

Photostability of PMMA-TiO₂ micro composites and PMMA-TiO₂ nano composites

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Abstract

Comparison for the optical energy gap between pure PMMA, PMMA-TiO₂ micro composites and PMMA-TiO₂ nano composites have been investigated under UV – radiation, the effect of time irradiation (0,6,12,24,48,72,96 and 120) have been studied for these specimens to study the photic stability. The results show that the photostability of the PMMA-TiO₂ nanocomposite is higher than that of the pure PMMA and PMMA-TiO₂ micro composite under UV-light irradiation.

Keywords

PMMA-TiO₂ micro composites
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الاستقرارية الضوئية لمتراكبات PMMA-TiO₂ المايكروية والنانوية

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الخلاصة

تم في هذا البحث مقارنة بين قيم فجوة الطاقة لمتراكبات البولي مثيل ميثا اكريليك وثاني اوكسيد التيتانيوم المايكروية والنانوية نتيجة تأثير اشعاع الفوق البنفسجية على هذه المسود، لدراسة الاستقرارية الضوئية تم تشيع العينات بفترة زمنية مختلفة للتشيع (0،6،12،24،48،72،96 ساعة). اظهرت النتائج استقرارية للضوء لمتراكبات البولي مثيل ميثا اكريليك - ثاني اوكسيد التيتانيوم النانوي اكثر من العينات النقية والمايكروية.

Introduction

Titanium oxide film is a very important material due to its multifunctional application in photocatalysis, hydrophobic material, photovoltaic cells, photochromic and electrochromic devices, gas sensor, biosensor, corrosion protection, bactericide, optical device, among others. TiO₂ can occur in a number

of crystalline forms, the most important of which are anatase, rutile and brookite. Nowadays, it is one of the most extensive studied metal oxide, both as particulate and thin film form. Their properties depend on the crystalline phase, roughness, porosity, and particle size and distribution. When the particle size is sufficiently small it is

possible to observe quantum size effects[1].

PMMA is one of the most versatile polymeric materials for applications in various technological areas including optics and electro-optics. While the current applications of PMMA in optics and electro-optics are limited by their linear optical behavior [2].

Long term exposure to sunlight leads to the degradation of plastic materials. In particular, the non-visible UV radiation characterized by short wavelengths is responsible for photo-degradation, a process that generally results in breaking down the polymer chains. This frequently results in a deterioration of the physical properties, changes in color or chalking of the part [9,10].

Theoretical part

1- Interaction of UV radiation with plastics

UV energy absorbed by plastics can excite photons, which then create free radicals. Absorption of electromagnetic radiation in the UV-region transfers the right amount of energy levels of the bonds of a molecule and result in excitation of electrons from the ground state into an excited state .However, absorption will only occur if the energy of the photon corresponds exactly to that of the transition. we will see that higher energy , shorter wavelength, light is necessary to excite σ bonds than π bonds as there is a larger energy difference between the bonding and antibonding σ – orbitals compared with the bonding and antibonding π – orbitals .In spectroscopic nomenclature the structural features of a molecule responsible for absorption of the UV light are referred to as chromophores [4-6].

2- Optical energy gap

The study of optical absorption spectra provides a very useful tool for the investigation of optically induced transitions and an insight in the energy gap and band structure of crystalline and non

crystalline materials. The experimental results on optical absorption in glassy materials have been reported by Mott and Davis [7].

One important difference of amorphous solids as compared with crystalline solids is that; whereas in crystalline nonmetallic solids there is a sharp well defined lattice absorption edge E_g given by the relation.

$$E_g = h c / \lambda \dots(1)$$

(where E_g = energy gap, h = Plank's constant, c = velocity of light), in amorphous materials the absorption edge is less sharp and is not well defined.

The optical absorption coefficient $\alpha(\omega)$ was calculated for each of the specimens at various photon energies ($\hbar \omega$) by using the relations

$$I_t = I_o e^{-\alpha d} \dots(2)$$

$$\alpha(\omega) = (1/d) \ln(I_o/I_t) \dots(3)$$

where d is the thickness of the sample, I_o and I_t are the incident and transmit intensities of the radiation, respectively. The experimental value of the absorption coefficient α near the edge was calculated using Eq. (3):

$$\alpha = 2.303 A / d \dots(4)$$

where A = normalized optical absorption and is given by $A = \log(I_o/I_t)$. The optical gap E_{opt} can be calculated from the curves representing the square root of the quantity ($\alpha \hbar \omega$) versus photon energy ($\hbar \omega$) using Eq. (1).

Obviously, the magnitude of the energy gap is higher for insulators than it is for semiconductors, but otherwise the same photophysical processes apply. Electrons can only be excited into the conduction band if an absorbed photon has sufficient photonic energy to allow the electrons to jump the energy gap leaving a positive hole in the valence band. Once in the conduction band, however, these electrons are free to contribute to the photoconductance and the photodegradation responses for a material; that is, all excited electrons have an equal probability of causing a photochemical change regardless as to whether excitation

into the conduction band was caused by UV radiation, ionizing radiation, or X-rays

The developed power law which identify optical property is [8]

$$(\alpha h\nu)^{1/r} \sim (h\nu - E_g) \dots (5)$$

where α : is the absorption coefficient , ν :

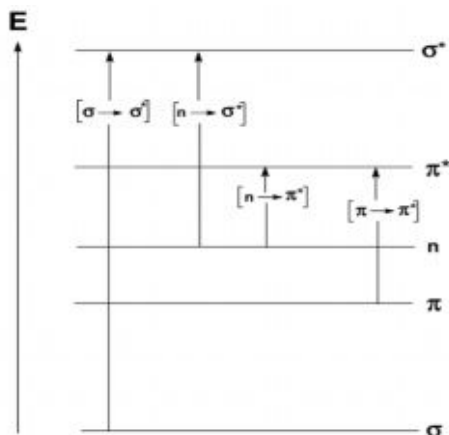
is the frequency

(Hz) and E_g : is the optical energy gap(eV).

r : is constant for field electronic transition (the value of r is 0.5 for direct transition ,3/2 for forbidden direct transition , 2 and 3 for indirect transition The values of E_{opt} were estimated from the extrapolation of the linear portion of the curves $(\alpha h\nu)^{1/r}$ vs. $h\nu$.

3- Molecular Orbital

When a molecule in its ground state absorbs a photon, an electron occupying a σ , π , or n orbital is promoted to a higher-energy σ^* or π^* orbital. In principle, fig(1) shows that the following transitions are possible:



Fig(1) : Molecular orbital and electronic transitions induced by the absorption of photon [5]

It follows that under conveniently practicable conditions ($\lambda > 200$ nm), photon absorption initiates transitions of n or π electrons rather than those of σ electrons [8].

In the case of polymers containing carbonyl groups, the absorption bands located at long wavelengths correspond to n to π^* transitions with low extinction coefficients, Table (1) i.e. low values of

the transition moment. At shorter wavelengths, π to π^* transitions with larger transition moments are excited [5].

Table (1): Typical chromophoric groups[5]

Chromophore	Typical compound	λ_{max} (nm) ^{a)}	ϵ_{max} (L mol ⁻¹ cm ⁻¹) ^{b)}	Mole of electron transition
	Ethene	193	10^4	$\pi \rightarrow \pi^*$
	Ethyne	173	6×10^3	$\pi \rightarrow \pi^*$
	Acetone	187	10^3	$\pi \rightarrow \pi^*$
		271	15	$n \rightarrow \pi^*$
	Azomethane	347	5	$n \rightarrow \pi^*$
	t-Nitrosobutane	300	100	$\pi \rightarrow \pi^*$
		665	20	$n \rightarrow \pi^*$
	Amyl nitrite	219	219	$\pi \rightarrow \pi^*$
		357	357	$n \rightarrow \pi^*$

a) Wavelength of maximum optical absorption.

b) Decadic molar extinction coefficient ($\log_{10} I_0/I = \epsilon cd$).

Experimental Part

Pure PMMA was prepared by solution cast techn. ,each 2g of PMMA was dissolved in 10 ml of methylene chloride to prepare thin film.

Mixture of pmma with 0.02 g of micro TiO2 powder and the same mixture for 0.02 g of nano TiO2 powder (50 nm) were prepared to get PMMA-TiO2 micro composites and PMMA-TiO2 nano composites.

Samples were was exposed to UV irradiation with a Mercury-Xenon lamp of 200 W for (6,12,24,48,72,96 and 120) hours , then uv- visible spectroscopy was used to analysis the absorbance spectra for the exposed and un exposed samples.

Results and Discussion

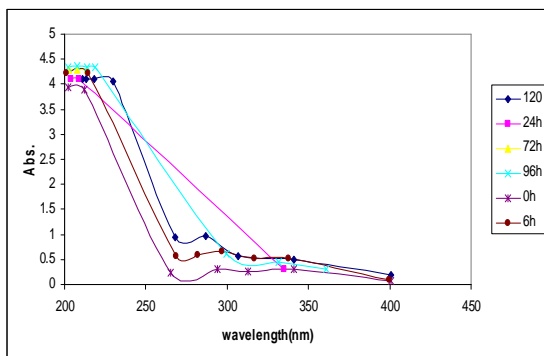
The bonds between the atoms in many polymer have dissociation energies that are very similar to the quantum energy present in UV radiation . UV radiation in the region of 300 to 400 nm is therefore capable of breaking the bonds in the polymer to cause rapid degradation of the

basic structure of the polymer as a function of exposure time.

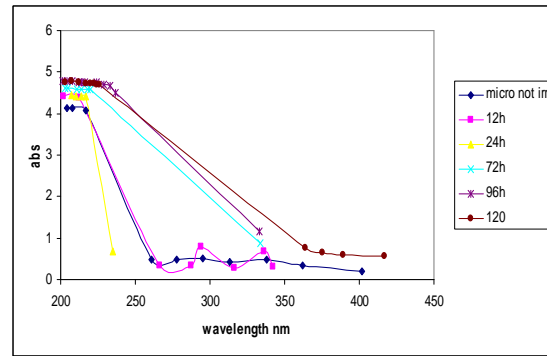
The experimental results were used to calculate the optical energy gap according to Tauc relation, these results indicate that the electronic transition for these polymer equal to $(r=2)$, which shows indirect electronic transition.

The absorbance of pure PMMA was slightly little increased with the increasing in time of radiation, Fig(1) in the wavelength ranged (200-217 nm) the polymer show higher absorption, after that wavelength the PMMA become transparence, because photon absorption initiates n to π^* transitions. In PMMA-micro TiO_2 composites, The absorbance increased with the increasing in time of radiation, Fig(2) in the wavelength ranged (200-220 nm) the polymer show higher absorption, for (0,6,12,24,48, and 72 h) and absorbance for (96 and 120 h) will be higher in the wavelength ranged (200-240 nm). The width of absorbance spectrum will higher in PMMA-nano TiO_2 composites, this is attributed to the photo stability of PMMA-nano TiO_2 composites under uv- radiation, Fig.(3).

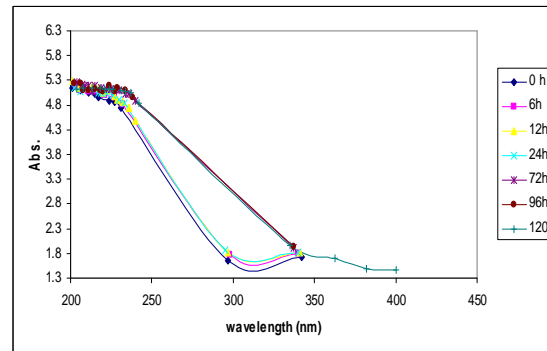
Fig.(4) shows the variation of energy gap with time of radiation for pure PMMA, PMMA-micro TiO_2 composites and PMMA-nano TiO_2 composites, it shows that the optical energy gap of PMMA-nano TiO_2 composites shows a higher stability rather than pure PMMA and PMMA-micro TiO_2 composites, because nano TiO_2 powder participate in the photostability of nano composites [11].



Fig(1): absorbance of PMMA as a function of wavelength



Fig(2): absorbance of PMMA-micro TiO_2 composites as a function of wavelength



Fig(3): Absorbance of PMMA-nano TiO_2 composites as a function of wavelength

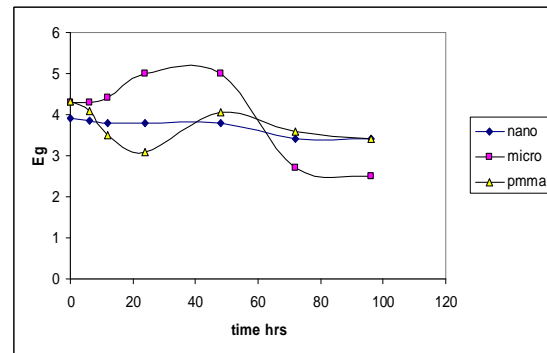


Fig (4): E_g values as a function of time of irradiation

Conclusions

The photostability of PMMA- TiO_2 nano composites is higher than for micro composites and pure PMMA under uv radiation.

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