Luminescent polyurethane composite with real-time thermal response via visible signal

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Abstract
Visible signals are vital to human communication. Thermal signals are often difficult to observe unless they are in physical contact with the subject or an infrared thermal imaging system is used. In this study, we prepared a luminescent polyurethane composite (LPC), which can intelligently alter its colour and luminescence based on temperature. The LPC is fabricated from rare-earth luminescent materials (Sr₂ZnSi₂O₇: Eu²⁺, Dy³⁺ and Y₂O₂S: Eu³⁺, Mg²⁺, Ti⁴⁺), a heat-sensitive rose-red TF-R1 thermochromic pigment (TP), polyurethane (PU), and polyester fabric. Microstructure and crystal structure analyses were carried out to determine the basic material properties of the LPC. The reflectivity and K S values under different temperatures indicate that blue and green light were absorbed by LPC at 25 °C and the absorption decreased at 45 °C. This results in the LPC turning white. The emission spectra demonstrate that the quinoid structure of TP blocked the light of Sr₂ZnSi₂O₇: Eu²⁺, Dy³⁺. Meanwhile, the lactone structure of TP allowed the light emission of Sr₂ZnSi₂O₇: Eu²⁺, Dy³⁺ and Y₂O₂S: Eu³⁺, Mg²⁺, Ti⁴⁺. As a result, LPC emits red light at low temperatures and blue light at high temperatures. The advantage of the fabricated LPC is that the output can be easily manipulated into patterns. The uncured PU could form various graphics to cooperate with visible signals. Therefore, the LPC has significant potential as a functional material in smart clothing, flexible electronics, and wearable devices.

1. Introduction

Visible signals are one of the most important communication methods, not only for humans, but also in nature to track prey, deter predators, and attract mates [1]. The ability of animals, such as cephalopods and jellyfish, to change their appearance by changing their colour, light, and geometry, inspired researchers to develop soft, smart materials that are capable of responding to changes in ambience [2, 3]. Therefore, smart materials that can exhibit changes in colour, light, or geometry have attracted significant research interest. Functional fabrics, which have soft mechanical properties, have been used to create smart clothes and intelligent devices that can interact safely and effectively with humans [4]. Sensing materials can exceed human sensory capabilities to perceive invisible signals, such as thermal signals [5, 6]. Hence, thermochromism is an effective strategy to render visibility to thermal signals, thus promoting the intelligence of the fabric [7, 8]. It exhibits potential for expanded usage in smart skin for robots and wearable electronic clothing [9, 10].

Rare-earth phosphors are exceedingly important luminescent materials that are widely used in electroluminescent and photoluminescent products [11, 12]. The high-energy storage efficiency of rare-earth phosphors is ascribed to the special 4f and 5d electronic orbitals of rare-earth ions [13–15]. Sr₂ZnSi₂O₇: Eu²⁺, Dy³⁺ (SZSOED) and Y₂O₂S: Eu³⁺, Mg²⁺, Ti⁴⁺ (YOSEMT) are outstanding blue and red phosphors, respectively, because of their excellent initial brightness and long afterglow [16, 17]. The europium ion usually serves as an activator in the phosphorescence system [18]. These two phosphors are endowed with long-lasting...
luminescent properties by co-doping with dysprosium or other metal ions. Therefore, the afterglow of SZSOED and YOSEMT can be detected by the human eye for several hours after only a few minutes of excitation [19].

Among the coating materials, polyurethane (PU) is an excellent soft material used in several commercial and industrial fields, such as coatings, adhesives, textile size, and leather [20, 21]. It can be easily combined with functional particles to fabricate soft functional materials [22]. Luminescent PU is a common material made from rare-earth phosphors [23]. PU is an ideal material to load SZSOED, YOSEMT, and TP because of its adjustable viscosity and ease of processing. Thermochromic luminescent polyurethane (TLPU) is the most suitable material to combine with all types of fabric, as it exhibits superior adhesion for the fabrication of flexible composites [24].

Rare-earth phosphors have been developed for numerous interesting and practical functions, for example, as an anti-fake material [25], in solid-state lighting applications [26], and as a biomedical drug [27]. However, the emission spectra or colour of conventional phosphors cannot be shifted or changed. There are numerous strategies to achieve a change on colour. The development of novel systems based on thermochromic materials with phosphors is an effective strategy to induce shifts in the emission spectra [28]. A suitable design would allow this system to convert thermal signals to visible luminescence signals. Moreover, thermochromic PU could alter the colour of the luminescence [29]. The three components of thermochromic materials include fluoror as a leuco dye, weak acids as colour developers, and alcohols as solvents. These components determined the colour-changing temperature [30]. They can be mixed to form a reversible thermochromic system, where the thermochromic reaction is triggered by the interactions of these components. The colour developer is an electron acceptor compound, while the leuco dye is an electron donor. Typically, the complex is coloured because the leuco dye has a quinoid structure below the melting point of the solvent [31]. Colour change always occurs at the melting temperature of the solvent. When the solvent melts, the leuco dye and colour developer complex is destroyed; the leuco dye changes to the lactone structure, and the system acquires a natural colour [32].

This study aims to fabricate and assess a material that can respond to thermal inputs by changes in colour and luminescence. We exploited the thermal behaviour of the rose-red TF-R1 thermochromic pigment (TP) and incorporated TP into luminescent polyurethane composite (LPC). Moreover we explored the influence of the TP on the colour and luminescence signals. This research could have significant contributions toward wearable devices and e-skins for robotics. The study also investigates visual graphics using the fabricated LPCs, which could also have broad industrial and commercial applications.

2. Materials and methods

2.1. Raw materials

SrCO₃, ZnO, SiO₂, Eu²⁺, Dy³⁺, Y₂O₃, S, TiO₂, MgCO₃·6H₂O, and Na₂CO₃ of analytical reagent grade were used as the starting materials and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Polyurethane (PU) was purchased from Milanduo Co., Ltd. (Hong Kong, China). Polyester fabric was purchased from Kangfuding Technology Co., Ltd. (Shenzhen, China). Commercial TP with a thermochromic temperature of 44 °C was purchased from Shenzhen Aobo Co. Ltd. The main component of TP is heat-sensitive rose-red TF-R1 fluorane (TF-R1).

2.2. Preparation of rare-earth phosphors

Sr₁.₉₅ZnSi₂O₇: Eu²⁺₂⁻, Dy³⁺₀.₃ and Y₂O₃:S: Eu³⁺₀.₄₄Mg²⁺₀.₅₅Ti⁴⁺₀.₃₅ were synthesised via a high-temperature solid-state method. After preliminary milling, the raw materials were respectively dissolved in appropriate amounts of absolute ethanol. This was followed by ultrasonic dispersion for 30 min and mechanical mixing for 30 min to obtain a homogeneous mixture. The samples were heated by adding flux (the ratio of H₃BO₃ to Sr₁.₉₅ZnSi₂O₇: Eu²⁺₂⁻, Dy³⁺₀.₃ was 10 mol. %; the ratio of Na₂CO₃ to Y₂O₃:S: Eu³⁺₀.₄₄Mg²⁺₀.₅₅Ti⁴⁺₀.₃₅ was 20 mol. %) to a high temperature of 1300 °C for 3 h in a reducing atmosphere. The sintered products were re-milled in ball mill and sieved with a 600 mesh to obtain the desired size.

2.3. Preparation of LPC

SZSOED, YOSEMT, and TP were added in PU to prepare the pre-coating solution. SZSOED and YOSEMT were uniformly mixed in PU by the mass ratios of 4% and 6% respectively. TP was added in quantities of 5 wt%, 10 wt%, 15 wt%, and 20 wt% to PU. The prepared TLPU was applied to the fabric evenly and dried at 60 °C for 1 h to obtain the LPC. The samples containing 5 wt%, 10 wt%, 15 wt%, and 20 wt% TP were labelled as LPC 5, LPC 10, LPC 15, and LPC 20, respectively. The preparation scheme is shown in figure 1(a).
2.4. Characterisation

The microstructures of the LPC were examined using a Hitachi TM3030 scanning electron microscope. X-ray diffraction (XRD) patterns were obtained using Bruker D8 Advance (Bruker, Germany). Reflectivity measurements were carried out using a Macbeth Colour-Eye 7000A spectrophotometer. The emission spectra were obtained using a fluorescence spectrophotometer (FS5 Fluorescence Spectrometer, Edinburgh Instruments). The samples were excited at a wavelength of 365 nm for 5 min using a handheld UV lamp (20 W) before the tests; the slit used was 2 nm wide. The excitation wavelengths were in the range of 400–700 nm; the dwell time was 0.2 s. Afterglow decay curves were obtained using a PR-305 afterglow brightness metre by exciting the samples at 1000lx for 15 min. The decay curves of SZSOED and YOSEMT were obtained at 25 °C, while the decay curves of LPC 10 were obtained at 25 °C and 45 °C.

3. Results and discussion

3.1. Concept of luminescent polyurethane composites

Figure 1 (a) illustrates the process of preparation of the LPC, as well as its structure. We used mixtures of SZSOED and YOSEMT because blue-violet light and red light are easily distinguishable. The materials were chosen based on a previous study, on account of their superior properties, such as viscosity, ease of processing, and luminescence performance [14, 22]. TP can interact with light of Rare-earth phosphors to achieve a reliable visible signal that is easy to identify. Heat triggers a change in the visible absorption of TP, which acts as a luminescence signal conversion species. This leads to a change in the observed phosphorescence of LPC.

Figure 1 (b) displays the microstructure of TP, SZSOED, YOSEMT, and LPC. Most of the spherical TP microcapsules exhibited diameters <10 μm. The particle sizes of SZSOED and YOSEMT were larger than those of TP, with distinctly different shapes. The geometry of SZSOED was cuboid-like, with an average diameter of approximately 30–40 μm. YOSEMT was irregularly shaped, with an average diameter of approximately 15–25 μm. The blend of TP, SZSOED, and YOSEMT exhibited significant effects on the morphology of the LPC. The surface of LPC was found to be exceedingly rough. Furthermore, some particles were exposed and formed nodules, while most of them remained buried in the PU.

Figure 1 (c) illustrates the XRD patterns of TP, SZSOED, YOSEMT, and LPC. The diffraction peaks of SZSOED and YOSEMT belong to space groups P-421 and P-3m1 and were ascribed to tetragonal and hexagonal crystal systems. The XRD patterns of SZSOED and YOSEMT were in good agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) database. This indicates that the co-doped ion only
occupies the chemical substitutional sites of the alkaline earth metal oxide, and does not disturb the crystal structure of SZSOED and YOSEMT. The characteristic peaks of TP, SZSOED, and YOSEMT were identified in the XRD pattern of LPC. These results demonstrate that TP, SZSOED, and YOSEMT maintain steady crystal phases after the milling and spinning processes. This indicates that there is no apparent chemical interaction of TP, SZSOED, and YOSEMT in the crystal structure.

3.2. Thermal response via colour signal

There are numerous types of fluoran pigments that can output colour signals in response to temperature \[19, 33\]. However, TP is an ideal species for the colour conversion of light. We sought to demonstrate the thermochromic mechanism of TP under ambient light (figure 2(a)). In an ambient environment, the TP turns white upon sufficient heating. The results indicate the triggering temperatures of thermochromism. Moreover, the temperature of thermochromism is determined by the melting point of the TP. Therefore, there are many different commercial pigments available with a wide range of colour-changing temperatures \[7\]. The melting solvent can drive TF-R1 to accept protons. Therefore, TF-R1 transforms the chemical structure from a quinoid to a lactone structure. Theoretically, TF-R1, being a proton donor, loses a proton and the opened lactone ring goes into a sp2 hybrid orbital. After heating, the central carbon atom of the spiro forms sp3 hybrid orbitals with the other carbon atoms. The absorption of the TF-R1 blue shifted to the ultraviolet band, and the white lactone structure was observed at 45 °C (figure 2(b)). This indicates that TF-R1 TP serves as a real-time thermal response material and output colour signal.

Figure 2 (b) also displays the reflectivity curves of LPC 10, which reveal the colour signal of the LPC under different temperature conditions. It can be observed that the reflectivity curves of LPC are similar to those of TP. The quinoid TP corresponds to the LPC at 25 °C and the lactone TP corresponds to the one at 45 °C. The LPC reflects most of the wavelengths ranging from 600 nm to 700 nm, regardless of the temperature. This indicates that LPC does not absorb the red waveband, regardless of whether TF-R1 is discoloured. However, the blue and green wavebands are almost completely absorbed at 25 °C. Consequently, LPC exhibits a red colour at 25 °C and changes to white at 45 °C (figure 2(b) inset). Therefore, it is inferred that the TP content has an evident effect on...
the reflectivity of LPC. The reflection of LPC changes slightly in the red band. Thermochromism is mostly induced by the change in the blue and green bands.

The $K S^{-1}$ of LPCs with different contents of TP are calculated in figure 2(c) to demonstrate the effect of TP content on the colour depth. A larger $K S^{-1}$ implies a deeper colour. The equation of $K S^{-1}$ value is as below:

$$K S^{-1} = \frac{(1 - 0.01R)^2}{2(0.01R)}$$

where $R$ is the reflectivity, $S$ is the scattering coefficient and $K$ is the absorption coefficient. It is evident from figure 2(c) that temperature has a significant effect on colour. The colour at 45 °C is significantly lighter than that at 25 °C. The sample with a higher TP content exhibits strong absorption. This indicates that high TP content can make the LPC darker. However, there is negligible overall difference in the colours. The CIE 1931 chromaticity coordinates of the LPCs at 25 °C, are LPC 5 = (0.5238; 0.3104), LPC 10 = (0.5318; 0.3081), LPC 15 = (0.5423; 0.3121), and LPC 20 = (0.5502; 0.3021). Furthermore, hot water was poured on the LPCs and the thermochromic phenomenon was recorded. The results demonstrate that the LPC can respond to heat in real-time via easily observable colour signals. (Video S1).

3.3. Thermal response via luminescence signal

To evaluate the luminescence performance of LPC, we studied the emission spectra of SZSOED and YOSEMT (figure 3(a)). From the emission spectra of SZSOED and YOSEMT, it is evident that the emission peaks of SZSOED at 470 nm are generated by the representative $^4F_0$ to $^5D_1$ transition from Eu$^{3+}$. The emission peak of Dy$^{3+}$ is not observed because Dy$^{3+}$ is the co-doping ion that generates the hole trap to improve afterglow. The red emission of YOS comprises several significant emission peaks generated from the $^5D_0 \rightarrow 7F_J$ transitions of Eu$^{2+}$ and the $^5D_0 \rightarrow 7F_J$ transition of Eu$^{3+}$. Mg$^{2+}$ and Ti$^{3+}$ act as assistive ions, which significantly promote the afterglow of YOSEMT.

The afterglow decay curves of SZSOED and YOSEMT at 25 °C are shown in figure 3(b). The afterglow decay curves of LPC 10 at 25 °C and 45 °C were also included to demonstrate the effect of TP on the afterglow. From the results, we can observe that the decay trend of the LPC is that of conventional exponential decay. This indicates that TP did not change the decay law of SZSOED and YOSEMT. It can be observed that the decay curve of LPC at 25 °C is close to YOSEMT. This is because the quinoid TP is beneficial for transmitting red
luminescence. However, quinoid TP still blocks some of the light energy. Therefore, the intensity of LPC at 25 °C is slightly lower than that of YOSEMT. In contrast, the decay curve of LPC at 45 °C is exceedingly similar to SZSOED. In this case, TP has a lactone structure that has a high reflection, to transmit blue and red light. However, the initial intensity of LPC is higher than SZSOED, and the decay rate is faster. This result can be ascribed to the temperature, because electron transitions are faster at high temperatures.

To demonstrate the response of the luminescence signal to heat, figure 3(c) exhibits the emission spectra of LPC 10 at 25 °C and 45 °C. The emission peak at 450 nm was generated from SZSOED. It can be observed that there is a 20 nm blue-shift of the blue peak. The blue luminescence is shifted by TP when it is transmitted in PU. At 25 °C, most of the blue luminescence from SZSOED was blocked by quinoid TP. When the temperature was raised to 45 °C, the lactone ring was closed, and the reflection drastically increased. In this case, the blue luminescence from SZSOED was emitted. The emission peak in the blue band is significantly more intense. Figure 3(d) exhibits the intensity of the peaks at 450 nm and 626 nm under different temperature conditions. The different contents of the TP have different results. It can be observed that the intensity of the peak declines as the TP content increases. This indicates that more TP leads to stronger luminescence colour conversion. The change in the emission spectrum can lead to a change in light colour. The CIE 1931 chromaticity coordinates of LPC 10 at 25 °C and 45 °C are (0.4504; 0.2985) and (0.2494; 0.2193), respectively. Red and blue-violet are easily distinguishable colours; hence, the colours of the luminescence signal are easy to perceive (Video S2).

3.4. Graphic design of LPC

The most outstanding advantage of LPCs is that they are easily manipulated into visual graphics. We used a conventional silk screen to pattern TLPU (figure 4(a)). Uncured TLPU is outflowed from the top layer of the screen and is patterned to the designed graphics. The text signal 'luminescence' was patterned on the fabric. From figure 4(a), it can be observed that the heated letters of 'lumine' emit blue light and the letters of 'scence' are red. Graphic signals are frequently used in day-to-day life and can contain a lot of information. For example, the two-dimensional code of Jiangnan University, in figure 4(b), demonstrates the output with multiple visual signals. These graphics emit different colours, and the luminescence signal depends on the temperature. Here, we only exhibited a limited number of examples; however, many more academic and commercial applications can be accessed using this strategy.

4. Conclusions

This study proposed the fabrication of LPC, which can be used to indicate temperature via change in colour. The LPCs comprise SZSOED, YOSEMT, PU, and TF-R1 TP. REPs formed uniform dispersions in PU, and the crystal structure of TF-R1 TP was stable. The LPC emits red luminescence at 25 °C, because the quinoid structure of
TF-R1 TP can block the light of SZSOED at low temperatures. At high temperatures, the lactone structure of TF-R1 facilitated the transmission of blue light. Therefore, the heat-triggered chemical structure change of TF-R1 allowed the visual response of the LPC with a change in the external temperature. The incorporation of TF-R1 TP, SZSOED, and YOSEMT enabled the LPC to serve as a real-time thermal indicator for temperature sensing applications by transforming the information from heat to a visible signal. LPC is an ideal material to obtain graphic signals and can emit the luminescence signals without external equipment for several hours. The concept of LPC is particularly interesting because it enables the simultaneous output of colour, luminescence, and graphic signals. Therefore, the LPC has potential for use as e-skins in soft robots, prosthetics, and wearable devices.

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Data availability statement

All data that support the findings of this study are included within the article and any supplementary files.

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