Influence of zinc oxide in a polar polymer matrix

Influencia de óxidos de zinc en una matriz polimérica polar

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Abstract	Resumen
<p>The creation of films constituted by semiconductor oxides of zinc oxide (ZnO) incorporated into a polar polymer matrix was proposed, looking for such films to be easy to apply, friendly to the environment and compatible with materials. Within the experimental process, the synthesis of styrene copolymers with a polar monomer (methyl methacrylate) was carried out through the suspension and emulsion polymerization processes.</p> <p>Styrene, Suspension Polymerization, ZnO</p>	<p>Se propuso la creación de películas constituidas por óxidos semiconductores de ZnO incorporados a una matriz polimérica polar, buscando que dichas películas sean de fácil aplicabilidad, amigables con el medio ambiente y compatibles con otros materiales y que se mejoren las propiedades conductoras. Dentro del proceso experimental, se llevó a cabo la síntesis de copolímeros de estireno con un monómero polar (metacrilato de metilo) mediante los procesos de polimerización en suspensión y emulsión.</p> <p>Estireno, Polimerización en Suspensión, ZnO</p>

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Introduction

The articles of common use suffer wear (yellowing) due to UV radiation, an alternative to this problem, consists of the use of coatings, which provide greater protection, without altering the intrinsic properties of the material on which it is applied. For the purposes of this experimental development, we propose the creation of films made of ZnO incorporated into a polar polymeric matrix, looking for such films to be easy to apply, friendly to the environment and compatible with materials that are applied. Within the experimental process, the synthesis of styrene copolymers with a polar monomer (alkyl acrylate) will be carried out by means of the suspension and emulsion methods, then the synthesis of Zinc oxides will be carried out, which upon incorporation into the polymer matrix is expected to generate a synergy, potentiating the properties of resistance to yellowing of the composite.

Morphological, electrochemical and structural characterization tests will be carried out. The best particle-matrix weight ratio will be found to avoid yellowing of the films and the best matrix particle ratio will be determined when evaluating the dispersion of the oxides in the polymer matrix.

Polymers play an important role in the needs of human consumption today. That is why, for many years, science has worked on the modification of physical and chemical properties of these compounds, in order to produce diverse materials according to the application they require.

In the field of polymer production, we have been working on the search for synthesis processes that can improve the final properties of the polymer or improve the industrial production process. [I].

– Suspension Polymerization

In it, the polymerization occurs in the liquid phase in the monomer droplets (normally dispersed in water), using a soluble initiator in organic phase (azo- or peroxides) and a stabilization or suspension agent that does not form micelles (used to prevent the coalescence of the drops). The two-phase system is unstable, in the sense that polymerization in suspension is not maintained in the absence of agitation.

– Emulsion polymerization

The monomer is insoluble in the continuous medium and is suspended to form emulsion drops stabilized using surfactants (surfactants). The initiators used are soluble in water (or in the solvent). In such a way that the polymerization process does not occur in the drops, but in entities formed by the surfactant called micelles, which are fed by the monomer that travels by diffusion through the medium. [II].

Nanotechnology is an emerging interdisciplinary field that has become very popular in many areas over the last decade, including the science of materials, mechanics, electronics, optics, medicine, plastics, textiles, etc.). ZnO belongs to a group of metal oxides that are characterized by the following properties: photocatalytic capacity, electrical conductivity, UV absorption, photooxidant capacity against chemical products and biological species, antimicrobial and self-sterilization. In addition, ZnO is generally considered as a safe material for humans and animals, and has been widely used in the formulation of personal care products. [III]. ZnO) is a semiconductor that in nanoscale presents an ordered structure, and a great activation energy. The scientific interest in this material arose to recent dates, because it was observed that it is a solid with high mobility of electrons, good conductor of electricity, thermodynamically stable and capable of absorbing visible light.

The production of nanostructured fibers is an area where nanotechnology has had a great impact, since it presents the possibility of manufacturing antimicrobial textiles, which are very useful in the medical field, or the search for materials such as ZnO that, when irradiated by ultraviolet light, has an antibacterial effect [IV]. Inorganic ZnO semiconductor exists in two different phases such as zinc blend and hexagonal wurtzite. Among these, hexagonal wurtzite is the commonly observed structure at room temperature. [V].

This project aims to incorporate semiconductor oxide particles in a vinyl-type copolymer to achieve a good dispersion and to evaluate the synergy between the properties of the zinc oxide (ZnO) in combination with the polymers which will generate protective films against deterioration caused by the UV rays.

Metodology

Synthesis of ZnO nanoparticles (wurzite) by the Sol-Gel method.

Synthesis of polymers

Prior to any synthesis method, the ZnO nanoparticles were ground in an agatha mortar and the appropriate amount was weighed according to the desired incorporation either at 1% or 0.3% w/w, placing them in a flask with methanol immersed in a sonicator for 30 min.

Emulsion polymerization

Prior to initiating the emulsion synthesis, of 0.68% Potassium Persulfate solution was prepared. A stirrer, distilled H₂O, sodium Dodecyl sulfate SDS (surfactant) was placed in a beaker and the stirring was started at the appropriate revolutions (rpm) according to the polymer to be obtained as well as the heating in order to reach the desired temperature. Once the reaction temperature was reached, the nanoparticles were added in case of being a polymer with incorporation of nanoparticles. Next, 0.68% potassium persulfate (used as initiator) and then monomer (s) used were added and then left for the appropriate time for the monomer (s) polymerization.

Suspension polymerization

A stirrer, the desired continuous medium as well as its dispersing medium was placed in a beaker, stirring and heating was carried out in order to reach the necessary reaction conditions for each polymer.

Once the reaction temperature was reached, the nanoparticles were added in case of being a polymer with incorporation of nanoparticles. Next, 0.68% potassium persulfate (used as initiator) and then monomer (s) used were added and then left for the appropriate time for the polymerization of each monomer (s). At the end of the reaction, 2 washes were made with tap water and one with distilled water.

The polymer is dried in an oven at 70 °C for 24h. The polymers obtained are listed in table 1.

Polymer	Meth.	Monómer mL	Disp. mL	Disp.	Initiator	ZnO (%)	T °C	Stir rpm	Time hours
PS	Em.		H ₂ O	SDS 0.225g	K ₂ S ₂ O ₈ (0.68%) 2mL	0	85	00	3
PS	Em.		H ₂ O	SDS 0.225g	K ₂ S ₂ O ₈ (0.68%) 2mL	1	85	00	3
PS	Em.		H ₂ O	SDS 0.225g	K ₂ S ₂ O ₈ (0.68%) 2mL g	0.3	85	00	3
PS	Susp.		H ₂ O	PVA 0.075g	PBO 0.0181g	0	85	50	3
PS	Susp.		H ₂ O	PVA 0.075g	PBO 0.0181g	1	85	50	3
PS	Susp.		H ₂ O	PVA 0.075g	PBO 0.0181g	0.3	85	50	3
PMMA	Susp.		Gly 40	Cell. 0.15g	PBO 0.0181g	0	75	80	3
PMMA	Susp.		Gly 40	Cell. 0.15g	PBO 0.0181g	1	75	80	3
PMMA	Susp.		Gly 40	Cell. 0.15g	PBO 0.0181g	0.3	75	80	3
PS - PMMA 50 - 50 %	Susp.	03/0.9	Gly 40	Cell. 0.15g	PBO 0.0181g	0	75	80	3
PS - PMMA 50 - 50 %	Susp.	03/0.9	Gly 40	Cell. 0.15g	PBO 0.0181g	1	75	80	3
PS - PMMA 50 - 50 %	Susp.	03/0.9	Gly 40	Cell. 0.15g	PBO 0.0181g	0.3	75	80	3

Table 1 PS = Polystyrene, PMMA = Polymethylmethacrylate, SDS = Sodium Dodecyl Sulfate NaC₁₂H₂₅SO₄, PVA = Polyvinyl Alcohol (C₂H₄O) x, PBO = Benzoyl Peroxide C₁₄H₁₀O₄, K₂S₂O₈ = Potassium Persulfate

Results

Characterization of ZnO

XRD

ZnO diffractogram synthesized via sol-gel

With these results the hexagonal wurzite phase is confirmed whose characteristic peaks are located at 32.24 ° (31.79 °), 34.42 ° (34.47 °), 36.25 ° (36.28 °), 47.54 ° (47.60 °), 56.84 ° (56.66 °), 62.86 (62.91), and 68.76 ° (68.01 °).

UV-Vis

UV-Vis absorption spectrum of ZnO film

The presence of ZnO is confirmed since it is known that UV-Vis has an absorption band at approximately 370 nm (382 nm).

Characterization of polymer films

Spectrum of electrical impedance of polystyrene, polystyrene with incorporation of ZnO at 0.3% and polystyrene with incorporation of ZnO at 1% in KCl

Spectrum of electrical impedance of polymethylmethacrylate with incorporation of ZnO at 0.3% and copolymer polystyrene-polymethylmethacrylate with incorporation of ZnO at 0.3% in KCl.

Impedance spectroscopy is a technique that indirectly allows us to measure the conductive character and the materials. The resistance to the transfer of load is related to the diameter of the semicircles that are obtained from the graph.

We can see that the sample has no ZnO is the one that has the largest diameter, therefore the greatest resistance and with the highest concentration of ZnO that is 1% resistance decreases, indicating that it increases its conductivity as they are reverse measurements.

Conclusions

The results obtained are conclusive to affirm that the polymerization processes were performed correctly in both emulsion and suspension, the characterization of the PS and PMMA polymers as well as the copolymer gave the expected result, as well as the characterization of the ZnO nano particles confirms that the sol-gel method was performed correctly.

The experimental methods used gave favorable results, however due to lack of time, more characterization tests are still pending such as SEM microscopy, NMR spectroscopy and FT-IR by diffuse reflectance in order to analyze the dispersion level of the ZnO particles in the polymer networks synthesized.

As the ZnO is a material that adsorbs the UV light, we can also say that the higher concentration in the polymer matrix will favor the protection to the solar radiation and the yellowing.

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