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Blends of polyurethane-polymethyl methacrylate/TiO_2-based composites

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Abstract−Polyurethanes (PUs) prepolymer was prepared by the reaction of toluene-2,4-diisocyanate (TDI) and poly caprolactone diols and the chain was further extended with 1,4-butane diol (1,4-BDO) to get final polyurethane (PU). FTIR spectra of the monomers, PU prepolymer, chain extender and final PU confirmed the reaction progress. A series of blends were prepared by varying the percent compositions of prepared PU, procured polymethyl methacylates (PMMA) and titanium dioxide (TiO_2). Pellets were formed from the prepared blends (PU-PMMA/TiO_2) using a self-designed mechanical tool. Scanning electron microscope (SEM) images were also taken to confirm the incorporation of the TiO_2 contents into the prepared blends. Mechanical properties such as hardness and compressive strength were studied and discussed. The results of the study reveal that the blended sample having 80% PU, 20% PMMA content with 2.5 g TiO_2 in 100 g mixture of PU and PMMA is very suitable for suggesting dental materials.

Key words: Polyurethane, PMMA, Titanium Dioxide, FTIR, SEM, Compression Strength

INTRODUCTION

Studies of tooth-related genetic disorders and knockout enamel demonstrate that the correct formation of the dentin-enamel interface is essential for proper tooth function. The problem of interface stability is also very important with respect to tissue repair, where implant failure often occurs due to a weak interface between tissues and repair materials. It is likely that interactions between dentin and enamel tissue during initial mineralization events play an important role in the proper formation of the interface [1]. Polymers can be modified for better and critically important interfaces. Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers as they can be molded, injected, extruded, recycled [2] and can be easily modified by varying the diisocyanate structure [3] and chain extender (CE) length using a, w-alkane diols [4,5]. Synthesis, characterization of UV-curable and waterborne polyurethane dispersions [6,7], effect of blocked polyisocyanate based PU composites [8] and PU/natural rubber blends [9,10] have been studied comprehensively. Bio-based hyperbranched PU [11-14], PLA-based hybrid bio-composite [15], PP/nitroxide-mediated radical graft polymerization of styrene [16] and influences of clay type, content and dispersion state on PET/clay nanocomposites [17,18] have been documented in the established literature.

Among the many materials used, polyacrylate (PA) is the most frequently used in water borne polyurethane (WPU) modifications due to its excellent properties in terms of hardness, weather ability, water resistance and gloss [19]. Urethane acrylates are explored as biomaterials useful in contact lenses, radiation, thermally sensitive materials, and dental materials [20]. A large number of reports on the use of reinforcing materials in polyurethane acrylate copolymers are available in the literature [21,22]. Modified clay has been used as a filler to improve the mechanical properties [23,24]. The contrast between composites containing conventional glass fillers and those containing glass-ceramic revealed that the latter increased flexural strength and modulus significantly, although it did not affect the diametric tensile strength (DTS). Among porous fillers (glass-ceramic), the porosity increased flexural strength significantly but did not affect flexural modulus and DTS. Therefore, porous fillers can be considered as an important and applicable way to reinforce dental composites [25]. At the resin-dentin interface, the adhesive layer has the lowest elastic modulus among the components of the bonded complex. Inclusion of fillers into an adhesive causes an increase in its elastic modulus providing a layer with an elastic modulus between dentin and restoration [26,27]. Incorporation of zirconium oxide into the dental material has also been reported in the literature [28]. Titanium is known as a good, biologically safe material for various medical applications. In bulk form, it is used for the production of implants [29], whereas in the form of porous structures, it provides support for living cells [30]. Resin composites with 0.1-0.25% titanium dioxide nanoparticles could simulate the opalescence of human enamel [31]. Titanium shows excellent mechanical strength, fatigue resistance [32], good corrosion resistance and biocompatibility [33]. Due to its excellent properties in biomedical applications, some reports are also available using titanium oxide (TiO_2) films for implant-applications by electrochemical process in an electrolyte with sodium silicate solution as an additive [34]. To achieve all the required properties in a single material, molecular engineering is required. Polyurethanes (PU) can present better mechanical stability, good solvent and chemical resistance, excellent biocompatibility [35-37] and toughness against loading. Acrylic (AC) component, on the other hand, shows high outdoor resistance, pigment ability, and lower cost [38]. The incorporation of TiO_2 will definitely improve the mechanical properties and enhance the biocompatibility. It is noteworthy that

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no report is available on the preparation of blends of polyurethane (PU)-polymethyl methacrylate (PMMA)/TiO_2-based composites. It is a common procedure to prepare polyurethane by step growth reaction of diisocyanate and polyol, and the chain is further extended with diols or diamines, and hence incorporation of nanofillers into the matrix of polyurethane. However, we did not find any report regarding the preparation of PU-PMMA/TiO_2 based composites. Blending of properties of AC, PU and TiO_2 definitely will help in getting such a polymer with the required properties. Keeping in view the excellent requisite characteristics of the component material and to tailor the dental material for the required properties, this study has been conducted.

EXPERIMENTAL

1. Materials

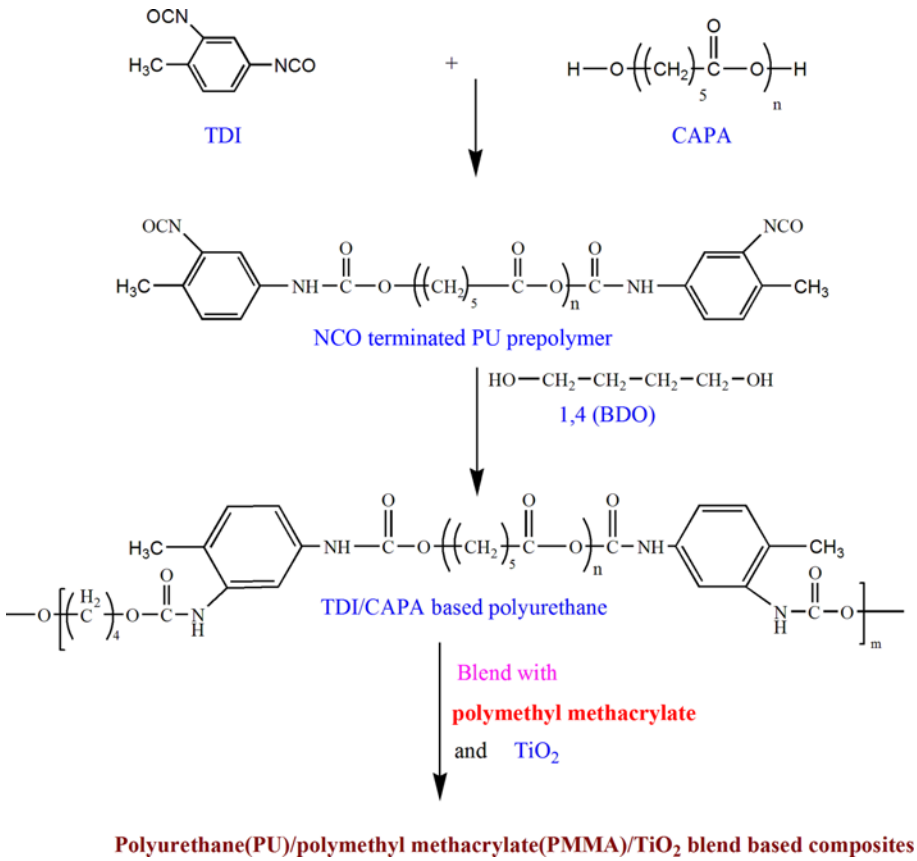
1-1. Chemicals

Toluene diisocyanate (TDI), 1,4-butane diol (BDO), titanium dioxide and dimethyl formamide (DMF) were purchased from Sigma Chemical Co. (Saint Louis MO, USA). Polycaprolactone diol CAPA 2403A (molecular weight 4000) was kindly gifted by Perstorp Polyols (Solvay Chemicals), Inc. Toledo, Ohio. Poly-methyl methacrylate was purchased from Merck Chemicals (Darmstadt, Germany). Its molecular weight was confirmed following the method reported in the literature [39]. The polyol and BDO used in this study were

Table 1. Sample code designation and different formulation of polyurethane and PU/PMMA/TiO_2 blends

Sr. no.	Sample code	Formulation of polyurethane			Composition (PU[d]/PMMA[e]) % by mass	Percentage of TiO_2 in the blends	Hardness data of blends (Shore A)
		TDI[a]	CAPA[b]	BDO[c]			
1	PUACT 1	10	1	9	0/100	2.5	88
2	PUACT 2	10	1	9	20/80	2.5	88
3	PUACT 3	10	1	9	40/60	2.5	91
4	PUACT 4	10	1	9	80/20	2.5	95
5	PUACT 5	10	1	9	100/0	2.5	90

[a]Toluene-2,4-diisocyanate (mole ratio)
[b]Polycaprolactone diol (mole ratio)
[c]1,4 Butane diol (mole ratio)
[d]Polyurethane (%)
[e]Polymethyl methacylates (%)



Scheme 1. Synthetic route for the preparation of polyurethane/polymethyl methacrylate/TiO_2 based composites.

dried at 80 °C in vacuo for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. TDI and all of the other materials were used as received. All of the reagents used in this study were of analytical grade.

1-2. Step 1: Synthesis of Polyurethane

The synthesis of PU prepolymers was carried out according to the recommended procedure [5]. First, 1 mole (Table 1) of hydroxyl terminated poly caprolactone diol (polyol) CAPA2403A (Molecular weight 4000) was charged into a four-necked round bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, heating oil bath and a nitrogen gas inlet system. The temperature of the oil bath was increased to 60 °C. Poly caprolactone diol was melted and stirred continuously under the blanket of nitrogen gas for 30 min. Then 10 moles (Table 1) of toluene-2,4-diisocyanate (TDI) was added to the reaction vessel and temperature was raised to 80 °C. During optimization of the experimental conditions it is confirmed that the formation of isocyanate (NCO) terminated polyurethane (PU) prepolymer completes in one hour. Fourier transform infrared (FTIR) spectrum of the PU prepolymer was also obtained to confirm the progress of polyurethane (PU) prepolymer reaction. The NCO contents of the PU prepolymer were determined and the experimental values found close to the theoretical value (experimental value 9.27%; theoretical value 9.29%). The PU prepolymer was converted into the final PU by stirring the prepolymer vigorously and then adding a previously degassed chain extender, 1,4-butane diol (9 moles). When homogeneity was obtained in the reaction mixture, the dispersion of chain extender was considered complete and the liquid polymer was cast into a Teflon plate to form a uniform sheet of 2-3 mm thickness. The synthesized polymer was then placed in a hot air circulating oven at 100 °C and cured for 24 h. The synthetic route for the synthesis of polyurethane is shown in Scheme 1.

1-3. Step 2: Preparation of Blends of Polyurethane-poly Methyl Methacrylate (PMMA) and TiO_2

A series of blends was prepared by dissolving different compositions of PU and PMMA (Table 1) in dimethyl formamide (DMF). Titanium dioxide-TiO_2 (2.5% of weight of polymer) was added to the blends of PU and PMMA. Complete dispersion of TiO_2 in the blends was obtained by continuous stirring with a magnetic stirrer for three hours. The solvent was evaporated by drying in an oven at 110 °C. The synthetic route for the preparation of polyurethane-polymethyl methacrylate/TiO_2 is shown in Scheme 1.

1-4. Step 3: Preparation of Pellets from Blends

Pellets were prepared by using the following parts of the self-designed mechanical tool. The cylinder 'a' is placed into the cylindrical volume 'd'. The material whose pellets are required is placed inside through the open mouth of the 'd', and the bolts 'b' and 'c' are fixed at the both end of the cylindrical volume 'd'. The self-designed components of the mechanical tool are shown in Fig. 1(a).

Fig. 1. Pellet formation (a) Self-designed mechanical tool for pellet formation; (b) Torque wrench and self-designed mechanical tool for pellet formation; (c) Pressure being applied with a torque wrench; (d) Pellet formed using the self-designed assembly.

A torque wrench as shown in the Fig. 1(b) is used to press the material placed inside the cylindrical volume between the solid cylinder 'a' and bolts 'c' inside 'd'. For this purpose 0.5 g of the prepared material was placed inside the self-designed mechanical tool for the pellet formation. The material inside the cylindrical volume was pressed using a pressure of 112 Nm^{-1} with the help of Torque wrench (Fig. 1(c)).

After applying pressure (112 Nm^{-1}) with the help of a torque wrench, the instrument is placed in an oven at 100 °C for 60 minutes. The instrument is then taken out from the oven and allowed to cool down. The pellet is taken out from the cylindrical volume by loosing the end of bolt 'c'. The pellet is taken out as shown in Fig. 1(d) by opening the knob 'c', and then the pellet comes out attached to the cylinder 'd'.

2. Molecular Characterization

Molecular characterization of the monomers used in the synthesis, the intermediate compounds and the final material formed at the end of complete polymerization were confirmed by Fourier transform infrared (FT-IR) spectroscopy. FT-IR scans of the prepared copolymer samples were obtained in the transmission mode using a Shimadzu Fourier Transform Infra-red (FT-IR) spectrometer.

3. Scanning Electron Microscopy (SEM) Analysis

A small sample of PU-PMMA/TiO_2 blends specimen was fit into the sample chamber, which could accommodate a specimen up to 15 cm in height. PU-PMMA/TiO_2 blends specimens were made electrically conductive by coating with a thin layer of gold film using JEOL sputter coater before analysis. Morphological studies were examined by scanning electron microscopy (JEOL JSM-6490A) at 20 kV.

4. Compression Test

Compression testing provides mechanical strength and properties of rigid cellular materials under compressive loads. The compressive strength and stiffness properties of polymer matrix composite materials were determined by using the standard test method-ASTM D6641 [39]. In this test specimens are centered between two compression platens and compressive load is applied at a constant crosshead rate of 2.5 mm (0.1 in/min) for each 1 inch of sample thickness. Crosshead travel and load are recorded throughout the test. Compressive strength can be determined in one of two manners depending on the characteristics of the stress-displacement curve. Strain can more accurately be determined using an extensometer that measures the distance between the upper and lower compression platens.

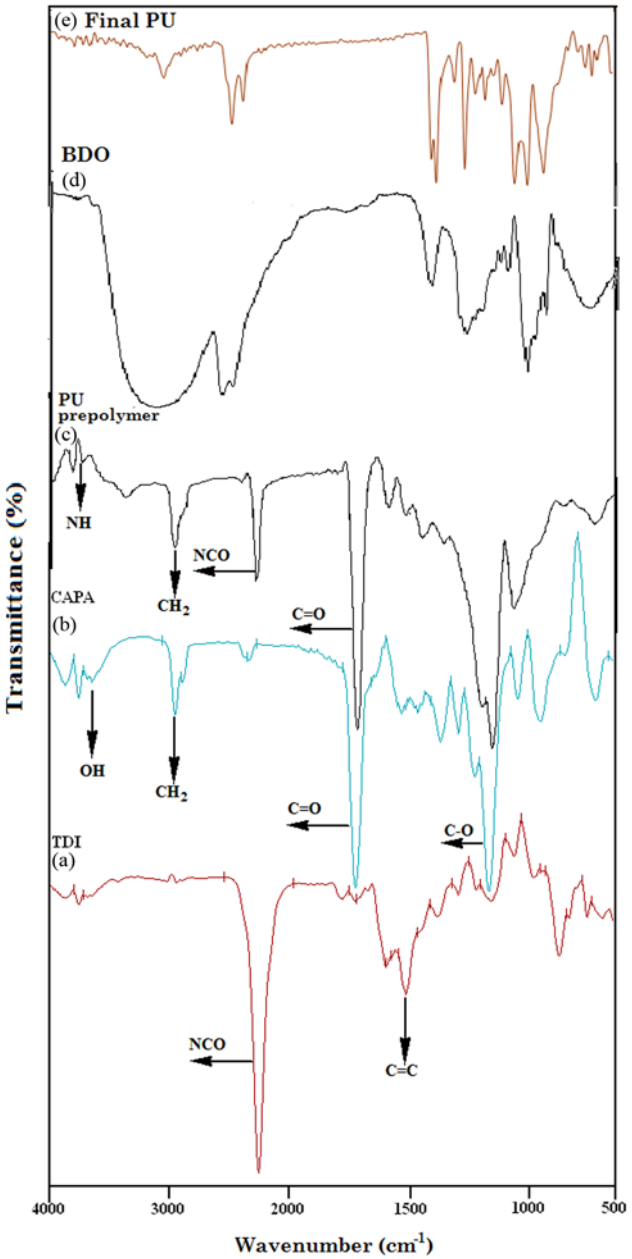


Fig. 2. FT-IR spectra: (a) toluene-2,4-diisocyanate (TDI); (b) Polycaprolactone diol (CAPA); (c) polyurethane (PU) prepolymer; (d) 1,4 butane diol (BDO); (e) Final polyurethane (PU).

RESULTS AND DISCUSSION

1. Structural Characterization

FTIR spectra of all the monomers and individual polymerization steps were recorded and presented in Fig. 2. FTIR spectra of toluene-2,4-diisocyanate (TDI), hydroxy terminated poly caprolactone diol, isocyanate and (NCO) terminated PU prepolymer obtained by the reaction of TDI and hydroxy terminated poly (caprolactone diol) are jointly presented in Fig. 2. The peaks assignments of the important functional group are presented and discussed. The FTIR spectrum of toluene-2,4-diisocyanate (TDI) (Fig. 2(a)) show a very sharp and an intense peak at 2,241.28 cm^{-1} which correspond to the isocyanate (-NCO) groups attached to the TDI structure. The FT-IR spectrum shows sharp peaks at 1,516.05 cm^{-1} attributed to the C=C stretching of benzene ring. The peaks assignment of FTIR spectrum of poly (caprolactone) diol (PCL) is presented in Fig. 2(b). The observed peaks in the functional group region of PCL were assigned as: 3,534 cm^{-1} (OH stretching vibration); 2,937.59 cm^{-1} (asymmetric CH_2 stretching); 2,876 cm^{-1} (symmetric CH_2 stretching); 1,724.36 cm^{-1} (C=O stretching); 1,168.86 cm^{-1} (C-O stretching). These two monomers (TDI & PCL) reacted in the reaction flask and the reaction lasted for 1 h at 100 °C. After optimization of the experimental conditions it was observed that formation of polyurethane prepolymer was completed in 1 h and isocyanate terminated PU prepolymer was formed. FT-IR spectrum of NCO terminated PU prepolymer is given in Fig. 2(c). It can be clearly observed from

the spectrum that isocyanate (-NCO) group has reacted with the OH group of the PCL, and therefore the signal for the OH groups disappeared and that of the intensity of isocyanate (-NCO) groups has reduced to some extent, resulting in that isocyanate terminated PU prepolymer has been formed with a signal for NH units appearing at 3,239 cm^{-1} (Fig. 2(c)). The other peaks observed in the FT-IR spectrum of PU prepolymer were assigned as: 2,930 cm^{-1} (CH symmetric stretching of CH_2); 2,893 cm^{-1} (CH asymmetric stretching of CH_2 groups); 2,267 cm^{-1} (isocyanate (-NCO) group); 1,726 cm^{-1} (C=O stretching of soft segment of poly (caprolactone) diol; 1,190 cm^{-1} (C-O stretching of soft segment). Disappearance of an intense peak 2,241.28 cm^{-1} (-NCO) and the appearance of a relatively weak peak at about 2,267 cm^{-1} (-NCO), confirm the formation of the NCO terminated PU prepolymer. To complete the polymerization, the PU prepolymer was further reacted with 1,4-butane diol to form final polyurethane. The peak assignment of FTIR spectrum of 1,4-butane diol is represented in Fig. 2(d). FT-IR spectra of 1,4-butane diols (Fig. 2(d)) showed that broad OH stretching vibration band appeared at 3,452 cm^{-1}. The peaks observed at 2,930 and 2,844 cm^{-1} correspond to CH symmetric and asymmetric stretching vibrations of CH_2 groups, respectively. To provide clear information about the vibrational mode changes due to involvement of 1,4-BDO into the polyurethane backbone during the polymerization reaction, FT-IR spectrum of PU based on 1,4-BDO obtained from the cast film is shown in Fig. 2(e). In the FT-IR spectrum of the PU sample, the appearance of N-H peak at 3,330 cm^{-1} and the disappearance of the NCO peak at 2,255 cm^{-1} confirmed the completion of polymerization reaction. The FTIR spectra of the predesigned PU obtained support the proposed structure of the final PU polymer. FTIR spectra showed characteristic bands of urethane groups at 3,330 cm^{-1} (N-H stretching); CH symmetric stretching vibrations of CH_2 at 2,947 cm^{-1}; CH asymmetric stretching vibrations of CH_2 groups at 2,810 cm^{-1}. The other peaks observed were assigned as: 1,728 cm^{-1}, 1,642 cm^{-1} (C=O bond); 1,599 cm^{-1}, 1,529 cm^{-1} (NH bending); 1,407 cm^{-1} (CH bending vibration); 1,311 cm^{-1} (CH_2 wagging). By further reaction of the PU prepolymer with 1,4-BDO, the FT-IR spectra showed a very strong, new peak at about 1,728 cm^{-1} which was assigned to C=O stretching of soft segment of PCL. Another new peak was also observed at about 1,464 cm^{-1} which was assignable to urethane -NH group. The other peaks related to the absorption of -NH, -CO, -CHN were appeared at 3,330 cm^{-1}, 1,728 cm^{-1} and 1,464 cm^{-1}, respectively, which indicates the newly synthesized proposed product has -NHCOO group.

2. Interaction between the PU-PMMA and TiO_2 Particles

Inorganic/polymer nanocomposites are a relatively new class of materials. Compared to conventional composites, the nanocomposites exhibit improved physical properties, such as thermal and mechanical, due to the much stronger interfacial interactions between the nanofillers and polymer matrices. Inorganic/organic nanohybrids could combine the advantages of organic polymers and nanomaterials. Possible interfacial interaction mechanism and the secondary structure of macromolecular chain could lead to the formation of extensive intermolecular interactions easily, which reduces the index of hydrogen deficiency and the unsaturated degree.

An FT-IR study of pristine PU-PMMA and PU-PMMA/TiO_2 was done to investigate the information about the interactions of TiO_2 with PU-PMMA molecules. The results revealed that the characteristic peaks of pure PU-PMMA copolymer and PU-PMMA/TiO_2 are still maintained in the spectrum, and there is no significant difference among the peaks in IR studies. It may be proved that the structure of PU-PMMA was not affected by the presence of TiO_2 implying that the TiO_2 did not react with the PU-PMMA molecules. Obviously, this result indicates a strong and uniform physical interaction between PU-PMMA and TiO_2 nanoparticles and may be owing to interfacial synergistic forces such as hydrogen bonding or electrostatic interactions between the organic and inorganic components. These interactions can alter the original vibration mode of molecules, atoms or pendant groups on the interface between organic and inorganic components, which may have some effects on the resultant properties of the material.

3. Scanning Electron Microscope (SEM) Analysis

SEM images were taken to investigate the micro-morphology of prepared PU-PMMA/TiO_2 blends with different mass percent of PU and PMMA in the blends (Fig. 3). From the SEM images (Fig. 3) of the prepared PU-PMMA/TiO_2 composite blends, it can be clearly observed that the TiO_2 particles are well dispersed in the polymer matrix and all the individual components can be easily identified. This homogeneity in dispersion of the TiO_2 contents in the PU/PMMA matrix will certainly help to improve the mechanical properties of the prepared blends. The red zone area in the Fig. 3(a) has been magnified (×500 to ×1,000) and presented in Fig. 3(b). It is worth mentioning that individual components, i.e., PU, PMMA and TiO_2, can be easily identifiable in the presented images.

As discussed above, SEM analysis was used to measure the distri-

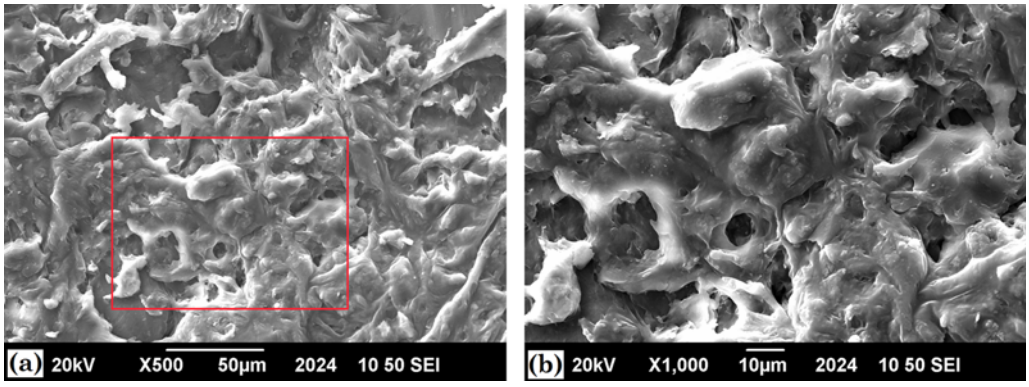


Fig. 3. Scanning electron microscope (SEM) images of PU-PMMA/TiO_2 blends.

bution of nano-TiO_2 particles in the PU-PMMA films. The micro-structure surface of the PU-PMMA based on TiO_2 particles shows a very compact multilayer net-work structure due to mutual net-working of PU and PMMA embedded TiO_2 particles in the resulting matrix. Moreover, the particles seemed to be very uniformly dispersed on the surface of the PU-PMMA, which provides direct evidence regarding the micro-structure and the formation of true PU-PMMA/TiO_2 nanocomposites. The micrographs confirmed that the PU-PMMA/TiO_2 nanocomposites present a homogeneous and fully dispersed micromorphology. It can observed from the micrograph images that the average size of PU-PMMA/TiO_2 nanocomposites is round about 60-70 nm. The obtained results accord with those of previous findings [40,41].

4. Mechanical Properties of the Blended Samples

The hardness data of the synthesized PU/PMMA/TiO_2 samples is presented in Table 1. The results revealed that all the blended samples have shown comparable hardness results; however, the samples having entire PMMA (PUACT 1) and sample having 20% PU and 80% PMMA (PUACT 2) have shown equal hardness. The hardness of the studied samples gradually increases with increase in the PU mass percent; however, the sample having 100% PU and 0% PMMA (PUACT 5) has shown comparable result to the sample PUACT 3 (having 40% PU and 60% PMMA). This trend of increasing rigidity of the sample attributed to the compatibility of the PU and PMMA with that of TiO_2. The existing trend of the hardness indicates that both the PU and PMMA are responsible for the production of tough material.

A compression test is simply the opposite of the tensile test with respect to the direction of loading. In compression testing the sample is compressed while the load and the displacement are recorded. The compression tests result in mechanical properties that include the compressive yield stress, compressive ultimate stress, and compressive modulus of elasticity. Compressive yield stress is measured in a manner identical to that done for tensile yield strength. When testing plastics, the compressive yield stress is measured at the point of permanent yield on the stress-strain curve. Moduli are generally greater in compression for most of the commonly used structural materials. The compression results are presented in Fig. 4(a) & (b). The results revealed that among all the studied samples, maximum applied load, i.e., 1,397 (Kgf), was observed by the sample PUACT 1 (0% PU and 100% PMMA), and this sample has shown maximum resistance against load. By decreasing the mass percent of the PMMA, the load-bearing capacity of the samples decreases, resulting in a slight fracture that was observed in sample PUACT 2, and a clear fracture was observed in sample PUACT 3. However, the sample PUACT 4 (80% PU and 20% PMMA) has shown good load bearing capacity (i.e., 1,101 Kgf) as compared to all the other samples having various mass percent of PU. Although the sample PUACT 5 (100% PU and 0% PMMA) has also shown load bearing capacity, the max applied load to this sample is 489 Kgf. Furthermore, some pores in the un-checked sample (PUACT 5) were also observed. In comparison to all the studied samples, no fracture was observed against the applied load in the samples PUACT 1, PUAT 4 and PUACT 5. Finally, concluding the best one among the above three, PUACT 4 is more suitable for suggesting dental materials because of the following reasons: (i) the sample PUACT 1 was prepared with 100% PMMA (and 0% PU) which shows less

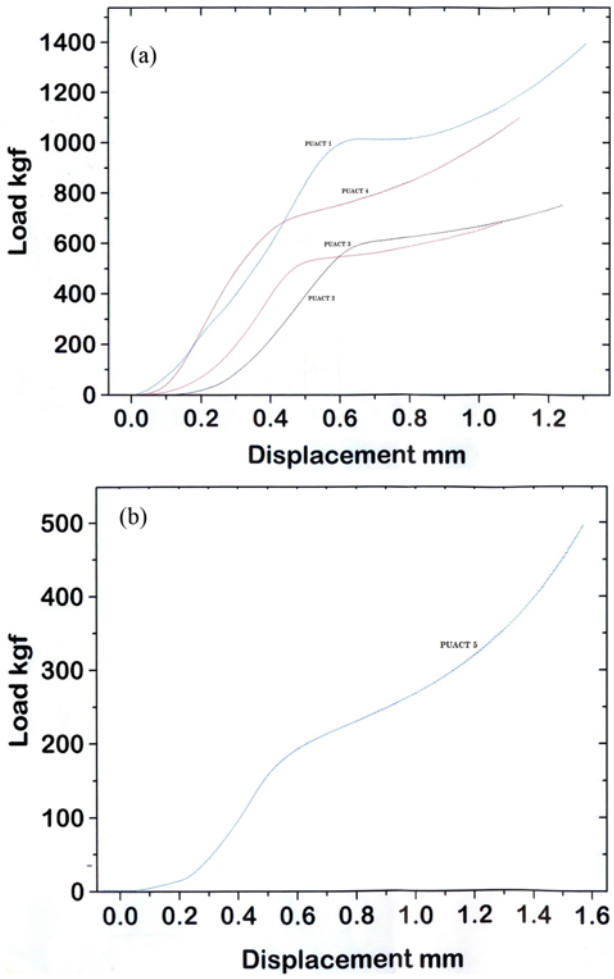


Fig. 4. Compression results of the prepared PU/PMMA/TiO_2 blends samples (a) PUACT 1 to PUACT 4; (b) PUACT 5.

biocompatible behavior and also least hardness factor (i.e., 88); (ii) the sample PUACT 4 has shown maximum load bearing capacity and maximum hardness (i.e., 95); and also may show less toxic effect during the cell culture assay because 80% (mass percent) of PU (20% PMMA) was blended in this sample. The established literature has reported the polyurethane is a biocompatible material and can be inserted inside the living organism, which does not result in any toxic effect [35,36]; (iii) the sample PUACT 5 was blended with 100% PU (and 0% PMMA) with hardness factor 90, max applied load was also much less, and further, having pores onto the surface of the sample is one of the other drawbacks of this sample. The value of the PUACT 5 is much harder to determine for a compression test since many materials do not exhibit rapid fracture in compression. Materials such as most plastics that do not rupture can have their results reported as the compressive strength at a specific deformation such as 1%, 5%, or 10% of the sample's original height. Same trend has been shown by the PUACT 5.

CONCLUSION

Polyurethane prepolymer was prepared using toluene-2,4-diisocyanate (TDI) and poly caprolactone diols (molecular weight 4,000

g/mol), and the chain was further extended with 1,4-butane diol to get final polyurethane. Spectroscopic data confirmed the proposed polyurethane structure. The prepared polyurethane and procured polymethyl methacylates were blended with different percent composition taking constant proportion of titanium dioxide. A self-designed mechanical tool was used for pellet formation to study the compressive behavior of prepared blended pellets. The results revealed that samples having 80% polyurethane (PU), 20% polymethyl methacrylates (PMMA) with 2.5 g titanium dioxide in 100 g mixture of PU and PMMA are very suitable for suggesting dental materials.

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