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Technical Note

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

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This study investigates the impact of incorporating clay nanoplatelets and waste eggshell particles into poly(methyl 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. The hybrid nanocomposites were prepared at a filler content of 5% (hereafter designated as 5 wt.%) 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) and the PMMA matrix. The mechanical behavior of the PMMA and the produced hybrid nanocomposites was also evaluated through tensile testing. 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 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, poly(methyl methacrylate) (PMMA) is an acrylic polymer and the most well-known member of the methacrylate family [1, 2]. It is widely used in different applications due to its excellent properties, such as low weight, low density, highly durable polymer providing excellent biocompatibility, high transparency, and great aesthetic properties [3–5]. Such properties make PMMA-based composite materials highly suitable 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, low flexural and impact strengths [4, 5, 7]. Hence, the PMMA polymer matrices require improvement to achieve greater mechanical performance.

Different approaches have been investigated to enhance and expand the range of applications of PMMA polymers, including the development of composites. Consequently, PMMA polymer matrices reinforced by natural nanoparticles, metal oxide nanofillers, carbon-based nanofillers, and synthetic or natural fibers 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 nanoclay, which comprises thin 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 (utilized as fillers) enhances the mechanical performance, thermal stability, and dimensional integrity of various composite materials [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 along with organic type X collagen (5 %) and 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 [19–21]. 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, other studies have evaluated the impacts of eggshell particles on the properties of PMMA polymer composites [25, 26]. However, 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 with nanotechnology to provide enhanced functionality for potential industrial applications. For this purpose, PMMA hybrid nanocomposites were fabricated by incorporating waste eggshell particles and clay nanoplatelets as hybrid fillers into PMMA. The morphological properties of the tensile fractured samples, as well as the filler distribution in the PMMA matrix, were examined using scanning electron microscopy (SEM). In addition, the chemical interactions between the waste eggshell particles and clay nanoplatelets were investigated using Fourier transform infrared (FTIR) spectroscopy. Moreover, the tensile properties (tensile strength and Young's modulus) of the pure PMMA and the fabricated nanocomposites were investigated.

2. Materials and methods

2.1. Materials

PMMA was used as the polymer matrix and supplied by Orthocryl-Dentaurum, Germany. MMT-based nanoclay and eggshell particles were used in this study as the reinforcement materials. The MMT nanolplatelets were purchased from Sigma-Aldrich, UK. These nanoplatelets were originally modified with approximately 30 % octadecylamine and were used in composites as received. The eggshell particles were prepared according to the procedure described in the following subsection.

2.2. Preparation of eggshell particles

Brown waste eggshells were collected from household waste. First, 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 washed shells were boiled in hot water for 15 min. Then, the cleaned shells were dried in an electric oven at 60 °C for 180 min. After that, the dried shells were crashed by hand into small pieces and then ground into a powder using a high-speed blender. For particle sizes less than 75 µm, 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 by mixing the resin with a hardener at a weight ratio of 100/2. Thereafter, specimens of PMM/5 wt.% of clay nanoplatelets were fabricated as follows. First, pure PMMA resin was stirred in a beaker using a mechanical stirrer (WiseStir/HS-50A). While stirring, the clay nanoplatelets were slowly added to the PMMA, and the mixture was stirred continuously for additional 5 min at a speed of 500 r/min. Thereafter, the mixture was sonicated using an ultrasonic probe sonicator (Misonix Sonicator 3000) for 3 min to improve the homogenization of the mixture. After the proper dispersion of the clay nanoplatelets in the PMMA matrix, the hardener was added at a ratio of 100:2. The solution was then poured into a tensile mold (an aluminum mold according to the ASTM D638, supplementary Fig. A1, see Appendix). The same procedure was followed to fabricate the PMMA specimens reinforced with 5 wt.% eggshell particles. However, for the hybrid nanocomposites, a total filler mass fraction of 5 % was achieved by mixing equal mass fractions (2.5 % clay nanoplatelets and 2.5 % eggshell particles), and then adding them to the matrix via the same procedure of mixing and sonification. Hereafter, the produced specimens (shown in supplementary Fig. A2, see Appendix) are 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) was examined using SEM (Tescan VEGA3). In order to eliminate the electrostatic surface charging effect, the specimens were coated with Au. Thereafter, the specimens were mounted onto an aluminum stud using double-sided carbon tape. The images were collected using an XFlash 410 M detector with a beam deceleration of 200 V.

2.5. FTIR spectroscopy

In order to investigate the chemical interactions between eggshell particles and clay nanoplatelets, FTIR was conducted. A PerkinElmer Frontier spectrometer (Waltham, MA, USA) with a single reflection diamond attenuated total reflectance (ATR) accessory was used. The analysis was conducted over a wavenumber range of $4000\,cm^{-1}$ to $500\,cm^{-1}$ at an angle of incidence of 16° from the perpendicular. For each specimen, a total of 8 scans were averaged at a spectral resolution of $2\,cm^{-1}$.

2.6. Tensile testing

Tensile properties (strength and modulus) of the pure PMMA polymer and its hybrid nanocomposites were tested using an HST WDW-100E 100 KN computer-controlled electromechanical universal testing machine. The test was performed according to the ASTM D638 standard at a constant crosshead displacement rate of 40 mm/min. The load-displacement 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 from the maximum stress obtained 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 °C ±3 °C). Three tests were carried out for each type of specimen, and the average values were reported.

3. Results and discussion

3.1. Fracture surface morphology

The surface morphology of each tensile fractured sample was observed using SEM, and the representative images are presented in Fig. 1. The tensile fracture morphology of pure PMMA exhibits a brittle failure mode with some cracks, sharp edges, and also exhibits a rapid crack structure, as shown in Fig. 1a. This confirms the nature of PMMA, which is intrinsically brittle [27]. However, after the addition of 5 wt.% clay nanoplatelets into the PMMA (Fig. 1b), the micrograph exhibited a comparatively rougher surface with varying morphological features. For instance, relatively uniform and flat surfaces are observed in some zones (Fig. 1b), whereas in others, sharp edges and rough surfaces are observed. Furthermore, the SEM micrograph in Fig. 1b shows some agglomerated clay nanoplatelets (highlighted by arrows) on the fractured surface. The high surface area of nanoplatelets and the strong attractive forces between them results in their agglomeration [28]. This agglomeration can reduce the potential im-

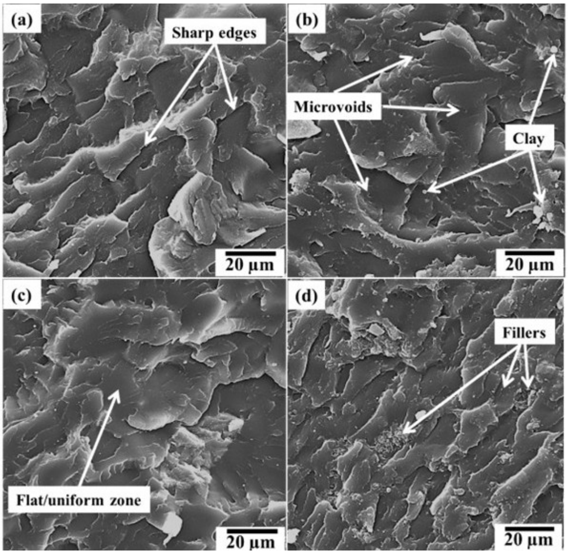

Fig. 1. SEM micrographs of: a) pure PMMA, b) PMMA/C, c) PMMA/E, and d) PMMA/C/E.

provement of mechanical properties (see Subsec. 3.3) due to a reduction in the interfacial area. Moreover, Fig. 1b shows some microvoids (indicated by arrows), which may be attributed to the pull-out of the agglomerated clay nanoplatelets. A similar fracture surface morphology was also observed for that of PMMA/E, as shown in Fig. 1c. However, after the addition of both fillers (clay nanoplates and eggshell particles) to PMMA, the SEM micrograph (Fig. 1d) shows a rougher surface with sharper edges than those of PMMA, PMMA/C, and PMMA/E. Although, agglomerated particles are also observed in Fig. 1d, which may be related to either or both filler types, a more uniform dispersion of fillers is observed (Fig. 1d, indicated by arrows) compared to the single-filler composites (PMMA/C and PMMA/E), when dual fillers were used. This may be attributed to the proper mixing of the clay and eggshell particles before adding them to PMMA. Moreover, eggshell particles could break down any agglomerated clay nanoplatelets during mixing, thereby enhancing the dispersion of nanoclay in the PMMA matrix. This dispersion contributes effectively to the improvement of the tensile properties of the produced hybrid nanocomposites (discussed in Subsec. 3.3).

3.2. Chemical analysis by FTIR

To further understand the actual interaction between the clay nanoplatelets and eggshell particles, FTIR absorption spectra of the powder samples were collected. Figure 2 displays the collected FTIR spectra of the clay nanoplatelets, eggshell particles, and the mixture of both fillers (clay and eggshell). The FTIR

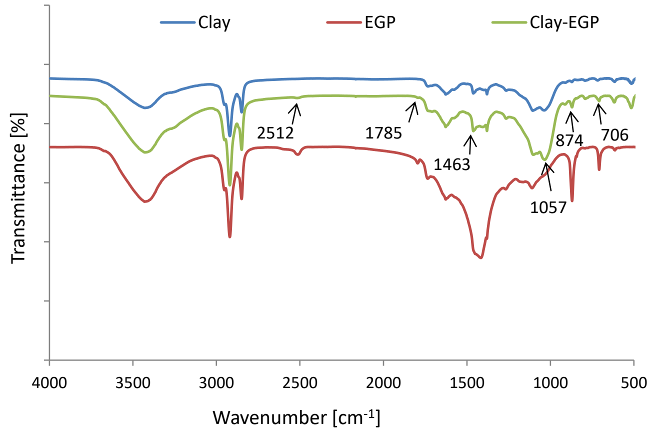

FIG. 2. FTIR spectra of clay nanoplatelets, eggshell particles, and clay/eggshell particles.

spectrum of the clay nanoplatelets in Fig. 2 shows absorption bands that are in good agreement with those presented in previous studies [29]. In Fig. 2, the spectrum of clay nanoplatelets shows characteristic peaks at 3462 cm^{-1} and 1659 cm^{-1}, which corresponds to the O-H stretching vibration of the clay silicate interlayers [29]. The characteristic bands at 1122 cm^{-1}, 1057 cm^{-1}, and 874 cm^{-1} can be ascribed to Si-O stretching vibrations of the clay nanoplatelets [30].

The FTIR spectrum of both fillers (clay nanoplatelets and eggshell particles) is presented in Fig. 2. The spectrum displays an almost identical pattern to that of clay nanoplatelets, except for some new bands indicated by arrows in Fig. 2. For instance, a characteristic band is observed at a wavenumber of 2512 cm^{-1} in the hybrid spectrum. In contrast, there was no absorption peak at this wavenumber range in the clay spectrum. However, this absorption band is clearly visible in the FTIR spectrum of eggshell (Fig. 2), which is 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 shoulder peak is observed in the spectrum of both filers (clay and eggshell) at about 1831 cm^{-1}. This peak could have resulted from the carbonyl group that existed in the eggshell structure [20]. Moreover, the spectrum of clay and eggshell showed two peaks at 1463 cm^{-1} and 1057 cm^{-1} that are not present in the spectrum of eggshell, whereas they exist in the spectrum of clay. The observed peak (1463 cm^{-1}) in the spectrum of clay is attributed to the CH_2 in-plane scissoring vibrations [31], whereas the band at 1057 cm^{-1} is assigned to Si-O stretching vibrations of clay nanoplatelets [30]. Furthermore, the spectrum of clay and eggshell in Fig. 2 also shows two absorption peaks at 874 cm^{-1} and 706 cm^{-1}. Compared to the spectra of clay and eggshell in Fig. 2, these two bands appear 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 cm^{-1} and 706 cm^{-1}) in the spectrum of eggshell is 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} is related to the bending vibration of O-H groups [33], whereas the band at 706 cm^{-1} is attributed to the CH_2 vibration absorption [27]. Therefore, from the FTIR results, it can be concluded that the clay nanoplatelets are successfully grafted onto the surface of eggshell particles. Thus, this confirms the improved mechanical properties of the PMMA/C/E hybrid nanocomposites, which showed higher tensile strength and modulus than those of the single-filler composites (see Subsec. 3.3).

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 Fig. 3. Moreover, the detailed results of the tensile tests, including the tensile stress, elongation at break, and Young's modulus for all tested samples, with standard errors, are presented in supplementary Table A1. It can be clearly observed from Fig. 3 that the PMMA/C nanocomposites demonstrate lower tensile strength than the pure PMMA. The average tensile strength of the pure PMMA is 30.722 MPa ±0.54 MPa. With the addition of 5 wt.% of clay nanoplatelets to the PMMA-based polymer, the average tensile strength decreased to 20.011 MPa ±1.41 MPa (Fig. 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 (Fig. 3) could also be attributed to the interfacial interaction between the exfoliated clay nanoplatelets and the PMMA matrix. Materials in the size range of less than 100 nm usually tend to cluster or

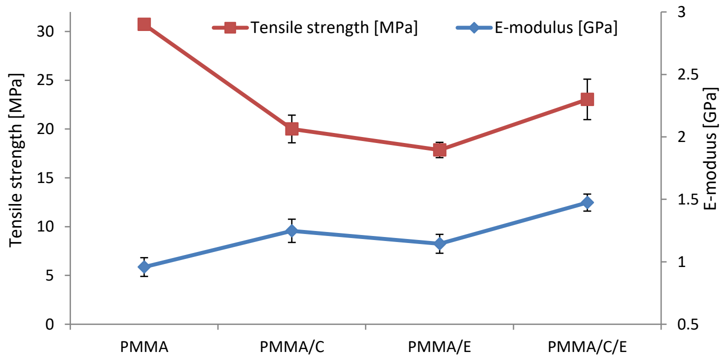

Fig. 3. Comparison of tensile strength and Young's modulus of pure PMMA, PMMA/C, PMMA/E, and PMMA/C/E, obtained from tensile stress-strain curves.

agglomerate, because of the dominant intermolecular van der Waals interactions between them [34]. This results in poor interfacial interaction between the clay and the PMMA matrix, consequently decreasing effective stress transfer within the polymer nanocomposite and weakening the mechanical properties [35]. It is also observed form Fig. 3 that the incorporation of eggshell particles into the PMMA matrix leads to a further decrease in tensile strength (17.857 MPa ±0.78 MPa) when 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]. The overall deformation behavior and mechanical response of these materials can be further observed in the stress-strain curves presented in supplementary Fig. A3 (see Appendix). 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 used as filler, as well as the processing technique.

On the other hand, the incorporation of both fillers (clay nanoplatelets and eggshell particles) into the PMMA polymer to produce hybrid nanocomposites shows an increase in tensile strength (23.043 MPa ±2.07 MPa) when compared with the single-filler composites (PMMA/C and PMMA/E), as shown in Fig. 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 the polymer and the micron-sized particles and reducing voids or weak regions [39, 40]. Therefore, the achieved tensile strength of PMMA/C/E in Fig. 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 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 Fig. 3. For example, the average tensile modulus of the pure PMMA is 0.958 GPa ±0.075 GPa. With the addition of clay nanoplatelets (5 wt.%) to the PMMA, the average tensile modulus was increased to 1.248 GPa ±0.093 GPa, as shown in Fig. 3. This could be attributed to the high modulus properties of clay nanoplatelets when they are dispersed at the nanoscale level in polymer matrices [41]. In contrast, the inclusion of eggshell particles into the PMMA matrix shows a lower tensile modulus (1.144 GPa ±0.075 GPa) than that of PMMA/C, as presented in Fig. 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 the 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 increases the modulus to a value of 1.474 GPa ±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 the SEM observations in Subsec. 3.1.

4. 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 when compared to those of single-filler composites. FTIR results revealed noticeable chemical interactions between the 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 the 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.

Appendix

Fig. A1. Tensile mold made of aluminum.

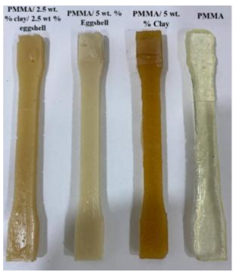

Fig. A2. Fabricated specimens of pure PMMA and its composites.

Table A1. Tensile stress, Young's modulus, and elongation at break for all tested samples.

	Tensile strength [MPa]	Young's modulus [GPa]	Elongation at break [%]
PMMA			
Sample 1	31.309	0.993	3.4
Sample 2	30.000	0.853	3.7
Sample 3	30.857	1.028	3.2
PMMA/5 wt.% clay			
Sample 1	20.178	1.327	1.6
Sample 2	18.200	1.300	2.2
Sample 3	21.657	1.116	1.4
PMMA/5 wt.% eggshell			
Sample 1	18.777	1.062	1.8
Sample 2	17.931	1.243	1.9
Sample 3	16.863	1.127	1.4
PMMA/2.5 wt.% clay/2.5 wt.% eggshell			
Sample 1	25.972	1.570	1.5
Sample 2	21.645	1.427	1.3
Sample 3	21.512	1.424	1.4

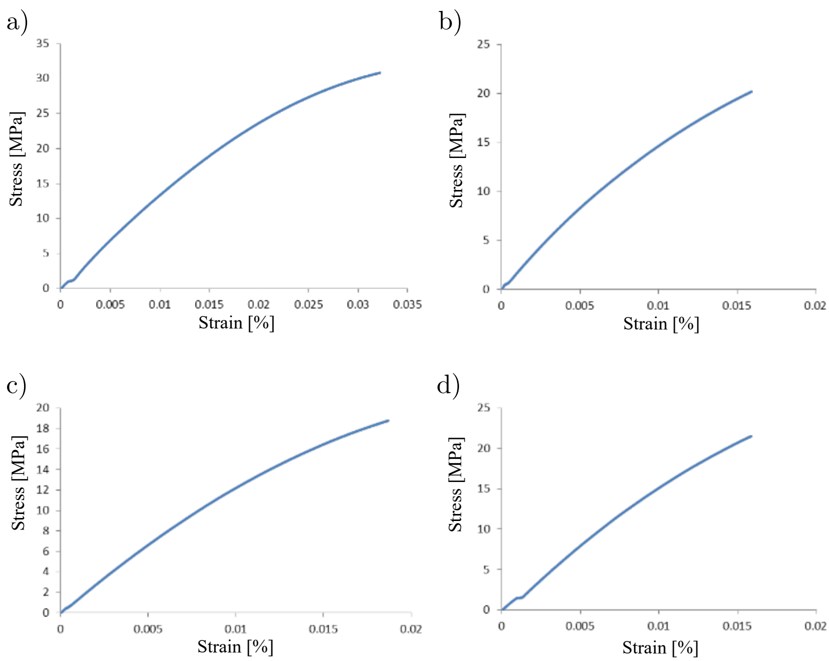

Fig. A3. Stress-strain curves of:
a) pure PMMA, b) PMMA/C, c) PMMA/E, d) PMMA/C/E.

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Conflict of interest

The authors declare that there are no known competing financial interests or personal relationships that could have influenced the work described in this paper.

Authors' contributions

All authors contributed to the study conception, methodology, data analysis, and manuscript drafting, and read and approved the final manuscript.

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