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Biocompatibility and Microscopic Evaluation of Polyurethane–Poly(methyl methacrylate)–Titnanium Dioxide Based Composites for Dental Applications

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ABSTRACT: We prepared and then blended polyurethanes (PUs) with poly(methyl methacrylate)s (PMMAs) and TiO_2 by varying the percentage compositions to form pellets. The chemistry of all of the blended samples was confirmed by Fourier transform infrared spectroscopy. The incorporation of TiO_2 into the PU–PMMA matrix was confirmed with scanning electron microscopy analysis. Differential scanning calorimetry analysis and compression testing was performed, and the results are discussed. The cytotoxicity level of the prepared blends displayed dependence on the composition ratio of the PU–PMMA blends. The results reveal that the optimum PU contents in the PU–PMMA–TiO_2 blend were responsible for its better biocompatibility. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39806.

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INTRODUCTION

Dentin and enamel are two mineralized tissues with strikingly different mechanical and structural properties that normally operate jointly for decades without any damage under the environment. The formation of dentin takes place before the formation of enamel and is initiated by the odontoblasts of the pulp. Unlike enamel, dentin continues to form throughout life, and its formation can be initiated in response to stimuli, such as tooth decay.[1] An outstanding mechanical endurance requires an extraordinarily strong bond between these two tissues. Studies of tooth-related genetic disorders and knockout enamel have demonstrated 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 because of the weak interface between the tissues and repair materials. It is well understood that interactions between dentin and enamel tissues during the initial mineralization process play an important role in the proper formation of this critically important interface.[2]

Polymers can be modified for better and critically important interfaces. PU elastomers are possibly the most versatile classes of polymers, as they can be molded, injected, extruded, and recycled[3] and can be easily modified by the variation of the diisocyanate structure and chain-extender length with α,ω-alkane diols.[4,5] Structural modifications in polyurethane (PU)[6–11] and PU acrylate copolymers for textile applications[12–14] have also been of interest to many researchers.

Among the many materials used, polyacrylate is the most frequently used in waterborne PU modifications because of its excellent properties in terms of hardness, weatherability, water resistance, and gloss.[14,15] The prepared PU–poly(methyl methacrylate) (PMMA)-based waterborne PU can be extensively used for textile applications;[14] however, the incorporation of TiO_2 into the structure of PU–PMMA is expected to provide excellent biocompatibility and other related properties. Urethane acrylate copolymers have been explored as biomaterials that are useful in contact lenses, thermally sensitive materials, and dental materials.[16] A large number of reports on the use of reinforcing

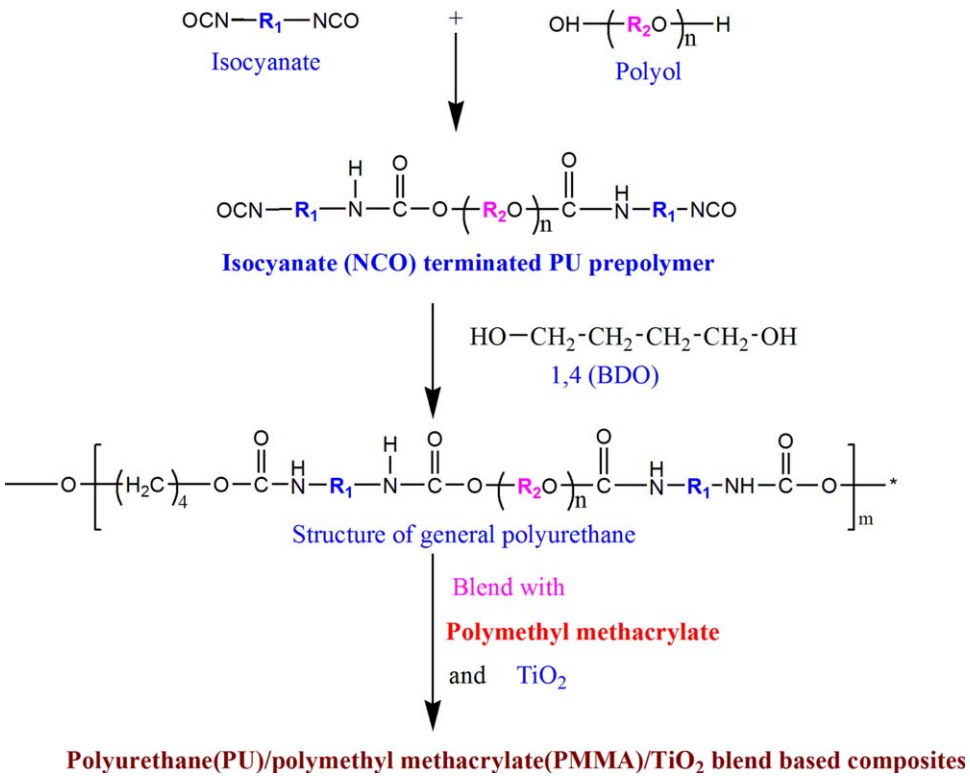

Figure 1. General schematic for the preparation of the PU–PMMA–TiO_2-based composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

materials in PU acrylate copolymers are available in the literature.[17,18] Modified clay has been used as a filler to improve their mechanical properties.[19,20] The contrast between composites containing conventional glass fillers and those containing glass–ceramic blends revealed that the latter showed significantly increased flexural strength and modulus, although the difference did not affect the diametric tensile strength. Among porous glass–ceramic fillers, the porosity increased the flexural strength significantly but did not affect the flexural modulus and diametric tensile strength. Therefore, porous fillers can be considered as an important and applicable way to reinforce dental composites.[21] At the resin–dentin interface, the adhesive layer has the lowest elastic modulus among the components of the bonded complex. The inclusion of fillers in an adhesive causes an increase in its elastic modulus and provides a layer between the dentin and restoration.[22,23] The incorporation of zirconium oxide into the dental material has also been reported in the literature.[24] Titanium dioxide is known as a good, biologically safe material for various medical applications. In bulk form, it is used for the production of implants,[25] whereas in the form of porous structures, it provides support for living cells.[26] Resin composites with 0.1–0.25% titanium dioxide nanoparticles could simulate the opalescence of human enamel.[27] Titanium dioxide containing binders showed excellent mechanical strength, fatigue resistance,[28] good corrosion resistance, and biocompatibility.[29] Because of its excellent properties in biomedical applications, some reports are also available on the use of titanium dioxide (TiO_2) films for implant applications by electrochemical processes in an electrolyte with sodium silicate solution as an additive.[30] To achieve all of the required properties in a single material, molecular engineering is required. PUs can present better mechanical stability, good solvent and chemical resistance, excellent biocompatibility,[31–33] and toughness against loading. The acrylic component, on the other hand, is a low-cost material having a high outdoor resistance and pigment ability.[34] It is considered that the incorporation of TiO_2 will definitely improve the mechanical properties and enhance the biocompatibility. It is noteworthy that no report is available on the preparation of blends of PU–PMMA–TiO_2-based composites. It is a common procedure to prepare PU by a step-growth reaction of diisocyanate and polyol, and the chain is further extended with diols or diamines. Hence, nanofillers are incorporated into the matrix of PU. However, we have not found any report on the preparation of PU–PMMA–TiO_2-based composites. The blending of the properties of the acrylic component, PU, and TiO_2 will definitely help in getting a polymer with the required properties. Keeping in view the excellent requisite characteristics of the component material and to tailor dental material for the required properties, we conducted this study.

EXPERIMENTAL

Materials

Chemicals. Toluene diisocyanate (TDI), 1,4-butane diol (BDO), titanium dioxide, and dimethylformamide (DMF) were purchased from Sigma Chemical Co. (Saint Louis, MO). Poly(caprolactone diol) (CAPA 2403A, molecular weight = 4000) was kindly gifted by Perstorp Polyols (Solvay Chemicals, Inc.,

Table I. Sample Code Designations and Different Formulations of the PU and PU–PMMA–TiO_2 Blends

Sample no.	Sample code	PU formulation (molar ratio)			PU–PMMA composition by mass (%)	TiO_2 in blend (%)
		TDI	CAPA[a]	BDO		
1	PUACT 1	10	1	9	0/100	2.5
2	PUACT 2	10	1	9	10/90	2.5
3	PUACT 3	10	1	9	20/80	2.5
4	PUACT 4	10	1	9	40/60	2.5
5	PUACT 5	10	1	9	60/40	2.5
6	PUACT 6	10	1	9	80/20	2.5
7	PUACT 7	10	1	9	100/0	2.5

[a] Poly(caprolactone diol).

Toledo, Ohio). PMMA was purchased from Merck Chemicals (Darmstadt, Germany). Its molecular weight was confirmed with a method reported in the literature.[35] The polyol and BDO used in this study were dried at 80°C *in vacuo* for 24 h before use to ensure the removal of all of the air bubbles and water vapors that may have otherwise interfered with the isocyanate (NCO) reactions. The molecular weight of the polyol we used was confirmed by a procedure reported in ASTM D 4274C.[35] TDI and all of the other materials were used as received. All of the reagents used in this study were of analytical grade.

Synthesis of PU and PU–PMMA–TiO_2 Blends

The synthesis of the PU prepolymers was carried out according to a recommended procedure.[5] During optimization of the experimental conditions, we confirmed that the formation of the NCO-terminated PU prepolymer was complete in 1 h. The Fourier transform infrared (FTIR) spectrum of the PU prepolymer was also obtained to confirm the completion of the PU prepolymer reaction. The NCO contents of the PU prepolymer were determined, and the experimental value found was close to the theoretical value (experimental value = 9.27%, theoretical value = 9.29%). We carried out the conversion of the PU prepolymer into the final PU by stirring the prepolymer vigorously and then adding a previously degassed chain extender, BDO. The detailed synthesis procedure was presented in our previous article.[36] The synthetic route for the synthesis of PU is shown in Figure 1.

After the preparation of PU, a series of blends of PU–PMMA–TiO_2 were prepared by the dissolution of different compositions of PU and PMMA (Table I) in DMF. Titanium dioxide (TiO_2; 2.5 wt % of the polymer) was added to the blends of PU and PMMA. The complete dispersion of TiO_2 in the blends was obtained by continuous stirring with a magnetic stirrer for 3 h. The solvent was evaporated by drying in oven at 110°C. The synthetic route for the preparation of PU–PMMA–TiO_2 is shown in Figure 1.

After the preparation of the PU–PMMA–TiO_2 blends, pellets were prepared with the self-designed mechanical tool; the detailed procedure for the formation of the pellets from the blends was presented elsewhere.[36] The final prepared pellets are shown in Figure 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 was confirmed with FTIR spectroscopy. FTIR scans of the prepared copolymer samples were obtained in the transmission mode with a Shimadzu FTIR spectrometer.

Hemolytic Activity

To evaluate the biocompatibility, a cytotoxicity test was conducted with cell lines. The hemolytic activity of the pellets was studied by the method reported by Sharma and Sharma[37] with some modifications. For this purpose, 3 mL of freshly obtained heparinized human blood was collected from volunteers after consent and counseling. Blood was centrifuged for 5 min at 2500 rpm. Plasma was discarded, and the cells were washed three times with 5 mL of chilled (4°C) sterile isotonic phosphate-buffered saline (PBS) at pH 7.4. Erythrocytes were maintained (10^8 cells/mL) for each assay. A volume of 100 μL

Figure 2. Pellets prepared from the PU–PMMA–TiO_2 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Setup of the Mutagenic Study with the Ames Bacterial Reverse-Mutation Test (Fluctuation Assay)

	Volume added (mL)				
Treatment	Mutagen standard	Extract	Reagent mixture	Deionized water	*Salmonella* test strain
Blank	—	—	2.5	17.5	—
Background	—	—	2.5	17.5	0.005
Standard mutagen	0.1	—	2.5	17.4	0.005
Test sample	—	0.005	2.5	17.5	0.005

of solution of each pellet dissolved in DMF was mixed with human erythrocytes (10^8 cells/mL) separately. The samples were incubated at 37°C for 30 min and agitated after 10 min. Immediately after incubation, the samples were placed at 0 to 4°C for 5 min and then centrifuged for 5 min at 2500 rpm. After incubation, 100 μL of supernatant was taken from each tube and diluted 10 times with chilled PBS (4°C). Triton X-100 (0.1% v/v) was used as positive control, PBS was taken as a negative control, and we carried out the same procedural steps. The absorbance was recorded at 576 nm with a μ Quant (Bioteck). The percentage of red blood cell (RBC) lysis for each sample was calculated.

Mutagenic Study by an Ames Bacterial Reverse-Mutation Test (Fluctuation Test)

A reagent mixture composed of Davis–Mingioli salt, D-glucose, Bromocresol Purple, D-biotin, and L-histidine were mixed aseptically in a sterile bottle. The reagent mixture, extract, sterile deionized water, strains, and standard mutagens were mixed in several bottles with the amounts indicated in Table II.

Two mutant strains of *Salmonella typhimurium,* TA98 and TA100, were used. A volume of 200 μL of the prepared contents was dispensed into each well of a 96-well microtitration plate. The plate was placed in an airtight plastic sample holder to prevent evaporation and incubated at 37°C for 4 days. The blank plate was observed first, and the rest of plates were read only when all wells in the blank plate were purple; this indicated that the assay was not contaminated. The background, standard, and test plates were scored visually, and all yellow, partially yellow, or turbid wells were scored as positive wells, whereas purple wells were scored as negative wells. The extract was considered toxic to the test strain if all wells in the test plate showed purple coloration. For an extract to be mutagenic, the number of positive wells had to be more than twice the number of positive wells in the background plate.

Scanning Electron Microscopy (SEM) Analysis

A small sample of PU–PMMA–TiO_2 blend specimen was fit into the sample chamber, which could accommodate a specimen up to 15 cm in height. The specimens of the PU–PMMA–TiO_2 blends were made electrically conductive by coating with a thin layer of gold film with a JEOL sputter coater before analysis. The morphological studies were performed by SEM (JEOL JSM-6490A) at 20 kV and at 33 and 100× magnifications.

Thermal and Mechanical Analyses

To comprehend the changes taking place in the thermal characteristics of the PU–PMMA–TiO_2 composites, we carried out differential scanning calorimetry (DSC) analysis. It was done with a PerkinElmer thermal analyzer under a nitrogen atmosphere.

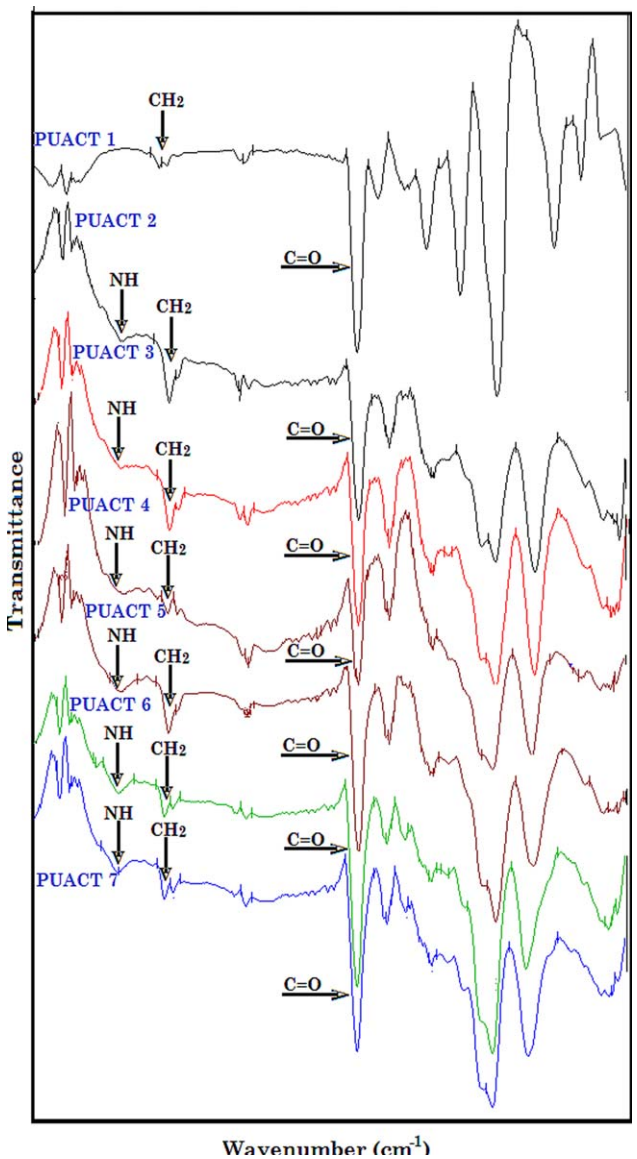

Figure 3. FTIR spectra: (a) PUACT 1 (100% PMMA/0% PU), (b) PUACT 2 (90% PMMA/10% PU), (c) PUACT 3 (80% PMMA/20% PU), (d) PUACT 4 (60% PMMA/40% PU), (e) PUACT 5 (40% PMMA/60% PU), (f) PUACT 6 (20% PMMA/80% PU), and (g) PUACT 7 (0% PMMA/100% PU). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Toxicity Levels of Samples of the PU–PMMA–TiO_2 Blends

Sample no.	Mean toxicity level (%)[a]	Standard deviation (%)
PUACT 1	9.24	0.68
PUACT 2	8.71	0.30
PUACT 3	7.45	0.59
PUACT 4	4.60	0.33
PUACT 5	2.33	0.45
PUACT 6	0.80	0.06
PUACT 7	0.64	0.09
DMF	0.1	0.02
PBS	0.00	0.03
Triton	100.00	0.05

[a] The values were the averages of three measurements. The scale was as follows: 1–10, nontoxic; 11–25, slightly toxic; 26–50, moderately toxic; and 50–100, highly toxic.

The compressive strength and stiffness properties of the polymer matrix composite materials were determined with the standard test method ASTM D 6641. In this test, specimens were centered between two compression platens, and a compressive load was applied at a constant crosshead rate of 2.5 mm (0.1 in/min) for each 1 in. of sample thickness. Crosshead travel and load were recorded throughout the test.

RESULTS AND DISCUSSION

Structural Characterization

FTIR spectra of all of the monomers and the product of individual polymerization steps were recorded and were presented in our previous study.[36] The detailed peak assignments of the important functional group appearing in the FTIR spectra were presented and comprehensively discussed elsewhere.[36] Seven samples with different compositions of the blends were prepared (Table I) and characterized. FTIR scans of all of the prepared samples are given in Figure 3. In the FTIR spectrum of PUACT 1 (pristine PMMA and TiO_2), the appearance of C═O and CH symmetric and asymmetric stretching vibrations of CH_2 confirmed the structure of PMMA. The FTIR spectra of the blends of PU–PMMA–TiO_2 are also presented in Figure 3 and are designated as PUACT 2, PUACT 3, PUACT 4, PUACT 5, and PUACT 6, whereas the FTIR scan of the pristine PU and TiO_2 is titled PUACT 7. All of the FTIR spectra of the PU–PMMA–TiO_2 blends (PUACT 2 to PUACT 6) clearly showed the appearance of N—H, C═O, and CH symmetric and asymmetric stretching vibrations of CH_2 at the proper frequency and confirmed the involvement of the PU–PMMA blends. The detailed FTIR peaks assignment appearing in the PU–PMMA blends was presented in a previous report.[36] The FTIR spectrum of PUACT 7 is also given in Figure 3; significant peaks were assigned at their relevant position. It could be noted in the comparison of all of the FTIR scans that there were no NH peaks in the PUACT 1 because this sample only contained pristine PMMA and TiO_2, and all of the other FTIR scans showed the prominent peaks of N—H, C═O, and CH_2 at the proper frequency region. The FTIR scans presented higher intensity C═O peaks in all of the spectra. It is worth mentioning that the DMF showed a lower C═O stretching frequency at 1675 cm^{-1} than an unsubstituted C═O bond when it remained in the sample. So, we confirmed that the DMF used as a solvent was completely removed.

Biocompatibility Evaluation

The hemolytic activity of the prepared PU–PMMA–TiO_2 blends was evaluated with the method discussed previously. For this purpose, PBS and 1% v/v Triton X-100 were used as references. The results are reported in Table III. The results revealed that no hemolysis (0%) and full hemolysis (100%) was observed in the presence of PBS and 1% v/v Triton X-100, respectively. As indicated by the scale (given at the bottom of Table III), the percentage lysis caused by the blends of the PU–PMMA–TiO_2 samples was within the range of no toxicity (as per scale of toxicity level). No sample showed any toxic behavior toward the living cells. In a comparison of all of the studied samples, the PUACT 7 sample (100% PU/0% PMMA) showed least nontoxic behavior, and this value toward toxicity increased with increasing content of PMMA; however, the mean values of the individual samples remained in the limit of nontoxicity. Although PMMA

Table IV. Mutagenic Activity of Compounds in the Ames Fluctuation Test with TA98 and TA100 with Different Standard Mutagens

	With TA98 and $K_2Cr_2O_7$ as the standard mutagen		With TA100 and NaN_3 as the standard mutagen	
Sample description	Number of positive wells per 96 wells	Result	Number of positive wells per 96 wells	Result
Background	24	—	25	—
Standard mutagen	92	Mutagenic	90	Mutagenic
PUACT 1	54	Mutagenic	52	Mutagenic
PUACT 2	66	Mutagenic	81	Mutagenic
PUACT 3	42	Nonmutagenic	34	Nonmutagenic
PUACT 4	21	Nonmutagenic	44	Nonmutagenic
PUACT 5	36	Nonmutagenic	43	Nonmutagenic
PUACT 6	45	Nonmutagenic	36	Nonmutagenic
PUACT 7	22	Nonmutagenic	48	Nonmutagenic

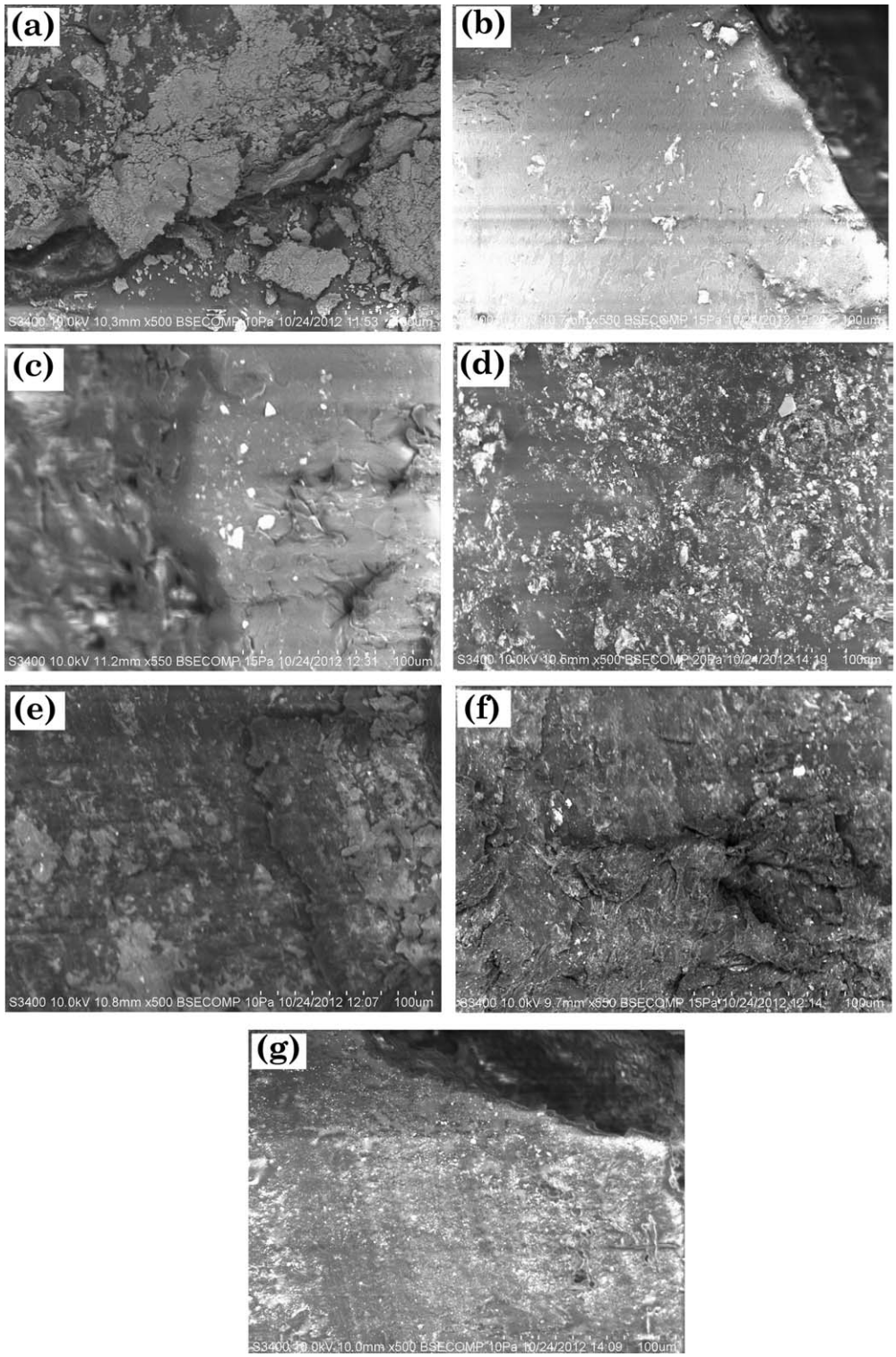

Figure 4. (a) SEM images of the PU–PMMA–TiO_2 blends: (a) PUACT 1, (b) PUACT 2, (c) PUACT 3, (d) PUACT 4, (e) PUACT 5, (e) PUACT 6, and (e) PUACT 7. (2) SEM images of the PU–PMMA–TiO_2 blends showing the dispersion of TiO_2.

also showed biocompatible behavior, we concluded that the contents of PU in the blends were responsible for higher level of biocompatibility, as shown by the samples. It has been presented in the literature that the noncytotoxic chemistry of PU makes these polymer blends good candidates for continued development as biomedical implants.[38] In a similar manner, a study was conducted on the cytotoxicity of PU–PMMA-based material.[39]

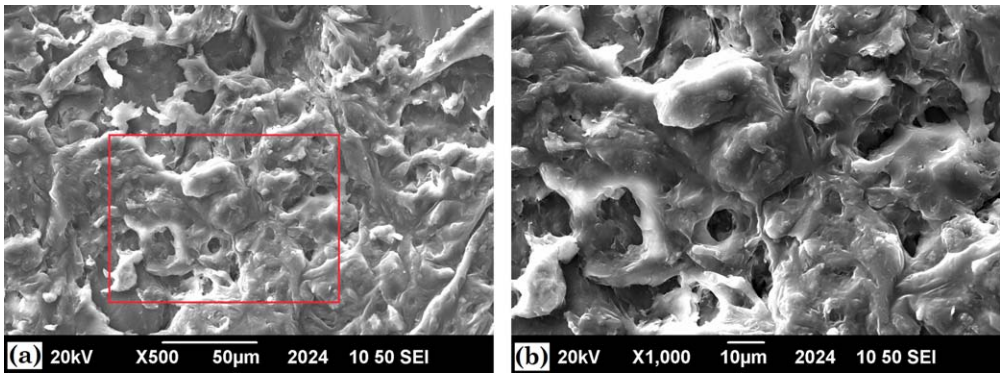

Figure 4. Continued [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mutagenic Activity

The mutagenic activity of the compounds were measured with the Ames fluctuation test according to the TA98 and TA100 methods with $K_2Cr_2O_7$ and NaN_3 as standard mutagens, respectively, and the results are presented in Table IV.

The results presented in Table IV reveal that the standard sample and PUACT 1 and PUACT 2 samples showed mutagenic behaviors with both test methods, although all of the other studied samples showed nonmutagenic behavior. This was attributed to the fact that the PU–PMMA–TiO_2-based composite showed improved biocompatibility and lower mutagenicity than the control and the level of biocompatibility increased with increasing % amount of PU in the blends. The biocompatibility encompasses many aspects of a material, including its physical, mechanical, and chemical properties and its potential cytotoxic, mutagenic, and allergenic effects, so that no significant injuries or toxic effects on the biological function of cells and individuals arise. It is worth mentioning that biocompatible materials cannot be mutagenic or influence inflammatory mediators to cause systemic responses, including toxicity, tissue injury, or teratogenic or carcinogenic effects. Such materials must be free of agents that may cause allergic responses to individuals sensitive to these substances. On the basis of the results presented in Tables III and IV, we concluded that although all of the samples showed biocompatible behavior, the level of biocompatibility increased with increasing contents of PU in the blends.

SEM Analysis

Polymers, like other substrates, can be scanned with SEM to show the surface morphology, but some factors can affect the image. The polymer chains are composed of carbon backbones, and the organic chain can be damaged by energetic electrons hitting the surface. SEM images were taken to investigate the morphology of the prepared PU–PMMA–TiO_2 blends with different mass percentages of PU and PMMA in the blends (Figure 4). From the SEM images (Figure 4) of the fractured surface of the of the PU–PMMA–TiO_2 composite blends, we could clearly see that the fractured surface of the composites became less rugged with increasing PU contents and decreasing PMMA contents; this suggested increasing interfacial bonding between the TiO_2 contents and PU–PMMA matrix. The homogeneity in the dispersion of the TiO_2 contents in the PU–PMMA matrix increased with decreasing PMMA ratio and vice versa. Moreover, we observed that the TiO_2 contents were well dispersed in the polymer matrix in PUACT5, PUACT6, and PUACT7, and there was well defined shadow around the particles in these images.

DSC Analysis

The glass-transition temperature (T_g) of a dental composite is merely of importance if it falls in the range of intraoral temperatures. Dental composites should possess T_g values greater than the maximum temperature in the oral cavity to preserve the material's physical and mechanical characteristics. In this study, the T_g of the PU–PMMA–TiO_2-based composites was 50°C, whereas their T_m was 352.4°C, and their heat of enthalpy (ΔH) was 1985.497 J/g, as obtained from DSC measurement (Figure 5). This value of T_g was slightly above the temperature of the oral cavity, as established in the literature.

Compression Testing for the Blended Samples

The compressive yield stress was measured in a manner identical to that used for the tensile yield strength. While testing plastics, the compressive yield stress was measured at the point of permanent yield on the stress–strain curve. The moduli are generally greater in compression for most commonly used structural materials. The compression results are presented in Table V. The results reveal that among all of the studied samples, the maximum applied load, that is, 1397 Kgf was observed for the PUACT 1 sample (0% PU and 100% PMMA), and this sample showed the maximum resistance against load. By decreasing the mass percentage of the PMMA, the load-bearing capacity of the samples decreased, and this resulted in the slight fracture observed in the PUACT 3 sample, and a clear fracture was observed in the PUACT 4 sample. However, the PUACT 6

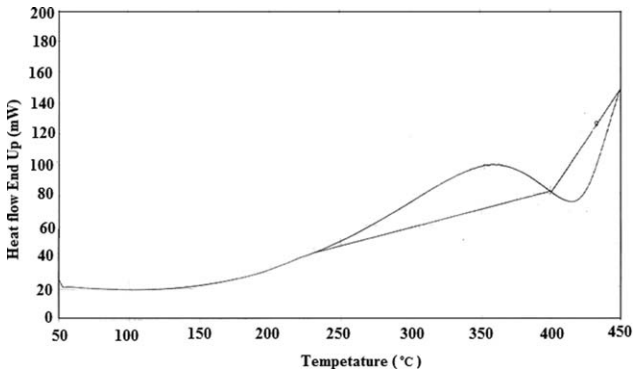

Figure 5. DSC scan of the PU–PMMA–TiO_2 blends.

Table V. Compression Results of the Prepared PU–PMMA–TiO_2 Blend Samples

Sample code	PU–PMMA composition by mass (%)	Shore A hardness	Load at yield (Kgf)	Load at fracture (Kgf)	Maximum applied load (Kgf)	Remarks
PUACT 1	0/100	88	1010.4	—	1397	No fracture observed
PUACT 3	20/80	88	593.2	753	—	Slight fracture observed
PUACT 4	40/60	91	524.2	685	—	Fracture observed
PUACT 6	80/20	95	693.9	1101	1101	No fracture observed
PUACT 7[a]	100/0	90	186.4	—	489.1	No fracture observed

[a] Pores on the untested samples were also observed.

sample (80% PU and 20% PMMA) showed a good load-bearing capacity (i.e., 1101 Kgf) compared to all of the other samples having various mass percentages of PU. Although the PUACT 7 sample (100% PU and 0% PMMA) also showed acceptable load-bearing capacity, the maximum applied load to this sample was 489 Kgf. Further, some pores in the pretested sample (PUACT 7) were also observed. In comparison to all of the studied samples, no fracture was observed against the applied load in the PUACT 1, PUAT 6, and PUACT 7 sample, and finally, we concluded that the best one among the previous three, PUACT 6, was more suitable for dental materials because of the following reasons: (1) PUACT 1 was prepared with 100% PMMA (and 0% PU), which showed less biocompatible behavior and also showed the lowest hardness factor (i.e., 88); (2) PUACT 6 showed the maximum load-bearing capacity and maximum hardness (i.e., 95) and also showed less toxic effects during the cell culture assay because 80 mass % of PU (20% PMMA) was blended in this sample, and (3) the sample PUACT 7 was blended with 100% PU (and 0% PMMA) with a hardness factor of 90; the maximum applied load was also much lower. Also, the fact that this sample had pores on the surface was another of its drawbacks. The value of PUACT 7 was much harder to determine for the compression test because many materials do not exhibit rapid fracture in compression.

CONCLUSIONS

PUs were prepared with TDI, poly(caprolactone diol)s (molecular weight = 4000 g/mol), and BDO. Spectroscopic data confirmed the proposed PU structure. The blends were prepared with various compositions with PU, PMMA, and TiO_2 with different mass percentages. Pellets were prepared from the blends, and FTIR scans confirmed their chemical structure. SEM analysis confirmed the incorporation of TiO_2 into the PU–PMMA matrix. The thermal and mechanical properties were also affected by the composition of the PU–PMMA blends. The results revealed that the mass percentage of PU in the blends of PU–PMMA–TiO_2 were responsible for their better biocompatibility. In addition to its structural and thermal characteristics, the other unique characteristic of these composites included its biocompatibility and compression resistance.

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