Boletín de la Sociedad Española de Cerámica y Vidrio
Vol 50, 4, 213-218, Julio-Agosto 2011 ISSN 0366-3175. eISSN 2173-0431.
doi: 10.3989/cyv.282011

BOLETIN DE LA SOCIEDAD ESPAÑOLA DE
Cerámica y Vidrio
A R T I C U L O

Preparation and characterization of photochromic effect for ceramic tiles

B. ATAY [1], A. GOKTAS [2], A. DOGAN [1, 3]

[1] Department of Material Science and Engineering, Anadolu University, Eskisehir, Turkey
[2] Department of Metallurgy and Material Engineering, Dokuz Eylul University, Izmir, Turkey
[3] Advanced Technologies Research Center, Anadolu University, Eskisehir, Turkey

Ceramic tile industry is developing due to the technological researches in scientific area and new tiles which are not only a traditional ceramic also have many multiple functionalities have been marketed nowadays. These tiles like photocatalytic, photovoltaic, antibacterial and etc. improve the quality of life and provide lots of benefits such as self cleaning, energy production, climate control. The goal of this study was to enhance the photochromic function on ceramic tiles which is the attitude of changing color in a reversible way by electromagnetic radiation and widely used in many areas because of its aesthetic and also functional properties. High response time of photochromic features of ceramic tiles have been achieved by employing of polymeric gel with additives of photoactive dye onto the ceramic surface. Photochromic layer with a thickness of approximately 45- 50 μm was performed by using spray coating technique which provided homogeneous deposition on surface. Photochromic ceramic tiles with high photochromic activity such as reversibly color change between ΔE= 0.29 and 26.31 were obtained successfully. The photochromic performance properties and coloring-bleaching mechanisms were analyzed by spectrophotometer. The microstructures of coatings were investigated both by stereo microscopy and scanning electron microscopy (SEM).

Keywords: Photochromism, Color Change, Ceramic Tile.

Preparación y caracterización de efecto fotocromático en las baldosas de cerámica

La industria de baldosa cerámica se está desarrollando debido a las investigaciones tecnológicas en el área científica y los nuevos azulejos no son sólo de cerámica tradicional, sino que también tienen múltiples funcionalidades que son valiosas en el mercado hoy en día. Estos azulejos tipo fotocatalítico, fotovoltáico, anti-bacteriano, entre otros, mejoran la calidad de vida y proporcionan muchos beneficios como la limpieza fácil o de uno mismo, la producción energética y el control del clima. La meta de este estudio es realzar la función fotocrómatica en las baldosas cerámicas y la capacidad de cambiar color de una manera reversible debido a la radiación electromágnetica, y que además, es ampliamente utilizada en muchas áreas debido a su estética y también características funcionales. Las baldosas cerámicas fotocromáticas de alta respuesta han sido preparadas aplicando gel polimérico incluyendo el tinte fotoactivo sobre la superficie cerámica. La capa fotocromática fue hecha con un grosor de cerca de 45 - 50 μm con la técnica de aerosol que proporcionó la deposición homogénea en la superficie. El resultado fue la obtención de cerámicas fotocromáticas con buenas características mecánicas y de alta actividad fotocrómatica como por ejemplo el cambio reversible de color entre ΔE= 0.29 y 26.31. Las propiedades del funcionamiento fotocromático y los mecanismos del colorante-blanqueo fueron analizados con un espectrofotómetro y se investigó la microestructura de la cubierta mediante estereomicroscopia y microscopía electrónica de barrido.

Palabras claves: Fotocromismo, cambio del color, baldosa cerámica.

1. INTRODUCTION

Ceramic tiles are no longer classified only according to their traditional characteristics but also special attention is paid to the functionality which makes them utilizable in various environments and enhances their industrial and commercial value. Many examples due to these performances can be given as antibacterial, photocatalytic, photovoltaic ceramic tiles. The technological approaches given by several functionalities create new applications of tiles as a building material that overcomes being only a flooring material (1). In accordance to these technological and manifold applications at tile industry, the aim of this study is to enhance photochromic performance to ceramic tiles. Photochromic phenomena refer to a reversible change of color under irradiation with visible or ultra-violet light. Reversible photo transformation of chemical species between two forms having different absorption spectra results as the color change of the material (2-3). On exposure to light, material transforms from colorless or pale yellow color form to colored form and when irradiation cut off material turns to its original uncolored state (4-5). Mechanisms of photochromism that cause the color change are the reactions occurred as trans-cis isomerism caused by rotation of a double bond, bond-cleavage, transfer of a H atom, and oxidation-reduction reactions. Under irradiation, by absorption of light and sufficient exciting energy, photochromic materials undergo reversibly these photochemical reactions that results as a color formation (6-7).

As the technology has developed, nowadays due to its functional and aesthetic properties photochromic materials have found many applications in the areas as of glasses, plastics, textiles, and optical data storage (8-10).

The objective of this paper was to gain the photochromic color change ability to ceramic tile surfaces. This should be achieved by incorporation of photoactive dye into appropriate matrix. First issue at combining organic photochromophores with inorganic ceramic surfaces was high temperature differences at processing. Organics can not survive temperatures above 200 ºC, but ceramic tiles are high temperature process products like 1000 ºC (11). Because of this reason the current matrix should have enough adhesion on ceramic surface at low temperatures that will not cause the decomposition of organic photochromic dye. The second issue was the matrix which should have sufficient free volume for photochromic structures that carry out structural changes during phototransformations (12). These matters were achieved by using photoactive compounds that are embedded in acrylamide based polymer system. We examined the preparation of photochromic coatings on ceramic tile surfaces and investigated the photochromic behavior of coatings, and special attention is paid to the color change mechanisms.

2. EXPERIMENTAL

2.1. Sample preparation

Firstly, as coating solution of ceramic tiles polymeric gel including photoactive material was prepared by using acrylamide based polymer and photochromic dye. 1-2 wt.% of polymer was added to 100 ml distilled water, and stirred vigorously for 2 hours. After completely dissolution of polymer, photochromic dye was added to transparent solution as 1 wt. % and stirred further for 1 hour at room temperature and this final solution was kept at dark for coating process. Coating of cleaned ceramic tiles (50 x 50 x 3mm) was performed by using spray coating technique at process parameters as coating distance, coating time were 10 cm and 5 minutes, respectively. Finally, the photochromic films on tiles obtained after heat treatments were used for optical measurements.

2.2. Surface Analyses

The microstructure of coated samples was analyzed by scanning electron microcopy (Zeiss Evo 50 EP). Au coating by sputtering was performed for 35 s on ceramic surface to enhance conductivity and inhibit the charging of polymer. SEM characterization was applied on the cross section area of ceramic tile at 20 KV as operating voltage and different magnifications such as 2000 KX were carried out. The thickness of photochromic film was also determined by using stereo microcopy (Leica M205 C) at various points on ceramic tile.

2.3. Hardness and Abrasion Resistance Measurements

For investigating hardness of coatings, Mohs Hardness Scale system that has been as a very basic method to classify the hardness of surface was performed on coated ceramic tile and also the resistance to surface abrasion of coated ceramic tiles was determined according to the test method specified in the Standard ISO 10545-7.

2.4. Photochromic Measurements

The excitation and emission spectra of samples were investigated to realize out the optical transition due to the photochromic effect. Firstly, full range at visible region was scanned through emission and excitation spectra and then due to the emission at specific wavelengths, the activation region was determined by means of fluorescence spectrometer (Perkin Elmer LS 55). According to the analyzed excitation wavelengths, samples were irradiated under UVA lamp and also sunlight to see the effect for outdoor application. Photochromic experiments for observing the coloring and bleaching responses as before and after irradiation over the range of 400-700 nm. were carried out by using spectrophotometer (Minolta 3600-d). In order to describe the degree of color change at the irradiated samples under UV lamp and sunlight, the differences in reflectance % and colorimetric values (ΔE, L, a, b) were measured by using illuminant D65 and 10 º observer data. In order to define the color, colorimetric values were investigated by using CIE (International Commission on Illumination) Lab color space which is a three-dimensional system with the coordinates a* (green/red), b* (blue/yellow), and L* (lightness). The CIELab color space is composed on the basis that colors can be considered as a set of combinations of red and yellow, red and blue, green and yellow, and green and blue. To determine the exact combination of colors of a sample, coordinates of a three dimensional color space are assigned. L* assumes values from 0 (minimum lightness) to 100 (maximum lightness) as lightness of product, a* denotes red when it is positive and green when negative. b* defines yellow when it is positive and blue when negative (13).

3. RESULTS AND DISCUSSION

By the experimental preparation as described above, pale yellow coatings containing photochromes have been obtained on ceramic tile surface. The utilization of acrylamide based polymer as matrix for organic photochromic dye provided enough inner free volume that has enabledthe transformation of dye structure during irradiation. Coating solutions were prepared by using these organic photochromics and polymer gel were applied on ceramic tiles by spray coating technique. The homogeneous layer formation on surface and uniform coating layer were acquired. Coating thickness was investigated by using both stereo microcopy and scanning electron microcopy. For the measurement of thickness by stereo microscopy, it was necessary to focus the image at one point; the measured thickness of film was about 46.75 μm as shown in Figure 1. The figure denotes that the coating can be easily seen as a glassy-like phase on ceramic tile. Investigation of the thickness at three different points, which

Bol. Soc. Esp. Ceram. Vidr. Vol 50. 4, 213-218, Julio-Agosto 2011. ISSN 0366-3175. eISSN 2173-0431. doi: 10.3989/cyv.282011

were close to each other on the same lateral section, showed a homogeneous level of thickness as of 47.48, 47.29, 48.10 μm as seen in Figure 1. An accurate characterization was proofed by scanning electron microscopy analyses as indicated in Figure 2. SEM image at 2000 KX magnification obviously shows that photochromic coating layer on ceramic tile has a uniform structure as a layer on surface which has a thickness approximately as 45-50 μm.

The surface of coated ceramic tiles has a considerable influence on the mechanical response to the various stresses coming from the environment. For investigation the hardness of coated surface, measurements were performed with Mohs hardness. Coated surface has a value of 3 according to Mohs hardness scale which is closes to standard ceramic tile surface value. Also, the resistance to surface abrasion of coated ceramic tiles was determined according to the test method specified in the Standard ISO 10545-7. This test results indicated that the resistance to surface abrasion of coating was at class 2: 600 revolutions. Mainly, tiles that are classified to the Standard ISO 10545-7, need higher resistance for real applications, but considering the low temperature process on ceramic tile to hold the photoactive material on surface that can not survive temperatures more than 200 ºC, the test results indicated an available value that shows us photoactive layer can not be easily abrade from surface. Also one important issue is that photochromic tiles have been mainly suitable for exterior wall applications due to the irradiation and color change ability of photochromism which do not need high resistance values as floor tiles, but test results has shown that coating has nearly appropriate mechanical properties despite the heat treatments at low temperatures when we compare with polymer coatings that generally can be easily wear out from the surface under a slight force.

The photochromic experiments were carried out by analyzing the emission and excitation wavelengths and activation region of photoactive material, the reflectance % variations due to irradiation and also colorimetric values of samples before and after irradiation. At dark, ceramic tile was pale yellow nearly colorless, but after exposure to light due to the phototransformations, color changing on surface was observed. When the coated samples were irradiated by light, it was seen that only a few minutes later, colorless surface turned to blue from pale to intense color due to the increasing irradiation time. Photochromic activities of coated tiles were analyzed after irradiation at different time intervals between 0-10 min.

Firstly, by excitation through full range at visible region, the emission spectra were acquired and the emission wavelength of photoactive layer was detected by using fluorescence spectrometer. It was observed that at the range between 620-680 wavelengths and also a smaller broad emission at 420-600 wavelengths have been occurred as shown in figure 3. To identify the specific wavelengths which are required to activate these emission intervals to provide the photochromic color change, the excitation spectra were performed for the emission at 648 nm that is the top point on the maximum emission band between 620-680 wavelengths. As seen obviously from figure 4, to activate sample it has been required an irradiation source mainly at wavelengths between 310-340 nm which is directly match with a UVA light. Also as seen from figure, excitation bands at 380-550 nm and 200-220 nm wavelenghts, the photoactive layer also can be

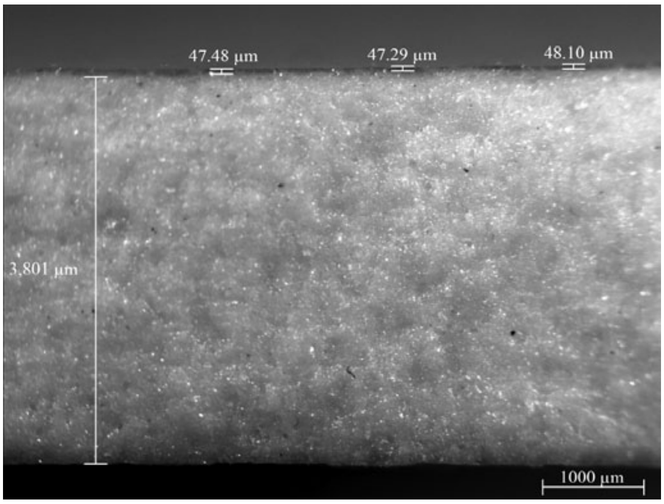

Figure 1. Stereo microcopy image of coating thickness at different parts on ceramic tile.

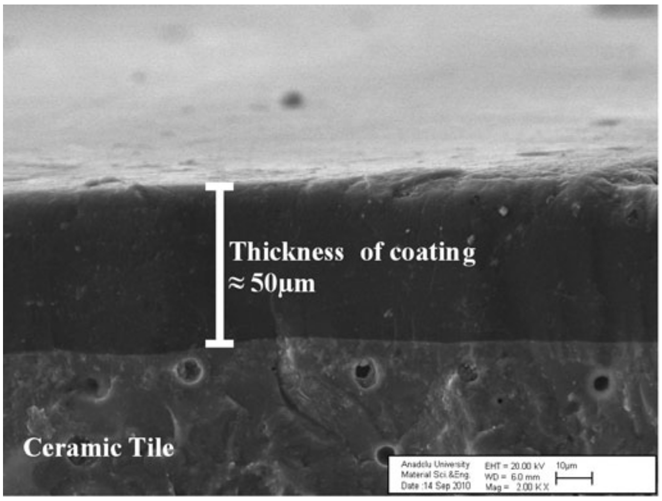

Figure 2. SEM image of coating thickness on lateral side of ceramic tile.

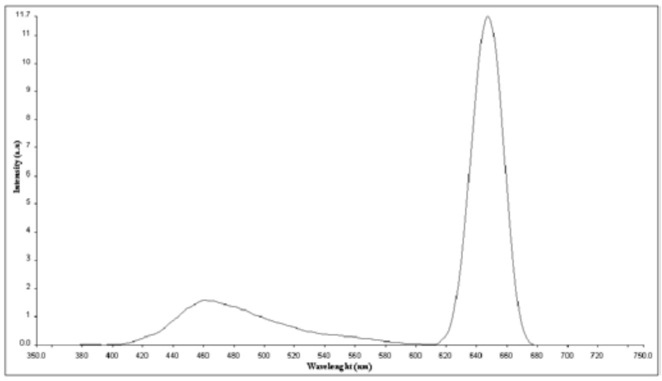

Figure 3. Emission spectra of sample at visible region by fluorescence spectrometer.

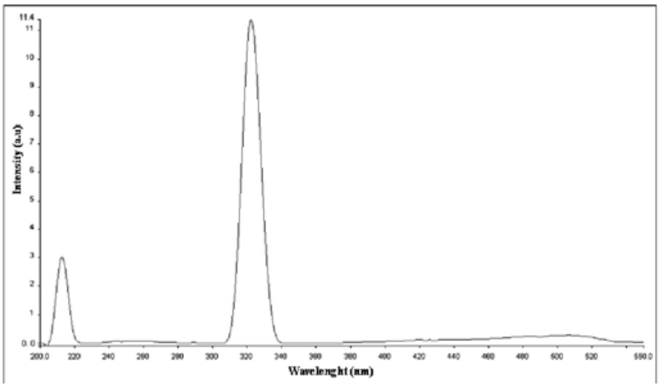

Figure 4. Excitation spectra of sample for 648 nm emission by fluorescence spectrometer.

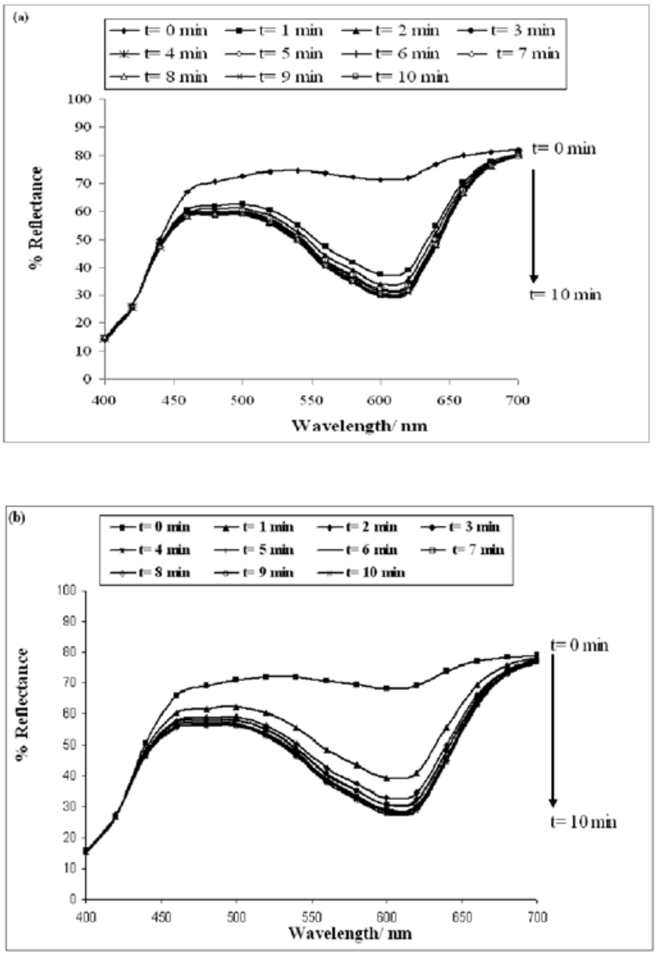

Figure 5. Reflectance spectra of coated ceramic tile under sunlight (a) and UV lamp (b) irradiation at different times.

irradiated at these wavelengths, but mainly the activation side is UVA region and sunlight. As a result of these analyses for photochromic effect characterization UVA lamp and sunlight were used to classify the reflectance changes under irradiation and without a filter or monochromatic flux due to the activation of photochromics through a range of wavelengths as detected from excitation spectra. It has been indicated that according to the emission and excitation spectra also 200-220 nm wavelengths can be used but these wavelengths are at UVC region which can not be directly get from sunlight for outdoor applications and also has a hazardous effect, cause of these reasons UVA lamp and also sunlight irradiation analyses were done for examining reflectance variations under irradiation.

The more the sample reflects light means the brighter it is and the less change in the color under irradiation. Figure 5 (a) shows the reflectance spectra of the coating under sunlight irradiation after different time intervals. As seen from the figure, at the initial state without irradiation there has no distinctive absorption at visible region, but after irradiation almost at 1 min the reflectance of coating indicated a sharp decrease from 71.15% to 30.78% at 600-620 nm wavelengths due to the increasing absorption and thus phototransformations that results as color change under sunlight. By increasing irradiation time, absorption has been increased and after 7 min the activated state was saturated. After this time period as seen, sample exhibited similar reflectance values at t= 8, 9, 10 min as 30.42%, 29.77% and 30.44 %. The reflectance of sample decreased while irradiation time was increasing, and it exhibited more color change upon light exposure, as expected. Likewise, Figure 5 (b) indicates the reflectance spectra of the coating under UVA lamp irradiation after different time intervals. After irradiation under UVA lamp, nearly at 1 minute reflectance of sample displayed a decrease from % 70.83 to % 27.53 at 600-620 nm wavelengths. When the reflectance of sample under UVA lamp has been compared with sunlight irradiation, the reflectance graphs seems nearly similar but due to the more intense irradiation of UVA lamp it has exposed more decrease at reflection which means more color change as a result of photochromic effect.

Furthermore color measurements were carried out for identification of color change by photochromic reactions with using principles of colorimetry based on CIE lab color space. This system uses a completely set of coordinates to define a color as L* (lightness), a* (green/red) and b* (blue/yellow) as mentioned before. The photochromic ceramic tile was irradiated under sunlight at different time intervals as 0-10 min. and L*, a* and b* colorimetric values were determined by using spectrophotometer as shown in Table 1. It was observed that at initial state when there was no irradiation, lightness of sample were higher, while a* values were at green side and b* values at yellow side at color space. But under irradiation where absorption of the light and further photochromic reactions took place, color change occurred and L* values decreased, while a* and b* values increased at negative direction which are at the color side of more intense green and blue, respectively. Specially b* values showed a rapid increase from 15.09 to -4.52 and demonstrates the transformation from initial pale yellow color to blue color. For denoting the color change more quantitatively, it is well known that the total color difference (ΔE*) can be used and calculated as the

TABLE1. COLORIMETRIC VALUES OF COATED CERAMIC TILE AFTER IRRADIATION UNDER SUNLIGHT AT TIME INTERVALS BETWEEN 0-10 MINUTES.

Irradiation Time (min)	L*	a*	b*	ΔE*
0	88.24	-7.07	15.09	0.29
1	76.65	-13.74	-0.41	20.75
2	75.16	-14.37	-2.27	23.21
3	74.20	-14.76	-3.51	24.82
4	73.81	-14.92	-3.77	25.29
5	74.15	-14.84	-3.29	24.71
6	73.86	-15,04	-3.72	25.27
7	73.41	-15.18	-4.33	26.02
8	73.19	-15.20	-4.62	26.38
9	72.87	-15.40	-4.97	26.89
10	73.23	-15.29	-4.52	26.31

geometrical distance between the three dimensional positions in the CIELAB color space by the formula,

$$\Delta E^* = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})} \qquad [13]$$

As illustrated in Table 1, the color change (ΔE*) increased with the irradiation time. After irradiation under sunlight, ΔE* raised very quickly and at t= 1 min already reached up to 20.75 which was 0.29 at t= 0 initially that revealed the fast color change of ceramic tile.

After irradiation, when the sample was left in the dark, photochromic compound displayed bleaching and recovered naturally to its initial colorless state. For investigating bleaching mechanism, after exposure to irradiation, sample was left at the dark and the reflectance spectra were taken with time intervals. The reflectance of photochromic structure quickly increased and there was nearly no absorption after 14 minutes in the dark as illustrated in Figure 6. The reflectance of the sample again reached 71% and sample transformed to its original colorless state from blue color at activated state. When colorimetric data of coated samples were examined at bleaching stage, it was observed as seen in Table 2 that at bleaching stage, L* was increased, while a* was decreased and b* was shifted significantly from negative blue side to positive

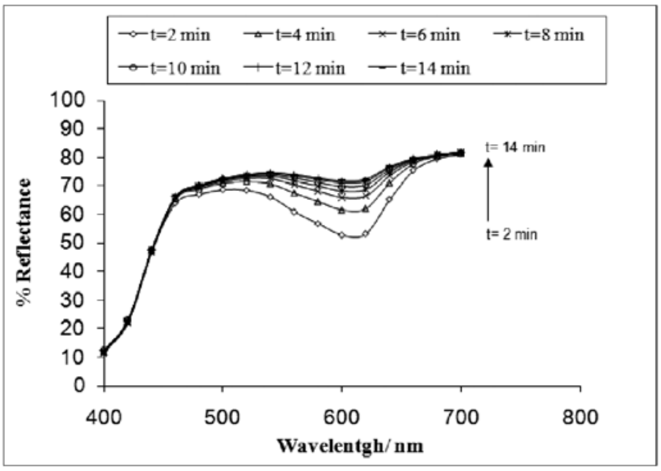

Figure 6. Bleaching of coated ceramic tile at dark after irradiation under sunlight.

TABLE 2. COLORIMETRIC VALUES OF COATED CERAMIC TILE AT BLEACHING STATE AT DIFFERENT TIME INTERVALS.

Duration time at dark (min)	L*	a*	b*	ΔE*
2	82.90	-12.23	8.88	11.07
4	85.63	-10.14	12.76	5.90
6	86.84	-9.10	14.85	3.30
8	87.43	-8.38	15.35	2.28
10	87.81	-7.90	15.86	1.52
12	88.11	-7.60	16.36	0.86
14	88.32	-7.43	16.62	0.50

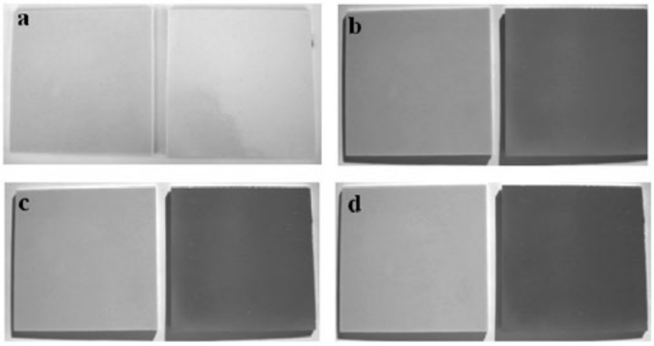

Figure 7. Color changing of photochromic ceramic tile under sunlight, a: initial, b: after 30 s, c: after 60 s, d: after 90 s (at all images left side tile is standard ceramic tile, right side is photochromic ceramic tile).

yellow side due to the transformation to uncolored form. At the end of 14 minutes, ΔE* values were decreased from 34.79 to 0.50 and approached similarly to the original uncolored form ΔE* value which was 0.29 without irradiation.

The photochromic coloring of developed photochromic ceramic tile is shown in Figure 7. As it can be seen, under exposure to sunlight ceramic tile changed its color in which it turned very quickly to intense blue color from initial colorless state.

4. CONCLUSION

Photochromic coating including active organic photochromes were successfully formed on ceramic tiles. The coating process was performed by using spray coating method. This technique provided homogeneous layer formation on the ceramic surface which has a thickness nearly 45-50 μm. By using polymeric gel, even though heat treatments at low temperature, photochromic coating exhibited good adhesion on the surface that was a value of 3 according to Mohs hardness scale and was also at class 2: 600 revolutions to standard ISO 10545-7 test. The photochromic mechanism of the ceramic tiles indicated quick response and replaced its color in a few minutes under irradiation. Ceramic tile surface showed maximum absorption at 600-620 nm and altered its color from colorless to intense blue color under sunlight. The intensity of the obtained color was increasing by irradiation time and reached the saturation after nearly 7 minutes. When irradiation was cut off, system exhibited bleaching and turned to its original colorless state due to the decreasing at absorption. In this work, photochromic ceramic tiles were developed and the ceramic surface gained novel aesthetical properties because of the functionality of photochromism that is widely used in many industrial areas and has an increasing demand. The experiments were performed at pilot scale under laboratory conditions, but it should be considered that for industrial applications at large production scales, system modifications different from traditional processing such as spray coating systems may be set up and due to the applied low temperature, researches for mechanical enhancement should be carried out and also because of the organic based compounds, durability of these photoactive materials should be investigated as planned future work for us.

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Recibido: 14/11/2010
Aceptado: 28/07/2011