Wear response and mechanical behaviour of silicone-based photoluminescent coatings

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HIGHLIGHTS

- The thickness of the photoluminescent coatings depends on deposition technology.
- Pigment size and concentration influence the morphology of the coatings.
- Pigment size and concentration influence the tribological and scratch response.
- Sprayed coatings are characterized by the lowest wear volume and best scratch resistance.
- Photoluminescent intensity is correlated to pigment size and concentration.

ABSTRACT

Photoluminescent coatings were manufactured by dispersing different sized hydrophobic silane surface-modified SrAl₂O₄:Eu²⁺, Dy³⁺ photoluminescent pigments in a waterborne, silicone-modified 1-pack polyurethane binder. The resulting emulsions were deposited by spraying and automatic drawdown applicator on medium density fiberboard (MDF) panels covered with decorative paper. After automatic drawdown applications, half of the photoluminescent coatings were recoated with a transparent acrylic topcoat for protection purpose. The visual appearance of the coatings was analyzed by combined contact gauge profilometry and field emission gun scanning electron microscopy. Mechanical and tribological properties of the coatings were then analyzed by progressive and continuous load scratch as well as by linear reciprocating ball-on-flat sliding wear tests. High resistant, flexible and partially transparent photoluminescent coatings are achieved with a very simple, reproducible and eco-sustainable procedure, which can be easily extended to industrial applications for a wide range of substrates.

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1. Introduction

Photoluminescence has always drawn people attention. Some pigments, also known as phosphors, can absorb light energy when irradiated by sunlight or lamping. Once the cause of the excitation elapses, the pigments can release the stored energy slowly and in the form of low-frequency visible light in the dark [1]. Nowadays, particular interest is being focused in pigments doped with rare earth ions as SrAl₂O₄:Eu²⁺, Dy³⁺, since they have the longest persistence time of photoluminescent decay [2]. Their photoluminescence can last more than 20h, which means it may last over night [3]. The persistence comes from the Sr²⁺ and Dy³⁺ defect related hole traps which ensure the photo-charging effect and the persistence of luminescence enhancing [4]. Furthermore, photoluminescent decay occurs in a three-level fashion and weak excitation intensity is preferred to strong ones, which quickly saturates the traps hindering the trapping and detrapping of electrons in long persistent phosphor [5].
Photoluminescent pigments might have many industrial applications [6]. They can be used in road marking, public and emergency lighting, accessorizes, paint and furniture. Further, they can be installed in fluoroinmunnoassays, spectroscopic structural probes in biologically relevant systems, lasers, optical amplification, organic light emitting diodes as well as in stairwells [7].

Low-level lighting way-guidance photoluminescent systems performed better than conventional emergency lighting. Studies with smoke stated the continuity of information of photoluminescent lines ensures an uninterrupted visual reinforcement, providing a significant advantage over conventional emergency lighting, which becomes obscured by the smoke [8].

The industrial applications of photoluminescent materials rely all on the common principle of dispersing the pigments inside the bulk of the materials which must be functionalized. Accordingly, a huge amount of pigments should be used at any time the aim of manufacturing large components with good optical performance must be pursued. This leads to a loss of efficiency as most of the pigments are embedded inside the core of the component where their optical performance is refrained from the shielding effect of the material around them.

An attractive alternative could be the usage of photoluminescent and transparent resins suitable to a wide range of deposition processes. The pigments would be dispersed in a layer of nearly transparent material with which to coat and make large sized components photoluminescent. This would lead to a good efficiency, as the pigments would stand only on the surface of the components, where they could explicate all their photoluminescent potential.

Some efforts to produce photoluminescent coatings made from an organic or organic–inorganic binder and pigments as filler are in progress. Qiu et al., in their early studies, proposed an eco-friendly dispersion of photoluminescent pigments inside a waterborne styrene-acrylic binder [9]. However, such formulations needed for continuous pH monitoring and only allowed pigment concentrations of approximately 10–20%. In 2009, Pathak et al. proposed the dispersion of photoluminescent pigments inside waterborne polyurethanes [10]. They were found to ensure satisfactory properties and minimize the environmental impacts. Yet, such coating systems might ensure high hardness with limited flexibility which was even worsened by the presence of the highly concentrated photoluminescent pigments. Such drawbacks limited the viability of such a coating class in several industrial applications, as the deposition on flexible substrates like plastics or fabrics where the ductility of the coatings cannot be put aside. Subsequently, Alcon et al. added the pigments to solventborne polyester resins which required radiative curing process. The resulting material was characterized by good optical and mechanical properties, but it was not suitable for coating complex shaped components as a result of the compulsory radiative drying [11]. Further, the usage of solventborne resins is awkward, as they demand for massive amount of solvents and are severely environmentally impacting. Recently, Wang et al. proposed two photoluminescent resins based on covalently bonded silica–polymer hybrid materials synthesized from the sol–gel technique [7,12]. The comparison between two kinds of xerogel, the former based on Si–O–Si/Ti structure and the latter on Si–O–B emphasized how Si–O–B systems allowed improved thermal stability and excellent luminescent properties [12]. Yet, sol–gel formulations can be troublesome and not suitable to several industrial applications as they require very time-consuming and stringent synthesis procedures.

In this context, the present work focuses on the development of a new photoluminescent resin with the following features: (i) easiness in the synthesis or preparation; (ii) suitability to industrially compliant deposition and drying processes; (iii) responsive to stringent requirements in terms of optical and mechanical performance; (iv) respondent to stringent requirements in terms of pollution and environmental impact; (v) low cost and time consumption compliant with industrial needs. Such aims were pursued investigating the dispersion of hydrophobic silane surface-modified SrAl2O4:Eu2+, Dy3+ photoluminescent pigments in a waterborne silicone-modified 1-pack polyurethane binder. The manufacturing of the photoluminescent resins was pursued by dispersing a variety of combinations among different sized (5, 15 and 30 μm) photoluminescent pigments inside the silicone-modified polyurethane binder. The resulting stabilized photoluminescent emulsions were then deposited by spraying and automatic drawdown applicator on medium density fiberboard (MDF) panels covered with decorative paper. After automatic drawdown applications, half of the photoluminescent coatings were recoated with a transparent acrylic topcoat for protection purpose.

The morphology and the visual appearance of the resulting photoluminescent coatings were tested by combined contact gauge profilometry and field emission gun scanning electron microscopy. Their mechanical and tribological responses were characterized by progressive and constant load scratch and linear reciprocating ball-on-flat sliding wear tests, respectively. The photoluminescence of the manufactured coatings was characterized by capturing high resolution images of the surface with a digital camera and monitoring the decay of the intensity of the photoluminescent emitted radiations.

The experimental results showed high resistant, flexible and partially transparent photoluminescent coatings with good optical performance could be achieved by a very simple and environmentally sustainable procedure, making such a class of material very promising in a large share of industrial applications.

2. Materials and methods

2.1. Materials

5 and 30 wt.% of hydrophobic silane surface-modified SrAl2O4:Eu2+, Dy3+ photoluminescent pigments (5, 15 and 30 μm in diameter, Luedcentro srl, Modena, Italy) were dispersed in 10 g of waterborne silicone-modified 1-pack polyurethane binder (Evonik Tego Chemie GmbH, Essen, Germany) together with a dispersant agent (120 wt.% on pigments) based on modified polyether with groups of high pigment affinity. The silane-coupler has an organic functional and alkoxyl groups, and the alkoxyl group is changed into a silanol group (Si–OH) by hydrolysis according to [13]. The siloxane-modified polyurethane dispersion is proprietary, however, further details about their typical synthesis procedure can be found elsewhere [14]. The constituents were thoroughly mixed using a magnetic stirrer until a homogenous dispersion of the pigments was achieved. Defoamer, thickener and wetting agents, based on siloxane ether copolymers, were added drop wise while keeping on stirring the emulsions. The resulting formulations are reported in Table 1.

2.2. Coating process

The photoluminescent formulations were deposited on commercially available Medium Density Fiberboard (MDF) panels

<table>
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<tr>
<th>Table 1</th>
<th>Full factorial experimental design.</th>
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<td>Factors</td>
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covered with white decorative paper. The panels were cut in slabs, approximately 100 × 100 mm² in order to have surface large enough for practical purposes and improve handling.

The photoluminescent formulations were then applied by spraying and automatic drawdown applicator. Diluted formulations were sprayed using an air-mix spray gun with a nozzle of 0.8 mm using a feeding pressure of ~1.75 bar. During spraying, the gun was keptstatic and the nozzle stand-off distance was 400 mm. This setting ensured the spraying cone was wide enough to invest all of the sample surface and coat it uniformly. Automatic drawdown application was performed setting the bar speed at 0.5 m/min. The amount of material deposited on the substrates was always ~25 ml. Half of the substrates coated by automatic drawdown application were then recoated by commercially available self-drying acrylic-based transparent enamel supplied by Arexons (Petronas Lubricants, Cernusco sul Naviglio, MI, Italy). The enamel was applied as topcoat on the photoluminescent coatings for protection purpose.

After the deposition, the coated substrates were left overnight in a climatic chamber (Binder KBF240; Binder GmbH, Tuttlingen, Germany) at 40 ± 2% Relative Humidity (RH) and 20 ± 0.2 °C temperature for drying purposes.

2.3. Coating characterization

Morphology and visual appearance of the resulting photoluminescent coatings were examined by Field Emission Gun – Scanning Electron Microscope (FEG-SEM Leo Supra 35, Cambridge, UK) using both the secondary electrons (SE) and in-lens detectors and by a contact gauge Taylor Hobson SurfTop System (Taly-Surf CLI 2000, Taylor Hobson, Leicester, UK), using the intermediate range mode (2.3 mm). The morphology of the coatings were measured by probing areas 2 × 2 mm² with a lateral resolution of 2 μm and storing 500 points × mm along the measurement direction. The surface roughness was analyzed by recording a number of patterns (10), each 20 mm long, to cover an area (20 × 5 mm²). The surface waviness was analyzed by recording a number of patterns (10), each 50 mm long, to cover an area (50 × 5 mm²) wide enough to be representative of the entire surface structure. In both cases, 1000 points per mm were stored. TalyMap software Release 3.1 was used to get the roughness parameters and, in particular, the standard amplitude, spacing and hybrid parameters for both waviness and roughness profiles (Gaussian filter, 0.8 mm). The thickness of the photoluminescent coatings was measured using a digital palmer (Mitutoyo IP65, Kawasaki, Japan).

Scratch tests on the photoluminescent coatings were performed using a micro-scale scratch tester (CSM micro-Combi Tester, Peseux, Switzerland). Scratching procedures were carried out with a Rockwell C-type conical indenter with a rounded tip (800 μm tip radius), operating in progressive mode (track 3 mm, scratch speed 1 mm/min, load 100 mN to 5 N) at ~20 °C (±0.2 °C) and 40% (±2%) RH. The photoluminescent coatings were tested at 1 N load (frequency 4 Hz, sliding distance 100 and 500 m, track 3 mm long) of the upper SAE52100 steel ball (6 mm diameter). The surface imaging tool used to study the shape of residual wear pattern after the tribological tests was the Field Emission Gun-Scanning Electron Microscope. Wear rate of the coatings was assessed by the contact probe surface profiler (lateral resolution, 5 μm), measuring the area involved by the action of the counterpart, the wear volume and the minimum and maximum height of the wear pattern as well as the friction coefficient.

The photoluminescence was measured by exciting the surface of the coatings for 1 h under daylight. To avoid any initial excitement, the samples were kept in the dark for at least 48 h before testing. The photoluminescent decay as well as the light emitted were assessed in a darkroom using a high resolution digital camera (Canon D60 macro lens 100F28, Canon Italia, San Donato Milanese (MI), Italy). Images were collected in a time range of 0–15 min and they were analyzed with Image J (NIH, Bethesda, Maryland, USA). Background was subtracted from all the experimental data. For each sample, a constant area was drawn and monitored during the experimental analysis. Performance comparison was done normalizing the emission between 0 (i.e., no emission), and 255 (i.e., maximum emission) and reporting it according to the emission time.

3. Results and discussions

3.1. Coating characterization

The thicknesses were measured over four different locations of the surface of the photoluminescent coatings. Experimental data are summarized in Table 2. The coatings deposited by drawdown applicator were thicker (i.e., 126–226 μm), whilst spraying produced thinner layers of photoluminescent material (i.e., 31–71 μm). As the final purpose was the achievement of uniform coatings as much thinner as possible, spraying was found to be the most respondent technology. The deposition process performed by drawdown applicator required more material to achieve uniform coating. In fact, when lower thicknesses were deposited, surface defects and large inhomogeneity were found as a result of the pigments displacement inside the ‘as-deposited’ coatings. Such defects were then emphasized by the sliding bar which spread them over larger sizes of the surface. Pigments size and concentration had both a major role in determining the final coating thickness.
In particular, an increase in the size of pigments or, less apparently, in the amount of pigments dispersed inside the binder led to a corresponding increase in the thickness.

The size of the pigments was crucial to the thickness as they had to be surrounded by the binder to attain a uniform coating. The silane surface-modified \( \text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+} \) photoluminescent pigments had a good affinity with the silicone-modified 1-pack polyurethane binder. Therefore, when bigger pigments were dispersed inside the resin, much more binder was drained around them and, accordingly, much more binder was necessary to embed them. As a result, thicker coatings were achieved. Differently, the capability of the smaller sized pigments to drain binder around them was lower and thinner coatings were achieved. The pigment concentration had a role in determining the coating thickness, as well. This role was particularly apparent in the coatings deposited by drawdown applicator, where the increase in pigment concentration determined a corresponding increase in the capability of the pigments to drain binder around them and concur to the final coating thickness. In spraying process, this effect was less apparent. This is probably ascribable to the lower amount of material which was deposited by this technology, which limited the relationship between the draining capability of the pigments and their concentration in the formulation.

The protection of the photoluminescent coatings with the acrylic-based topcoat determined a significant increase in the thickness of the final coating system. Increase in the range of 50–100 \( \mu \text{m} \) was measured as reported in Table 2.

### 3.2. Coating morphology

SEM images of the morphologies of some photoluminescent coatings are reported in Fig. 1. The deposition technology, the size and the concentration of the pigments, the thickness of the topcoat were all found to be influential in determining the final morphology of the coatings. The morphology of the coatings deposited by drawdown applicator was found to depend on the pigments involved (Fig. 1a and b). The coating surface is smoother when smaller pigments or lower pigment concentrations are involved. Conversely, large pigments at high concentration lead to bumpier morphology, with big agglomerates distributed over the coating surface. The usage of the acrylic-based topcoat leads to a very smooth morphology (Fig. 1c). Coatings deposited by spraying are characterized by a spikier morphology, with smaller agglomerates distributed over the surface (Fig. 1d).

Figs. 2–4 show the 3D morphological maps. Fig. 2 shows the morphology of the coatings deposited by drawdown applicator. As shown before, the morphology was found to change according to the size and concentration of the pigments. The coating with the large-sized 30 \( \mu \text{m} \) pigments at either 30 or 5 wt.% concentration showed the presence of a highly corrugated texture characterized by individual grains (i.e., the pigments surrounded by the binder) uniformly spread over the surfaces and sticking out from the average areas (Figs. 2a and d). After the deposition process, the pigments were surrounded by the heavy diluted binder. After drying, the solvent part (i.e., water) was evaporated and the binder withdrew leaving the ‘covered’ pigments sticking out from the baseline of the coating morphology. When the lowest pigment concentrations (5 wt.%) were used, less grains stack out from the baseline of the coating surface (Fig. 2d). The corrugation was weaker (Fig. 2b and e) also when smaller-sized pigments were used as in the case of the 15 \( \mu \text{m} \) grain at both 5 and 30 wt.% concentration. In this case, the smaller pigments were easily embedded inside the binder and their influence on the final coating morphology was definitely limited. A special mention deserves the coating characterized by the mixture of the pigments 5, 15 and 30 \( \mu \text{m} \) in diameter. Even in this case, some pigments kept on sticking out from the baseline of the coating surface. Nevertheless, only some of them were clearly visible. In fact, the specific concentration of the large-sized 30 \( \mu \text{m} \) pigments was lower and, therefore, only a small fraction of pigments could stand out from the surface and gave rise to the corrugation.
Fig. 2. 3D map of the morphologies of the photoluminescent coatings deposited by drawdown applicator: (a) 30 μm 30%; (b) 15 μm 30%; (c) 5 + 15 + 30 μm 30%; (d) 30 μm 5%; (e) 15 μm 5%; (f) 5 + 15 + 30 μm 5%.

Fig. 3. 3D map of the morphologies of the photoluminescent coatings deposited by spraying: (a) 30 μm 30%; (b) 15 μm 30%; (c) 5 + 15 + 30 μm 30%; (d) 30 μm 5%; (e) 15 μm 5%; (f) 5 + 15 + 30 μm 5%.

Fig. 4. 3D map of the morphologies of the photoluminescent coatings deposited by drawdown applicator, recoated with an acrylic-based topcoat: (a) 30 μm 30%; (b) 15 μm 30%; (c) 5 + 15 + 30 μm 30%; (d) 30 μm 5%; (e) 15 μm 5%; (f) 5 + 15 + 30 μm 5%.
of the coating morphology (Fig. 2c and f). This is the same phenomenon observed for those samples characterized by the biggest pigment size (30 µm) and the lowest concentration of them inside the binder (5 wt.%). Similar considerations can be drawn in the case of coatings deposited by spraying technology. Although the coating thicknesses were less than the half of those applied by drawdown applicator, the coating morphology was found to be coarser when the biggest-sized 30 µm pigments were used (Fig. 3a and d). The smoothest morphology was achieved when the smallest sized 15 µm pigments were dispersed inside the binder (Fig. 3b and e), with the intermediate scenario being applicable to the mixture of the pigments with the three different mesh sizes (Fig. 3c and f).

The addition of the acrylic-based self-drying topcoat on the photoluminescent coatings deposited by drawdown applicator made the resulting coating systems definitely smoother whatever the investigated scenario (Fig. 4). As a matter of fact, the organic topcoat filled all the gaps among the sticking out pigments, thus giving rise to a flat texture, even flatter than the starting surface of the MDF substrate (Fig. 5).

Amplitude, spacing and hybrid roughness parameters reported in Fig. 6 support the aforementioned results. The usage of the biggest-sized pigments (30 µm) with their highest concentration (30 wt.%) led to large values of the amplitude parameters \( R_a \), and \( R_t \), and slope \( R_{\Delta a} \), especially for coatings deposited by spraying technology (~7 and ~40 µm for \( R_a \) and \( R_t \) and ~16.5° for \( R_{\Delta a} \), respectively). The reduction in pigment concentration from 30 to 5 wt.% determined a decrease in the amplitude parameters and slope regardless the deposition technology. Such decrease was particularly apparent in the case of the coatings deposited by drawdown applicator, with \( R_a \) and \( R_t \) lowering from ~6 and ~18 µm to ~1.5 and ~8 µm and \( R_{\Delta a} \) from ~15 to ~6°, respectively. Under such circumstance, even the spacing parameter \( R_{Sm} \) was heavily affected increasing from ~0.32 to ~0.44 mm. The increase in the spacing \( R_{Sm} \) is related to the different way by which the pigment was dispersed inside the binder at the lowest concentration of 5 wt.%.

In such case, less pigments stack out from the baseline of the surface. Accordingly, the distance among two consecutive pigment peaks or adjoining valleys was increased, thus leading to an enlargement in the spacing.

The usage of the small-sized 15 µm pigments or of the mixture of 5, 15 and 30 µm pigments caused a decrease in the amplitude parameters and slope as well as an increase in spacing in agreement with the aforementioned results. The decrease in the pigment size or in its concentration in the binder caused similar effects. In fact, just a few number of pigments stack out from the baseline and less. This determined: (i) a reduction in the amplitude parameters as they are related to how much the pigments emerge from the baseline; (ii) a reduction in slope which is related to how much an incident light is scattered when projected on a surface and a smoother surface reflect the light better; (iii) an increase in spacing which is related to the distance between two consecutive peaks or adjoining valleys which are closer or farther in strict relation with how much pigments emerge from the coating baseline.

The acrylic-based topcoats caused a significant alteration in all the roughness parameters. The coating surface became smoother as the topcoat filled the gap among the pigments inside the binder. The amplitude parameters \( R_a \) and \( R_t \) went down to less than 1 and 5 µm, respectively. Similarly, the slope \( R_{\Delta a} \) went down to ~5° and spacing \( R_{Sm} \) kept its value pretty low (~ or ~0.3 mm) if compared with the coatings without the topcoat. The hybrid parameter
kurtosis $R_{ku}$ was found to increase whatever the deposition technology, thus indicating that the deposition of the coatings tends to generate a morphology which is distributed more evenly around the centre line. In addition, the hybrid parameter skewness turned in most of the cases positive from the negative values typical of the uncoated substrate. This result can be ascribed to the prevalently spiky or bumpy morphologies induced by the coatings filled with the photoluminescent pigments sticking out from the centre area of the surface. Such morphologies substituted the starting morphology of the uncoated substrate characterized by many voids and porosity typical of the MDF panels. The trend of hybrid dimensionless parameters $R_{sk}$ and $R_{ku}$ deserves a special mention in case of the coating systems involving the acrylic-based topcoat, pigments 30 $\mu$m in diameter and concentration of 30 wt.%. In such case, $R_{sk}$ and $R_{ku}$ measured on topcoat approached very large values. The highest value of $R_{ku}$ can be related to the good distribution of the profile very close to the centre line of the surface as a result of the pretty flat morphology. The highest value of $R_{sk}$ can be related to the symmetry of the profile, characterized by few peaks and large valleys located below the centre line of the surface, thus emphasizing the overall smoothing effect on the morphology of the topcoat.

3.3. Analysis of the scratch response: progressive load

Figs. 7–9 report the trends of the penetration and residual depth increasing the load from 0 to 5 N during the progressive load scratch tests. Whatever the investigated scenarios, the trends of the penetration depth follows nearly linear branches, with a faster increase in the penetration depth according to the normal force only at the beginning of the scratch tests (i.e., at very low load). Similarly, the residual depth trends follow linear branches, although, at very high load, there is a sudden decrease of the residual depth. This can be ascribed to the accumulation of some coating materials at the very last contact position between the advancing indenter and the coating surface during the progressive load scratch tests. This phenomenon is known as pile-up [15] and it is related to the displacement of coating material by plastic deformation (micro-ploughing mechanism). Comparing the maximum penetration depths among the photoluminescent coatings deposited by both automatic drawdown applicator and spraying with the 30 wt.% pigment concentration and those with the 5 wt.%, it is possible to emphasize how the latter coatings are apparently more penetration resistant (Figs. 7–8). Coatings deposited by spraying are characterized by smaller values of the maximum penetration depths, but this is the result of the starting coating thickness rather than of the intrinsic stiffness of the coatings themselves. As a matter of fact, the coatings deposited by spraying are definitely thinner than the coatings deposited by automatic drawdown applicator. Being the coatings deposited by spraying thinner means that the substrate surface is closer to the indenter tip during the progressive load scratch test. This induces an increase in the stiffness of the overall substrate–coating system and, accordingly, lower value of the maximum penetration depth. However, the crucial role of the substrate in determining the deformation response of polymeric coating was well known since early studies on thermo-mechanical behaviour of
organic materials [16] and, later on, in more specific analysis which Barletta et al. led on epoxy-polyester powder coatings deposited on micro- and macro-corrugated substrate as well as on silicon-based release layer [17].

The coatings with the protective topcoats exhibited a different response. In fact, such coating systems are so thick that the effect of the pigment concentration is pretty small and it does not affect significantly the maximum penetration depth during the progressive load scratch tests. Contrarily, the increased thickness makes the system composed by the underlying photoluminescent coatings and the topcoats even less stiff and, therefore, subject to higher deformation during the application of the load and, accordingly, to corresponding higher values of the maximum penetration depths (Fig. 9).

The trends of the penetration depth of the coatings deposited by spraying are very close to those achieved by automatic drawdown applicator without topcoat. They are influenced by the pigment size. When large-sized pigments (30 μm) are dispersed inside the binder, the penetration depth trends are characterized by several irregular jumbling (Fig. 7a, b and e, Fig. 8a, b and e) along the sliding distance (i.e., at the different values of the applied normal loads). Such jumbling can be ascribed to the interaction between the advancing indenter tip and the pigments in the binder according to the model proposed by Jardret and Morel, first, in their studies on the scratch resistance of polymers [15] and, later on, by Jiang et al. in their studies on the establishment of the fish-scale mechanism in the polymers [18]. The indenter tip penetrates inside the coatings and it comes in touch with the pigments. In particular, the compressive stress field which is generated ahead of the advancing indenter compresses the pigments towards the binder around them. The pigments are abrasive and when they are pushed towards the coating material by the advancing indenter, they can act as cutting tools, thus contributing to cut away the softer binder. Moreover, the presence of the pigments along the sliding distance hinders the movement of the sliding indenter, which is forced to overcome the pigments, thus generating further irregularity in the penetration depth trends. When the small sized 15 μm pigments are used, the jumbling phenomenon is strongly reduced (Figs. 7c, 8c). The pigments are smaller and they interact less with the advancing indenter tip and with the binder around them. The resulting effect is the formation of smaller jumbling events, that is, the formation of peak-valley features characterized by a smaller amplitude and larger spacing. Such effect is further reduced when the pigment concentration is lowered at 5 wt.% (Figs. 7d, 8d). The effect of concentration is easily understandable by watching the trends of the penetration depth in Figs. 7f, 8f and comparing them with the analogous trends in Figs. 7e, 8e. Such trends refer to the coatings in which mixture of pigments 5, 15 and 30 μm in diameter are dispersed inside the binder at 5 and 30 wt.% concentration. As said before, at the highest concentration the part of pigments 30 μm in diameter plays an important role and generates the jumbling phenomenon. When their concentration is strongly reduced at 5 wt.%, the jumbling phenomenon is extremely reduced, as the possibility of interactions between the advancing indenter tip and the biggest pigments is very low.

The residual depth trends are expression of the penetration depth trends. After the load is removed, the coating material recovers part of the deformation. Yet, it keeps on taking memory of the jumbling phenomenon. The effect of plasticization at the end of the scratch patterns is, at a certain extent, correlated with the pigment concentration, as well. Coatings involving higher pigment concentrations are characterized by bigger plastic pile-up at the end of the scratch pattern. This result can be ascribed to the coating thickness that the higher pigment concentration determines rather than to the massive presence of pigments inside the coating material. In fact, thicker the coating less stiff the overall coating system results (i.e., the stiffer substrate surface is farther from the indenter tip during the progressive load scratch test and the coating system is more compliant to accommodate the advancing indenter along its pattern). The coating material is therefore more prone to plasticize and gives rise to bigger pile-up formation at the end of the scratch pattern.

A special mention deserves the trends of penetration and residual depths measured for the coating system involving the topcoats. As said before, the trends of the penetration depth are very smooth and almost linearly increasing whatever the pigment size and concentration. Yet, the residual depth trends are very different and they seem to strongly depend on the pigment concentration. Whilst the coatings characterized by a pigment concentration of 30 wt.% present a pretty smooth residual depth trends, the rest of the coatings, characterized by a pigment concentration of 5 wt.%, presents uneven trends. The difference can be ascribed to the stiffness of the photoluminescent coatings on which the acrylic-based topcoat is deposited. In the former case, the underlying coatings sustain better the topcoats as a result of the large amount of pigments dispersed in the binder, which confer compactness to the overall coating system. Accordingly, the topcoats do not fail after the release of the load at the end of the progressive load scratch tests. In the latter case, the low amount of pigments inside the underlying photoluminescent coatings does not explicate a sufficient sustaining action of the topcoats. The overall coating system is less compact. Therefore, once the load is released, the topcoats broke in a brittle way, as witnessed by the residual depth trends and the corresponding SEM image (Fig. 10).

The difference in the residual depth trends in Fig. 9 among coatings characterized by high and low pigment concentration can be also the result of interfacial adhesion between the acrylic-based topcoats and the underlying photoluminescent coatings. At high pigment concentration, a sort of mechanical coupling or interlocking (hook and eye) adhesion mechanism between the underlying coatings and the topcoats can be claimed [19,20]. This mechanical interlocking is favoured by the angular geometry of pigments as well as by the coarseness of the morphology of the underlying layers. In fact, at high pigment concentration, the photoluminescent coatings are substantially rougher and this simplifies the anchoring between the topcoats and the underlying layers. At low pigment concentration, such effect is definitely limited as a result of fewer amounts of pigments dispersed inside the binder. The low amount of pigments ensures a limited number of anchoring points between the topcoats and the underlying layers, thus making less...
favouring their mechanical matching. Similarly, the photoluminescent coatings characterized by low pigment concentration have a substantially smooth morphology, which, once more, is not favouring the anchorage between the topcoats with the underlying layer.

In addition to mechanical coupling, molecular bonding among the silane surface-modified SiAlO2:Eu²⁺, Dy³⁺ photoluminescent pigments and the silicone-modified 1-pack polyurethane binder could be inferred [19,21]. Accordingly, higher the pigment concentrations inside the binder higher should be the chemical affinity between the binder and pigments themselves.

Although the current debate about mechanical adhesion between polymers and interfaces involves a share of researchers believing that mechanical coupling provides higher adhesion strength and the rest of researchers believing that cosponding of the surface is just increasing the contact area for more molecular bonding interactions, the increase in the contact surface at the polymer/filler or substrate interface is often found to be useful to promote better adhesion apart from the basic mechanisms implicated [22].

3.4. Analysis of the wear response

The analysis of the tribological behaviour of the photoluminescent coatings is summarized in Fig. 11. The wear volume after 100 and 500 m sliding distance is reported for all the application technology, pigment size and concentration. Coatings deposited by spraying are characterized by the lowest wear volume. This is probably related to the superior stiffness showed by such coating class, which was ascribed to the smaller thickness and to the proximity of the coating surface with the substrate. The stiffer substrate being closer to the coating surface is able to sustain better it against the action of the counterpart during the tribological tests and determines a better wear endurance in agreement with the pertinent literature [23]. Lack of stiffness of the photoluminescent coatings deposited by automatic drawdown applicator and, at a greater extent, of the coating system composed by the photoluminescent coatings and acrylic based topcoat determines a bigger wear rate and volume. Under these circumstances, the coating surface is far from the substrate surface, which is not able to ensure extra-rigidity to the coating system. Accordingly, the counterpart can be more invasive and removes much more material from the coatings during the tribological tests.

Pigment concentration is influential in determining the wear endurance of the photoluminescent coatings, too. Lower the pigment concentration better the wear response is found to be. The pigments are extremely hard. When the coating surface comes in contact with the counterpart, the pigments contained inside the binder are quickly removed and slide between the surface and the counterpart itself. Accordingly, loss of material takes place quickly as a result of three-body abrasion mechanism. Abrasive wear is very efficient to determine material removal from the photoluminescent coatings and when the pigment concentration inside the binder is very high, the material removal is very fast, too. Reducing the amount of pigment inside the binder means less efficient wear by abrasion and, therefore, slower material removals by abrasive wear. Finally, pigment size seems to have a minor role in determining the wear rate. This is particularly true when thicker coatings deposited by automatic drawdown applicator are considered. In those cases, the pigments are completely embedded inside the binder and they come in contact with the counterpart inducing abrasive wear after comparable time span. The situation of the coatings deposited by spraying is different. The lower coating thickness of such samples causes the large sized pigments to come in touch with the counterpart from the beginning of the tribological tests. Despite this should activate abrasive wear, the large-sized pigments seem to confer extra wear endurance to the coatings. This can be probably due to the counterpart response, which, coming in touch from the beginning of the tribological test with the hard and tough pigment, is quickly abraded. The contact surface between the counterpart and the coating surface becomes quickly flatter as a result of the abrasion, the contact pressure decreases and the wear rate goes correspondingly down.

3.5. Analysis of the optical property

The photoluminescent intensity of the investigated coatings is reported in Fig. 12. Coatings deposited by drawdown applicator are characterized by the highest photoluminescent intensity. The application of an acrylic-based topcoat was found to reduce the photoluminescent intensity of the overall coating system. The worst photoluminescent performance characterizes the coatings deposited by spraying. The better effectiveness of the coatings deposited by drawdown applicator is related to the coating thickness. Being the thickness higher, much more pigments are dispersed on the coating surface and, accordingly, more powerful the photoluminescence results to be. Coatings deposited by spraying
are thinner. Less pigment is dispersed inside the coating surface and the photoluminescent power is reduced. Differently, the usage of the acrylic topcoats reduces the photoluminescent potential as they interpose a barrier between the photoluminescent coating and the actual coating surface.

The photoluminescent intensity is found to be a function of the pigment size and concentration. Obviously, an increase in pigment size and concentration reflects in a significant increase in the photoluminescent potential of the coatings regardless the deposition technology [11,24,25]. Coatings which include the large sized 30 µm pigments and the mixture among 5, 15 and 30 µm pigments present the highest photoluminescent intensity. In the former case, the good results can be ascribed to the size of the pigments which, as well known in the pertinent literature, express their best photoluminescent potential with the increase in their diameter. The mixture of the pigments with the three different mesh sizes behaves efficiently. In fact, the pigments with the different sizes combine well in closing all the gaps of the surface, which is uniformly photoluminescent. Despite, the lower average dimension of the pigment, their good geometrical matching confers extra photoluminescent power to the coatings, which perform efficiently.

The photoluminescent decay is summarized in Fig. 13. The decay time is pretty short (i.e., only 10 min) as the excitation time used was very short (i.e., just 1 h under solar light). This is probably related to the superior stiffness showed by such coating class, which was ascribed to the smaller thickness and to the proximity of the coating surface to the substrate.

4. Conclusions

- The development of photoluminescent formulations, the analysis of the related deposition processes as well as the characterization of the mechanical and optical performance of the resulting coatings were the matter of the present investigation.
- Based on the experimental evidence, the following conclusion can be draw:
  - The approach to the deposition of uniform layer of photoluminescent material on the substrate surface influences the minimum thickness of the photoluminescent coatings: coatings deposited by automatic drawdown bar result to be always thicker than coatings deposited by spraying whatever the pigment size and concentration;
  - Pigment size and concentration are very influential in determining the morphology of the photoluminescent coatings. Bigger the pigment size and higher its concentration inside the binder, coarser is the corresponding morphology. The usage of the acrylic topcoats fills the gap among the pigments inside the binder and gets to smoother morphology;
  - Pigment size and concentration were found to influence significantly the scratch response of the photoluminescent coatings, as well. In particular, the biggest pigment at the highest concentration contribute to coating failure as a result of their compression towards the softer binder pushed by the advancing indenter;
  - Photoluminescent coatings deposited by spraying are apparently more scratch resistant. Such extra scratch resistance is conferred to those coatings from their thinner thicknesses. Under such circumstances, the substrate is closer to the coating surface and with its stiffness contribute to sustain better the coating against the penetrating indenter;
  - The acrylic topcoats are subject to the highest deformation under the action of the indenter tip during the progressive load scratch tests. After the release of the load, the system characterized by the lowest pigment concentration exhibits brittle failure which was ascribed to the minor capability of the underlying layer to sustain the topcoat when filled with a lower concentration of pigments and, above all, to the poor mechanical interlocking and molecular bonding between the photoluminescent underlying layers and the topcoats due to the limited number of anchoring points available (i.e., the pigments present low concentration);
  - Coatings deposited by spraying are characterized by the lowest wear volume. This is probably related to the superior stiffness showed by such coating class, which was ascribed to the smaller thickness and to the proximity of the coating surface to the substrate.
  - The lack of stiffness of the photoluminescent coatings deposited by automatic drawdown applicator and, at a greater extent, of the coating system composed by the photoluminescent coatings and acrylic based topcoat determines a bigger wear;
  - Pigment size and concentration influence the tribological response of the coatings. The pigments are removed from the binder by the action of the counterpart during the tribological tests and activate material removal by abrasive wear. Higher the pigment size and concentration quicker is generally found to be the corresponding wear rate;
  - Photoluminescent intensity was found to be correlated to the amount of pigments deposited on the substrate surface as well as to their size and concentration. Photoluminescent decay was found to be independent on deposition technology and strongly related to pigment size and concentration.
References


