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Synthesis and incorporation of ZnO/TiO_2 in PMMA to study its thermal properties

Síntesis e incorporación de ZnO/TiO_2 en PMMA para estudio de sus propiedades térmicas

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Abstract

The creation of films formed by the incorporation of ZnO or TiO_2 in poly(methylmethacrylate) PMMA matrices was proposed in order to improve their properties as resistance to high temperatures. ZnO and TiO_2 nanoparticles were synthesized by the sol-gel method, which does not require the use of surfactants and is easily scalable. In the present work, zinc oxide (ZnO) or titanium oxide (TiO_2) incorporations were carried out in a polymeric matrix of Poly(methylmethacrylate) PMMA. Both oxides were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD) and diffuse reflectance UV-Vis spectroscopy. PMMA was obtained by the suspension free radical polymerization method and PMMA composites containing ZnO or TiO_2 were obtained. Polymer characterization was performed using Fourier transform infrared spectroscopy (FTIR). The composites were analyzed by thermogravimetric analysis (TGA) and its thermal resistance was found to be the best incorporation of TiO_2 in 1%.

PMMA, Suspension Polymerization, ZnO, TiO_2

Resumen

Se propuso la creación de películas formadas por la incorporación de ZnO ó TiO_2 en matrices de PMMA con el fin de mejorar sus propiedades como resistencia a altas temperaturas. Las nanopartículas de ZnO y TiO_2 se sintetizaron por el método sol-gel, el cual no requiere el uso de tensoactivos y es fácilmente escalable. En el presente trabajo se llevaron a cabo incorporaciones de óxido de zinc (ZnO) u óxido de titanio (TiO_2) en una matriz polimérica de Polimetacrilato de metilo PMMA. Ambos óxidos fueron caracterizados por espectroscopía infrarroja por transformada de Fourier (FTIR), espectroscopía de difracción de rayos-X (DRX) y espectroscopía UV-Vis de reflectancia difusa. El PMMA se obtuvo por el método de polimerización por radicales libres en suspensión y se obtuvieron compositos de PMMA conteniendo ZnO ó TiO_2. La caracterización del polímero se realizó mediante la técnica, espectroscopía infrarroja por transformada de Fourier (FTIR). Se analizaron los compositos mediante análisis termogravimétrico (TGA) y se encontró que aumenta su resistencia térmica siendo la mejor incorporación la de TiO_2 en 1%.

PMMA, Polimerización en Suspensión, ZnO, TiO_2

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Introduction

The polymer industry is one of the most active sectors in the world economy due to the sustained demand of its products in many technological applications.

Synthetic polymers have become an essential part of our daily lives by being part of various objects and materials with which we are in contact throughout the day. Its great variety and numerous applications, increasingly specific and of greater added value in different areas such as electronics, optics and biomedical, have made polymer science an area with a lot of research and innovation potential both academic and industrial [I].

Poly(methylmethacrylate) PMMA is a well-known amorphous polymer (mainly), it has two asymmetric side groups along the spine: methyl ($–CH_3$) and polar and larger ester ($–COOCH_3$) side groups [II].

It is an important member of the family of polyacrylic and methacrylic esters. It has several desirable properties, including exceptional optical clarity, good weather resistance, high strength and excellent dimensional stability [III].

Polymers are characterized by having two types of main transition temperatures: the crystalline melting temperature Tm (or crystalline melting point) and the glass transition temperature Tg.

The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample. The glass transition temperature is the temperature at which the amorphous domains of a polymer assume the characteristic properties of the glassy state such as fragility, hardness and stiffness.

The values of Tg and Tm of a polymer affect its mechanical properties at any particular temperature and determine the range of temperatures at which the polymer can be used.

Some of the factors that decrease the tendency to crystallize a polymer also lead to an increase in the values of Tm (and also Tg).

The reason for this is that the degree of crystallinity developed in a polymer is controlled both kinetically and thermodynamically, while the melting temperature is controlled only thermodynamically. Polymers with rigid chains are difficult or slow to crystallize, but the portion that crystallizes will have a high melting temperature.

Ceramic materials are usually designed for use at high temperatures, their resistance to thermal creep is a very important property. Thus, the crystalline ceramics have a resistance to thermal creep due to their high melting points.

ZnO is a ceramic photoactive material that at its nanometric scale sees its properties enhanced. TiO_2 is an inorganic ceramic material widely used in the industry due to its optical, mechanical and chemical properties, as well as its relative accessibility.

Sol-Gel Method

The sol-gel method involves a colloidal suspension of particles where the precursor can be an alkoxide metal such as an aluminate, titanate, borate, silicate, thiosulfate, among the most commonly used. The sol-gel method is a technique that leads to the formation of oxides by polymeric inorganic reactions. It has 4 characteristic stages: hydrolysis, polycondensation, drying and thermal decomposition [IV]. Therefore, its advantages of the Sol-Gel method are the ease and the low temperature of synthesis [V].

Suspension Polymerization

In suspension polymerization the initiator is soluble in the monomer (dispersed phase) which in turn is immiscible in water (continuous phase), which contains the stabilizing agent and which is soluble in it. It is important to mention that it is important to maintain a stir in the system; likewise, the stabilizer hinders the coalescence of monomer droplets and polymer particles, whose tendency to agglomerate can cause problems [VI]. A reverse suspension polymerization involves an organic solvent as a continuous phase, with dispersed drops of a water soluble monomer (acrylamide, acrylic acid and soluble acrylates), which may be pure or dissolved in water, and the initiator.

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Commonly used items made of polymers undergo modifications are favored by the isolated or combined action of certain environmental conditions, for example wear (yellowing) due to UV radiation as well as deformation due to heat.

This significantly decreases its useful life, therefore, it is important to implement a technological route to prolong the useful life of polymers, mainly diminished by their interaction with ultraviolet radiation and high temperatures.

It is reported that zinc oxide and titanium dioxide have an excellent absorption of UV radiation, with application in different industries, their incorporation in polymeric matrices to manufacture composites can achieve that their properties (thermal resistance, resistance to photodegradation), Be remarkably improved.

Therefore, this work was aimed at finding a composite that gives better thermal resistance to PMMA by making 2 different types, one incorporating ZnO and the other with TiO_2.

At the same time looking for what proportion gives better results between the options 1% and 0.3%.

Thus, the hypothesis was that the incorporation of the metal oxides ZnO or TiO_2 in the polymeric matrices of PMMA will make a synergy relationship improving the properties of the polymer films. In particular, a higher thermal resistance is expected.

Methodology

For ZnO synthesis a 0.06 M solution of zinc acetate Zn $(CH_3COO)\ 2 \cdot (H_2O)_2$ in 400 mL of methanol (CH_3CH_2OH) and a 0.5 M solution of sodium hydroxide (NaOH) in 250 mL of methanol were prepared. The zinc acetate solution was placed in an Erlenmeyer flask under constant magnetic stirring at 800 rpm and the NaOH solution was added dropwise to adjust to a pH = 11. The flask was then placed in an oil bath at a temperature of 60 °C maintaining magnetic stirring at 800 rpm for 1h. After the time elapsed, the reaction flask was immediately subjected to an ice bath for 20 minutes to stop the growth [VII].

The nanoparticles were recovered in 50 mL Falcon tubes subjected to centrifugation at 6000 rpm for 20 min. At the end of the centrifugation, methanol was discarded and the recovered nanoparticles were placed in a crucible which was left for 12 hours at 60 ℃ in a convection oven. Finally, the crucible was placed in a flask at 100 °C for 1 hour.

TiO_2 nanoparticles were obtained through the aging process accompanied by hydrolysis/polycondensation.

Titanium tetraisopropoxide (TTIP) was used as the starting material. 5 mL of TTIP and H_2O in a molar ratio of 100 H_2O/Ti were placed in a flask, the reaction flask was subjected to constant magnetic stirring at 1000 rpm and temperature of 90 °C (using a cooling system to prevent evaporation of H_2O). The reaction was allowed to be carried out for 72 hours, taking care to keep the temperature constant after the first 30 minutes, which were critical to stabilize the reaction and thus optimize aging. The TiO_2 solution will be transformed into a one-phase paste solution, and a peptizing agent was added, in this case HNO_3 at a molar ratio of 0.25 HNO_3/Ti. For the preparation of the TiO_2 powder, the solution was dried at 100 ° C for 24 h in a convection oven and finally calcined at 500 °C for 2h in a flask. Finally the powder was ground in agate mortar [VIII].

To perform the synthesis of PMMA by the free radical polymerization method in suspension, glycerol was used as a continuous medium and as a microcrystalline cellulose dispersing medium (DS-0 cellulose powder), placed in a beaker at 75 °C and magnetic stirring constant at 380 rpm, adding as initiator benzoyl peroxide (BPO) dissolved in the monomer (methyl methacrylate) [IX].

NOTE: For the incorporations, the ZnO or TiO_2 nanoparticles (which were previously sonicated for 30 min in a glass with 3 mL of methanol) were added at the beginning of the polymerization.

Sample	Matrix	% ZnO	% TiO_2
1	PMMA	0	0
2	PMMA	0.3	0
3	PMMA	1	0
4	PMMA	0	0.3
5	PMMA	0	1

Table 1 Synthesized samples

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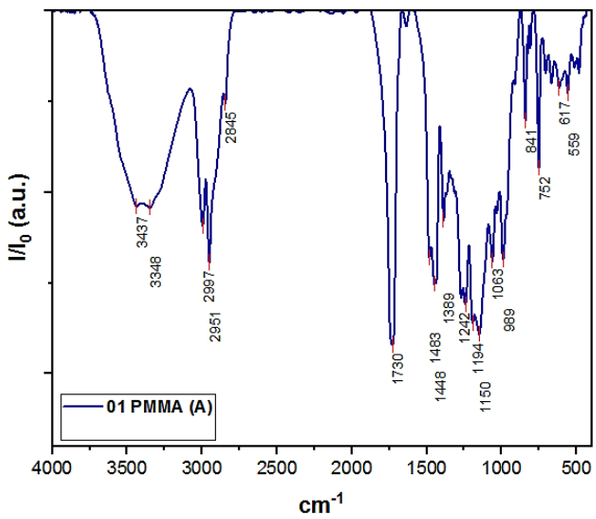
Results

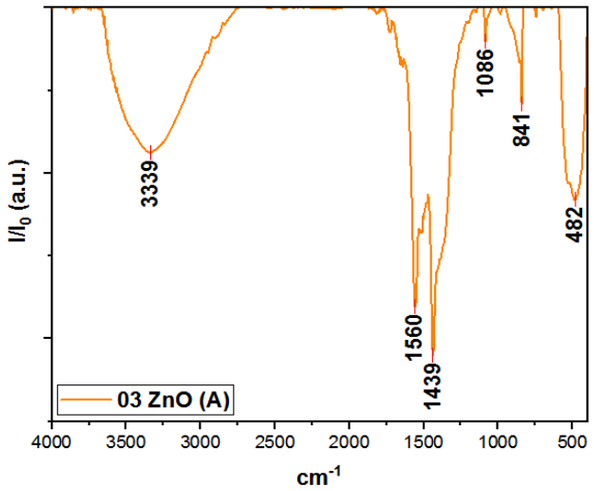
FTIR

The spectrum of the PMMA sample shows that the bands at 2997, 2951 and 2845 cm^{-1} are due to CH type elongation vibrations of methyl and methylene, the band at 1732 cm^{-1} is due to a stretch C = Or of the ester group present in the PMMA, the bands in 1483,1450,1437 and 1387 cm^{-1} are due to deformation vibrations of CH bonds typical of PMMA methyl and methylene, the bands in 1271 and 1242 cm^{-1} are due At the C–O elongation of the ether group, the 1194 and 1150 cm^{-1} bands are due to vibrations of the CH flap and torsion link out of plane respectively, the 1061 cm^{-1} band is due to a C-OH bond due to to possible presence of glycerol). The 989 cm^{-1} band is due to the elongation of the DC link, the 841 cm^{-1} band is due to the rolling methylene vibration in the plane and the 750 cm^{-1} band is due to the C=O vibration link torsion out of plane [X].



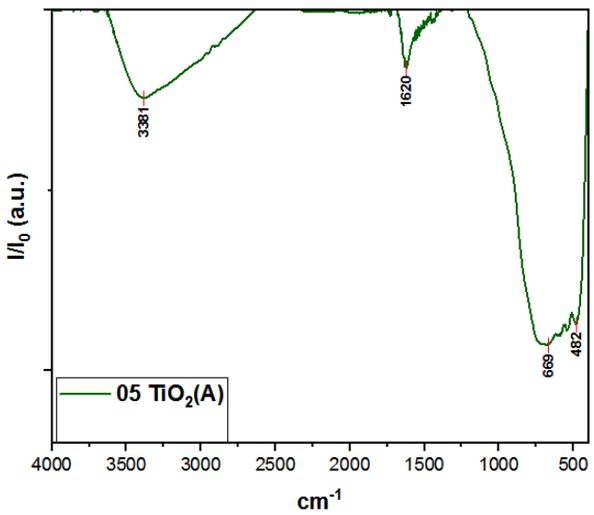
Graphic 1 Infrared spectrum in KBr plates for the sample 1 PMMA in chloroform

The spectrum of the ZnO sample shows a peak is observed in 482 cm^{-1} belonging to the stretch band of the Zn-O bond, the peak of 841 cm^{-1} belongs to the Zn-Zn bond and corresponds to the tetrahedral coordination of Zn, the peak in 1086 cm^{-1} it is due to the elongation band of the zinc acetate precursor. The peaks in 1439 cm^{-1}, 1512 cm^{-1} and 1560 cm^{-1} are due to symmetric and asymmetric stretching vibrations C=O probably of zinc acetate precursor, finally the weak wide peak in 3339 cm^{-1} is due to OH stretch vibration [XI].



Graphic 2 Infrared spectrum in KBr plates for sample ZnO in MeOH

The spectrum of the TiO_2 sample shows a peak in 669 cm^{-1} of the Ti-O-O bond which confirms the presence of titanium dioxide. In addition, the signals in 3381cm^{-1} and 1620 cm^{-1} belonging to the O-H and N = O bonds of the nitric acid used in the synthesis of TiO_2 can be observed.



Graphic 3 Spectrum in KBr plates for sample TiO_2 in MeOH

DRX

From the X-ray diffraction it is possible to determine the crystallite size. Scherrer's formula was used to calculate crystallite size using the equation:

$$B = \frac{K\lambda}{L\cos\theta} \quad (1)$$

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Sample	Position 2θ (°)	B (FWHM)	Crystal size L (nm)
ZnO	36.29	0.29	37.35
TiO_2	25.25	0.88	10.37

Table 2 Crystal size calculations using the Scherrer equation with values of XRD.

Diffuse reflectance UV-Vis

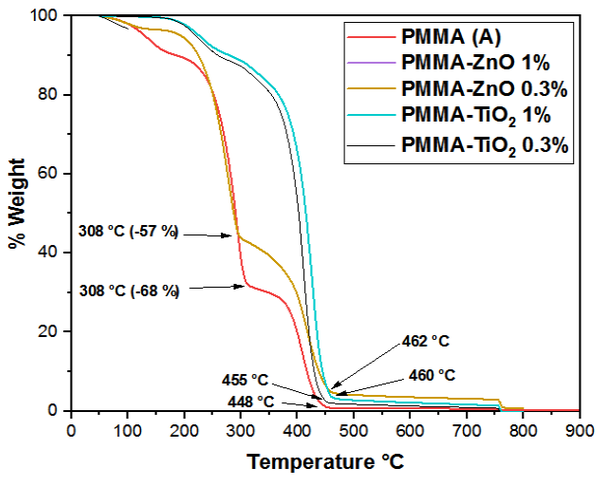
For TiO_2 sample it is reported that the experimental values obtained from Band gap (Egap) are due to the high synthesis temperature (90 ° C) since lowering the temperature results in higher values of Egap [XII].

Sample	Theoretical Egap (eV)	Experimental Egap (eV)
ZnO	3.37	3.09
TiO_2	2.8 – 3.3	3.15

Table 2 Comparison between the theoretical and experimental band gap calculated

TGA.

The TGA shows that the thermal resistance of PMMA-ZnO (for 0.3% and 1%) increases, at 308 °C the loss of mass was reduced 11%, the decomposition of most mass goes from 448 °C to 462 °C, while for PMMA-TiO_2 the thermal resistance increases, going from breaking down the PMMA from 448 °C to 455 for 0.3% or up to 460 °C for 1%.



Graphic 4 TGA studies for samples PMMA, PMMA-ZnO and PMMA-TiO_2

Conclusions

The sol gel method is a good method for synthesis of nanoparticles of metal oxides (ZnO and TiO_2) since it is simple, with a high level of conversion and cheap, making it a scalable process. The polymer with the highest thermal resistance was with 1% TiO_2 which showed a difference greater than 100 °C to begin most thermal decomposition.

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