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Influence of ZrO₂ nanoparticles and thermal treatment on the properties of PMMA/ZrO₂ hybrid coatings

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ABSTRACT

In this work, ZrO₂ nanoparticles were synthesized by the sol-gel method, treated thermally at different temperatures (400, 600 and 800 °C), and added to a polymer matrix in two different weight percentages (0.5 and 1) by single screw extrusion in order to determine the influence of these parameters on the thermal stability and UV radiation resistance of PMMA/ZrO₂ composites. Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD), transmission electron microscopy (TEM), confocal laser scanning microscopy (CLSM), ultraviolet-visible spectroscopy (UV-Vis), thermogravimetric analysis (TGA) and nanoindentation techniques were used to evaluate the structural, morphological, optical, thermal and mechanical properties of as-prepared composites. The average crystallite sizes for ZrO₂ sintered at 600 and 800 °C were about 17 and 26 nm, respectively. It was found that the incorporation of a low percentage of ZrO₂ nanoparticles increased the thermal properties of PMMA as well as its hardness and elastic modulus. The degradation temperature at 10 wt.% loss of the PMMA/ZrO₂ (0.5 wt.%, 400 °C) nanocomposite was approximately 48 °C higher than that of pure PMMA. The absorption in the UV region was increased according to the ZrO₂ heat treatment temperature and amount added to the polymer matrix.

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1. Introduction

Poly (methyl methacrylate) (PMMA), an important thermoplastic polymer, displays excellent properties such as transparency, lightness, hardness and high elastic modulus [1,2]. Furthermore, it is a common substitute for inorganic glass due to its higher impact strength and fracture behavior (ductile rather than brittle fracture prone) [3]. It is widely used in many optical, automotive and consumer applications. Nevertheless, it is limited in many applications including computer/electronics, aerospace industry and architectonic materials due to its low thermal stability and poor resistance to UV radiation. A possible alternative to improve these properties is to combine it with different inorganic nanoparticles to obtain hybrid polymers or polymer nanocomposites. These materials, also known as inorganic–organic hybrids, constitute a multicomponent system in which the major constituent is a

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http://dx.doi.org/10.1016/j.jallcom.2014.10.040 0925-8388/© 2014 Elsevier B.V. All rights reserved. polymer or blend, whereas the minor constituent is at least one dimension below 100 nm [4]. Recently, polymer/inorganic particle nanocomposites have garnered considerable interest since they can improve properties such as optical, thermal, mechanical, and chemical, as a result of the inorganic contribution to the polymer matrix [5–8]. Thus, the final properties of these nanocomposites depend on several factors including: composition, particle size, surfactant, dispersion of particles in the polymer matrix, thermal properties of inorganic particles, polymer-particle interface, and the fabrication method [9,10]. Among the fillers, SiO₂ is one of the most widely used in PMMA nanocomposites due to the fact that it has demonstrated its ability to enhance the mechanical properties of PMMA [11-13]. Other possible materials with excellent properties like chemical resistance, good mechanical strength and good thermal stability, which can be used to reinforce the polymeric matrix, are the ZrO₂ nanostructures [14]. A few reports are related to the addition of ZrO₂ to the PMMA matrix and, as a consequence, the interaction between the organic and inorganic parts is still far from being fully understood [15,16]. The PMMA/ZrO₂ system is commonly produced by two conventional methods: in situ polymerization or mixing solution. The melt mixing method is commercially more attractive than the methods mentioned above [17] due to the fact that it is inexpensive, environmentally friendly, straightforward, and seems to be a valuable method for industrial application [18,19]. Additionally, different strategies such as the non-aqueous-sol-gel method have demonstrated that they provide an easily controllable way to increase reactivity, including ternary systems (PMMA/ZrO₂/TiO₂) with potential applications in optical and mechanical fields [20]. In the present work, different PMMA/ZrO₂ polymer composites were successfully obtained by single screw extrusion to evaluate the influence of different sintering temperatures (400, 600 and 800 °C) and amounts of ZrO₂ nanostructures (0.5 and 1 wt.%) on their thermal stability and UV radiation resistance. ZrO₂ nanoparticles were synthesized by the low-cost-sol-gel method and thereafter samples were characterized by proper techniques to determine size, shape, dispersion and hardness in the polymer matrix.

2. Experimental procedure

2.1. Materials and synthesis of ZrO₂ nanoparticles

ZrO₂ nanoparticles were synthesized by the sol–gel method starting from zirconium n-propoxide [Zr(OCH₂CH₂CH₃)₄ 70 wt.% in 1-propanol, Aldrich] as precursor, acetylacetone (CH₃COCH₂COCH₃, Aldrich 99%) as chelating agent (to control the hydrolysis rate of the zirconia precursor and its reactivity) and isopropanol [(CH₃)₂₋ CHOH, Sigma–Aldrich 99.9%] as solvent, using the following procedure: zirconium n-propoxide was mixed with n-propanol (0.6 M) applying vigorous magnetic stirring for 30 min. The obtained solution was complexed by using acetylacetone at a 1:1.5 M complexing agent/alkoxide ratio. The solution was quickly stirred at room temperature for 120 min, maintaining pH fairly constant during the synthesis process (pH \sim 7). The sols were found to be stable and transparent with no precipitate or turbidity. The ZrO₂ powders were obtained by gelification of the solutions and drying of the gels at 120 °C for 24 h to remove organic material; afterwards, the xerogel samples were ground in an agate mortar and then thermally treated at 400, 600 and 800 °C for 2 h in air to study the effect on the structure and particle size. Finally, the powders were crushed by a horizontal ball mill at 350 rpm for 10 h.

2.2. Preparation of nanocomposites

A commercial grade poly (methyl methacrylate) (PMMA, PlexiglasV825, Altuglas International, Arkema) in pellet form was used; the reported melt flow rate of this material at 230 °C/3.8 kg is 3.7 g/10 min. PMMA pellets were first ground in a Thomas-Wiley laboratory mill using a 2-mm sieve to obtain fine PMMA particles. Thereafter, polymeric particles were dried at 80 °C for 1 h before being processed. PMMA-ZrO₂ nanocomposites were prepared using a laboratory single-screwextruder (D = 19 mm, L/D = 30 mm) with three heating zones. Two different amounts of ZrO₂ nanostructures (0.5 and 1 wt.%) were added to the polymer matrix. The blending temperature profiles on the extruder were 235, 235 and 240 °C, from hopper to die zone, and the screw rotating speed was 80 rpm; in the last step, nano-composite extrudates (filaments or narrow films) were cooled in a water bath at room temperature.

2.3. Characterization and measurements

FT-IR studies were carried out to determine the functional groups and bonding types in the samples. These studies were performed using a Spectrum One Perkin-Elmer spectrometer equipped with an attenuated total reflectance probe (ATR). The IR spectra of the nanocomposites were obtained in the transmittance mode, in the 450–4000 cm⁻¹ spectral region with 15 scans and at a resolution of 4 cm⁻¹.

To determine the interaction between the organic and inorganic phases, ¹H NMR and ¹³C NMR spectra were carried out using a Bruker Ascend 750 (750 MHz) NMR spectrometer for liquids at room temperature with deuterated chloroform (CDCl₃, ¹H: δ = 7.26 ppm, ¹³C: δ = 77.0 ppm) as a solvent and tetramethylsilane (TMS, δ = 0.00 ppm) as the internal reference. The syndiotactic percentage (*r*) in each sample was obtained by using the following equation:

% Syndiotacticity =
$$(r) = \frac{A_{(m)} + \frac{1}{2}A_{(mr)}}{A_T} \times 100$$
 (1)

where $A_{(rr)}$ and $A_{(mr)}$ are the areas of the signals corresponding to the syndiotactic and heterotactic configuration, respectively. A_T is the sum of all the areas within the PMMA tacticity $(A_{(rr)} + A_{(mr)} + A_{(mm)})$ [21]. The relative peak intensities were calculated with an electronic integrator. Crystalline phase identification of the ZrO₂ powders and nanocomposites was performed using a D8 Advance Bruker X-ray diffractometer with Cu K α monochromatic radiation. The XRD patterns were collected in the 20–80° 2 θ range at room temperature. The average crystallite size of ZrO₂ was estimated using the Scherrer formula [22].

$$D = \frac{0.9\lambda}{B\cos\theta_B} \tag{2}$$

where *D* is the average crystallite size, λ is the X-ray wavelength (1.54056 Å), *B* is the FWHM width of the diffraction peak, and θ_B is the corresponding diffraction angle of the diffraction peak.

 ZrO_2 nanoparticles were examined by TEM using a JEOL-2000 FX-II microscope coupled with an energy dispersive X-ray spectrometer (EDS) operating at 200 kV.

The nanocomposites were also characterized by CLSM using a Carl ZEISS microscope, model LSM 700. This tool is equipped with a spectral channel used to detect autofluorescence signals, which come from sample components. The fluorescence intensity measurements were performed using the built software ZEN of the LSM 710. The intensity peak, characteristic of a fluorescence emission signal, was 461 nm for PMMA and 598 nm for the ZrO₂ nanoparticles. UV–vis absorption spectra of the studied nanocomposites were measured in the 200–1100 nm wavelength range using a Perkin–Elmer Lambda 40 UV–vis spectrometer. The thickness of the analyzed samples was about 0.5 mm.

TGA studies were carried out using a Simultaneous Thermal AnalyserLabsysEvo 1600 of Setaram. Samples were placed in aluminum crucibles. An empty aluminum crucible was used as reference. The heating ramp applied to the samples was from 25 to 450 °C at a constant heating rate of 5 °C/min under argon atmosphere.

Nanoindentation technique was employed to evaluate the mechanical properties. Measurements were carried out with the CSM Instruments Nanoindentation Tester (TTX-NHT) with a Berkovich triangular diamond pyramid indenter. A loading rate of 15 mN min⁻¹ was maintained until reaching a maximum load of 5 mN. The load was held at maximum value for 10 s in order to study the creep behavior before the indenter was unloaded. The hardness (*H*) and elastic modulus (*E*) were estimated from the initial gradient of the unloading curves using the Oliver and Pharr model [23]. Five indents were performed on each sample on randomly selected locations to obtain average values of hardness and elastic modulus of the nanocomposites.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra of pure PMMA and different PMMA/ZrO₂ nanocomposites acquired in the 4000–450 cm⁻¹ range are shown in Fig. 1. For pure PMMA, the bands around 2996, 2952 (asymmetric) and 2844 cm⁻¹ (symmetric) are assigned to C—H stretching vibrations. The bending vibration bands of the methyl (—CH₃) group appear at 1484 and 1436 cm⁻¹ in the FTIR spectra, whereas the deformation mode of the methylene (—CH₂—) group appeared around 1387 cm⁻¹. In addition, the sharp and intense band at 1728 cm⁻¹ is attributed to the stretching vibrations of the carbonyl





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(C=O) group. The strong band at 753 cm^{-1} is attributed to the out of plane bending vibration of the C=O group. The PMMA/ZrO₂ nanocomposites show absorption bands that matched with pure PMMA, indicating a weak interaction between PMMA and ZrO₂ nanoparticles. Only the intensity of the C=O group at 1728 and 753 cm⁻¹ is reduced in the PMMA/ZrO₂ nanocomposites, which is characteristic of the weak interaction between the ZrO₂ nanoparticles and PMMA with the adsorption of the polymer on the inorganic surfaces *via* the methoxycarbonyl group $(-C(0)OCH_3)$ [24,25]. Bands corresponding to the vibration absorption of Zr–O groups (between 450 and 750 cm⁻¹) are not observed owing to the incorporation of a low percentage of nanoparticles. In agreement with previous reports, in the range between 1050 and 1300 cm⁻¹, there are five infrared absorption bands associated with the ester group of syndiotactic poly(methyl methacrylate), s-PMMA, which so arises from specific interactions [26]. Among them, the $v_1(C-C-O)$ coupled with the v(C-O) vibration at 1272 and 1242 cm⁻¹ (v_1 and v_2) associated with the trans and cis conformation of the ester group, respectively, are found. The bands at 1192 and 1150 cm⁻¹ (v_3 and v_4) are assigned to skeletal stretching coupled with internal C-H deformation. Finally, the band at 1065 cm⁻¹ (v_5) is attributed to the planar zigzag arrangement of the backbone carbon atoms [13]. Thus, the PMMA/ZrO₂ synthesized in this work shows mainly a syndiotactic configuration. It is well known that the thermal stability of PMMA changes according to the molecular weight and tacticity: in an inert atmosphere, the syndiotactic form of PMMA displays a higher degradation temperature than the isotactic one, which is attributed to the slower chain mobility of the first one [26,27].

3.2. NMR studies

¹H NMR spectra of pure PMMA and PMMA/ZrO₂ (0.5 and 1 wt.%, 800 °C) nanocomposites are reported in Fig. 2a. The methoxy protons $(-OCH_3)$ of PMMA show a peak at 3.60 ppm, whereas methylene protons ($-CH_2$) show peaks at the 2.2–1.5 ppm range. In addition, the peaks at 1.22, 1.01 and 0.83 ppm are related to the isotactic (mm), heterotactic (mr) and syndiotactic (rr) configurations of α -methyl protons (–CH₃), respectively. It can be seen that all the spectra have the same number of peaks without any modification in their shape. However, with the addition of ZrO₂ nanoparticles (0.5 and 1 wt.%) thermally treated at 800 °C, the peak at 1.59 ppm related to the methylene group of PMMA is shifted towards lower values. These small shifts suggest the existence of electrostatic interactions between the PMMA structure and ZrO₂ nanoparticles via methoxycarbonyl groups (-C(O)OCH₃), which is proposed in the inset scheme. The content of the different triads were determined by the electronic integration of the α -methyl signals, thereby obtaining a percentage of syndiotactic PMMA of 69%. Fig. 2b shows the ¹³C NMR spectra of pure PMMA and PMMA/ZrO₂ (0.5 and 1 wt.%, 800 °C) nanocomposites. The peaks between 22 and 16 ppm are assigned to the methyl group; peaks at 44 ppm are related to the quaternary carbon of the polymeric chain; the peak at 52 ppm is related to the methoxy group; the peak at 54 ppm is associated with the methylene group and peaks between 177 and 178 ppm are related to the carbonyl carbon. No modification in the chemical shift is observed in the nanocomposites, indicating that no chemical bond occurred. From the analysis of the carbonyl, quaternary carbon and α -methyl signals of the ¹³C NMR spectra, an average percentage of the syndiotactic configuration of about 70-71% was obtained. It has been reported that the possible measurement error by NMR is about 3-4% [28]; therefore it can be considered that these values are similar to those obtained by ¹H NMR analysis. Finally, these results confirm the high degree of syndiotacticity observed by FT-IR.

3.3. Structural and morphological characterizations

Fig. 3a and b shows XRD patterns of the ZrO₂ nanoparticles treated thermally at three different temperatures 400, 600 and 800 °C, pure PMMA and PMMA/ZrO₂ nanocomposites. Fig. 3a shows the evolution of the crystalline phase. It was found that at 400 °C, the ZrO₂ nanoparticles show low intensity broad peaks at around $2\theta = 30.2^{\circ}$, 50.3° and 60.2°, which are assigned to reflections from planes (011), (112) and (121), respectively, corresponding to tetragonal ZrO₂ (t-ZrO₂). It is clearly seen that these reflection peaks become sharper and narrower with higher treating temperatures (600 °C), indicating the increase in the average crystallite size and the improvement of the crystallinity of the ZrO₂ nanoparticles. In addition, the emergence of peaks at 34.8° (002), 35.2° (110), 59.6° (013), 62.9° (202), 74.5° (220), 81.9° (123) and 84.9° (222) can be observed, confirming the presence of a tetragonal phase. The diffraction pattern for the ZrO₂ treated at 800 °C is dominated by the more intense, characteristic peaks of the monoclinic phase $(m-ZrO_2)$, $(\overline{1}11)$, (111) and (220), centered at 28.1°, 31.4° and 50.1°, respectively. That is to say that the ZrO_2 nanoparticles present, basically, the monoclinic phase. However, a peak centered at $30.2^{\circ}(101)$ is observed, indicating the presence of a small content of the tetragonal structure at 800 °C. Additionally, the average D crystallite sizes of ZrO₂ nanoparticles were calculated on the basis of Eq. (1) and were found to be 17.1 ± 0.4 and 26.4 ± 0.9 nm for ZrO₂ nanoparticles treated thermally at 600 and 800 °C, respectively. Fig. 3b shows XRD patterns of the PMMA/ ZrO₂ nanocomposites. The diffraction pattern of pure PMMA shows a broad diffraction peak at $2\theta = 14.5$, typical of an amorphous material, together with two bands of lower intensities centered at 30.7° and 42.1°. The diffraction patterns of all PMMA/ZrO₂ nanocomposites show the same three bands observed in pure PMMA, indicating that neither the presence of the nanoparticles nor the preparation process change the orientation of the PMMA chains.

Polymer nanocomposites synthesized from annealed ZrO_2 nanoparticles at 400 and 600 °C display a sharp tendency to show an amorphous structure with narrow peaks at about ~30.2°, which seems to correspond to the tetragonal structure (011), whereas hybrid materials using sintered nanostructures at 800 °C show two low intensity peaks at 28.1° and 31.4°, corresponding to the ($\overline{1}$ 1 1) and (111) planes of the monoclinic ZrO_2 . It is important to highlight that the structural phase of ZrO_2 nanoparticles does not modify the amorphous nature of PMMA, only observing ZrO_2 crystalline domains embedded in the PMMA matrix.

Fig. 4a-c shows TEM images in bright field mode with their corresponding selected area electron diffraction pattern (SAEDP). The TEM micrographs show that the ZrO₂ nanopowders consist of crystal-faced-shaped nanocrystals with variable size distributions along with a high agglomeration degree. The size of crystals seems to be decreased with the treatment temperature, forming bigger agglomerates. As it is well known, nanoparticles are aggregated due to the large specific surface area and high surface energy; then it is expected to enhance the agglomerate size with the treatment temperature as in our case. The ZrO₂ nano powders, treated thermally at 400 °C, are constituted of aggregates with sizes between 0.2 and 0.3 μm and composed by crystals of about 50–100 nm in diameter. ZrO₂, thermally treated at 600 °C, shows aggregates between 0.35 and 4 µm with irregular smaller crystals of about 20 nm, while ZrO₂, thermally treated at 800 °C, consists of aggregates with sizes ranging from 0.33 to 0.45 µm with even smaller crystallite sizes. The large zirconia agglomerates are built up of aggregates of smaller units. The observed reduction in the crystal size with temperature seems to resemble the statement regarding the decrease in the crystallite size by Zener, which pins the effect in combination with the polymorphic transformation from the t-phase to the m-phase or both.

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Fig. 2. NMR spectra of pure PMMA and PMMA/ZrO $_2$ nanocomposites by (a) ^1H NMR and (b) ^{13}C NMR.



Fig. 3. XRD patterns of (a) nanocrystalline ZrO₂ powders thermally treated at different temperatures and (b) pure PMMA and PMMA/ZrO₂ nanocomposites.

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Fig. 4. TEM images and SAEDPs of ZrO₂ thermally treated at different temperatures (a) 400 °C, (b) 600 °C and (c) 800 °C.

The SAEDPs of ZrO_2 thermally treated at 600 and 800 °C show concentric rings, which also indicate that the crystallite size is on nanoscale. The SAEDPs were indexed according to the ICDD cards of tetragonal and monoclinic phases; thus, the results are consistent with XRD patterns, corroborating that as the temperatures is increased an increase in crystallite size is obtained.

To corroborate the TEM results, dynamic light scattering (DLS) also known as photon correlation spectroscopy was used to measure the particle size distribution (PSD) in anA Malvern Zetasizer-Nano ZSP, model ZEN5600. Different particle diameter moments (number-average diameter D_n ; weight-average diameter D_w and *z*-average diameter) were calculated using Eqs. (3)–(5), and the polydispersity index (PDI) was determined using Eq. (6):

$$D_n = \frac{\sum n_i D_i}{\sum n_i} \tag{3}$$

$$D_{w} = \frac{\sum n_{i} D_{i^{4}}}{\sum n_{i} D_{i^{3}}}$$
(4)

$$D_z = \frac{\sum n_i D_{i^5}}{\sum n_i D_{i^5}} \tag{5}$$

$$PDI = \frac{D_w}{D_n} \tag{6}$$

where n_i is the number of ZrO_2 NPs with diameter D_i . The particle size distributions (PSD) as well as average particle size and polydispersity index for the evaluated samples are shown in Table 1. From these data, it can be observed that the ZrO_2 particle size was increased with temperature and it can be considered as a polydispersed system (PDI > 1). The tendency to form bigger agglomerates with temperature, observed in the TEM micrographs, was confirmed with dynamic light scattering measurements.

To evaluate the dispersion degree of ZrO_2 nanostructures, the PMMA/ ZrO_2 nanocomposites were characterized by CLSM. This

technique allows scans at various x-y planes corresponding to different depths of the sample, and, thus to reconstruct the 3-D region of the specimen [29]. In this case, the three-dimensional structure reveals the spatial position of the particles in all directions, which is helpful to evaluate the effects on the optical, thermal and mechanical properties. It is well recognized that the distribution of the nanoparticles play an important role in the final properties. Fig. 5 shows the 3D-CLSM images of the PMMA/ZrO₂ nanocomposites with 0.5 and 1 wt.% of particles thermally treated at different temperatures. From the measurements, it can be seen that the ZrO₂ nanoparticles show a uniform dispersion within the PMMA matrix, but tend to form agglomerates with irregular morphology. In addition, it is clearly observed that the ZrO₂ particles tend to form bigger agglomerates as the heating treatment temperature is increased and only a small quantity of nanoparticles can be seen. This result is due to crystal size increments, which consequently decreases their fluorescence emission intensity.

3.4. Optical properties

The transmission spectra in the UV–Vis region (200–1100 nm) for pure PMMA and PMMA samples with 0.5 and 1 wt.% of ZrO₂ at different heating treatment temperatures are shown in Fig. 6a. It can be seen that the transmittance response of PMMA/ZrO₂ nanocomposites is attenuated in comparison with pure PMMA in the visible region. The transmittance of the nanocomposites is strongly decreased as the content of the inorganic moiety and the heating treatment temperature of the ZrO₂ nanoparticles are increased. Then, as the ZrO₂ content is decreased, the transmittance percentage is increased up to the highest value obtained in the PMMA sample with 0.5 wt.% of ZrO₂ thermally treated at 400 °C. Even in the previous case, the transmittance is reduced about 25% compared to pure PMMA, whereas PMMA with 1 wt.%

ZrO ₂ 400 °C		ZrO ₂ 600 °C		ZrO ₂ 800 °C	
Size d (nm)	Mean number (%)	Size d (nm)	Mean number (%)	Size d (nm)	Mean number (%)
78.82	7	396.1	12.5	458.7	0.8
91.28	32	458.7	37.5	531.2	8.9
105.7	43	531.2	37.5	615.1	24.5
122.4	18	615.1	12.5	712.4	31.7
-	-	-	-	825	22.9
-	-	-	-	955.4	9.5
-	-	_	-	1106	1.7
$D_z = 109.4 \text{ nm}$		$D_z = 536.9 \text{ nm}$		$D_z = 845 \text{ nm}$	
Polydispersity index = 1.0436		Polydispersity index = 1.0483		Polydispersity index = 1.0977	

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Fig. 5. 3D CLSM representations of pure PMMA and PMMA/ZrO₂ nanocomposites.



Fig. 6. (a) UV-vis spectra of pure PMMA and PMMA/ZrO₂ nanocomposites, and (b) optical images of pure PMMA and PMMA/ZrO₂ nanocomposites.

of ZrO₂ nanocomposites, treated at 800 °C, showed the lowest value. From these results and optical images (Fig. 6b), it is evident that the presence of even a small percentage of ZrO₂ leads to a dramatic transparency loss, which can be attributed either to the obtained structural phase or to the presence of agglomerated ZrO₂ nanoparticles since these can act as a strong scattering center [30], and therefore, causes haze or even turbidity; in fact, previous studies have shown that size, structural phase and distribution of

inorganic particles have critical importance for transparency of polymer/inorganic particle composites [31,32]. Besides, the formations of small crystalline domains embedded in the amorphous PMMA also contribute to the percentage reduction of transmittance in the visible range. Synthetic polymers are susceptible to degradation by UV and visible light, however, it has been reported that photodegradation of PMMA has taken place by irradiation at 260–300 nm, but not under irradiation at $\lambda > 320$ nm [33], which

furthers the photostability of aliphatic acrylic and methacrylic polymers, which is generally very high in comparison with polyolefins [34]. Additionally, spectra of pure PMMA and PMMA/ZrO₂ nanocomposites show two absorption bands at about 272 and 315 nm. These bands may be attributed to the $n-\pi^*$ transition of the C=O group in the PMMA [35,36].

3.5. Thermal studies

It is widely accepted that the degradation of PMMA is initiated by the scission of head-to-head linkages (155-220 °C), followed by β -scission at the vinylidene chain ends (230–300 °C), and finally by random main chain scission (>300 °C) [37]. TGA curves of pure PMMA and PMMA/ZrO₂ hybrid materials under argon atmosphere are presented in Fig. 7a. It can be observed that the thermal stability of the hybrid materials was greatly improved by the addition of ZrO₂ moieties. It can be seen that the improvement of the thermal stability of the nanocomposites is almost independent of the ZrO₂ content, but strongly dependent on the heating treatment temperature. This may explain the behavior of the PMMA/ZrO₂ (0.5 wt.%, 800 °C) nanocomposite, where low thermal stability compared with all nanocomposites is seen, perhaps because ZrO₂ nanoparticles are aggregated in the PMMA matrix. Fig. 7b indicates the effect of ZrO₂ content and thermal treatment on the decomposition temperature at 5 and 10 wt.% loss of the nanocomposites. In comparison with PMMA, the degradation temperature of PMMA/ ZrO₂ (1 wt.%) nanocomposites at 5 and 10 wt.% loss was increased in about 33-47 °C and 45-50 °C, respectively. These results imply that the nanocomposites are more thermally stable than pure PMMA due to the electrostatic interaction between the ZrO₂ nanoparticles and PMMA matrix. It is well recognized that the effective dispersion of inorganic nanoparticles in the polymer matrix enhances the thermal resistance of the nanocomposites because the increasing number of active sites increases the decomposition temperature, which is in agreement with CLSM observations [8]. The improvement of thermal stability is explained by the restriction of mobility of polymer chains resulting from the steric hindrance and radical trapping effect of inorganic fillers.

3.6. Hardness tests

Nanoindentation tests were used to study the ZrO₂ load effect on the mechanical properties of PMMA/ZrO₂ nanocomposites at higher thermal treatment. Fig. 8 displays the typical load–displacement curves at a maximum indentation load of 5 mN on the



Fig. 8. Load-displacement curves of pure PMMA and PMMA/ZrO₂ nanocomposites.

PMMA/ZrO₂ nanocomposites. The incorporation of ZrO₂ nanoparticles into the PMMA matrix resulted in a higher penetration resistance compared to that of pure PMMA. For example, for PMMA, the maximum indentation depth at the maximum load was 1049 nm, whereas with 0.5 and 1 wt.% of ZrO₂ thermally treated at 800 °C, the maximum depth was about 1003 and 985 nm, respectively. Similar values and trends were observed for asprepared composites from ZrO₂ nanoparticles sintered at 400 °C. The results of the nanoindentation experiments are in good agreement with the mechanical properties of nanocomposites obtained by standard macroscopic methods [38]. Hardness is important since it is related in many cases to the strength or fracture toughness of the specimen. A high hardness generally corresponds to a high abrasive wear resistance [39]. The hardness, elastic modulus and creep for PMMA and PMMA/ZrO₂ nanocomposites are summarized in Table 2. It is evident that the hardness and elastic modulus are increased with the addition of stiff ZrO₂ nanoparticles into the matrix [40,41]. However, a significant change in these values when the ZrO₂ content is increased from 0.5 to 1 wt.% is not observed. The creep percentage at the maximum hold segment was decreased (i.e., increasing the creep resistance) with the addition of a low content of nanoparticles, indicating that the PMMA/ZrO₂ nanocomposites provide greater stiffness than pure PMMA, further suggesting that the nanocomposites are less ductile than pure PMMA.



Fig. 7. (a) TGA curves of pure PMMA and PMMA/ZrO₂ nanocomposites, and (b) effect of ZrO₂ on the decomposition temperature of nanocomposites.

Table 2

Values of hardness (H_{IT}), elastic modulus (E_{IT}) and creep (C_{IT}) for pure PMMA and PMMA/ZrO₂ nanocomposites.

Sample	H _{IT} (MPa)	E_{IT} (GPa)	C _{IT} (%)
PMMA	254 ± 4	4.10 ± 0.03	6.97 ± 0.06
PMMA/ZrO ₂ (0.5 wt.%, 800 °C)	287 ± 9	4.17 ± 0.04	6.47 ± 0.07
PMMA/ZrO ₂ (1 wt.%, 800 °C)	297 ± 9	4.33 ± 0.09	6.39 ± 0.06

Preliminary experiments indicate that the PMMA without ceramic nanoparticles display similar values of syndiotacticity between pure PMMA and PMMA/ZrO₂ nanocomposites (about 70%); thus, changes in the mechanical properties are only attributed to the interaction degree between the PMMA structure and inorganic nanoparticles, which have a larger elastic modulus (241 GPa) than that presented by the PMMA polymer matrix (4 GPa).

In summary, the PMMA/ZrO₂ with 0.5 wt.% of ZrO₂ treated at 400 °C was the optimum nanocomposite with low reduction of transparency and high thermal stability compared with all the prepared nanocomposites. Hence, low percentages of ZrO_2 nanoparticles thermally treated at low temperature can improve the thermal properties of the PMMA.

4. Conclusions

Polymer nanocomposites of PMMA containing ZrO₂ nanoparticles were prepared by the melt-blending procedure as a function of the amount and heating treatment temperature of inorganic nanoparticles. The nanoparticles of m- and t-ZrO₂ were successfully synthesized using the sol-gel method. FT-IR and ¹H NMR spectral measurements help conclude that an electrostatic interaction between the polymer and ZrO₂ nanoparticles was formed. CLSM results show a homogenous dispersion of nanoparticles into the polymer matrix, however, agglomerates with irregular morphology can be observed. The prepared nanocomposites have better UV protection than pure PMMA. However, the structural phase and agglomeration of ZrO₂ nanoparticles in a polymer matrix play an important role in the transparency reduction of composites. The thermal stability of the PMMA is increased in the presence of ZrO₂ nanoparticles due to the electrostatic interaction between the ZrO₂ nanoparticles and PMMA matrix in addition to the possible radicaltrapping ability of the ZrO₂ nanoparticles during the thermal degradation of polymer chains. PMMA/ZrO2 nanocomposites show local higher values of elastic modulus and hardness. Finally, the results reveal that independently from the size or the shape of the nanoparticles, their addition to the PMMA matrix improved the thermal and mechanical properties as compared to the pure polymer, but a good dispersion and a t-phase is required to obtain maximum transparency.

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