Nano Oxides UV Protectors for Transparent Organic Coatings

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This paper deals with the synthesis and structural characterization of iron doped rutile (TiO_2) nanopowders and a mixture of nano rutile and transparent iron oxide by Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED), X-ray Diffraction (XRD) and Energy Dispersive X-ray analysis (EDAX). The optical properties of the dried acryl-polyurethane polymer films containing the mentioned nano powders (UV-Vis spectra, transparency and colours) have been studied and compared with coating containing others nano oxides (like nano-CeO_2, nano-ZnO or nono-Fe_2O_3) used as UV absorbers for transparent organic coatings.

Keywords: rutile, transparent iron oxide, nanopowders, UV-Vis absorption spectroscopy

The exterior durability of most organic coatings is highly dependent upon the use of light stabilizers. The choice of these light stabilizers is critical for protection of sensitive substrates such wood, especially due to sensitivity to the humidity and photo-oxidation of lignin [1].The colourless and transparent coatings based on organic polymer, must to be protected against damage (include loss of gloss, colour change, flaking and film delamination) from the sun light. The photo degradation of polymers involves the broke of chemical bonds at the certain energy [2] :

E_{C-H} = 415 kJ/mol (UV B)
E_{C-O} = 350 kJ/mol (UV A)
E_{O-H} = 463 kJ/mol (UV B)
E_{C-C} = 344 kJ/mol (UV A)

The two main light stabiliser categories are UV light absorbers (UVA) and hindered amine light stabilisers (HALS). The organics UVA include benzophenones, triazine, benzotriazole, cyanocrylates and oxanilides. These compounds do not affect the colour of coats, but due to the low extinction coefficient they can not ensure the permanent protection of polymer at sun light.The long term protection of the polymers can be obtained using the nanooxides due to the high extinction coefficient.

Light stabilisation of transparent coatings, using nanooxides as UV filters [3] must preserve the colourless and transparent aspect of coats [4]. These oxides absorb the energy of the light and turn it as heat which is dissipated in the system through ireversible intramolecular proton transfer, reducing the rate of aging polymer.

Transparency of system (lacquer) means the intensity of light scattered and is determined by: diameter of the particles (d), refractive index (η), wavelength (λ), particle concentration in the film the distance to the particle (R) , the scattering angle (θ) and is given by Rayleigh scattering relation [5]:

$$I = I_0 \frac{1+\cos^2\theta}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

The TiO_2 different crystalline modifications (anatase, rutile, brookite [6]) manifest different electric, magnetic, optical and photocatalitic properties. The two modification of TiO_2 - rutile and anatase- are used in coatings industry and their specific optical properties (reflection and/or absorption of UV and visible light), together with crystal structure, size and morphology of the individual particles and distribution of dopants play the key role for the different functions of TiO_2 [7].

In the present work the preparation and optical properties of acryl-polyurethane polymer films containing iron doped titania and mixture of titania and iron oxide nano powders (UV-Vis spectra, transparency and colours) have been studied and compared with coating containing others nano oxides (like nano-CeO_2, nano-ZnO or nono-Fe_2O_3) used as UV absorbers for transparent organic coatings.

Experimental part

The raw materials used were: Titanium tetraiso-propanolate (Dorf Ketal Chemicals), ethanol (>99% Chimopar), ethylene glycol (Sigma Aldrich), $Fe(NO_3)_3{\cdot}9H_2O$ (>98% Merck), acetyl acetone (Sigma Aldrich), APU 1062 (Alberdingk and Boley), 10 nm CeO_2 (Byk Chemie), 20 nm ZnO (Umicore), iron oxide with needles size 10x 100 nm (BASF).

Synthesis of iron doped rutil nanopowders

Fe (III) doped TiO_2 was prepared using organic precursors: Ti $(O\text{-}i\text{-}C_3H_7)_4$ and Fe $(acac)_3$. First, $Fe(acac)_3$ (prepared in reaction of $Fe(NO_3)_3$ with acetyl acetone) was solved in a mixture (1:1) of pure water and i-C_3H_7-OH. Then, 10 mL of Ti $(O\text{-}i\text{-}C_3H_7)_4$/ i-$C_3H_7$-OH (1:5) and 2 mL etilengilcol were added, under continuous stirring to the $Fe(acac)_3$ initial prepared solution (Ti:Fe = 100:5 molar ratio). After 3 days of hydrolysis, a gelatinous substance was formed, that was washed with isopropyl alcohol and dried in air. A slightly yellowish powder was obtained heating the gel at 600° C/1h, in air.

$$Fe(NO_3)_3 + 3\ acac = Fe(acac)_3 + 3HNO_3$$
$$Ti(O\text{-}i\text{-}C_3H_7)_4 + Fe(acac)_3 => TiO_2{:}Fe + i\text{-}C_3H_7\text{-}OH + + 3\ acac$$

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Preparation of transparent coatings based on polymer and nanopowders

Transparent coatings were prepared through ultrasonic dispersion of acryl-polyurethane polymer with 2% w/w of different nanooxides as Fe doped rutile (Sample P1), mixture of nano rutile and transparent iron oxide (Sample P2), 10 nm CeO_2, 20 nm ZnO, Fe_2O_3. Beside the main components of the formulation of the coatings they contain for dispersion additive and *p*H buffer.

The dried films based on polymer and nanoparticles were obtained by application with doctor blade applicator on the support at 120 microns thickness wet and dried 24 h at room temperature.

The crystallinity and the structure

Of the iron doped nano rutile obtained by synthesis (sample P1), and nano rutile mixed with iron oxide (sample P2) were studied by:

- transmission electron microscopy (TEM) and high resolution TEM (HRTEM), using TEMBF (Bright Field TEM imaging) and selected area electron diffraction (SAED);
- energy Dispersive X-Ray microanalysis was made with Spectrometer (EDAX) with resolution 133 eV at MnK_α;
- X ray diffraction was done in order to characterize crystalline structure, using a X- ray analytical diffractometer, X'PERT PRO MPD using Cu-K_α radiation.

Investigations of particle morphology and nanostructure were performed on a TECNAI F 30 G^2 STWIN transmission electron microscope (TEM) with linear resolution 1Å and punctual resolution 1.4 Å. The samples were prepared by ultrasonic dispersing the powder products as a slurry in ethanol, which was then deposited and dried on a holey carbon film mounted on a Cu grid.

Topography and elemental composition of the dried film

The micrographs of the film surfaces of formulations containing sample P1 and sample P2, was performed using scanning electron microscopy (SEM) in high pressure regime at an accelerating voltage 30 kV by secondary electron detector (ETD); For this analysis was used Quanta Inspect F with FEG (field emission gun) equipment used at magnification of 1,2 nm.

The elemental composition of dried film was obtained using X-Ray Energy Dispersive Spectroscopy.

The optical parameters

The coatings based on polymer and nanopowders were analyzed by UV-Vis absorption spectra, using an Able Jasco V560 spectrophotometer, and opacity /transparency and color measurements with spectrophotometer with sphere optical geometry Lab Scan.

Results and discussions

X ray diffraction patterns of both Fe-doped TiO_2 synthesized powder (sample P1) and the mixture of the commercial TiO_2 and Fe_2O_3 (sample P2) are presented in figure 1. It could be observed that only the diffraction lines of TiO_2, rutile phase were identified. In the case of the Fe-doped TiO_2 samples (fig. 1 a) this fact could be assigned to the formation of a solid solution with rutile structure, while in the case of the mixture of the oxides (Sample 2 - fig.1 b) the presence of the Fe_2O_3 could not be identified due to either its low amount in the mixture or the overlapping of its specific diffraction lines with those of the rutile phase.

The accurate information about crystalline structure, shape and size of samples P1, was obtained using Bright Field Transmission Electron Microscopy (TEMBF) and High Resolution Transmission Electron Microscopy (HRTEM); the

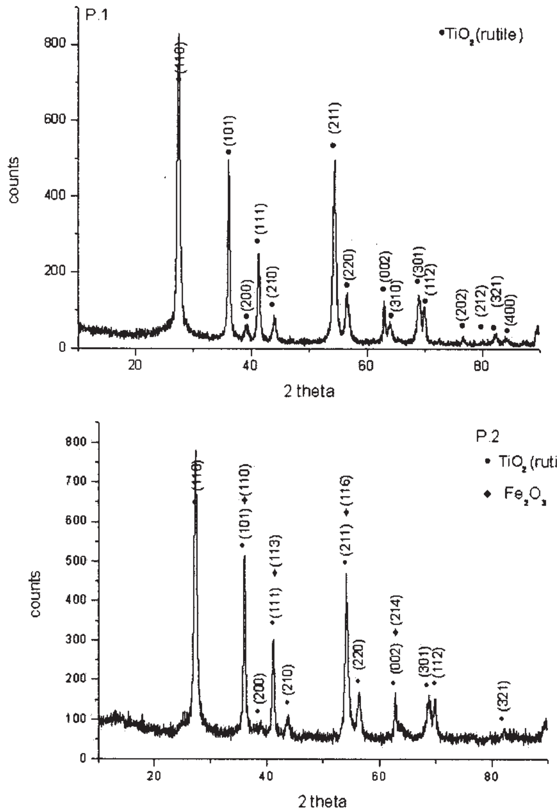


Fig.1 XRD pattern for Sample P1 (iron doped TiO_2) and Sample P2 (mixture rutile and Fe_2O_3)

average size of crystals from Sample P1 is 71 nm x 14-21 nm and is illustrated in figure 2. The HRTEM image shows the crystallographic planes' family of rutile (101) and (112) (fig.3.a) and the rings in the SAED pattern (fig.3.b) can be indexed as (110), (101), (200), (111), (210), (211), (220),(002), (301) reflection of rutile structure in agreement with XRD.

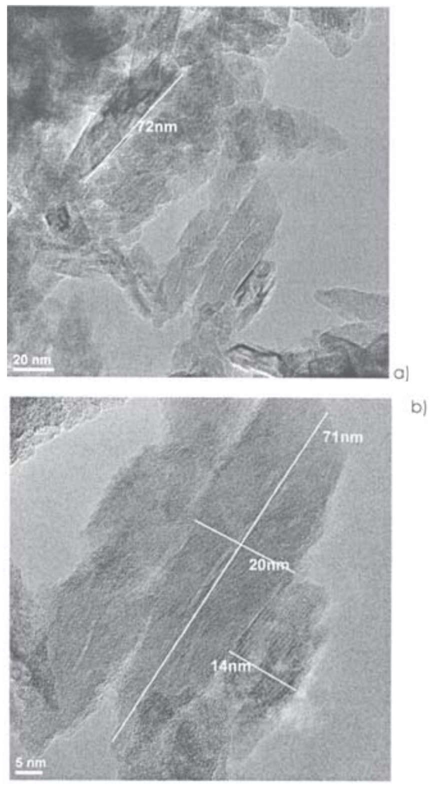


Fig. 2. Size and shape of crystals of sample P1, performed by TEMBF (image a) and by HRTEM (image b)

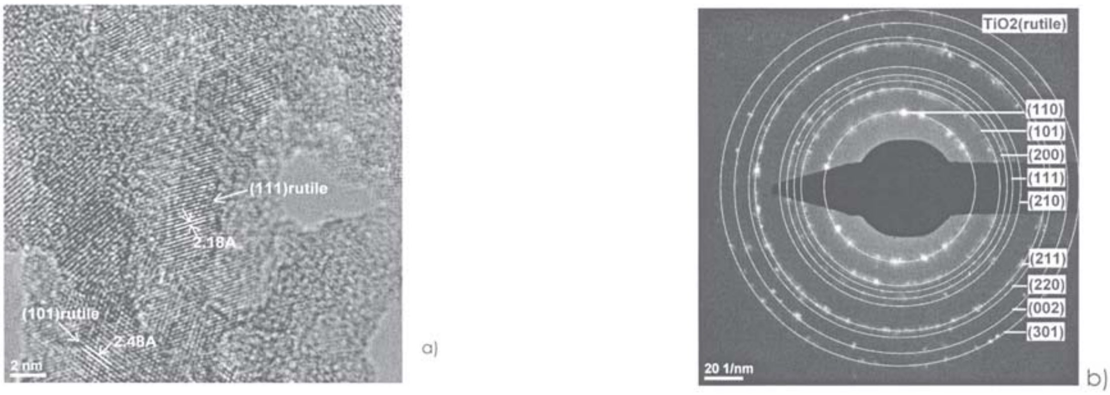


Fig.3 Sample P1; a) HRTEM image with crystallographic planes (101), (111); b) SAED pattern associated to site from image a)

The SEM image of the coating containing the sample P1, reveals the homogeneity of the powder dispersion in polymer matrix and EDAX spectrum shows the elements from the dried film: main elements C, O, Ti, Fe and secondary elements from surface treatments like Al and Si are shown in figure 4.

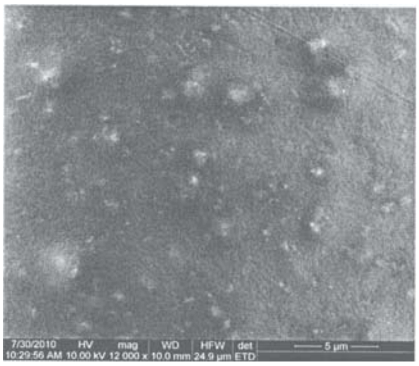
The TEMBF image confirms the size of the rutile crystals: 12-12 nm x 85-94 nm in fig. 5.a and the and the high resolution TEM reveals two phases being rutile and Fe_2O_3; The distance corresponding to the interplanar spacing of the (110) in 3.25Å for rutile and 2.51Å for plane (110) of Fe_2O_3 .The results are in accord with XRD pattern from figure 1.

The SEM image of the transparent coating containing sample P2 reveals the homogeneity of nanopowders dispersion and EDAX spectra point the elemental composition of the matrix: main elements C, O, Ti, Fe and secondary elements from surface treatments like Al and Si are showed in figure 6.

Optical properties of acryl-polyurethane polymer coatings containing UV absorbers (iron doped rutile and mixture of nano rutile and nano iron oxide have been investigated through UV -Vis spectra (200-800 nm) registration and compared with those of other absorbers like: CeO_2, ZnO and Fe_2O_3.

From the evaluation of the color (ΔL^*, Δa^*, Δb^*, ΔE_{cmc}, C^*, h^*), and opacity of the dried films, presented in figure 9, we observe that the most transparent coat is formulation which contain sample P1 (iron doped rutile) with lowest spectral opacity 4.45 and the closest color of coat to the standard is formulation which contain sample P1, having the smallest difference in color $\Delta E^*=7.45$ and $\Delta E_{CMC}=6.10$.

a



b

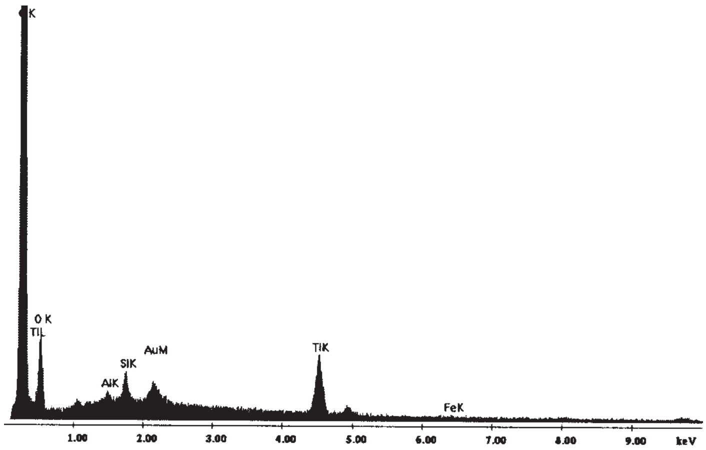


Fig 4. Dried polymeric film containing sample P1; a) EDAX results and b) SEM image (X 12000) using secondary electron detector (ETD)

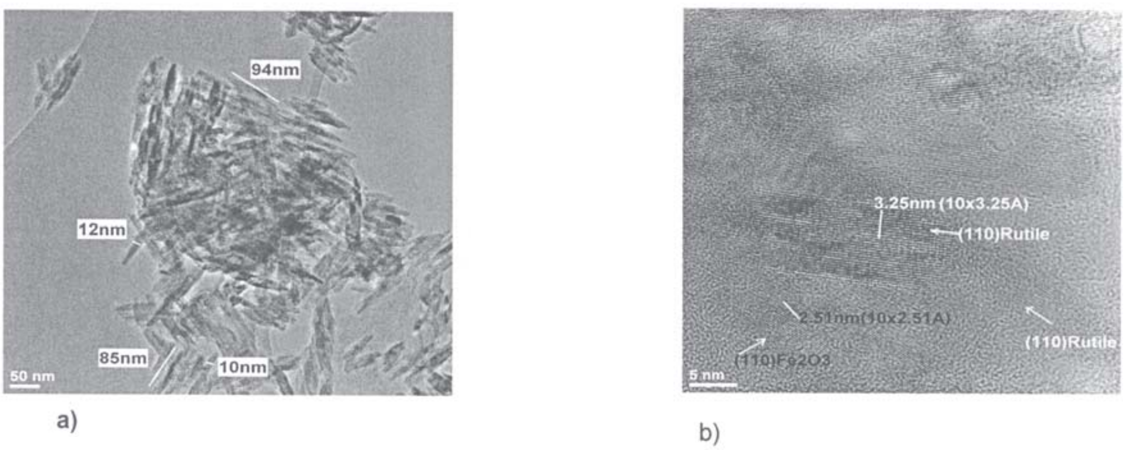


Fig.5. Sample P2; TEMBF image for powder a) and HRTEM image b)

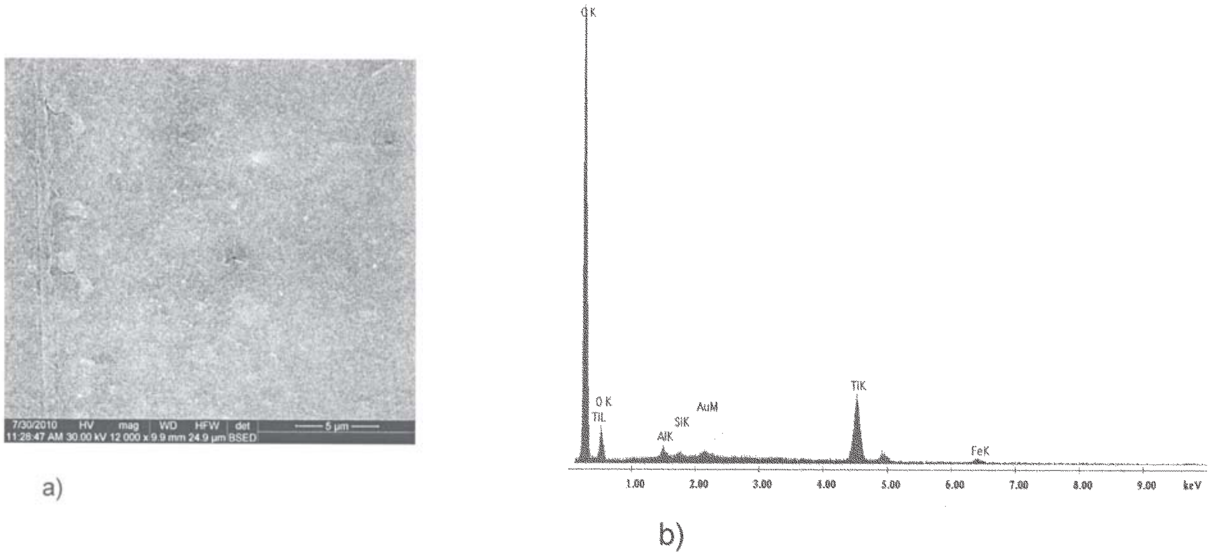


Fig..6. Dried transparent polymeric film containing sample P2; a) SEM image (X 12000) using EDT and b) elemental composition using EDAX

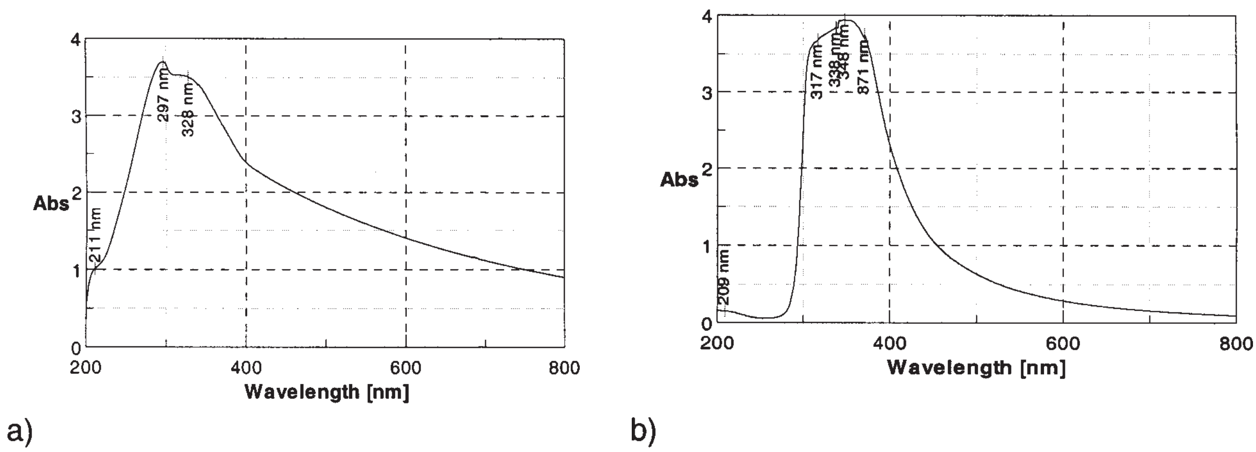


Fig.7. UV Vis spectra for dried film containing 2% w/w iron doped TiO_2 presented in graph a) and mixture of nano rutile and nano iron oxide (Fe_2O_3) showed in b)

The analysis of these spectra UV Vis and color and opacity of coatings containing UV absorbers conduct to the following conclusions:

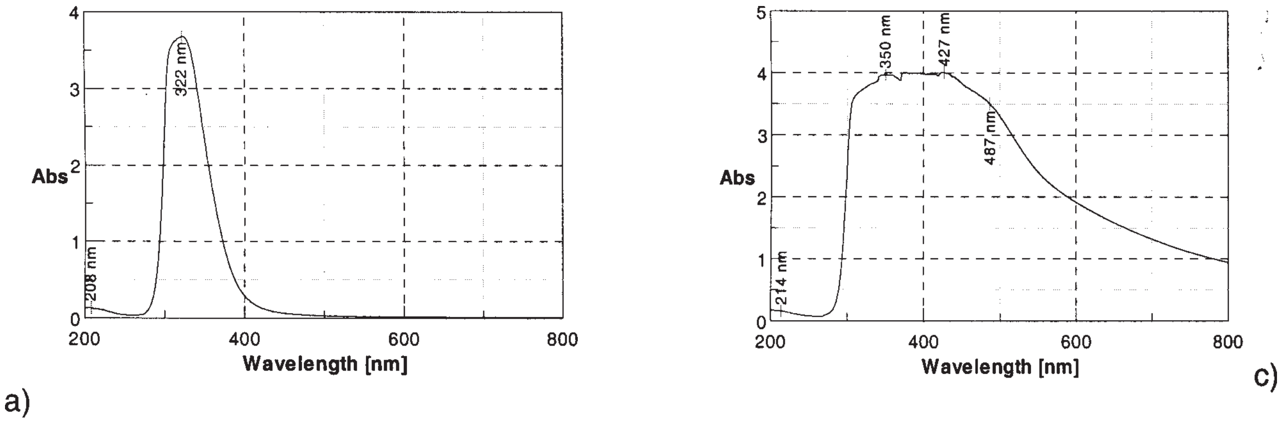
- the matrix based on polymer and iron doped rutile absorbs in large range comprising UV A, UV B and a part of Vis range, and has the best value of opacity/transparency and difference in color (ΔE cmc) ; this oxide prove the stability of the polymer system;

-the coating containing the mixture of nano rutile and nano iron oxide (Fe_2O_3) is stable. It absorbs the light in the range of 300-450 nm and determine the change of the color into yellow hue and increases the opacity;

-the film containing 10 nm CeO_2, is stable, transparent and is protected against UV B;

-the film which contains 20 nm ZnO absorbs the UVA and UV B, in 300-400 nm range, the color and transparency are preserved; the polymer must be carefully chosen due to the stability of dispersion matrix.

These parameters and the UV absorption capacity depend on the type and size of crystal, the homogeneity of dispersion of crystals in the polymer and the compatibility between of the nature of polymer and reactivity of nano oxide.



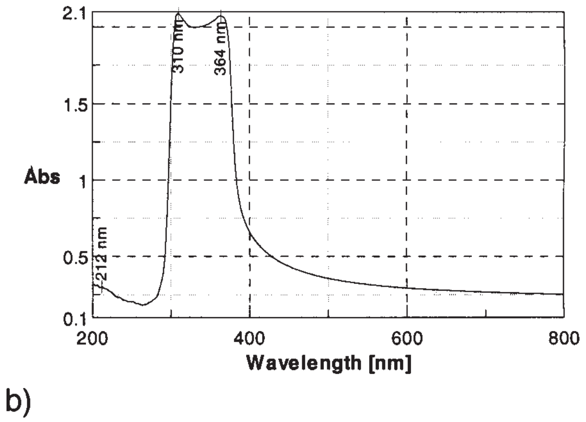
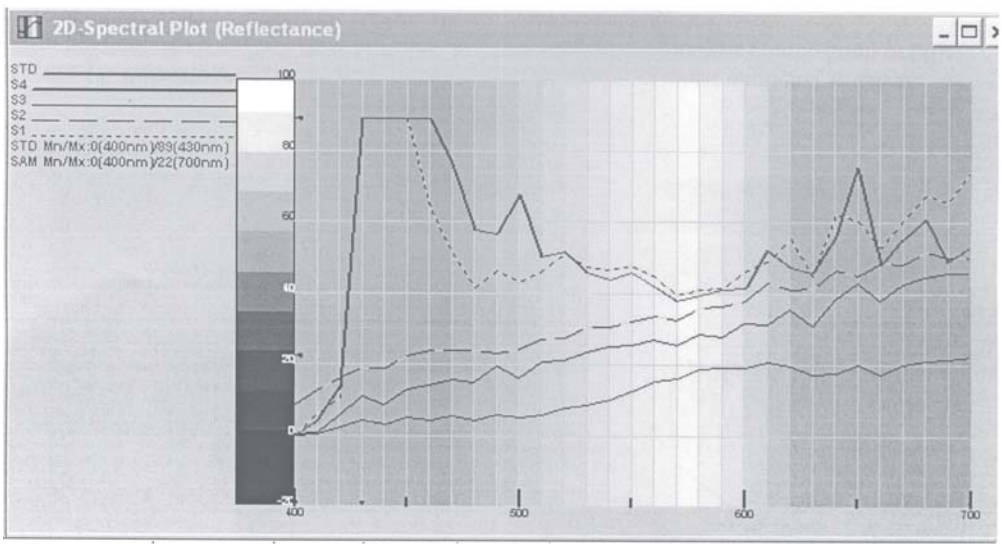


Fig.8. UV Vis spectra for dried film containing 2% w/w: a) 10 nm CeO_2, b) 20 nm ZnO and c) nano iron oxide (10x 100 nm needles)



	ID	L*	C*	h*	Opacity (Spectral)	MI	WI CIE
Standard	ET	75.18	24.89	284.70	3.83		176.67
Tolerance +							
Tolerance -							
Trial 4	FE2O3	42.07	33.45	66.61	15.58	0.00	-222.72
Trial 3	CEO2	57.10	27.60	78.92	5.09	0.00	-153.80
Trial 2	MIXTURE	63.56	19.31	68.62	15.05	0.00	-78.17
Trial 1	FE/TIO2	74.24	20.34	299.57	4.45	0.00	142.35

Color Difference Data (CIELAB 10 * /D65

	ID	Date	Time	DL*	Da*	Db*	DE*	DEcmc
Standard	ET	08/16/201	18:53:47	75.18	6.32	-24.07		
Trial 4	FE2O3	08/16/201	18:57:44	-33.10	6.96	54.77	64.37	53.77
Trial 3	CEO2	08/16/201	18:56:57	-18.08	-1.01	51.15	54.26	49.29
Trial 2	MIXTURE	08/16/201	18:56:21	-11.62	0.72	42.05	43.63	40.17
Trial 1	FE/TIO2	08/16/201	18:54:23	-0.94	3.72	6.38	7.45	6.10

Fig.9. Color analysis (values of color, opacity and reflectance diagram) of transparent film containing (Standard, considering the transparent film without UV filter) comparing with iron doped rutile (Trial 1), mixture of nano rutile and transparent iron oxide (Trial 2), CeO_2 (Trial 3) and transparent iron oxide (Trial 4)

Conclusions

In this paper nano powder of iron doped rutile was synthesized and was studied as UV absorber in an acryl-polyurethane polymeric film.

The structure and morphology of the synthesized nano powder, as well as that of the polymeric film doped with this powder was investigated by XRD, HRTEM, SEM, EDAX analysis.

Optical properties of the film based on iron doped rutile (UV Vis absorption, opacity and color) were determined and compared with those of others UV protectors.

The iron doped rutile can ensure the protection at light radiation incuding UVA, UVB and Vis up to 450 nm, preserve the transparency and color of the organic film and can be used in different polymer systems like UV filter without influence in stability of coatings.

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