On Physical and Chemical Characteristics of Poly(methylmethacrylate) Nanocomposites for Dental Applications. I.

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The objective of this paper is to present the thermal behavior of various PMMA/TiO_2 nanocomposite for complete dentures fabrication with 3D printing technology. There have been prepared and thermally characterized polymeric composites with varied nanofiller content ranging between 0.2% and 2.5% (w/w%). The nanocomposites proved a better thermal performance than that of pure copolymer PMMA-MMA or 3D printing PMMA polymer complex matrix. A small difference in glass transition (T_g) temperature for all compounds studied was recorded.

Keywords: 3D printing, PMMA nanocomposite, functionalized TiO_2, thermal analysis, denture

Despite the modern preventive dentistry and treatments, loss of teeth cannot be avoided, edentulism being among the 50 most common diseases, affecting 2.3% of the total global population in 2010, especially elderly persons [1]. For fully edentulous patients, complete removable prosthesis still remains the elective non-implant restorative approach [2].

The conventional techniques for complete dentures manufacturing have not significantly changed in the past fifty years [3]. The use of CAD-CAM technology in removable prosthodontics encompassed significant improvements by reducing the number of appointments [4], improving fit/retention [5] and electronic archiving of denture design for an easy reproducibility [6].

The biocompatible polymer poly (methyl methacrylate) (PMMA) is one of the oldest and most commonly organic material used in dentistry, being obtained through the methyl metacrylate monomer polymerization [7]. It is a material with good transparency and light transmission (approx 93%), pleasent esthetic aspect and scratching resistance.

Among its numerous employments in dentistry, since 1937 when introduced by Dr. Walter Wright to the National Society of Denture Prosthesis at Atlantic City, USA [8], PMMA has become a common material for producing denture bases and artificial teeth in clinics due to its various specific advantages: biocompatibility, excellent esthetic appearance, stability in the oral environment, ease use and repair, non-irritating, with relatively low cost and also due its tasteless and odorless properties, e.g. According to American National Standard Institute (ASI) and American Dental Association (ADA), PMMA materials used for producing denture base have being grouped in four categories by polymerization procedures (fig. 1). The poly (methyl methacrylate) (PMMA) properties as: bactericidal properties, glass transition temperatures, modulus, mechanical, optical properties [9] have been significantly improved by introducing nanofillers. Such procedure allowed to overcome its drawbacks (low mechanical resistance, high bacterial contamination, monomer leakage or thermal perception) as denture base material. Special attention has been addressed lately to poly (methyl methacrylate) (PMMA) nanocomposite with titanium oxide nanoparticles.

Considering the high physical and chemical stability of titanium oxide nanoparticles, together with the proved nontoxicity and bio-compatibility, photocatalytic behavior, safe to use and no secondary pollution to the environment [10], electrochemical properties, low cost, resistance to photo-induced reaction [11], various methods have been

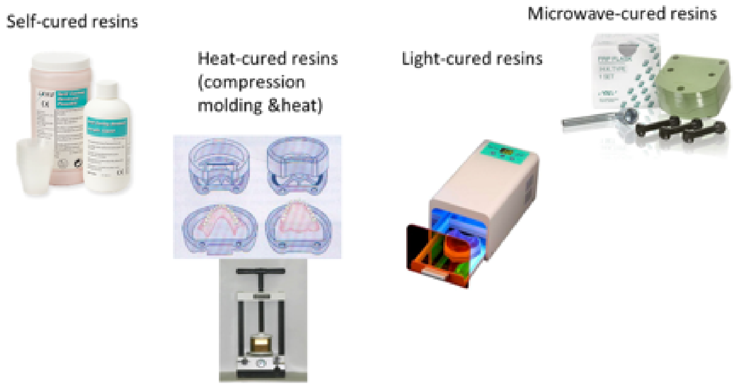

Fig. 1 Denture base polymers-reticulation according to ANSI/ADA classification (ISO 1567 replaced by ISO 20795-1:2013)

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developed to produce materials with nanosized TiO_2 for a wide range of applications [12], among which the medical ones are of the greatest importance. Lately, titanium dioxide is recommended by itself as the best alternative as polymeric filler in order to improve the characteristics of PMMA for denture usage.

The objective of this paper is to outline the some physical-chemical characteristics and future development of PMMA/TiO_2 nanocomposite and simplified protocol for complete dentures fabrication with 3D printing technology [13-17]. It was considered as primary interest the study of thermal properties of the composite material suitable for 3D printing.

Experimental part

Reagents and apparatus

The poly(methylmetharcrylate) – co-methacrylic acid (PMMA-MA) (Aldrich), 2-propanol (Aldrich), methacrylic acid (MA) and poly(methylmetharcrylate)(PMMA) – methylmethacylate (MMA) - benzoyl peroxide (BPO) – reinforcing additives solution (eD) (Envision TEC GmbH) were used in experiments as provided. The used nanoparticles of titania were titanium (IV) oxide, anatase variety (Aldrich). The dental prosthesis has been obtained by Stereolithography (SLA) as rapid prototyping technique, with an Envision TEC device. Details related to the 3D printing procedure are introduced elsewhere [2, 15].

Obtaining the nanocomposite PMMA/TiO_2

There are different methods applied to synthesize the titania nanoparticles [18, 19] each technique presenting its own benefits and specific characteristic depending on the intended applications. However, the hydrothermal and sol-gel process to obtain the TiO_2 nanoparticles are frequently used due to their materials availability, easy procedure and better physical and chemical properties of the final product [20]. In order to have a solid reference,

Type of TiO_2	Properties	Type of study	Reference
Coating with TiO_2 films	Excellent photoinduced antibacterial effect for the sterilization of bacteria under indoor natural light, and about 100% of both bacteria (Staphylococcus aureus (gram positive) and Escherichia coli (gram negative)) are inactivated within 2 h illumination	In vitro	Su et al. 2010 [22]
PMMA filled with 5% Al_2O_3/ZrO_2. The ratio of Al_2O_3 to ZrO_2 added was from 0 to 100	Al_2O_3/ZrO_2 of 80:20 ratio shows the highest values of fracture toughness and flexural properties. Therefore, addition of Al_2O_3/ZrO_2 in PMMA improves the mechanical properties of this denture base material.	In vitro	Alhareb et al 2011 [23]
6 groups: acrylic resin containing nanoparticles TiO_2, SiO_2 and TiO_2 with SiO_2 - two concentrations of 1% and 0.5%, and a control group	TiO_2 and SiO_2 nanoparticles into acrylic resins for antibacterial effect reduces the flexural strength of the final products, and this effect is directly correlated with the concentration of nanoparticles	In vitro	Sodagar et al. 2013 [24]
0.5 and 1 % concentration of TiO_2 nanoparticles (NP)	Addition of TiO_2 NP (for antibacterial effect) into acrylic resin can adversely affect the flexural strength of the final product and is directly proportional to the concentration of NP.	In vitro	Nazirkar et al. 2014[25]
0-5%TiO_2 nanotubes(n-TiO_2)	3% n-TiO_2 exhibited superior mechanical properties to those of control, with a minimum effect on flowability and radiopacity	In vitro	Dafar 2014 [26]
TiO_2-spray-coating technique	Self-cleaning and antibacterial denture properties. Denture base resin coated with TiO_2 does not cause irritation or sensitization of the oral mucosa, skin or intracutaneous tissue and has, therefore, good biocompatibility	In vivo: hamster for oral mucosa irritation test, guinea pig for skin sensitization test and rabbit intracutaneous test	Tsuji et al. 2015[27]
TiO_2-spray-coating technique	This application of titanium dioxide coatings not only improves the self-cleansing action of dentures, but also increases the surface glossiness without influencing the color of the base material.	In vitro	Mori et al. 2015 [28]
10% TiO_2 powder	Tested for thermal conductivity and flexural strength – not significant improvements. SEM images of the TiO_2added group showed that the hexagons formed as a result of polymerization were not fully compatible with PMMA.	In vitro	Kul et al. 2016 [29]
PMMA mixed with 0.4%, 1%, 2.5% weight nano-TiO_2	Antibacterial effects on Candida species (*C scotti*)	In vitro	Totu et al. 2017 [2]

Table 1
TiO_2 BASED FILLERS UTILIZED TO IMPROVE PMMA CHARACTERISTICS FOR DENTURE BASE MANUFACTURING

commercial titania nanoparticles, anatase variety have been used.

When preparing PMMA matrix reinforced with various fillers it is important to avoid the agglomeration of the filler materials which could lead to hybrid composite with a poor performance [21]. In table 1 some of the TiO_2 based fillers utilized to improve PMMA characteristics for denture base manufacturing are presented.

The methacrylic acid acts as functionalization agent [30] in order to obtain a workable composite material PMMA with TiO_2 nanoparticles. MA, as coupling agent, could allow a chemically link of TiO_2 nanoparticles to the polymeric skeleton following the bond formation between titanium oxide nanoparticles – carboxylic group present in MA.

Therefore, the surface of TiO_2 nanoparticles have been functionalized with MA. The titania nanoparticles (10g) - iso-propanol (250mL) dispersed solution was subsequently introduced together with MA (125mL) in a thermostated (80^0C) ultrasonic bath for 8h. The obtained compound was dried at 85^0C after its filtration and careful washing with deionized water.

Once functionalized, the titania nanoparticles were mixed to a corresponding amount of the PMMA-MMA-BPO mixture (eD). Subsequently, the resulted compound has been manually mixed up to an homogeneous, consistent state.

The resulting nanocomposite material has been further used for printing dental devices (complete dentures).

Thermal Analysis

The thermal analysis (TGA and DSC) was done using an equipment Universal V4.5A TA Instruments from 25^0C to 1000 °C at a heating rate of 10°C/min and 5^0C/min under nitrogen atmosphere (flow rate 50 mL/min), using alumina as reference material. The sample weights varied between 4 mg (PMMA-MA) and 14 mg (eD and nanocomposites).

The characterization analysis was performed for nanocomposite mixtures as well as for PMMA-MA (as reference material), PMMA-MMA-BPO mixture (eD) and the UV polymerized material resulted from the 3D printer.

Results and discussions

A realistic evaluation of polymers' thermal stability could be achieved applying the thermal gravimetric analysis. Performing thermal analysis, one can establish the moisture level of a polymer, but also the thermal decomposition through the specific kinetic parameters [31] can be study intimately. Figure 2 presents the thermogravimetric curve for 0.4% TiO_2 – PMMA nanocomposite. In order to decelate all the thermal decompositions possibly overlapping, the thermal analysis has been run at lower heating rate, 5^0C/min. In these conditions it was easier to follow and accurately evaluate the first and the last thermal decomposition steps, and differentiate between the second and the third stage.

All the thermogravimetric curves for PMMA-MA, PMMA-MMA-BPO, various nanocomposites and the 3D printed 0.4% TiO_2 – PMMA nanocomposite are similar presenting same features.

The study of TG curves put in evidence the presence of four decomposition steps for all nanocpomposites, including the compounds without nanoparticles. However, the 3D printed nanocomposite decomposed in only three steps. Although, for the PMMA-MA copolymer the first decomposition stage is very reduced, 0.80% of mass loss, and the the last stage between 480 - 700^0C is assigned to a final mass loss of 0.05% for the range 500 – 900^0C. Based on the recorded TG curves there were established the temperature ranges for each decomposition step, the temperatures where the major weight loss occurs (T_{max}) as well as the corresponding mass loss. These data are presented in table 2.

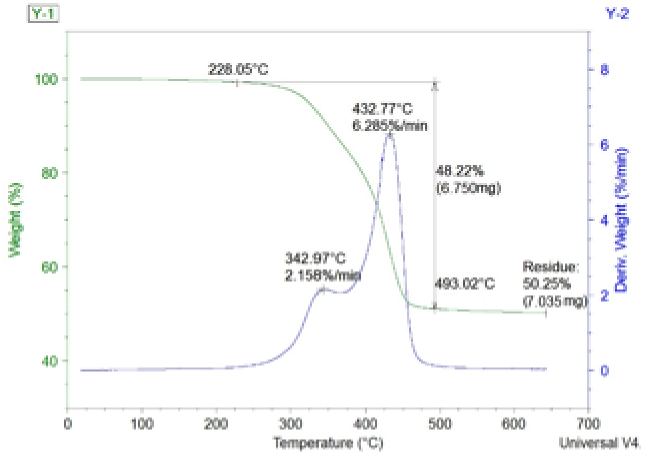

Fig. 2. Thermogravimetric (TG) curve for 0.4% TiO_2 – PMMA nanocomposite

The first thermal decomposition stage corresponds to the evaporation of physically absorbed water and also to the constitutional water loss. The first loss is very small which starts under 100^0C and continues towards 200^0C. This amount of lost water is smaller for composites compared with eD. However, the weight loss recorded for eD and nanocomposites suggest that not only the water was lost, but possibly volatilization of some molecule or even formation of various molecular fragments (monomer sppliting) occurred. Also, within the first decomposition stage, the evaporation of solvent and volatilization of small molecules/residual monomers should be considered.

In case of the 3D printed material, the initial decomposition stage could be assigned to the lost of absorbed water on the material surface. The temperatures where the significant weight loss was recorded presented greater values for eD and nanocomposites compared with PMMA without nanoparticles. The mass decrease for nanocomposites was smaller than the weight loss for eD, exception for the nanocomposite with 2.5% TiO_2 nanoparticles. All materials presented an endothermic effect up to 150^0C. If for the 3D printed material the mass is then constant up reaching 220^0C, for nanocomposites the mass is decreasing, without a null thermal influence. The initial decomposing temperature associated with the *dismantaling* of the composite polymeric matrix was increasing for the composites correlated with higher amounts of nanosized titania. Considering that at 10% weight loss it is recorded the start of the thermal decomposition (onset temoerature) for our compounds the following values were determined: for eD with 0.4% TiO_2 was 322^0C, for eD with 0.6% TiO_2 was 327^0C, and for eD with 2.5% TiO_2 was 331^0C, while for the 3D printed eD with 0.4% TiO_2 was 352^0C. Considering the similar determined temperature for eD of 311^0C it is easily noticed a clear increase of this temperature even by 40^0C for the 3D printed material. The increasing amount of titania nanoparticles in the polymeric matrix lead to an increasing decomposition temperature for nanocomposites. For the second and third steps, huge mass losses can be associated with degradation of different elements of the complex structure and backbone. Under nitrogen atmosphere, residues are mainly formed by non-volatile char and minerals. TiO_2 nanoparticles, especially if they

Table 2

THERMAL DECOMPOSITION STAGES FOR VARIOUS NANOCOMPOSITES

Decomposition stages		PMMA-MA	PMMA-MMA-BPO	Nanocomposites with different amounts of TiO_2 nanoparticles (wt/wt%)					3D printed material
				0.2	***0.4***	***0.6***	***1***	***2.5***	
1st stage	Temp. Range (^{0}C)	25-230	25-245	25-248	25-252	25-250	25-267	25-275	25-280
	% weight loss	0.80	8.29	6.80	4.02	7.42	8.22	9.16	1.25
	T_{max}	120	205	205	210	205	188	228	140
2nd stage	Temp. Range (^{0}C)	230- 355	245-405	248-415	252-420	250-426	266-440	275- 452	280-460
	% weight loss	53.45	17.24	16.89	20.57	13.94	15.85	15.60	41.59
	T_{max}	335	346	341	343	338	334	340	385
3rd stage	Temp. Range (^{0}C)	355-480	405-485	415-480	420-493	426-475	440-482	452 - 490	460-650
	% weight loss	45.22	22.29	21.83	23.63	21.83	17.88	16.35	6.72
	T_{max}	420	445	450	432	452	437	430	545
4th stage	Temp. Range (^{0}C)	480 – 620	485-670	480-670	493 – 675	497-680	502-680	510-700	
	% weight loss	0.05	5.64	6.08	1.53	6.16	6.95	7.07	
	T_{max}	520	525	516	545	512	515	510	

Table 3

TOTAL MASS LOSS (%)

Compound	PMMA-MA	PMMA-MMA-BPO	Nanocomposites with different amounts of TiO_2 nanoparticles (wt/wt%)					3D printed material
			0.2	***0.4***	***0.6***	***1***	***2.5***	
Total mass loss (%)	99.51	53.46	51.6	49.75	49.35	48.90	48.18	49.56

are nanostructured, may interact with polymer chain in the form of a hydrogen bond or a coordination bond, with direct result increasing thermal stability. Even without interacting, there is a possibility that TiO_2 particles consumed some heat and therefore increased the thermal stability.

During the second decomposition stage for eD and nanocomposites there have been recorded small endothermic peaks at: 340.4^{0}C for eD; 351.4^{0}C for 0.2% TiO_2 composite; 337.5^{0}C and 337.7^{0}C for 0.4%, respectively 0.6% TiO_2 composite; while for 1.0% and 2.5% TiO_2 composite there were recorded at 333.7^{0}C, respectively 335^{0}C. For the thermal decomposition stages over 300^{0}C is likely that non-oxidative process are involved. The second thermal degradation step could correspond to the scission of the polymeric chain and the degradation of the unsaturated ends for all composites considered. It is likely that the -$COOCH_3$ groups suffer a hemolytic scission. Reaching temperatures over 405^{0}C, as presented in Table 1, all materials further decomposed recorded an important exothermic effect. The fourth degradation stage could be assigned to a final random scission (-C-C) of the polmeric skeleton. The polymeric matrix thermally decomposes mainly to methyl methacrylate and further to small products as CO and CO_2, methanol and char. The thermal composition was complete for temperatures ranging between 620 -700^{0}C for all compounds (tabel 2). Over 600^{0}C it is likely that PMMA matrix is sized down to simple compunds as: water, carbon monoxide, dioxide and, for nanocomposites, the calcinated TiO_2. The study of the thermogravimetric curves put in evidence that the second endothermic peak and the important exothermic peak are shifted towards higher temperatures for nanocomposites compared cu the polymer mixture without nanoparticles. Table 3 presents the total mass loss for all compounds studied. It is noticed that the mass of the residue finally obtained by the end of the thermal degradation is increasing with incresing quantities of titania nanoparticles added to the initial polymeric matrix. In other words, by adding a larger amount of of TiO_2 nanoparticles to eD, lower values for the total mass loss is recorded.

For the 3D printed material we found similar amount of residue 50.25 to 50.44 % for the 0.4% TiO_2 nanocomposite, which is perfectly reasonable taking into account the fact that for 3D printing it was used the eD - 0.4% TiO_2 compound. Consequently, we could state that the thermal stability of the TiO_2 nanocomposites with PMMA matrix is improved as far as a smaller mass loss is recorded during the thermal decomposition, compared to PPMA-MA or eD.

Differential scanning calorimetry (DSC) measurements, to determine the values for the glass transition temperature (T_g) and the melting temperature (T_m), have been carried out. As general remark, all recorded curves for studied matrix and nanocomposites presented similar behavior being noted small deviations in endotherms and exotherms, depending on each component thermal degradation.

The PMMA mixture – eD, is syndiotactic PMMA being a mixture of PMMA and co-monomers, therefore higher values for T_g are expected. The glass transition temperatures (T_g) and the melting temperature (T_m) obtained are presented in table 4. As observed, there are not major differences between PMMA and nanocomposites regarding the T_g values.

The small increase recorded for T_g is definitely associated with the various amount of the titania filler. The most significant variance exists in the case of the 3D printed material, maybe due to a dramatically reduced intercrystallites distance. However, a monotonically

Table 4
GLASS TRANSITION TEMPERATURES FOR VARIOUS NANOCOMPOSITES

Compound	PMMA-MA	PMMA-MMA-BPO	Nanocomposites with different amounts of TiO_2 nanoparticles (wt/wt%)					3D printed material
			0.2	*0.4*	*0.6*	*1*	*2.5*	
T_g (^0C)	98	115	99	118	120	128	124	132
T_m (^0C)	162	329	333	335	337	340	342	358

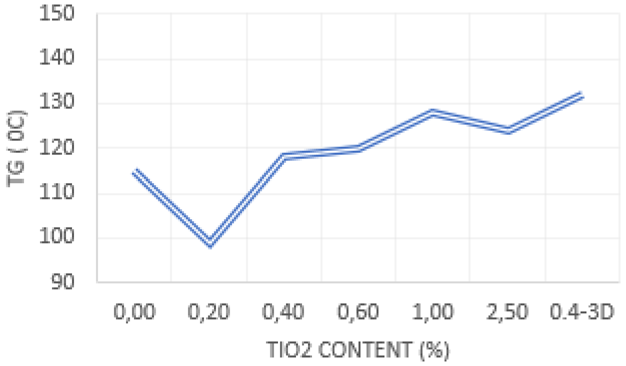

Fig. 3. Variation of glass transition temperature (T_g) for the studied nanocomposites

increase of the T_g values with the increasing amount of the titania nanoparticles has been observed figure 3. Also, it has to be noted the lowest T_g value for the composite with 0.2 TiO_2 content, 99^{0}C.

The DSC investigation allowed to assess the influence of various concentrations of titania nanoparticles in eD composites on the recorded thermal transitions. The DSC curve put in evidence the existence of an extended endothemic peak for a temperature range between 30^{0}C and 150^{0}C becoming broader with an increase of nanotitania in composite. Much more, the specific area of the endothermic peak became smaller with an incresed amount of titania filler. This could be assigned to a reduced content of free hidroxyl anions, either to their blocking through hydrogen bonding, or to their interaction with our nanofiller. Correlating these observations with the increased values for the T_g and T_m it could be considered that the crystallinity degree of the nanocomposites decreased against the increasing of the crosslinking due to the presence of TiO_2 nanoparticles. As the second endothermic peak for the eD - 0.2% TiO_2 nanocomposite and the 3D printed material could not be put clearly in evidence, the evaluation of the melting temperatures has been done by the heat flow change. Regarding the heat flow recorded there were obtained similar behaviour with reduced changes, exception for the 2.5% TiO_2 nanacomposite and for the 3D printed material when there has been a significant variation in the heat flow.

Considering that the heat flow is heat given off in time (s), the area of the endothermic peak could be calculated reporting the value to the mass of sample. To calculate the total heat for the polymer melting, the heating rate was taken into account, as well. The values presented in figure 4 for the melting enthalpy, H_m, have been calculated according to:

$$A = \frac{\Delta Q\cdot\Delta T}{\Delta t\cdot m}\left[\frac{J\cdot K}{s\cdot g}\right] \quad (1)$$

$$\frac{A}{\beta} = \frac{\Delta Q}{m}\left[\frac{J}{g}\right] \quad (2)$$

$$\Delta H_m = \frac{A}{\beta}\cdot m[J] \quad (3)$$

where A is the endothermic peak area, ΔQ the heat difference (J), ΔT the temperature difference (K), Δt is time range when the ΔQ is recorded (s), m stands for the amount of substance (g), β is the heating rate equal with ΔT/Δt (K/s), ΔH_m is the melting enthalpy (J). The calculated values of enthalpy for melting of the nanocomposites studied are synthetically presented in figure 4.

It is easily noticed that H_m is lower for nanocomposites compared with the PMMA matrix without nano-metallic oxide filler. Again, it could be observed that the behavior of the 3D printed material clearly put in evidence the presence a complete reticulated compound. The presence of the exothermic peak characteristic for crystallization of the polymeric matrix was not possible to be put in evidence for all compounds; therefore, the heat for crystallization was not calculated. As consequence, the degree of crystallization for the nanocomposites was not evaluated.

Subsequently to the melting, an important heat flow has been recorded for an exothermic peak, present for all nanocomposites at temperatures above 500^{0}C, corresponding to oxidative reactions of the already fragmented polymer and combustion of the formed residue.

The temperature of the exothermic peak (fig. 5) is around 520^{0}C with small variations for nanocomposites as follows: eD – 523.5^{0}C; eD-0.2% TiO_2 – 515.7^{0}C; eD-0.4% TiO_2 – 544.5^{0}C; eD-0.6% TiO_2 – 512.6^{0}C; eD-1.0% TiO_2 – 512.2^{0}C; eD-2.5% TiO_2 – 508.7^{0}C; 3D printed eD-0.4% TiO_2 – 552.5^{0}C. Studying these data it came out the high values for eD-0.4% TiO_2 and its 3D printed form. As the decomposition temperature is influence by the polymeric matrix crystallinity degree, it is known that a higher temperature corresponds to a larger crystallinity within nanocomposite. Therefore, for the mentioned compounds: eD-0.4% TiO_2 and its 3D printed composite we could conclude that they present a higher degree of crystallinity when compared to

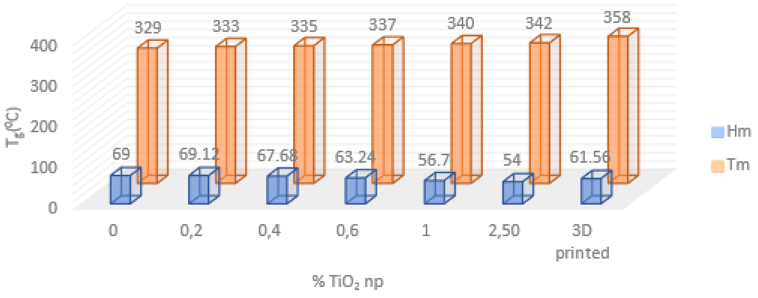

Fig.4. Values for T_m and H_m resulted from DSC analysis

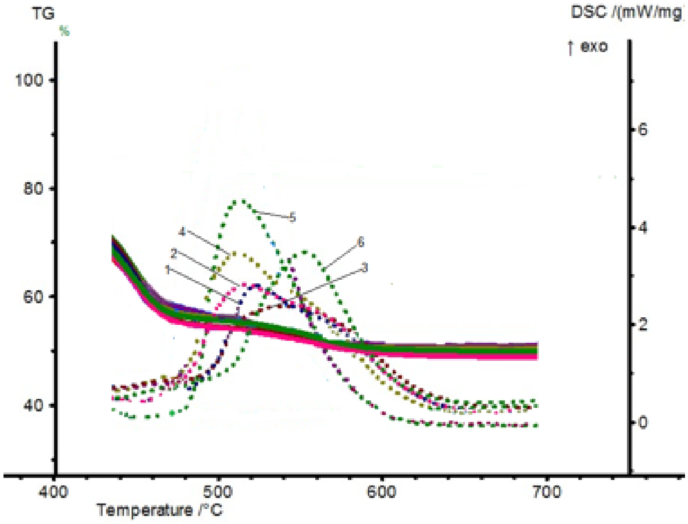

Fig. 5. Overlapping of the exothermic peak for: 1- eD; 2- eD-0.2% TiO_2; 3- eD-0.4% TiO_2; 4- eD-0.6% TiO_2; 5- eD-1.0% TiO_2; 6- 3D printed eD-0.4% TiO_2

the others, although there were encountred some difficulies in evaluating the degree of crystallinity. As general remark, the nanocomposites presented better thermal stability compared to initial PMMA matrix.

Conclusions

The complex nanocomposite PMMA and functionalized titania nanoparticles has been obtained.

In the present work, thermal methods such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are employed to study the change in the thermal stability of the PMMA/TiO_2 nanoparticles composites under investigation. The obtained results offer an insight over some structural changes occurring in a compelx PMMA matrix which has been mixed with various amounts of functionalized nanosised titanuim oxide particles.

The TG curves point out the displacement of the decomposition temperatures towards higher values for the PMMA based nanocomposites. Correlating these observations with the T_g values calculated from DSC plots and the higher residue content obtained we could assume that the nanocomposites under study presents an improved thermal stability. The recorded and calculated thermal data is an indication for a good dispersion of titania nanoparticles within the polymeric matrix. Therefore, such nanocomposites could be used to manufacture dental devices (dentures, bridges) through the new technology of 3D printing. Much more, obtaining important information on the inner structural evolution of the systems under study, we could forsee the evolution of various physico-chemical paramenters. Further investigations (morfological, structural, mechanical) should be carried on for confirming the findings of the presented work.

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