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Fabrication and characterization of polymethylmethacrylate/polysulphone/β-tricalcium phosphate composite for orthopaedic applications

Kalambettu Aravind Bhat · Padmavathi Rajangam · Sangeetha Dharmalingam

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Abstract Polymethylmethacrylate (PMMA) and polysulphone (PSu) are biocompatible polymers and are used widely for biomedical applications. In this study, a blend membrane of PMMA/PSu was fabricated using methylene bisacrylamide (MBA) as the blending agent and its properties were studied. Subsequently, a composite membrane consisting of β-tricalcium phosphate (β-TCP) filler dispersed in a polymer matrix of PMMA/PSu was fabricated and evaluated for application as an orthopaedic prosthetic material. Fourier Transform Infrared Spectroscopy spectra of the blend confirmed the interaction of PMMA and PSu with the blending agent MBA. The X-ray diffraction analysis showed that PMMA/PSu membranes exhibited a higher degree of crystallinity when compared with that of the individual polymers. The thermal properties of the samples studied by thermogravimetric analysis showed an increase in the thermal stability of the PMMA/PSu when compared with individual PMMA and PSu membranes. The morphology of the composite samples analysed through SEM showed that the fillers were widely distributed and agglomerated at certain places. The tensile strength of the PMMA/PSu/β-TCP was found to be inferior to that of PMMA/β-TCP although much superior to that of PSu/β-TCP composite membranes. Hardness testing performed using durometer hardness tester (Shore D) showed that the PMMA/PSu/β-TCP samples exhibited higher hardness than the composites having individual PMMA and PSu matrices. Analysis of the optical properties of the polymer membranes suggested good blend formation between PMMA and PSu. The in vitro bioactivity study suggested that the density of the calcium phosphate layer formed on the surface of PMMA/PSu/β-TCP was much higher than that of composites made of either PMMA or PSu matrix. The results of the study showed that the blended composite membranes exhibited favourable properties for biomedical applications such as for orthopaedic prostheses.

Introduction

Polymethylmethacrylate (PMMA) is an interesting polymer for the prosthetic industry exhibiting fairly good compatibility with human tissues. In medicine, it is mainly used as a prosthetic device for applications in artificial lenses, dentures and artificial limbs [1]. PMMA also has an important application as bone cement for the cementation of metallic and non-metallic prostheses to bone [2].

Arias et al., in their review [3], described the role of sulphate groups in inducing nucleation of calcium carbonate. Amongst the various sulphur group containing polymers, polysulphone (PSu) has been widely accepted for biomedical applications. It is a stable and biocompatible polymer and has been used for haemodialysis and catheters [4].

Universally, the most popular and widely followed procedure for fixing artificial limb prostheses is by the use of bone cements. However, this is beset with the problem of loosening over long term usage thus often necessitating a second revision surgery [5]. An important limiting factor of the existing polymers for application as bone substitutes is their lack of bioactivity [2, 6]. Bioactivity is a desired advantage due to which osseointegration can be achieved through the formation of hydroxyapatite on the surface of the polymer thus eliminating the requirement of bone cements [7, 8].

K. A. Bhat · P. Rajangam · S. Dharmalingam (✉)
Department of Chemistry, Anna University, Guindy,
Chennai 600 025, India
e-mail: sangeetha@annauniv.edu

Cross linking of PMMA is usually achieved using dimethacrylates such as 2,2-bis-[4-(2-hydroxy-3methacryloyloxypropyl)phenyl]propane (bis-GMA), triethylene glycol dimethacrylate (TEGDMA), 1,6-bis-[2-methacryloyloxyethoxycarbonylamino]-2,4,4-trimethylhexane (UDMA), and decanediol dimethacrylate (D3MA), ethylene glycol dimethacrylate (EGDMA) or triethylene glycol dimethacrylate (TREGDMA). Amongst the difunctional acrylamides, *N*,*N*-ethylene bisacrylamide (EBA) and *N*,*N*-methylene bisacrylamide (MBA) are popular cross-linking agents [9, 10]. The use of bisacrylamides results in a more hydrolytically stable polymer than that obtained using dimethacrylates [9]. In addition, the presence of amide groups provides a possibility for blend formation between incompatible polymers such as PMMA and PSu [11]. In this article, we report for the first time the use of MBA as a blending agent as well as the fabrication of PMMA/PSu composites for biomedical applications. The proposed interaction between PMMA, PSu and MBA is illustrated in Fig. 1.

The introduction of ceramic particles into the polymers results in an alteration in chemistry along the surface which would facilitate a biochemical attachment with the bone [12]. One such material is tricalcium phosphate (β-TCP) ceramic particles which are biocompatible, biodegradable and partially water soluble [12, 13].

In this study, a composite comprising of PMMA/PSu blend matrix and β-TCP filler was fabricated and their suitability for application as an orthopaedic prosthesis possessing a desired level of bioactivity was evaluated. The bestowing of bioactivity on orthopaedic prosthetic implants is expected to bring about osseointegration of the implant with the bone at the site of implantation. The novelty of this study lies in the fabrication of a composite membrane with a matrix of traditionally incompatible polymers, PMMA and PSu, blended using MBA. In addition, the optical properties of the blend polymer were evaluated as a supporting evidence for homogenous blending of the polymers.

Although for load-bearing applications, the traditional three-dimensional fabrication processes such as injection moulding and compression moulding are preferred, and in this study, the samples were fabricated as membranes due to its ease of fabrication and small scale of the study. In addition, for applications involving filling of bone defects which arise due to trauma, disease or surgery, the composites in the form of flexible membranes would be ideally suited.

Materials and methods

PMMA was purchased from Asian Acrylates, Mumbai, India, whilst PSu was purchased from Sigma-Aldrich. The solvent Tetrahydrofuran (THF) and the filler β-TCP were purchased from Sisco Research Laboratories, Mumbai and Sigma-Aldrich, respectively. For the bioactivity study, simulated body fluid (SBF or Kokubo solution) was prepared in the lab as per the procedure described by Kokubo [14].

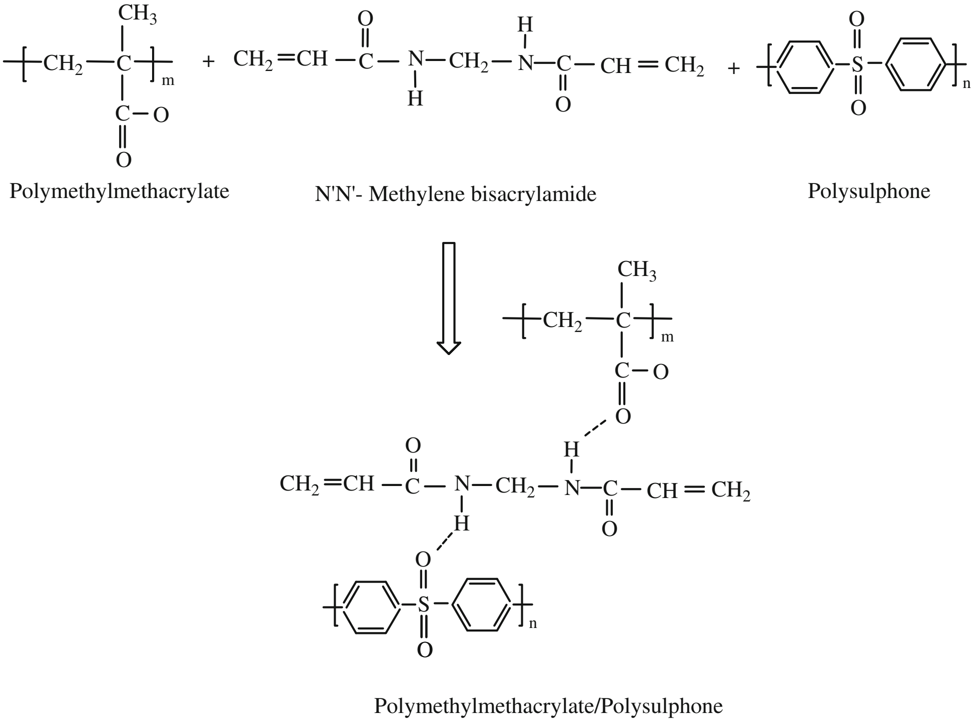

Fig. 1 Proposed structure of blend formation between PMMA and polysulphone via MBA

Preparation of polymer membranes

In order to compare the properties of the blend membrane with those of the individual constituent polymers, the experimental samples were divided into three groups. The first, second and third groups were comprised of PMMA, PSu and PMMA/PSu blend, respectively. The blending agent used was MBA.

THF was the common solvent that was used for the fabrication of all the membranes. In brief, 2 g of PMMA powder and 2 g of PSu pellets were dissolved in THF separately under constant overnight stirring. The blend polymer was prepared by stirring of the mixture of the polymer solutions taken in weight ratio of 1:1 along with 1 ml of MBA. The polymer solutions were then cast into petridish and the solvent evaporated by heating them in an oven at 40 °C. The obtained polymer membranes were then separated from the petridish and washed repeatedly with deionized water.

Characterization studies

Fourier Transform Infrared Spectroscopy (FTIR)

The interaction between the two polymers and MBA was analysed using FTIR. The FTIR spectra of PMMA, PSu and their blend were recorded in transmission mode using Perkin Elmer RX I FTIR spectrometer in KBr disc form from 400 to 4000 cm^{-1} with a resolution 4 cm^{-1}.

X-ray diffraction (XRD)

The membrane sample was subjected to powder XRD studies with Rich Seifert X-ray diffractometer using CuKα radiation of wavelength 1.5418 Å with a scan speed of 0.2°/s.

Thermogravimetric analysis (TGA)

The thermal analysis was carried out using TGA model Q50 V20.6 build 31 systems. The measurements were conducted by heating from room temperature to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Optical properties

The optical properties of the three groups were studied using a UV–Visible spectrophotometer and a refractometer. The Perkin Elmer Lambda 950 UV–Visible spectrophotometer was used to measure and record the difference in the UV absorbance of the three polymers. The Atago digital pocket refractometer with a range from 0.0 to 53.0% Brix, and a resolution of 0.1% Brix was used to determine the refractive indices of the polymers.

Preparation of the polymer composite membranes

In order to achieve bioactivity, it was essential to incorporate a bioactive agent such as β-TCP into the polymer matrix. The composite membranes were prepared in the same procedure as was followed for the preparation of the polymer membranes as discussed in "Preparation of polymer membranes". The only additional step was the incorporation of the β-TCP particles (0.25 wt%) into the polymer solution followed by ultrasonication before casting it in petridish. Hence, three sets of composite membranes were obtained—PMMA/β-TCP, PSu/β-TCP and PMMA/PSu/β-TCP. The surface morphology, bioactivity and mechanical properties of the obtained composites were studied.

Preparation of SBF

SBF was prepared according to the procedure described by Kokubo et al. [14]. In this fluid, the inorganic ions are maintained at a concentration and pH that is highly similar to that found in the human body. The concentration of the various ions in the human body and that in the SBF (Kokubo solution) are known to be very similar [15–17].

Testing of the composite membranes

Surface morphology

The surface morphology of the samples was studied using scanning electron microscope (SEM). The samples were sputtered with gold and viewed under SEM (S-3400, Hitachi, Japan) with an accelerating voltage of 5 kV.

Mechanical properties

The mechanical properties of the composite membranes were analysed by estimating their tensile strength and hardness. The tensile test was performed as per ASTM standard D-638 type V with UTM (Hounsfield). Hardness was measured according to ASTM D 2240 standard using a durometer hardness tester (Shore D).

Bioactivity study

The bioactivity property of the polymers was evaluated by analysing the calcium phosphate layer formed on the surface of the samples after immersion in the Kokubo solution for 4 days. The samples were then retrieved, dried in an oven at 40 °C for 4 h, and then examined under SEM. The samples were also subjected to EDS elemental analysis for further confirmation of the formation of the calcium phosphate layer.

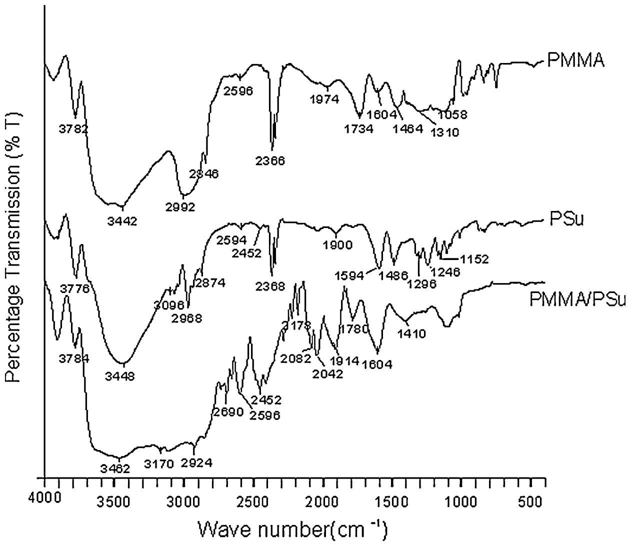

Fig. 2 FTIR spectra of PMMA, PSu and PMMA/PSu membranes

Results and discussion

Analysis of the polymer membranes

FTIR studies

The FTIR spectra of the polymer membranes of PMMA, PSu and their blends are given in Fig. 2. In the spectrum of PMMA, the peak appearing at 1058 cm^{-1} was assigned to the C–H stretching. The weak peak at 1242 cm^{-1} was due to O–CH$_3$. The peak at wave number 1464 cm^{-1} was assigned to the CH$_2$ stretching vibrations whilst the peaks at wave numbers 1604 and 1734 cm^{-1} were attributed to the stretching of the C=O bond. The peak seen at 1310 and the double peak at 2366 cm^{-1} represents O=C–O vibration, whilst the broad peak at 2596 cm^{-1} is due H–C=O stretching vibrations. The alkane CH stretching is interpreted by the occurrence of peaks at 2846 and 2992 cm^{-1}. The sharp peak observed at 3442 points to the OH stretch which is probably due to hydrogen bonding.

In the spectrum of PSu, the peak seen at wave numbers 1152 and 2368 cm^{-1} were due to the O=S=O symmetric stretching which is characteristic of sulphone groups. The C–H wag is observed from the medium peak at 1246 cm^{-1}. The strong peak seen at 1594 cm^{-1} and the weak peaks at 1900 and 2036 cm^{-1} were due to the C–C stretching and phenyl ring substitution overtones, respectively in the PSu polymer. The peaks at 2368 and 2452 cm^{-1} were assigned to the asymmetric stretching of O=S=O, respectively. The C–H stretching of the aromatic ring is evidenced by the presence of two small sharp peaks at 2968 and 3096 cm^{-1}, whilst the C–C stretching of the aromatic ring is observed with the peaks at 1594 and 1486 cm^{-1}. The broad peak at 3448 cm^{-1} indicates the presence of O–H vibrations which are due to hydrogen bonding.

From the spectrum corresponding to PMMA/PSu, it was observed that the peaks at 1410 and 1604 cm^{-1} corresponded to the C–C stretch in the aromatic ring. The appearance of a strong peak at 1780 cm^{-1} was considered to be due to C=O which was shifted from the 1734 cm^{-1} position as observed in the spectrum of PMMA. The presence of strong peaks at 1914, 2042 and 2082 cm^{-1} were assigned to the phenyl ring substitution overtones which were now shifted and also stronger than that observed in the spectrum of PSU (1900 and 2036 cm^{-1}) as a result of interaction between PSU and MBA. The appearance of a medium peak at 1100 cm^{-1} was assigned to C–N stretch of amine from the MBA. The strong peaks at 2402 and 2452 cm^{-1} were considered as a shift of the corresponding peaks of PMMA (2366 cm^{-1}) and PSu (2368 cm^{-1}) as a result of interaction of both the polymers with MBA. It was also noted that the peak at 1152 cm^{-1} in the PSu corresponding to the O=S=O did not appear in the spectrum of the blend. The shift in the peak for H–C=O (2690 cm^{-1} for the blend as compared to 2596 and 2594 cm^{-1} for PMMA and PSu, respectively) also indicated the presence of a strong interaction between PMMA, PSu and MBA. The peaks of 2924 and 3170 cm^{-1} were assigned to the asymmetric C–H stretch of the methyl group and the free amide groups from MBA, respectively. The broad peak at 3462 cm^{-1} indicates the O–H vibrations due to extensive hydrogen bonding. Thus, the FTIR

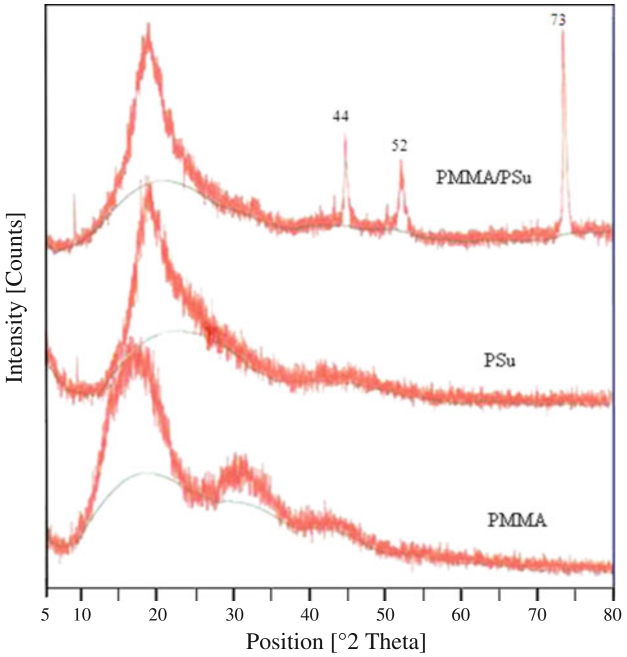

Fig. 3 XRD spectra of PMMA; PSu and PMMA/PSu polymer samples

analysis of the samples gives evidence of a strong interaction of PMMA and PSu with MBA resulting in the formation of a blend polymer.

XRD

The XRD analysis (Fig. 3) yielded interesting results. From the diffraction patterns of PMMA and PSu, their amorphous nature is noticed. On the other hand, the PMMA/PSu membrane showed new peaks at 2θ values of 44, 52 and 73, which were indicative of an increase in its crystallinity when compared with PMMA and PSu membranes. This was significant considering that both the starting polymers were amorphous. The increase in the crystallinity of the PMMA/PSu suggested a strong interaction of PMMA and PSu with MBA which resulted in their good blending.

TGA

The thermal properties of the polymers were compared by studying their TGA curves. The TGA curves of PMMA, PSu and PMMA/PSu polymers are shown in Fig. 4. From the TGA curve of PMMA, a gradual weight loss up to a temperature of 400 °C was observed which was attributed to the solvent and water molecules. Since the melting point of PMMA is 108 °C, it would be safe to assume that the degradation of the polymer chains would have occurred. The steep curve observed between 400 and 460 °C was due to the breakdown of the polymer backbone.

PSu exhibited a two-step degradation wherein, the initial weight loss (up to a temperature of 133 °C) was indicative of the removal of solvent and water. The gradual decrease in weight thereafter, up to a temperature of 450 °C, indicated the high thermal stability due to the aromatic portion of the polymer. A further steep drop in the curve (between 433 and 550 °C) was indicative of degradation of the polymer backbone.

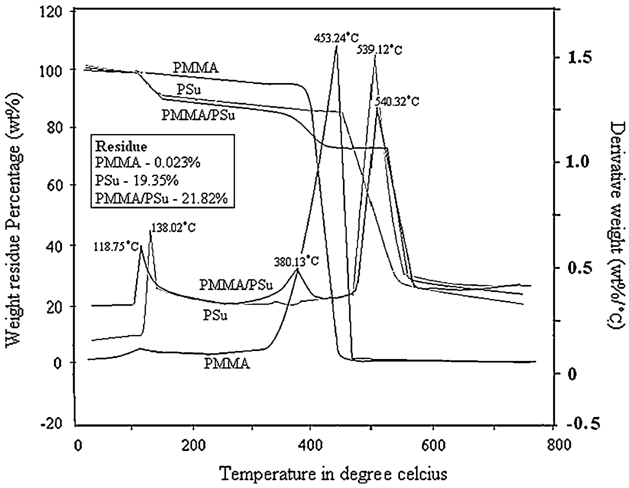

Fig. 4 TGA curves of PMMA, PSu and PMMA/PSu blend

In comparison, the PMMA/PSu polymer showed three-step degradation. The initial weight loss of up to 113 °C was due to the removal of water and solvent molecules. The subsequent drop in weight was attributed to the degradation of PMMA not involved in interaction with MBA. Further gradual decrease in weight up to 550° C was attributed to the effect of blending by MBA. In contrast to the rapid weight loss witnessed between 400 and 450 °C for the PMMA, the blend polymer showed a loss of only 15 wt% up to a temperature of 550 °C. A sudden drop in weight seen at 550 °C was in contrast with similar weight loss seen in the PSu membrane at 433 °C which indicated that the blend polymer had better thermal stability.

Optical properties

It is expected that if good blending occurred between any two polymers, then the refractive index (RI) of the blended polymer system would be different from those of the constituent polymers. On the other hand, if there was a phase separation, then the RI would be either of the two polymers. It is also known that, in the case of immiscible fully amorphous polymers, solvent evaporation would result in the formation of either a transparent or a two-layered film depending on whether they had the same or different refractive indices [18]. Some investigators have reported that, in a polymer system composed of two miscible polymers, there was a linear variation in the RI of the polymer system on varying the ratio of the constituent polymers [19–21]. Hence, the study of optical properties is important for determining the interaction between two incompatible polymers such as PMMA and PSu.

The optical properties of the polymers were studied using a refractometer and UV–Visible spectroscopy. The RIs of PMMA, PSu and PMMA/PSu blend are given in Table 1. It was observed that whilst PSu had a RI of 0.8 which was greater than that of PMMA (0.7), the blend polymer exhibited the highest RI (1.1). It is well known that crystalline materials have high RI whilst amorphous materials have low RI [22]. The increase in the RI of the blend polymer was reasoned as occurring due to the increase in the crystallinity. The increase in crystallinity is attributed to the greater interaction between PMMA chains,

Table 1 Measured refractive index of the polymer samples

Polymer sample	Refractive index
PMMA	0.7
PSu	0.8
PMMA/PSu	1.1

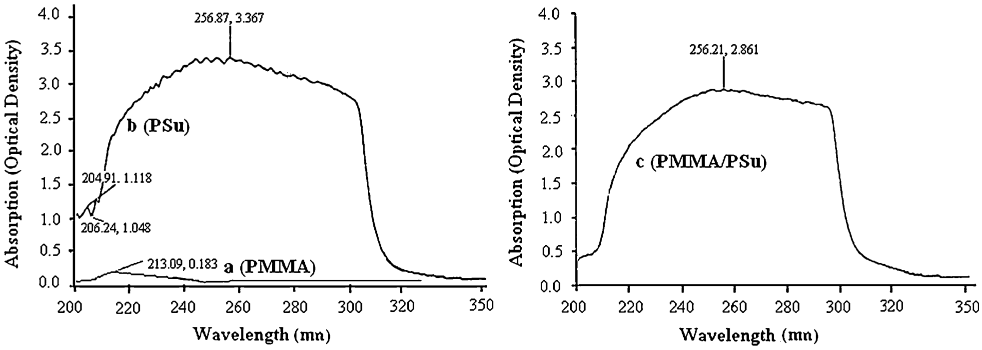

Fig. 5 UV absorption spectra of (*a*) PMMA; (*b*) PSu and (*c*) PMMA/PSu

MBA and PSu. This result corroborates with the interpretations of the FTIR and XRD studies.

The UV–Visible spectroscopic graphs are displayed in Fig. 5. From the figure, it is seen that there is a peak absorbance at a wavelength of 213 nm for PMMA (Fig. 5a) and at 256 nm for PSu (Fig. 5b). There is a visible change in the peak absorbance value (optical density (OD) = 3.3) for the blend polymer at wavelength of 256 nm (Fig. 5c) from that observed for PSu (OD = 2.8) indicating that the blend polymer showed different absorbance of UV radiation than that exhibited by the PSu. Optical density is always expressed as the negative logarithm of transmission.

$$\mathrm{OD} = -\log_{10}T \quad (\mathrm{or}) \quad T = l0^{-\mathrm{OD}}$$

where T is the transmittance of the sample (polymer).

It is noteworthy that the peak for PMMA (wavelength at 213 nm) was not seen in the spectra of the blend polymer indicating that the interaction between the two polymers masks the absorbance of the UV light by PMMA. This interaction also resulted in the shift in the absorbance value at 204 nm (for PSu) from 1.18 to a lower value of 0.4 in the polymer blend. This study is significant as it suggests that homogenous blending of the two polymers was achieved with the use of MBA.

Mechanical properties of the composite membranes

Tensile testing

The tensile strength and percentage elongation of the samples are given in Table 2.

Table 2 Tensile and hardness properties of the composite samples

Sample	Tensile strength (MPa)	Percentage elongation (%)	Durometer hardness
PMMA/β-TCP	21	2.65	48
PSu/β-TCP	9.7	4.4	42
PMMA/PSu/β-TCP	17.30	2.3	51

It is seen that the tensile strength of the PMMA/β-TCP sample was much higher than that of the PSu/β-TCP sample. The values of tensile strength and percentage elongation of the PMMA/PSu/β-TCP measured were close to those the of PMMA/β-TCP samples. The PMMA/PSu/β-TCP exhibited inferior tensile properties when compared with the pure PMMA/β-TCP samples. In the same scale, it was observed that the PMMA/PSu/β-TCP composite had greater tensile strength than that exhibited by PSu/β-TCP membrane. It is also to be noted that the percentage elongation of PSu/β-TCP was higher than that of both PMMA/β-TCP and PMMA/PSu/β-TCP. This observation is indicative of the brittleness of PMMA-based composites whilst underlining the higher strength of PMMA over PSu.

Hardness testing

The hardness of the composite membranes was tested using a Durometer hardness tester as per ASTM D 2240 standard. The hardness values determined are tabulated in Table 2. It is evident that the PMMA/PSu/β-TCP composite membrane exhibited higher hardness value than either PMMA or PSu composite. The increase in hardness can be explained as being associated with higher crystallinity of the blend polymer composite due to the interaction of MBA with PMMA and PSu polymer chains as discussed in the XRD and optical properties sections. The increase in the crystallinity implies that the macromolecules were more orderly arranged resulting in less displacement and eventually exhibiting higher hardness values.

Morphology studies

The SEM images of the surface of PMMA/β-TCP, PSu/β-TCP and PMMA/PSu/β-TCP composite membranes are shown in Fig. 6. The Fig. 6a and b showed the smooth surfaces of the PMMA and PSU composites, respectively. From Fig. 6c, it was seen that β-TCP particles were distributed throughout the membrane surface whilst exhibiting some amount of agglomeration. It was also noted that the filler particles were partially exposed on the surface of the matrix. This implied good wetting of the β-TCP particles by the polymer matrix. Whilst it is expected that good wetting of the filler particles would result in their complete immersion within the matrix, in this case, some of them (filler particles) were exposed on the surface of the matrix due to an increase in their size as a result of agglomeration. The thickness of the fabricated composite membrane was estimated to be 500 μm (±10 μm) using a thickness gauge instrument (Innolab).

Bioactivity studies

Bioactivity, here, refers to the capability of the polymer membrane to induce nucleation of $Ca_3(PO_4)_2$ on its surface which then subsequently enlarges and resembles either a plaque or a coat when viewed under SEM. Figure 6d, e and f is the SEM images of the composite membranes (PMMA/β-TCP, PSu/β-TCP and PMMA/PSu/β-TCP, respectively) retrieved after 4 days of immersion in SBF for the visualization of calcium phosphate layer ($Ca_3(PO_4)_2$) formed on their surface. The density of the $Ca_3(PO_4)_2$ was seen to be higher for the PMMA/PSu/β-TCP membranes (Fig. 6f) than for the other samples. Bioactivity, to a small extent, was also observed on the surface of the PMMA and PSu membranes (Fig. 6d and e). Hence, it can be deciphered that the presence of the inorganic material (β-TCP) in the composite increased the bioactivity [23, 24]. Higher bioactivity witnessed in the case of the PMMA/PSu/β-TCP sample could possibly be attributed to the presence of the amide groups (from MBA) which could additionally induce the nucleation of $Ca_3(PO_4)_2$ in larger numbers than compared with those of PMMA and PSu composite membranes.

Though the formation of $Ca_3(PO_4)_2$ apatite on the surface of the composite was supported by the energy dispersive spectroscopy (EDS) analysis, in the present case, it was considered that due to the presence of β-TCP in the membranes, the results of the EDS elemental analysis would not be justified and convincing. The authors are of the opinion that, as far as confirming the bioactivity of the composites was concerned, in vivo studies would be more reliable. Nevertheless, the incorporation of β-TCP into the membranes would definitely impart credible bioactivity to the polymer membranes.

Conclusions

Two traditionally incompatible polymers, PMMA and PSu, were successfully blended using MBA and a composite membrane fabricated with the blend polymer as the matrix and β-TCP as the filler. The morphological analysis indicated that the filler particles were widely distributed and completely wetted by the matrix. The FTIR and TGA results showed that the use of MBA resulted in good blend formation between PMMA and PSu. This was further supported by the results of the study of their optical properties. The mechanical properties indicated that the PMMA/PSu/β-TCP composite exhibited superior hardness compared to the PMMA/β-TCP composite whilst there was a small decline in the tensile strength. The prepared

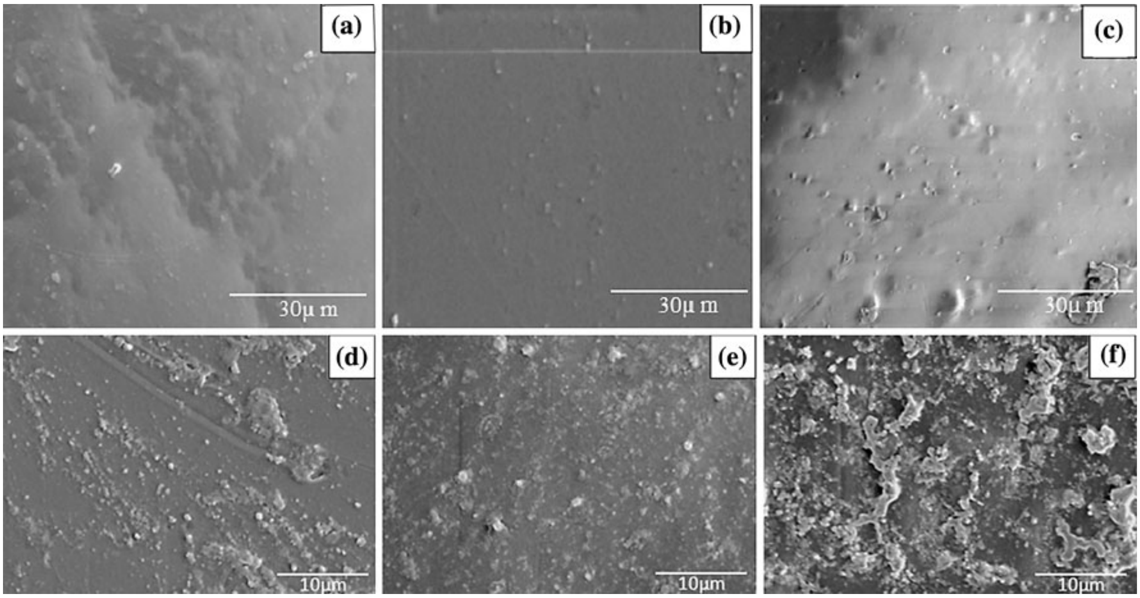

Fig. 6 SEM images of **a** PMMA/β-TCP; **b** PSu/β-TCP; **c** PMMA/PSu/β-TCP composite; **d** PMMA/β-TCP after 4 days in SBF; **e** PSu/β-TCP after 4 days in SBF; **f** PMMA/PSu/β-TCP after 4 days in SBF

composites possessed a good potential for bonding with bone as they were found to display good bioactivity. The presence of amide groups could enhance the nucleation of the apatite crystals due to their negative charge. No adverse cytotoxicity is expected as both polymers have been tried individually for various biomedical applications [25–27]. The fabrication of bioactive orthopaedic prostheses is a good alternative to the conventional prostheses as the former unlike the latter have the ability to bond with bone and thus reduce the failure due to loosening of the prostheses. Though this study demonstrated the successful blending of PMMA and PSu using MBA and the enhanced bioactivity due to the presence of amide groups, further studies are required to evaluate the ideal PMMA:PSu:MBA ratio and substantiate the same with in vivo studies. Furthermore, the study can be extended to involve 3D samples fabricated by injection moulding process. Future studies need to be focussed on studying the proliferation of osteoblast cells over the surface of the composite which is a more ideal indicator of bioactivity and also the ultimate goal of the study.

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