Possibilities to Improve the Colour Properties of the Yellow 17 Pigment by Treatment with Metallic Salts

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The objective of this work was the modification of the pigment Yellow 17 structure through a treatment with $ZnCl_2$ and Na_2SiO_3 in order to improve its properties. The modifications that appear in pigment structure were revealed by UV-visible diffuse reflectance and EDX analysis. The synthesized pigments were used to colour the polypropylene. The chromatic modifications appeared through pigment colouring with modified pigments were evaluated by measuring the colour intensity and colour difference. The light fastness and UV protection of the coloured polypropylene samples were also highlighted.

Keywords: organic pigments, polypropylene, colour measurements, light fastness, UV-protection

Polypropylene is one of the most used polymers due to its properties: fastness to water, chemical agents, organic solvents, temperature. The coloured plastic materials extended their area of application during the recent period. Both organic and inorganic pigments are used to colour it. Generally, the pigments are preferred to dyes for plastics coloration, mainly because of their superior fastness properties, especially migration resistance [1, 2]. By using the organic pigments, one can obtain various colours, as well as higher brightness and transparency as compared to inorganic pigments. The coloured plastics can change their shade under the influence of light and UV radiations [3-5]. Several factors influence the dyes and pigments light fastness, such as pigment chemical structure and physical shape, support structure, etc. [6]. During the last years, there have been several studies regarding the possibilities to improve the light and UV fastness. The utilization of some compounds containing zinc, cerium and titanium can be considered as promising materials for UV protection [7-10]. In the present work we meant to improve the light and UV fastnesses of the Yellow 17 pigment by treating it with $ZnCl_2$ and Na_2SiO_3. The synthesized pigments were used to colour polypropylene materials.

Experimental part

Materials and methods

The Yellow 17 pigment was purchased from Athena-Italy Company, while $ZnCl_2$ and Na_2SiO_3 were purchased from Merk Company. All the products involved in this study were used without any further purification. The pigment chemical structure is presented in figure 1.

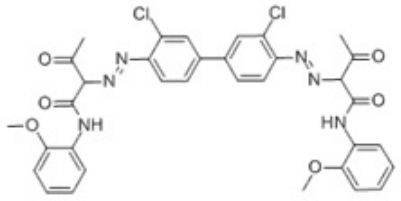

Fig. 1. Yellow 17 pigment

The synthesis of pigments

The synthesis of the new pigments was performed in alkaline medium under the following conditions: an aqueous solution of $ZnCl_2$ and Na_2SiO_3 respectively was added to the pigment Yellow 17 pasted with 10 mL ethyl alcohol. The mixtures of pigment: $ZnCl_2$ and pigment: Na_2SiO_3 respectively were stirred for 8 h. The pigments obtained in this way were filtered, washed with distilled water and dried at 80°C. The working conditions are presented in table 1.

Techniques of pigments analysis

The UV- visible diffuse reflectance spectra were measured with Shimadzu UV-2450 spectrophotometer equipped with an integrating sphere assembly. All spectra were recorded against barium sulphate in the 190÷800 nm wavelength range and plotted in terms of absorbance.

The EDX analyses were carried out with Quanta 200 (Fei) scanning electron microscope coupled with an energy dispersive X-rays analyzer. Samples were prepared by dispersing dry pigment on copper support and coated with gold by cathode deposition using an EMITECHK 550 apparatus.

Samples (Pigments)	Pigment Yellow 17 (mols)	Na_2SiO_3 (mols)	$ZnCl_2$ (mols)	NaOH (mols)
Zn1	0.003	-	0.006	0.005
Zn2	0.003	-	0.009	0.005
Si1	0.003	0.006	-	0.005
Si2	0.002	0.009	-	0.005

Table 1
WORKING CONDITIONS

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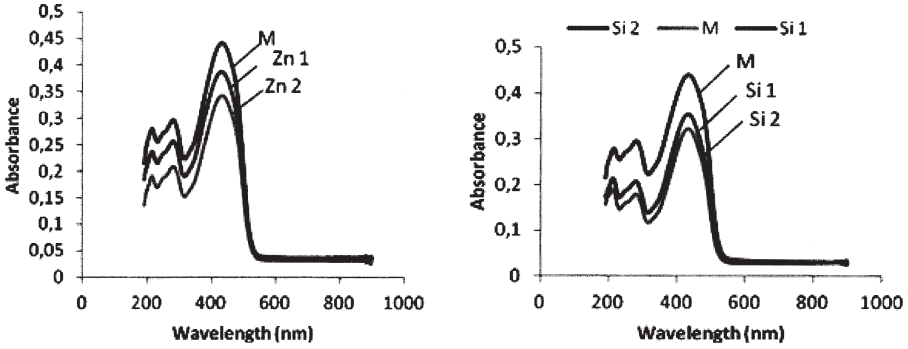


Fig. 2. UV- Vis. spectra of pigments

Polypropylene colouring with pigments

0.2 g pigment and 49.8 g polypropylene were mixed for homogenization and then introduced in a rectangular mould. The mould that contains the melted material is placed between two stainless steel plates and introduced together in a hydraulic press with two sets of cups (one for heating and another for cooling). In the first stage, the plates that contain the matrix with the material are introduced between the two cups that will be heated up to 190°C and pressed at 150 bars for 45 s, and then these are introduced between the cold cups where they are also pressed at 150 bars for 45 s. After cooling, the plates and the matrix are removed, remaining only the coloured polypropylene plate.

Testing the coloured polypropylene samples

The chromatic parameters [11-14] of the coloured polypropylene (remission (R%), colour difference (ΔE* CIELAB), luminosity (ΔL*), saturation (ΔC*) and chromatic parameters (Δa*)(Δb*) were calculated using the software Micromatch 2000, the measurements being made on a SPECTROFLASH SF-300 spectrophotometer from DATACOLOR Company.

The light fastness of the coloured polypropylene was determined as colour difference between the light exposed samples and unexposed samples.

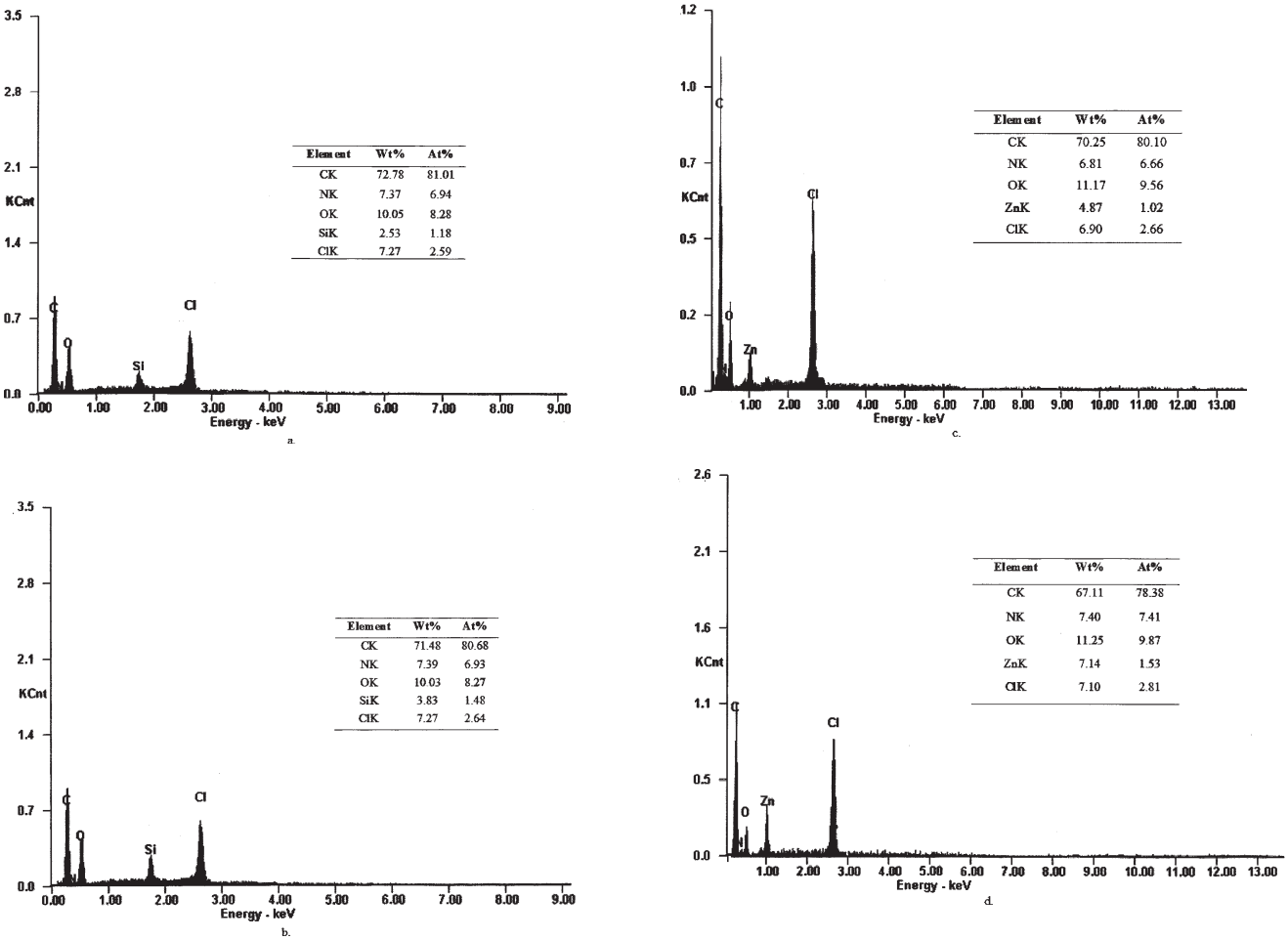
For the study of coloured polypropylene behaviour to UV radiations, the samples were irradiated with an UV source for 120, 240, 360 and 480 min. The colour difference for irradiated samples to the non irradiated samples was assessed using the CIELAB method [13-18].

Results and discussions

Pigments analysis

The modifications that appear in the structure of the pigments Zn1, Zn2, Si1 and Si2 were assessed through the UV-Vis and EDX analyses. The UV absorption spectra of the pigments are presented in figure 2.

The hypochloric effects that appear in the case of the pigments modified by treatment with $ZnCl_2$ and Na_2SiO_3 respectively can be explained through the interaction between the Zn^{2+} ions and the auxochrome/chromophore groups of pigment in the case of its treatment with $ZnCl_2$, and the formation of a thin film around the pigment treated with Na_2SiO_3 respectively.



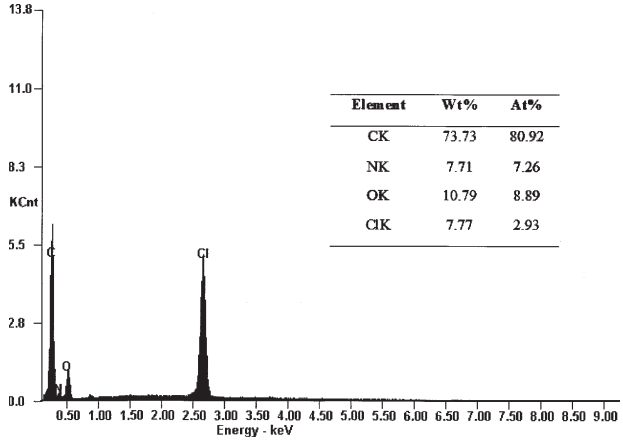
Element	Wt%	At%
CK	72.78	81.01
NK	7.37	6.94
OK	10.05	8.28
SiK	2.53	1.18
ClK	7.27	2.59

Element	Wt%	At%
CK	71.48	80.68
NK	7.39	6.93
OK	10.03	8.27
SiK	3.83	1.48
ClK	7.27	2.64

Element	Wt%	At%
CK	70.25	80.10
NK	6.81	6.66
OK	11.17	9.56
ZnK	4.87	1.02
ClK	6.90	2.66

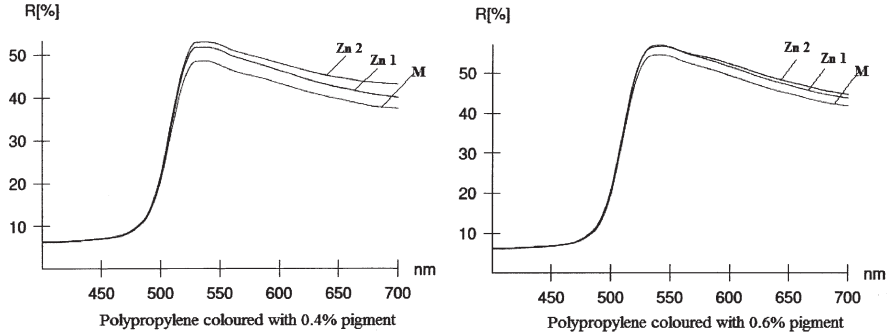
Element	Wt%	At%
CK	67.11	78.38
NK	7.40	7.41
OK	11.25	9.87
ZnK	7.14	1.53
ClK	7.10	2.81

Fig. 3. Analize EDX a. Pigment Si1; b. Pigment Si2; c. Pigment Zn1; d. Pigment Zn2



Element	Wt%	At%
CK	73.73	80.92
NK	7.71	7.26
OK	10.79	8.89
ClK	7.77	2.93

Fig. 3. Analize EDX e. Untreated pigment



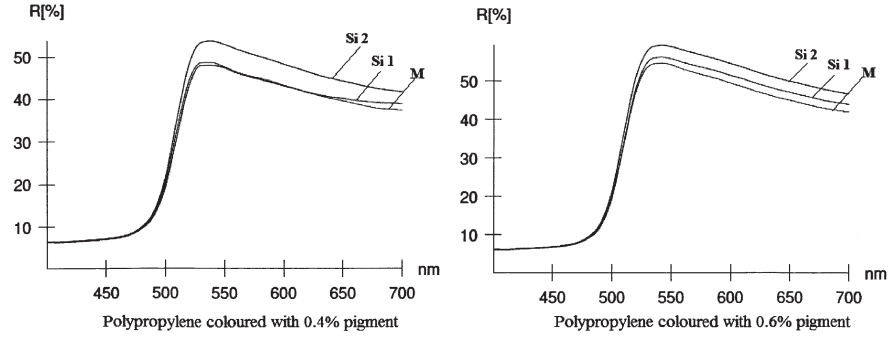


Fig. 4. Remission variation vs. wavelength for coloured polypropylene samples

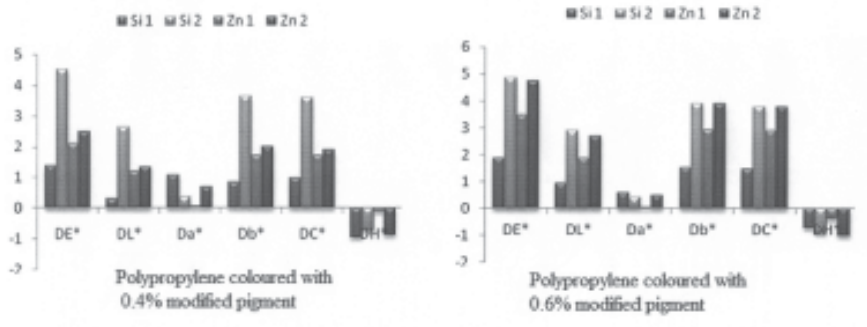


Fig. 5. Chromatic parameters for polypropylene coloured with modified pigments

The EDX spectra for the initial pigment and for the pigments modified by treating them with sodium silicate and zinc chloride are presented in figure 3.

The obtained spectra confirm that both zinc and silicon are found embedded in the synthesised pigments. The results are correlated with the amounts of $ZnCl_2$ and Na_2SiO_3 respectively used in the treatment of Yellow 17 pigment.

Analysis of coloured polypropylene samples

The modification of the chromatic parameters for the pigments modified through treatment with $ZnCl_2$ and Na_2SiO_3 respectively, as compared to the unmodified pigment is illustrated in figure 4.

According to the results presented in figure 4, one can notice that the samples coloured with pigments modified through treatment with $ZnCl_2$ and Na_2SiO_3 respectively have higher remission values than the samples coloured with the unmodified pigment. The remission modification can be explained by the interactions between pigments and $ZnCl_2$, and by the formation of a thin film at the pigment surface in the case of Na_2SiO_3 respectively.

The results presented in figure 5 show that the samples coloured with pigments modified by treatment with Na_2SiO_3 and $ZnCl_2$ (Si1, Si2, Zn1, Zn2) respectively are redder, more yellow and brighter than polypropylene coloured with unmodified pigment.

The values of light fastness for the samples coloured with the studied pigments were assessed by means of the colour difference between light exposed and unexposed samples. The obtained results are presented in table 2.

Sample/ pigmet concentration used for samples coloured	Colour Difference (ΔE)				
	Zn1	Zn2	Si1	Si2	Blank
0.4 %	1.333	0.773	1.981	1.522	3.271
0.8 %	2.481	1.76	2,651	1.983	5.153

Table 2
COLOUR DIFFERENCE (ΔE) BETWEEN IRRADIATED AND NON-IRRADIATED POLY-PROPYLENE SAMPLES

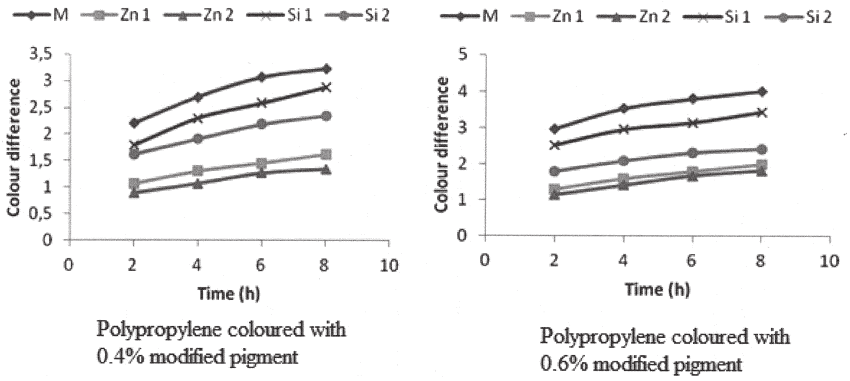


Fig. 6. Variation of colour difference in terms of irradiation duration

According to the obtained results, the light fastness of the polypropylene samples coloured with synthesized pigments is better than that of the samples coloured with unmodified pigment. The best light fastness belongs to Zn2 sample, which has the smallest colour difference. What concerns the influence of the pigment concentration used to colour the polypropylene samples, one can notice that higher pigment concentrations used to colour the polypropylene results in smaller light fastness, a fact confirmed by larger colour differences.

The modifications that appear as the result of irradiation of the studied pigments with UV radiation are presented as colour difference between the irradiated and non-irradiated sample, in terms of the irradiation time (fig. 6).

The colour difference increases with increasing irradiation time, which indicates that pigments photostability has changed. According to the obtained results, one can notice that the smallest colour differences between the irradiated and non-irradiated samples, therefore the best UV radiation fastness, belongs to the samples Zn1 and Zn2.

Conclusions

This study has presented the synthesis of new pigments using the treatment of pigment Yellow 17 with zinc chloride and sodium silicate. The presence of zinc and silicon in the obtained pigments was confirmed by EDX analyses. The modifications that appear in the structure of the pigment were highlighted by UV-Vis analysis and chromatic measurements. The polypropylene samples coloured with the pigment Zn2 show the best light fastness and the best radiation fastness to UV radiations.

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