Simple Preparation of Photoluminescent and Color-Tunable Polyester Resin Blended with Alkaline-Earth-Activated Aluminate Nanoparticles

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ABSTRACT: A simple inorganic/organic nanocomposite was used to generate long-lasting phosphorescent pebbles for easy commercial manufacturing of smart products. An organic/inorganic nanocomposite was made from low-molecular-weight unsaturated polyester and rare-earth-activated strontium aluminum oxide nanoparticles doped with europium and dysprosium. The polyester resin was mixed with phosphorescent strontium aluminate oxide nanoparticles and methylethyl ketone peroxide as a cross-linking agent to create a viscous mixture that can be hardened in a few minutes at room temperature. Before adding the hardener catalyst, the phosphorescent strontium aluminate nanoparticles were dispersed throughout the polyester resin in a homogeneous manner to ensure that the pigment did not accumulate. Long-lasting, reversible luminescence was shown by the photoluminescent substrates. The emission was reported at 515 nm upon exciting the pebble at 365 nm. In normal visible light, both blank and luminescent pebbles had a translucent appearance. As a result of UV irradiation, the photoluminescent pebbles produced an intense green color. The three-dimensional CIE Lab (International Commission on Illumination) color coordinates and luminescence spectra were used to investigate the color changing characteristics. Photophysical characteristics, including excitation, emission, and lifetime, were also investigated. Scanning electron microscopy, wavelength-dispersive X-ray fluorescence spectroscopy, and energy-dispersive X-ray analysis were employed to report the surface morphologies and elemental content. Without impairing the pebbles’ original physico-mechanical characteristics, the pebbles showed improved superhydrophobic activity. The current simple colorless long-lasting phosphorescent nanocomposite can be applied to a variety of surfaces, like ceramics, glassware, tiles, and metals.

1. INTRODUCTION

The development of energy-saving materials of high transmittance has been an exciting challenge. A smart product is a material that responds to an exterior stimulus like light and heat. For example, smart materials may change their color, emission, or even light up in patterns and show photos/videos upon exposure to an external stimulus. A broad variety of advanced applications may benefit from the incorporation of nanomaterials onto polymer substrates, including ultraviolet protection, electrical conductivity, preservation of transparency, optical sensors, and water repellency. A polymer matrix has been used to incorporate photoluminescent organic colorants, such as spiro-oxazines, into nanocomposites. However, various problems exist with the usage of organic colorants, such as limited photochromism owing to steric hindrance, deterioration due to prolonged light exposure, as well as poor photostability. It was reported that lanthanide-doped strontium aluminum oxide, an inorganic colorant, has better photostability, durability, and mechanical properties than organic colorants. The structure-related switching process occurring in organic colorants and limiting their photochromism does not exist in the photophysical performance of inorganic colorants, making them a better choice for the development of photochromic materials. Long-lasting luminescent materials have been used in a number of marketable goods. A variety of applications have benefited from this phenomenon, including protective garments, aesthetic decorations, anticounterfeiting barcodes, and safety signs. An external light source could be readily used to store light energy inside these long-lasting photoluminescent materials, which are made up of a carrier and a luminescent...
When the light source is removed, the photoluminescent pigment can gently discharge light. Strontium aluminum oxide (SAO) crystals and divalent europium energy traps are key components of the long-lasting phosphorescence process. With the help of a light source to excite luminescent materials, the traps can be charged, while the luminescent contents can be charged by exposure to light.15 Thus, as time goes on, the crystals continue to generate light by prolonging the emission time period after the light source is turned off. There are a variety of persistent photoluminescent compounds available on the market with different color emissions. For instance, Y₂O₂S:Mg²⁺, Ti⁴⁺, SrAl₂O₄:Eu³⁺, Dy³⁺, and CaAl₂O₄:Eu³⁺, Nd³⁺ have been reported as emitters of red, green, and blue colors, respectively.16–18 Those photoluminescent pigments have been reported as most durable on the market today because they can withstand solvents, chemicals, heat, and light. There show no toxicity or radioactivity, and they had high quantum efficiency as well as a highly extended phosphorescence time period.19–21

A polyhydric alcohol and a dibasic organic acid react to form a polyester resin, which is defined as an unsaturated synthetic resin. Polyesters have been used in the manufacture of various materials, such as sheets, bulk-shaped products, and fiberglass wall panels. Resistant to water, chemicals, ageing, and high temperatures, polyester resins are also known for being affordable and having a low shrinkage percentage after curing.22,23 Polyester resins have been attractive materials according to the previously reported high-temperature solid-state synthetic procedures.24–28 However, polyester-based luminescent materials with energy-saving properties have only been reported in a few research articles. To the best of our knowledge, photoluminescent pigments made from an unsaturated polyester and rare-earth-doped SAO have not been documented to date. The current research procedure can be reported as an inexpensive and straightforward approach for producing glow-in-the-dark pigments using low-molecular-weight unsaturated polyester and strontium aluminum oxide nanoparticles (SAON). Both X-ray diffraction (XRD) and transmission electron microscopy (TEM) were employed to characterize SAON. The photoluminescent pigments exhibited a smooth surface and good hardness. The present manufacturing method of the luminescent polyester/SAO nanocomposite is distinguished by its ease of use and low cost while also offering great durability, fatigue resistance, and excellent hardness. Scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDXA), and wavelength-dispersive X-ray fluorescence (WDXRF) spectroscopy were used to investigate the morphology and chemical content of the generated pebbles. The static water contact angles were utilized to characterize SAON. The photoluminescent compounds available on the market with different color emissions, lifetime, and luminescence spectra were also explored. The current pigment—polyester resin mixture can be readily made industrially under ambient conditions. The current photoluminescent composites have been reported for many potential applications ranging from mosaics, night work products, traffic and building directional signs, and coating for hard surfaces, including ceramics, tiles, glass, walls, and wood.

2. EXPERIMENTAL SECTION

2.1. Materials. The polyester resin (unsaturated; 189 fpt; purity is 99.9%, ~15–25 min solidifying period, yellow translucent liquid) was obtained from the marketplace in Egypt. Methylene ketone peroxide (MEKP, Merck) was utilized as a hardening agent. Eu²⁺ and Dy³⁺-doped SAO was synthesized as previously described.29,30 Ball milling was used through the top-down approach to lower the particle size of the produced pigment so that it could be more easily distributed and to achieve better transparency.3,29,30 The materials utilized to prepare the lanthanide-doped pigment were obtained from Aldrich (Egypt) and Merck (Egypt), including dysprosium(III) oxide (Merck), boric acid (Aldrich), europium(III) oxide (Aldrich), strontium carbonate (Merck), and aluminum oxide (Merck).

2.2. Synthesis of SrAl₂O₄:Eu²⁺, Dy³⁺ Nanoparticles. The Eu²⁺- and Dy³⁺-doped SAO phosphor was synthesized according to the previously reported high-temperature solid-state synthetic procedures.29,30 Al₂O₃ (200 mmol), SrCO₃ (100 mmol), Dy₂O₃ (1 mmol), H₃BO₃ (20 mmol), and Eu₂O₃ (2 mmol) were combined in absolute ethanol (450 mL) and stirred to allow a better dispersion. In order to guarantee that the solution is disseminated evenly, it was homogenized (25 kHz) for an hour. After 24 h of drying at 90 °C and three h of grinding, the mixture was exposed to 3 h of sintering at 1300 °C. Pigment microscale particles were provided by grinding and sieving the supplied powder. The pigment nanoparticles were obtained by grinding the provided microscale powder using the top-down approach.25 The microscale powder (12 g) was placed in a ball milling vial (stainless steel; 20 cm) on a vibrating sheet, where it was pulverized into a fine powder. The nanoparticles were produced after 24 h of grinding the pigment microscale particles placed in a vial on a vibrating system and repeatedly hitting with another ball mill (SiC with a diameter of 0.1 cm).

2.3. Preparation of Photoluminescent Pebbles. In a bowl, the polyester resin (Figure 1) was mechanically mixed for 5 min with the Eu²⁺- and Dy³⁺-doped SAO at various contents (0, 1, 3, 6, 9, 12, 15, 18, and 21% w/w). A hardener, MEKP (1.5% w/w), was then added to the admixture and cured for 5 min of stirring. The admixture was then subjected for drop-casting onto a Teflon plate, followed by 30 min of ambient curing to produce long-lasting phosphorescent pebbles. The generated pebbles were denoted by P₀, P₁, P₃, P₆, P₉, P₁₂, P₁₅, P₁₈, and P₂₁, respectively.

Figure 1. Chemical formulae of the polyester resin and MEKP.
2.4. Methods and Apparatus. 2.4.1. Morphological Properties. A JEOL 1230 (JEOL; Japan) transmission electron microscope was employed to inspect the pigment nanoparticle morphology. XRD was performed using a Bruker Advance D-8 (Karlsruhe; Germany). A SEM Quanta FEG250 (FEI; Republic of Czech) paired with an EDX spectrometer that is powered by the TEAM software was used to evaluate morphologies and compositions of the prepared samples. An Axios sequential wavelength-dispersion XRF spectrometer (Axios; Almelo, Netherlands) was utilized to examine the compositions of the prepared pebbles.

2.4.2. Contact Angles. The OCA15EC (Dataphysics, GmbH, Germany) was employed to measure the water contact angle using 10 L droplets. To create a flat surface, the photoluminescent polyester pebble was taped to the glass slip using double-sided adhesive tape.

2.4.3. Hardness Properties. The prepared pebbles were examined for hardness and resistance to scratching utilizing a Shore D (Otto Wolpert-Werke, GmbH, Germany) and HB pencil scratching testing machine, respectively.

2.4.4. Luminescence Spectra. An FP-8300 JASCO spectrofluorometer (JASCO, Tokyo, Japan) was used to measure the lifetime, emission, and excitation spectra.

2.4.5. Photostability and Reversibility. When exposed to UV light (365 nm) for 2 min, the pebble sample (P15) was held in the dark for 90 min to release light. After several cycles of UV irradiation and light release, the 515 nm emission intensity was recorded.

2.4.6. Coloration Measurements. A Hunter Lab Ultra Scan Pro (Hunter Associate Laboratory Inc., Reston, USA) was used to measure the colorimetric properties of pebbles before and after irradiation with UV light (365 nm). CIE $L^*$, $a^*$ and $b^*$ color space characteristics as well as color intensity ($K/S$) were examined. CIE Lab stands for the International Commission on Illumination and is abbreviated from the French name of Commission Internationale de L’éclairage, which is the international authority on color defined in three-dimensional coordinates, illumination, and light. $L^*$, $a^*$, and $b^*$ were used to characterize lightness (100)/darkness(0), red(+)/green(−), and yellow(+)/blue(−) color ratios, respectively. The photos of the photoluminescent pebbles were taken utilizing an A710IS Canon camera before and after UV irradiation.

3. RESULTS AND DISCUSSION

3.1. Morphologies and Elemental Compositions. In Figure 2, SEM was utilized to determine the morphologies of both blank and luminous pebbles. Phosphorescent pigment immobilization was confirmed by the SEM images showing no morphological differences among the blank and treated luminous pebbles. Aluminum in the phosphor molecule could coordinate with the polyester carbonyl groups (O=C=O), which might explain the pigment’s uniform distribution. In addition, SEM images showed that the surface of the SAO-loaded pebbles remained unchanged in comparison to a blank pebble. The phosphor pigment was evenly distributed in the polyester resin bulk as proved by EDXA spectra explored at three different spots on the pebble surface. The dispersion of pigment in the luminous pebbles was also verified uniformly and consistently by the mapping images (Figure 3).

An investigation of the pigment-immobilized P15 pebble chemical composition was performed by EDXA, as shown in Figure 3 and Table 1. The pigment was well integrated into the polyester bulk as shown by the identical chemical composition.
at three separate locations on the pebbles’ surface. The elemental analysis was also examined using WD-XRF. EDXA has shown to be a fairly accurate tool for determining the chemical composition. As reported by EDXA, the elemental contents displayed carbon and oxygen as major components due to the main bulk content of polyester. The minor contents of Al, Sr, Eu, and Dy were attributed to the lower ratios of SAON used in the preparation procedures. WD-XRF, on the other hand, typically has a detection limit of 10 ppm. Thus, XRF introduced a fractional analysis of a pebble’s chemical composition. Only strontium and aluminum were detected by WD-XRF in the luminescent pebbles, as indicated in Table 2.

As a consequence of their very low total concentration, however, WDXRF was unable to identify Dy(III) and Eu(II). Both XRF and EDXA were used to determine the molar percentages of various elements in the developed pebbles, which were found to match with the molar percentages employed in the preparation of both SAO and luminous pebbles. Ball milling was necessary to achieve homogeneous dispersion of the phosphorescent pigment to achieve the transparency of the manufactured photoluminescent pebbles. The diameters of the pigment nanoparticles are detected at 35–95 nm, as shown in Figure 4.

XRD spectra of SAON and its standard spectrum are illustrated in Figure 5. The diffraction signals of SAON matched the pure monoclinic phase of SrAl2O4 (JCPDS card number 34-0379). No crystal phase was observed to designate the presence of Eu2+ and Dy3+ within the SrAl2O4 crystal lattice. No other signals were observed for other materials to prove the low-temperature monoclinic phase of the precursor nanoscale powder. This also confirmed that the extremely low contents of europium and dysprosium demonstrated nearly no effects on the SrAl2O4 phase composition.

3.2. Contact Angles. Table 3 shows the contacting angles of the prepared pebbles. Strontium aluminate was observed to enhance the contact angle of the polyester pebbles from 131.5° (P0) to 133.2° (P1). The increased strontium aluminate concentration to reach P15 led to an increase in photoluminescent pebbles’ contact angles to 145.6°. However, after increasing the strontium aluminate concentration from P15 to P21, the angle decreased to 144.8°. Generally, increasing the SAON ratio resulted in an increment in the pebbles’ surface roughness. However, the further increase in the strontium aluminate concentration in the polyester pebble matrix led to a reduction in the spaces between SAO nanoparticles, which reduces roughness and, as a result, decreases the water contact angle. Figure 6 illustrates both emission and waterproofing ability of the polyester pebble (P15) upon immersion in water.

3.3. Colorimetric Results. CIE Lab and K/S data are shown in Table 4. Similar to the untreated polyester pebbles, the luminescent pebbles display a transparent appearance. The color strength of the luminescent pebbles was observed to rise marginally when the pigment concentration was increased from 1 to 15% before UV irradiation. Because the treated pebbles retain their transparent appearance, this minor increment in K/S confirms that the homogeneous distribution of the SAON content in the polymer bulk itself is responsible for maintaining their transparency. However, the colorimetric strength increased significantly at concentrations beyond 15%, indicating that the transparent look had been lost. Hence, the K/S showed that the optimum SAON content was at 15% (P15), at which no major variations in color intensity were identified compared to the blank pebble. The color strength of the luminescent pebbles after exposure to UV was reduced somewhat as a consequence of increasing the SAON content in the phosphorescent pebbles, which might be attributable to the concentration-dependent greener colorimetric character. The treated pebbles revealed a drop in color strength after exposure to UV light owing to the transition of pebbles from the less faded colorless appearance to the stronger green color strength. The +a* values of the luminous pebbles rose significantly, but the b* value decreased. A change in +a* values to −a* occurred due to UV irradiation, but b* remained almost unchanged. A color shift from transparent to green below UV and greenish-yellow in darkness might be a factor. With the SAO serving as crystals and the rare-earth constituent serving as a trap, an external UV source may readily excite SAO crystals allowing them to store light. Upon removing the source of light, this pigment will progressively release light. Luminous elements like crystals and lanthanide traps can be charged by a light supply. However, crystals have the advantage of holding light photons for extended periods of time. As a result, the crystals continue to generate green light even after the light source is turned off. Figure 7 shows the results of monitoring green phosphorescence under a UV supply, as well as in the dark following UV excitation.

### Table 1. Elemental Contents (wt %) of the Pristine and Luminescent Pebbles Determined by EDXA at Three Locations (a1, a2, and a3) on the Pebble Surface

| Pebble | C   | O   | Al  | Sr  | Eu  | Dy  |
|--------|-----|-----|-----|-----|-----|-----|
| P0     | 59.72 | 40.28 | 0   | 0   | 0   | 0   |
| P1     | 65.81 | 35.47 | 1.21 | 0.89 | 0.26 | 0.11 |
| a1     | 65.94 | 35.59 | 1.26 | 0.77 | 0.32 | 0.12 |
| a2     | 65.92 | 35.73 | 1.07 | 0.84 | 0.30 | 0.14 |
| a3     | 52.85 | 40.71 | 3.12 | 2.32 | 0.57 | 0.43 |
| P6     | 53.07 | 40.67 | 3.07 | 2.15 | 0.72 | 0.32 |
| a1     | 52.81 | 40.65 | 3.26 | 2.29 | 0.61 | 0.40 |
| a2     | 47.51 | 40.47 | 5.92 | 4.50 | 0.95 | 0.63 |
| a3     | 47.52 | 40.73 | 5.76 | 4.62 | 0.83 | 0.60 |
| P15    | 47.87 | 40.36 | 5.43 | 4.88 | 0.90 | 0.56 |
| a1     | 44.13 | 39.00 | 8.50 | 6.24 | 1.35 | 0.78 |
| a2     | 44.11 | 39.12 | 8.38 | 6.36 | 1.26 | 0.80 |
| a3     | 44.34 | 39.51 | 8.08 | 6.01 | 1.24 | 0.82 |

### Table 2. Elemental Composition of Pebbles Determined by XRF

| Elements | Oxide | P1 | P6 | P15 | P21 |
|----------|-------|----|----|-----|-----|
| Sr       | SrO   | 28.86 | 31.50 | 33.25 | 34.15 |
| Ca       | CaO   | 2.28 | 1.85 | 1.27 | 0.84 |
| Na       | Na2O  | 2.47 | 1.64 | 1.18 | 0.92 |
| K        | K2O   | 3.24 | 2.53 | 1.64 | 0.66 |
| Al       | Al2O3 | 55.39 | 57.17 | 59.30 | 60.05 |
| Mg       | MgO   | 3.16 | 2.06 | 0.87 | 0.73 |
| Si       | SiO2  | 4.60 | 3.25 | 1.49 | 1.65 |
escent composites. As a filler, the pigment was encased in the polyester resin. Composites with more than 1% pigment concentration had a slower reversibility of photoluminescence activity than those with lower concentrations of the pigment. Thus, only composite pebbles with 1% pigment concentration (P1) demonstrated fast reversibility of photoluminescence activity indicating fluorescence, whereas composites with more than 1% pigment concentration (P3–P21) had a slower reversibility to indicate long-persistent phosphorescence. Figure 8 depicts the emission spectra of composite pebbles that have been untreated and treated with the pigment. The emissive intensity rises with the increase in the SAON content; however, the emission wavelength was determined at the same value of 515 nm. Pigment-immobilized polyester pebbles

Figure 4. TEM images of pigment nanoparticles (SAON).

Figure 5. XRD spectrum of SAON (top) and its standard pattern (bottom).

Table 3. Contact Angle of the Prepared Blank and Luminescent Pebbles

| pebble | contact angle (°) |
|--------|------------------|
| P0     | 131.5            |
| P1     | 133.2            |
| P3     | 135.3            |
| P6     | 137.5            |
| P9     | 141.6            |
| P12    | 143.8            |
| P15    | 145.6            |
| P18    | 145.0            |
| P21    | 144.8            |
displayed long-lasting phosphorescence at 515 nm, which is almost the same wavelength monitored for a powder of strontium aluminum oxide (519 nm).29 As seen in Figure 9, the lifetime profile exhibited a nonlinear relation with time. It started with strong and fast decay, followed by slow and weak decay.

The colorless background was monitored to introduce a better optical identification of the color change to intense green below UV and greenish-yellow in darkness.35 After removing the UV irradiation source away from the pebble sample, the pigment-containing luminescent pebble P1 with the lowest pigment concentration demonstrated fluorescence emission with instant reversibility. In other words, this fluorescent pebble displayed no emission bands in darkness. The polyester pebbles from P3 to P21 with higher pigment nanoparticle concentrations showed slow reversibility to indicate long-persistent luminescence in the dark. Thus, the developed luminescent samples demonstrated concentration-dependent luminescence spectra. Broad and strong emissions were reported at 442 and 515 nm in the visible light spectral range. The $4f^65D_1 \leftrightarrow 4f^7$ transition of Eu$^{2+}$ has been known to

![Figure 6. Photographic images of $P_{15}$ upon immersion in water: colorless in daylight (a), green in UV (b), and greenish-yellow in darkness (c).](image)

**Table 4. Colorimetric Screening of Both Blank and Luminescent Pebbles Before ($C_1$) and Directly After ($C_2$) Excitation with UV Light**

| pebble | $K/S$ | $L^*$ | $a^*$ | $b^*$ |
|--------|-------|-------|-------|-------|
| $P_0$  | 0.49 | 87.05 | -1.75 | 1.70 |
| $P_1$  | 0.71 | 75.20 | -1.14 | 1.87 |
| $P_5$  | 0.76 | 72.73 | -1.09 | 1.78 |
| $P_6$  | 0.83 | 72.28 | -1.03 | 1.72 |
| $P_9$  | 0.92 | 70.57 | -0.99 | 1.67 |
| $P_{12}$ | 0.99 | 67.37 | -0.93 | 1.61 |
| $P_{15}$ | 1.07 | 65.34 | -0.88 | 1.55 |
| $P_{18}$ | 1.45 | 63.79 | -0.76 | 1.47 |
| $P_{21}$ | 1.84 | 63.37 | -0.67 | 1.35 |

![Figure 7. Color change of the luminescent polyester pebble (15%) between being transparent under daylight (a), green below ultraviolet (b), and greenish-yellow in darkness (c).](image)

![Figure 8. Phosphorescence spectral analysis of composite pebbles at various ratios of SAON.](image)
be responsible for the strontium aluminum oxide pigment emission. There was no emission band detected for Eu$^{3+}$ to confirm the complete transformation of Eu$^{3+}$ to Eu$^{2+}$.$^{13,29,30}$

3.5. Mechanical Performance. The mechanical behavior of the pigment-loaded polyester composite pebbles has a significant influence on their long-term stability. Light-emitting bulk material was prepared using a polyester resin matrix with the best transparency and minimal roughness. As a consequence, the mechanical performance of the nano-composite pebbles was evaluated by conducting hardness and scratch tests. A scratching test was performed on blank and pigment-immobilized polyester composite pebbles in order to measure scratch resistance. For measuring the resistance to scratch, the hardness of the scratch testing pencils has demonstrated a simple and effective procedure.$^{36,37}$ A sharpened scratch pencil was used to scratch the nano-composite pebbles. The resistance to the scratch experiment employed pencils with hardnesses ranging from 6B to 9H. The blank pebble (P$_{0}$) sample was unable to resist scratching beyond the F pencil. The composite pebbles from P$_{1}$ to P$_{21}$ were capable of resisting scratching with pencils of H, 2H, 2H, 2H, 4H, 5H, 5H, and 6H, respectively. It has been shown that when the pigment ratio is raised, scratch resistance is observed to rise. Deformation levels affecting material durability are influenced by a material hardness.$^{32,35}$ As a result, composite hardness is an important metric to employ when evaluating a material performance. As a bulk material, polyester was used because it is translucent and has a smooth surface. The toughness of the luminous polyester pebbles was tested with different pigment ratios, as shown in Figure 10. When the pigment ratio was raised from P$_{0}$ to P$_{19}$, the hardness fell from 8.59 to 5.32 kg/mm$^{2}$ before rising again from P$_{18}$ to P$_{21}$ (5.55 kg/mm$^{2}$), respectively. Raising the pigment concentration had lowered the impact from 8.81 to 5.16 MPa. Similarly, the impact was then raised again to 5.40 MPa for the composite pebble sample P$_{21}$. Aluminum in strontium aluminate could be responsible for the increased hardness of the polyester pebbles as aluminum may act as a cross-linking hardener during the polyester polymerization process to result in a homopolymer with a higher molecular weight. Aluminum may also act as a coordinating agent decreasing the distance between the polyester polymer chains during the polyester polymerization process leading to higher hardness.$^{38-40}$

3.6. Evaluation of Photostability. As illustrated in Figure 11, the photoluminescent polyester pebbles were tested for durability and fatigue resistance in the presence of ultraviolet light. A remarkable fatigue resistance was shown by the P$_{15}$ photoluminescent composite material. After being exposed to UV light for 2 min, the luminous P$_{15}$ pebble was put in darkness for 90 min to allow for light release and allow the pebble sample to return to its originally fading state. The emissive intensity measured after each UV excitation and fading cycle was found to be almost the same, indicating strong reversibility. Luminescent pigments have high reversibility because they include SAO crystals, which store light when exposed to UV excitation, as well as lanthanide traps, which can slowly release the light energy they have previously stored. The lanthanide trap is capable of retaining light for longer periods of time than the crystal, which may be charged under a light source.$^{41-44}$

4. CONCLUSIONS

With both the low-molecular-weight unsaturated polyester and rare-earth doped aluminate, glow-in-the-dark pebbles were produced while maintaining the inherent properties of the pigment-free polyester pebble, such as smoothness, hardness,
and appearance. A low-molecular-weight unsaturated polyester and SAON pigments were combined with MEKP as a hardener to create luminous pebbles. Before adding the catalyst, the pigment was dispersed in a homogeneous manner into the viscous polyester resin to avoid pigment agglomeration. Additionally, an even distribution of SAO nanoparticles in the polyester bulk was achieved to ensure a transparent pebble. The TEM images show that the pigment was milled to a nanoparticle size of between 35 and 95 nm. Luminescence spectra, coloration measurements, XRF, SEM, and EDXRA were used to investigate the morphologies, colorimetric changes, and photoluminescence properties of the composite pebbles. Both absorption and emission wavelengths were detected at 365 and 515 nm. Only photoluminescent pebbles exhibited green phosphorescence under a UV lamp and strong green phosphorescence for about 100 min in the dark. The static contact angles were studied to prove that the water repellency of the composite pebbles can be increased by increasing the pigment ratio. \( P_2 \) had a contact angle of 131.5°, whereas both \( P_1 \) and \( P_{2,5} \) had contact angles of 133.2 and 144.8°, respectively. The hardness performance only showed very modest variations as the pigment concentration increased. The present strategy can be used to introduce a straightforward and economical preparation approach to produce long-lived phosphorescent pebbles for electricity-free soft lighting. The current transparent long-lasting phosphorescent composite can be applied on various surfaces, including ceramics, glassware, metals, and wood, and is simple under ambient circumstances.

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