscopy (FTIR) was utilized to assess the powder chemical interactions and potential bonding between the fillers (clay nanoplatelets and eggshell particles). Mechanical behavior was also evaluated through tensile testing of PMMA and its produced hybrid nanocomposites. The results indicate a synergistic enhancement due to the combination of organic biowaste and inorganic nanoclay, offering a promising route for the development of sustainable, high-performance polymer nanocomposites.

*Keywords: Clay nanoplatelets; waste eggshell particles; PMMA; hybrid nanocomposites; tensile mechanical properties.*

## 1. Introduction

The development of polymer-based nanocomposites has garnered considerable attention in recent years due to their improved mechanical and thermal properties compared to

conventional polymer materials. Among polymer matrices, polymethyl methacrylate (PMMA) is an acrylic polymer and the most well-known member of the methacrylate family [1][2]. It is widely applied in different applications due to its enhanced properties, such as being a lightweight, low-density, durable polymer that gives excellent biocompatibility, high transparency, and aesthetic properties [3][4][5]. Such properties make PMMA-based composite materials a highly suitable material for various biomedical applications such as intraocular lenses, orthopedic devices, removable dentures, and bone tissue engineering. Moreover, PMMA and related linear acrylic polymers have also been utilized in other applications such as lightweight armor, electronics fabrication, transportation components, and glass replacement [4][6]. Nevertheless, PMMA resins demonstrate weak surface characteristics and poor mechanical specifications, including a lack of toughness, poor flexural, and impact strength [4][5][7]. Hence, the PMMA polymer matrices require improvement to achieve greater strengthening properties.

Different approaches have been investigated to enhance and expand the range of applications of PMMA polymers, including developing their composites. Consequently, PMMA polymer matrices reinforced by natural nanoparticles, metal oxide nanofillers, carbon-based nanofillers, synthetic or natural fibers, and more have been developed [8][9]. Among these fillers, clay nanoplatelets such as montmorillonite (MMT) provide high aspect ratios and surface areas, offering effective stress transfer and enhanced interfacial bonding within polymer matrices [10]. MMT is one of the most available forms of nanoclays, which comprises small layers with an internal octahedral layer interposed between two tetrasilicate layers [11][12] . Such a structure is reported to inhibit crack formation [13]. Accordingly, several investigations have confirmed that the utilization of clay nanoplatelets enhances the mechanical performance, thermal stability, and dimensional integrity of various composite materials when utilized as fillers [14] [15].

On the other hand, biologically derived waste materials have recently received considerable attention as sustainable fillers in various polymer composites due to their low cost, eco-friendliness, and wide availability. Among these fillers, eggshell waste has emerged as a potential reinforcing additive because it consists primarily of inorganic calcium carbonate

(95%) in the form of calcite and organic type X collagen (5%), sulfated polysaccharide components [16][17].

This high content of calcium carbonate makes eggshell powder functionally similar to traditional mineral fillers used in polymer composites [18]. Therefore, several investigations have reported the effective incorporation of eggshell as a reinforcing material into various polymer matrices, demonstrating enhancements in structural and mechanical properties [19][20][21]. Although eggshell is a biological material whose composition may vary slightly depending on different factors, such as the animal's diet and living conditions [22], appropriate processing steps—including cleaning, drying, and grinding into fine powder—can significantly enhance reproducibility and reduce variability. Consequently, the use of waste eggshell-derived fillers not only provides a sustainable approach for waste valorization but also offers a viable alternative to traditional inorganic fillers in polymer composite applications.

The combination of bio-derived fillers, such as waste eggshell particles and inorganic nanoplatelets, such as clay, presents an innovative approach to fabricating sustainable hybrid nanocomposites [23]. Based on the existing literature, several studies have investigated the impact of clay nanoplatelets on the properties of PMMA-based polymer nanocomposites [13][24]. Furthermore, some other studies have studied the impacts of eggshell particles on the properties of PMMA polymer composites [25][26]. However, still, none of these studies has addressed the reinforcement of PMMA polymer matrices with waste eggshell particles and clay nanoplatelets as dual fillers.

Therefore, this study aims to explore the synergistic effects of combining clay nanoplatelets and waste eggshell particles in a PMMA matrix, investigating how these fillers influence the morphological, chemical, and mechanical properties of the resulting hybrid nanocomposites. This research seeks to contribute to the advancement of green materials by integrating sustainable waste materials and nanotechnology, with enhanced functionality for potential industrial applications. For this purpose, PMMA hybrid nanocomposites were fabricated by incorporating the waste eggshell particles and clay nanoplatelets as hybrid fillers into PMMA. Morphological properties of the tensile

fractured samples, as well as the filler distribution on the PMMA matrix, were observed using Scanning Electron Microscopy (SEM). In addition to that, the chemical interactions between the waste eggshell particles and clay nanoplatelets were investigated using Fourier transform infrared (FTIR) spectroscopy. Moreover, tensile properties (strength and Young's modulus) of the pure PMMA and its produced composites were investigated.

## 2. Materials and Methods

### 2.1. Materials

Polymethyl methacrylate (PMMA) was used as a polymer matrix and supplied by Orthocryl-Dentaurum, Germany. Montmorillonite (MMT) based nanoclay and eggshell particles were used in this study as reinforcement materials. The MMT nanolplatelets were purchased from Sigma Aldrich chemicals, UK. These nanoplatelets were originally modified with approximately 30% octadecylamine and were used in composites as received. Eggshell particles were prepared as described in the following section (2.2).

### 2.2. Preparation of eggshell particles

Brown waste eggshells were collected from household waste. First of all, the thin inner membrane was removed as much as possible, as it is proteinaceous and may interfere with the polymer. Next, the shells were washed thoroughly with warm, soapy water to remove grease and egg residue. Thereafter, the waste shells were boiled in hot water for 15 minutes. Then, the cleaned shells were dried in an electric oven at 60°C for 180 minutes. After that, the dried shells were smashed by hand into small pieces and then ground into powder using a high-speed blender. For particle sizes less than 75 microns, a 200-mesh sieve was used.

### 2.3. Fabrication of hybrid nanocomposites

The solution casting method has been performed to fabricate PMMA hybrid nanocomposites. Specimens of pure PMMA were first cast with the use of hardener in the ratio of 100/2 (resin to hardener weight ratio). Thereafter, specimens of PMM/5 wt. % of clay nanoplatelets were fabricated as follows. First, pure PMMA was stirred in a beaker using a mechanical stirrer (WiseStir/HS-50A). While stirring, clay nanoplatelets were slowly added to the PMMA, and the mixture was stirred continuously for an additional 5 minutes at a speed of 500 r/min. Thereafter, the mixture was sonicated using an ultrasonic

probe sonicator (Misonix Sonicator 3000) for 3 minutes to improve the homogenization of the mixture. After a proper dispersion of clay nanoplatelets in the PMMA matrix, the hardener was added in a ratio of 100:2. The solution was then poured into a tensile mold (an aluminum mold (Figure S1) according to the ASTM D638). The same procedure was followed to fabricate the specimens of PMMA/5 wt. % of eggshell particles. However, the hybrid nanocomposites of PMMA/5 wt. % of clay nanoplatelets and eggshell particles were fabricated by mixing 2.5 wt. % of clay nanoplatelets and 2.5 wt. % of eggshell particles, and then adding them to the matrix, following the same procedure above. Hereafter, the produced specimens were referred to as PMMA, PMMA/C, PMMA/E, and PMMA/C/E.

## 2.4. Morphological observations

The surface morphology of the tensile fractured samples (PMMA, PMMA/C, PMMA/E, and PMMA/C/E) were observed using Scanning Electron Microscopy (Tescan VEGA3). In order to eliminate the electrostatic surface charging effect, the specimens were coated with Au. Thereafter, the specimens were mounted on an aluminum stud using double-sided carbon tape. The images were collected using the XFlash detector 410 M with 200 V of beam deceleration.

## 2.5. Fourier transform infrared (FTIR) spectroscopy

In order to investigate the chemical interaction between eggshell particles and clay nanoplatelets, an FTIR was conducted. A PerkinElmer Frontier spectrometer (Waltham, MA, USA) with a single reflection diamond ATR accessory was used. The analysis was conducted with a range of wavenumbers between 4000 cm$^{-1}$ and 500 cm$^{-1}$ and an angle of incidence of 16° from the perpendicular. The average of scan repetitions was 8 scans for each specimen at 2 cm$^{-1}$ of resolution.

## 2.6. Tensile testing

Tensile properties (strength and modulus) of PMMA polymer and its hybrid nanocomposites were tested using HST WDW-100E 100KN Computer control electromechanical universal testing machine. The test was performed according to the ASTM D638 standard at a constant crosshead displacement rate of 40 %/min. The force-strain values were recorded during the test, and the recorded values were used to calculate

the ultimate tensile strength and Young's modulus properties of the produced samples. The tensile strength of each specimen was determined at the maximum stress prior to fracture, while Young's modulus was calculated from the slope of the initial linear elastic region of the stress-strain curve. The tests were performed at room temperature ($22 \pm 3$ ∘C). Three tests were carried out for each type of specimen, and the average value was reported.

## 3. Results and discussion

### 3.1. Fracture surface morphology

The surface morphology of each tensile fractured sample was observed using SEM, and the images are presented in Figure 1. The tensile fracture morphology of pure PMMA exhibited a brittle fracture character with some cracks, sharp edges, and also exhibits a rapid crack structure, as shown in Figure 1a. This could confirm the nature of PMMA, which is intrinsically brittle [27]. However, after the addition of 5 wt. % of clay nanoplatelets to the PMMA (Figure 1b), the micrograph exhibited a comparatively rough surface with varying morphological features. For instance, relatively uniform and flat surfaces were observed in some zones (Figure 1b), whereas in others, sharp edges and rough surfaces were observed. Furthermore, the SEM micrograph in Figure 1b shows some agglomerated clay nanoplatelets (highlighted by arrows) on the fractured surface. The high surface area of nanoplatelets and the strong attractive interactions between them result in their agglomeration [28]. This could reduce the potential improvement of mechanical properties (see section 3.3) in polymer nanocomposites because of the restriction of the interfacial area. Moreover, Figure 1b exhibited some microvoids (indicated by arrows), which may be attributed to the agglomerated clay nanoplatelets pulling out. Similar fracture surface morphology was also observed for that of PMMA/E, as shown in Figure 1c. However, after the addition of both fillers (clay and eggshell particles) to PMMA, the SEM micrograph (Figure 1d) showed a rougher surface with sharper edges than those of PMMA, PMMA/C, and PMMA/E. Furthermore, agglomerated particles are also observed in Figure 1d, which may be related to one or both of the fillers. However, in comparison to those of single filler composites (PMMA/C and PMMA/E), a more uniform dispersion of fillers can be noticed in Figure 1d (indicated by arrows) when dual fillers were used. This may be attributed to the proper mixing of clay and eggshell particles before adding them to PMMA.

Moreover, eggshell particles could break down any agglomerated clay nanoplatelets during mixing, which could also enhance the dispersion of clay in the PMMA matrix. This contributes effectively to the improvement of the tensile properties of the produced hybrid nanocomposites (discussed in section 3.3).
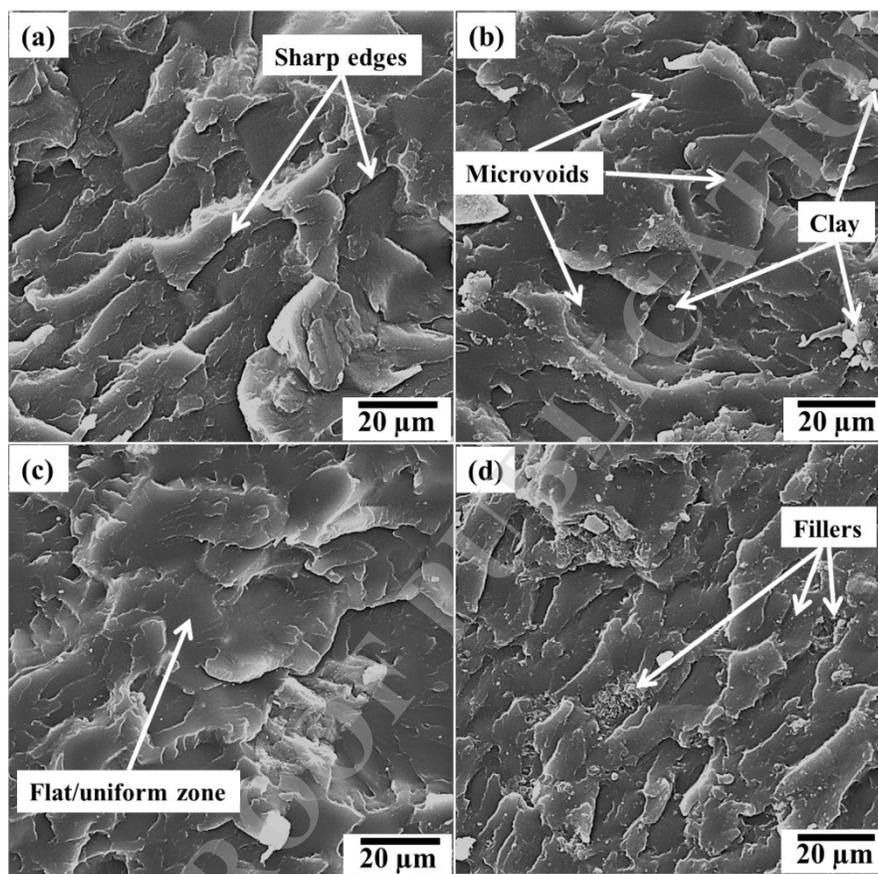


Figure 1. SEM micrographs of (a) pure PMMA, (b) PMMA/ 5 wt. % clay nanoplatelets, (c) PMMA/ 5 wt. % eggshell particles, and PMMA/ 5 wt. % clay and eggshell particles.

## 3.2. Chemical analysis by FTIR

To further understand the actual interaction between clay nanoplatelets and eggshell particles, FTIR absorption spectra of powder samples were collected. Figure 2 exhibits the collected FTIR spectra of clay nanoplatelets, eggshell particles, and a mixture of both fillers (clay and eggshell). The FTIR spectrum of clay nanoplatelets in Figure 2 showed absorption bands that are in good agreement with the previous studies [29]. In Figure 2, the spectrum of clay nanoplatelets shows characteristic peaks at 3462 and 1659 cm$^{-1}$, which

represent the OH stretching vibration of the clay silicate interlayers [29]. The characteristic bands at 1122, 1057, and 874 cm$^{-1}$ can be ascribed to Si-O stretching vibrations of clay nanoplatelets [30].

The FTIR spectrum of both fillers (clay nanoplatelets and eggshell particles) is presented in Figure 2. The spectrum displays an almost identical pattern to that of clay nanoplatelets, except for some new bands that were indicated by arrows in Figure 2. For instance, a characteristic band observed at a wavenumber of 2512 cm$^{-1}$ in the spectrum of clay and eggshell. In contrast, there was no absorption peak in this wavenumber range in the clay spectrum. However, this absorption band was clearly visible in the FTIR spectrum of eggshell (Figure 2), which was attributed to the existence of a hydrogen group in the eggshell structure [20]. Therefore, the observed peak (2512 cm$^{-1}$) in the spectrum of clay and eggshell could be assigned to the presence of eggshells. Another observed shoulder peak in the spectrum of both filers (clay and eggshell) at about 1831 cm$^{-1}$. This peak could have resulted from the carbonyl group existed in the eggshell structure [20]. Moreover, the spectrum of clay and eggshell showed two peaks at 1463 and 1057 cm$^{-1}$ that are not present in the spectru of eggshell, whereas they exist in the spectrum of clay. The observed peak (1463 cm$^{-1}$) in the spectrum of clay was attributed to the CH$_2$ in-plane scissoring vibrations [31], whereas the band at 1057 cm$^{-1}$ was assigned to Si-O stretching vibrations of clay nanoplatelets [30]. Furthermore, the spectrum of clay and eggshell in Figure 2 also showed two absorption peaks at 874 and 706 cm$^{-1}$. Compared to the spectra of clay and eggshell in Figure 2, these two bands appeared as very weak broad bands in the clay spectrum, while they were clearly visible in the eggshell spectrum. The existence of these two bands (874 and 706 cm$^{-1}$) in the spectrum of eggshell were associated with the out-of-plane deformation and in-plane deformation, respectively, which indicates the existence of calcium carbonate (CaCO$_3$) in the eggshell structure [32]. However, in the spectrum of clay nanoplatelets, the absorption band at 874 cm$^{-1}$ was related to the bending vibration of OH groups [33], whereas the band at 706 cm$^{-1}$ was attributed to the CH$_2$ vibration absorption [27]. Therefore, from the FTIR results, it can be concluded that the clay nanoplatelets were successfully grafted onto the surface of eggshell particles. Thus, could confirm the mechanical properties of PMMA/C/E hybrid nanocomposites that showed higher tensile strength and modulus than those of single filler composites (see section 3.3).
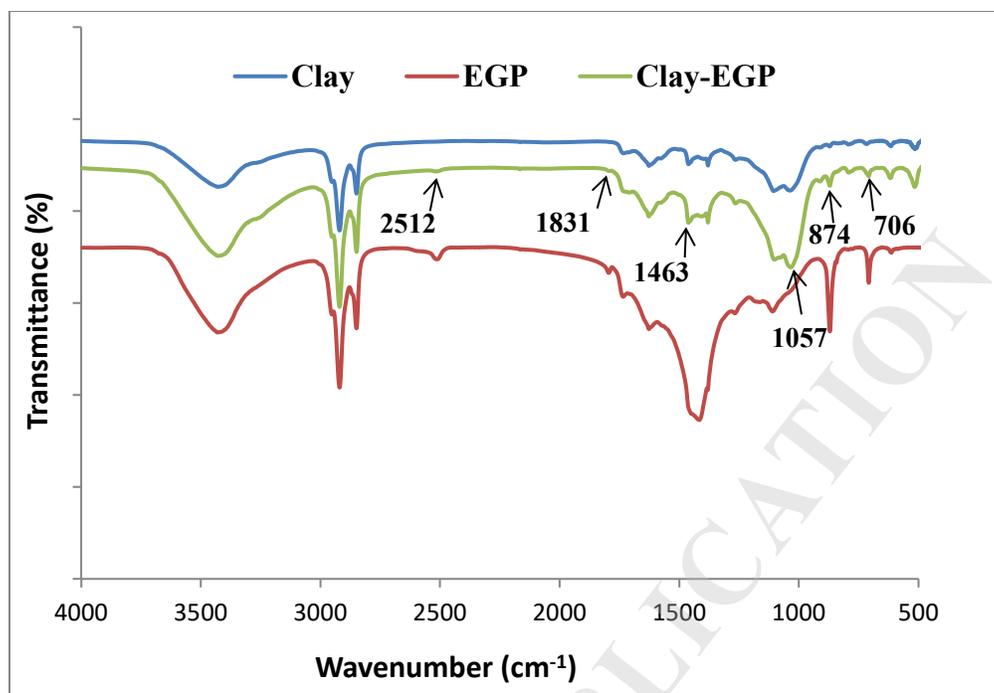
Figure 2. FTIR spectra of clay nanoplatelets, eggshell particles, and clay/eggshell particles.

## 3.3. Tensile properties

The tensile properties (strength and modulus) of pure PMMA and its hybrid nanocomposites (PMMA/C, PMMA/E, and PMMA/C/E) are presented in Figure 3. Moreover, the detailed results of the tensile tests, including the tensile stress, tensile strain, and Young's modulus for all tested samples, with standard errors, are presented in Supplementary Table S1. It can be clearly observed from Figure 3 that PMMA/C nanocomposites demonstrate lower tensile strength than pure PMMA. The average tensile strength of the pure PMMA was $30.722 \pm 0.54$ MPa. With the addition of 5 wt. % of clay nonoplatelets to the PMMA-based polymer, the average tensile strength was decreased to $20.011 \pm 1.41$ MPa (Figure 3). This can be attributed to the nature of the PMMA matrix, which is brittle to some extent [6], and the addition of clay nanoplatelets could provide further brittleness characteristics in the amorphous matrix [31]. Furthermore, the observed results (Figure 3) could also be attributed to the interfacial interaction between the exfoliated clay nanoplatelets and the PMMA matrix. Materials in the range of size less than 100 nm usually tend to cluster or agglomerate, because of the dominant intermolecular van der Waals interactions between them [34]. This has resulted in poor interfacial

interaction between clay and PMMA matrix, consequently decreasing effective stress transfer within the polymer nanocomposite, weakening the mechanical properties [35]. It is also observed that (Figure 3) the incorporation of eggshell particles into PMMA matrix leads to a further decrease in tensile strength (17.857 ± 0.78 MPa) if compared with those of PMMA and PMMA/C. This is in agreement with other studies that recorded a decrease in tensile strength when eggshell particles were incorporated into epoxy polymer matrices [36]. This drop in tensile strength might be related to the stress concentration effect produced by eggshell particles in the PMMA matrix [37]. However, another work reported an increase in tensile strength when smaller particle sizes (0.2 μm) of eggshells were incorporated into a polyvinyl chloride matrix [38]. Such an increase may be attributed to the size of eggshell particles that are used as filler, as well as the processing technique.

On the other hand, the incorporation of both fillers (clay nanoplatelets and eggshell particles) into PMMA polymer to produce hybrid nanocomposites showed an increase in tensile strength (23.043 ± 2.07 MPa) if compared with those values of single filler composites (PMMA/C and PMMA/E), as shown in Figure 3. Generally, the micron-sized particles in hybrid composites carry most of the load, while the nano-sized fillers fill the spaces around the micron-sized particles, improving the interfacial bonding between polymer and micron-sized particles and reducing voids or weak regions [39][40]. Therefore, the achieved tensile strength of PMMA/C/E in Figure 3 could be attributed to the inclusion of eggshell particles and clay nanoplatelets as hybrid fillers in the structure of PMMA. A similar trend was also reported, where the mechanical properties of the hybrid silica/epoxy composites show an improvement in tensile strength compared to the single filler composites [39].

It is noteworthy to mention that, although the tensile strength is reduced after the inclusion of clay nanoplatelets/ eggshell particles into PMMA, the modulus is constantly increased compared with that of pure PMMA, as presented in Figure 3. For example, the average tensile modulus of the pure PMMA was 0.958 ± 0.075 GPa. With the addition of clay nanoplatelets (5 wt. %) to the PMMA, the average tensile modulus was increased to 1.248 ± 0,093 GPa, as shown in Figure 3. This could be attributed to the high modulus properties of clay nanoplatelets when it is dispersed at the nanoscale level in the polymer matrices

[41]. In contrast, the inclusion of eggshell particles into the PMMA matrix showed a lower tensile modulus (1.144 ± 0.075 GPa) than that of PMMA/C as presented in Figure 3. The size of eggshell particles significantly affects the final mechanical properties of the produced composites [42]. The decrease in modulus after the incorporation of eggshell particles can be attributed to the large particle size of eggshells, which acts as a stress concentration. However, it is important to mention that the incorporation of both fillers (clay nanoplatelets and eggshell particles) into the PMMA matrix has increased the modulus to a value of 1.474 ± 0.068 GPa. This promising result could be attributed to the uniform distribution of clay nanoplatelets and eggshell particles in the PMMA polymer matrix, as confirmed by SEM observations in Section 3.1.
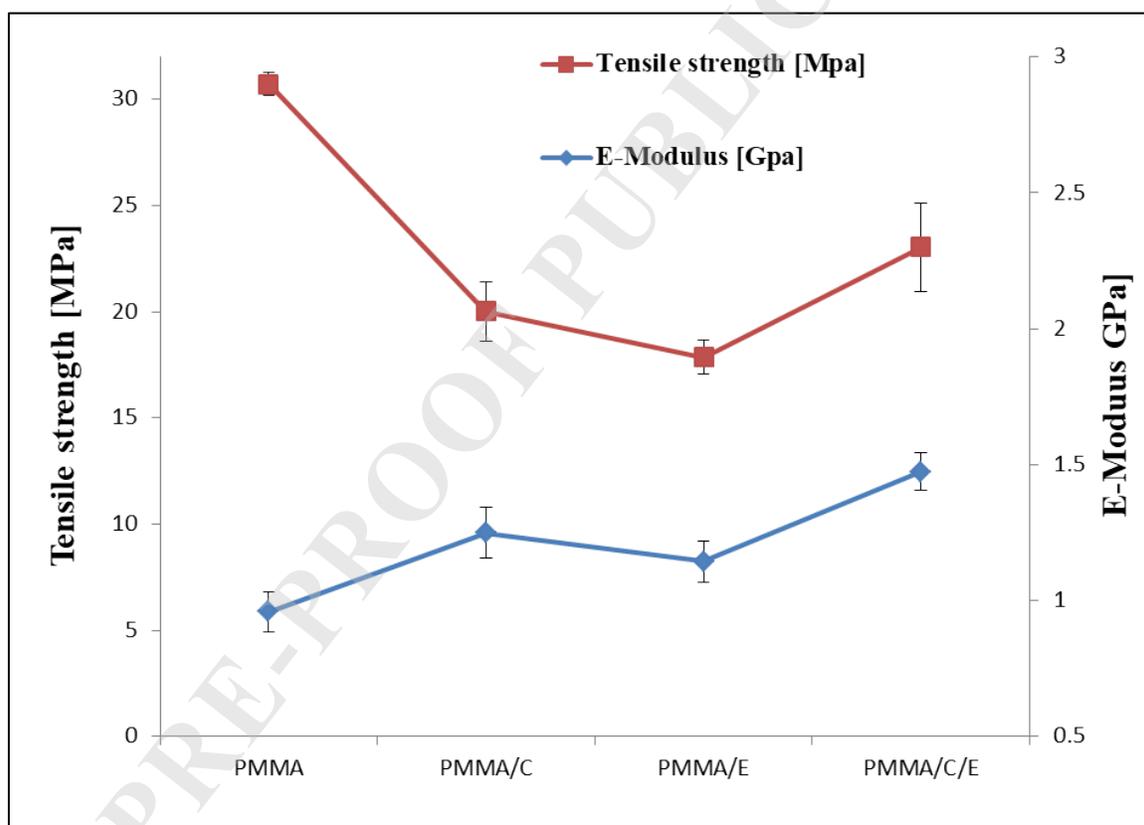


Figure 3. Comparison of Tensile strength and Young's modulus of pure PMMA, PMMA/clay nanocomposites (PMMA/C), PMMA/eggshell composites (PMMA/E), and PMMA/clay/eggshell hybrid nanocomposites (PMMA/C/E), obtained from tensile stress-strain curves.

## Conclusion

The incorporation of clay nanoplatelets and eggshell particles significantly influenced the structural, chemical, and tensile properties of PMMA hybrid nanocomposites. The structural analysis confirmed a more homogeneous distribution of both fillers within the PMMA polymer matrix, indicating good interfacial bonding and improved composite integrity if compared to those of single-filler composites. FTIR results revealed noticeable chemical interactions between clay nanoplatelets and eggshell particles, suggesting the formation of a stable hybrid network. Moreover, the introduction of clay nanoplatelets and eggshell particles resulted in a decrease in tensile strength compared with pure PMMA; nevertheless, Young's modulus increased, indicating a positive contribution of the fillers to the stiffness of the polymer composite matrix. This could be attributed to the synergistic reinforcing effect of clay nanoplatelets and eggshell particles. Overall, the study demonstrates that combining inorganic clay with bio-derived eggshell fillers offers an effective and sustainable strategy to enhance the mechanical performance and stability of PMMA hybrid nanocomposites.

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**Appendix:**

Figure S1. Tensile mold made of aluminum, Figure S2. Produced samples of PMMA and its composites, Table S1. The tensile stress, Young's modulus, and tensile strain for all tested samples, Figure S3. Stress-Strain curves of (a) pure PMMA, (b) PMMA/5 wt % of clay, (c) PMMA/5 wt % of eggshell, and (d) PMMA/2.5 wt % of clay/ 2.5 wt % of eggshell.



Figure S1. Tensile mold made of aluminum

Figure S2. Produced samples of PMMA and its composites

Table S1. The tensile stress, Young's modulus, and tensile strain for all tested samples

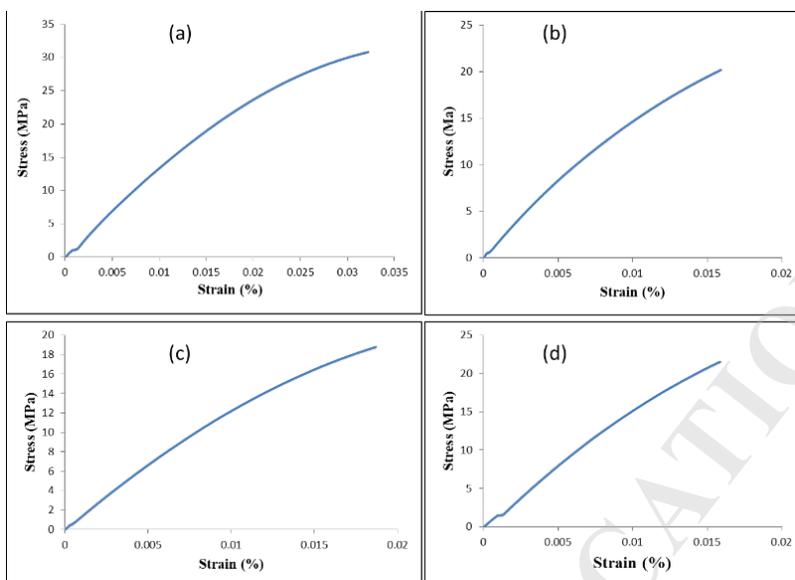| PMMA | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break % |
|---|---|---|---|
| Sample 1 | 31.309 | 0.993 | 0.034 |
| Sample 2 | 30.00 | 0.853 | 0.037 |
| Sample 3 | 30.857 | 1.028 | 0.032 |
| PMMA/ 5 WT % Clay | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break % |
| Sample 1 | 20.178 | 1.327 | 0.016 |
| Sample 2 | 18.2 | 1.300 | 0.022 |
| Sample 3 | 21.657 | 1.116 | 0.014 |
| PMMA/ 5 WT % Eggshell | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break % |
| Sample 1 | 18.777 | 1.062 | 0.018 |
| Sample 2 | 17.931 | 1.243 | 0.019 |
| Sample 3 | 16.863 | 1.127 | 0.014 |
| PMMA/ 2.5 WT % Clay/ 2.5 WT % Eggshell | Tensile strength (MPa) | Young's modulus (GPa) | Elongation at break % |
| Sample 1 | 25.972 | 1.57 | 0.015 |
| Sample 2 | 21.645 | 1.427 | 0.013 |
| Sample 3 | 21.512 | 1.424 | 0.014 |

Figure S3. Stress-Strain curves of (a) pure PMMA, (b) PMMA/5 wt % of clay, (c) PMMA/5 wt % of eggshell, and (d) PMMA/2.5 wt % of clay/ 2.5 wt % of eggshell.