Biodegradable Polylactide/Rare Earth Complexes in Light Conversion Agricultural Films

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Abstract: Rare earth luminescent material CaAlSiN$_3$:Eu$^{2+}$ (CEu) was applied and modified with (3-Aminopropyl) triethoxysilane (KH550) to obtain two types of rare earth conversion agents, CEu and KH550-modified CEu (KCEu). Two kinds of polylactide (PLA) conversion films were successfully prepared through solution blending. The results showed that the addition of rare earth complex increases the crystallinity of PLA. More importantly, both PLA/CEu and PLA/KCEu films showed good red-light conversion ability, which can accelerate plant growth.

Keywords: rare earth; PLA; light conversion film; Eu

1. Introduction

Sunlight consists of various types of light of different wavelengths, but only 380–750 nm is efficient for plants’ photosynthesis. The biggest contribution is red light around 600–700 nm, which is beneficial to the synthesis of starch and soluble sugar, and can accelerate the development of plant stem nodes [1–3]. Agricultural light conversion film is obtained by adding specific light conversion materials to the traditional film, which can convert high-energy ultraviolet (UV) light into low-energy short length visible light to promote plant growth [4].

However, nearly all agricultural conversion films are non-degradable polyolefin, the residue of which has a large impact on soil quality and hinders plant growth. Biodegradable agricultural films can be composted or ploughed into the soil after use, which can then be degraded by microorganisms into the nutrients needed for crops [5]. Polylactide (PLA) has good biodegradability, biocompatibility and transparency, and is expected to replace non-degradable polyolefin in the application of light conversion agricultural film [6,7].

At present, the main types of light conversion agents include metal sulfide, metal nitride, organic dyes, and rare earth complexes [8,9]. The luminescent complexes of europium (III) are promising because of its strong light absorption ability and high conversion efficiency [10]. CaAlSiN$_3$:Eu$^{2+}$ (CEu) has been considered as one of the most promising red phosphors, owning to the wide absorption and emission band in the UV-visible range, high efficiency, and high thermal and chemical stability [11]. Research in this area has focused on the development of various rare earth complexes, with little attention to biodegradable polymers. In any case, the study of biodegradable light conversion film can not only increase plant production and farmers’ income, but also ease environmental problems.

2. Materials and Methods

Materials. The applied PLA (grade 4032D, NatureWorks LLC, Minnetonka, MN, USA) was dried in a vacuum oven at 60 °C for 24 h before use. The ethanol, CH$_2$Cl$_2$, and KH550...
were bought from Admas LLC (Shanghai, China). The red phosphor CEu was supplied by Grirem Advanced Materials LLC (Beijing, China). KCEu was prepared with CEu grinding with 2 wt.% KH550 and 6 wt.% ethanol.

Sample preparation. A 5 g quantity of PLA was dissolved in 50 mL CH$_2$Cl$_2$, then a certain amount (0.2 wt.%, 0.5 wt.%, and 1 wt.%) of CEu and KCEu was mixed in the solution, respectively. After solvent evaporation, the PLA/CEu, and PLA/KCEu composites were prepared and labeled as PLA; PLA/CEu-0.2, PLA/CEu-0.5, PLA/CEu-1; PLA/KCEu-0.2, PLA/KCEu-0.5, PLA/KCEu-1. The composites were further hot-pressed under 40 MPa for 5 min to obtain 40 mm $\times$ 40 mm $\times$ 1.5 mm film.

Characterizations. Differential Scanning Calorimetry (DSC). Thermal analysis was performed with DSC (Q20, TA Instruments Inc., Newcastle, DE, USA) under nitrogen atmosphere. Each sample of 3–5 mg was heated from 30 to 200 $^\circ$C at 10 $^\circ$C/min to eliminate thermal history, then cooled to 20 $^\circ$C at 10 $^\circ$C/min, then reheated to 200 $^\circ$C at 10 $^\circ$C/min. The fluorescence spectra were performed with a 970CRT fluorescence spectrometer (Shanghai INESA Physico-Optical Instrument Co., Ltd., Shanghai, China). The light conversion effect of each sample was recorded under a ZF-1 ultraviolet analyzer (Shanghai Qinke Analytical Instrument Co., Ltd., Shanghai, China) equipped with visible light, 254, and 365 nm UV light.

3. Results

The melting behavior and non-isothermal crystallization of PLA/CEu and PLA/KCEu composites were studied through the first and second heating runs by DSC, and the results are presented in Figure 1A,B and Table 1. The endothermic stepwise change near 61.5 $^\circ$C belongs to the glass temperature (Tg) of PLA chain. The exothermal peak near 130 $^\circ$C belongs to the cold crystallization temperature (Tcc) of PLA. The endothermic peaks around 166 $^\circ$C corresponding to melting temperature (Tm) can be observed in neat PLA, PLA/CEu, and PLA/KCEu composites. The crystallinity (Xc) of PLA samples was calculated by the following equation: $X_c = (\Delta H_m - \Delta H_c) / (93.6 \text{ J} \cdot \text{g}^{-1})$. $\Delta H_m$ is the melting enthalpy, and $\Delta H_c$ is the cold crystallization enthalpy of PLA. The crystallinity of PLA (Xc) increased from 1.63% to 1.72% with 0.2 wt.% CEu, and increased to 3.44% with 1 wt.% CEu. After modification with KH550, the addition of KCEu showed the same trend as with CEu, but showed a better effect on the increase in the Xc of PLA/KCEu composites. The Xc of PLA/KCEu-0.2 and PLA/KCEu-1 was 1.77% and 3.55%, respectively.

![Figure 1.](image-url) The first (A) and second (B) heating curves of PLA/CEu and PLA/KCEu composites.
Table 1. The crystallinity of PLA with different CEu or KCEu contents.

| Sample       | Tg (°C) | Tcc (°C) | △Hc (°C) | Tm (°C) | △Hm (°C) | Xc (%) |
|--------------|---------|----------|----------|---------|----------|--------|
| PLA          | 61.53   | 133.63   | 24.21    | 166.56  | 25.74    | 1.63   |
| PLA/CEu-0.2 | 62.27   | 134.65   | 24.16    | 167.00  | 25.77    | 1.72   |
| PLA/CEu-0.5 | 62.37   | 130.90   | 28.58    | 166.97  | 30.52    | 2.07   |
| PLA/CEu-1   | 61.53   | 130.48   | 29.14    | 166.35  | 32.36    | 3.44   |
| PLA/KCEu-0.2| 61.68   | 135.71   | 22.12    | 166.98  | 23.78    | 1.77   |
| PLA/KCEu-0.5| 61.69   | 133.32   | 27.03    | 166.87  | 29.25    | 2.37   |
| PLA/KCEu-1  | 61.51   | 134.70   | 24.43    | 166.79  | 27.75    | 3.55   |

The excitation and emission spectra of PLA/CEu and PLA/KCEu films are shown in Figure 2. It can be seen from Figure 2A,B that PLA/CEu and PLA/KCEu show good excitation of UV light and blue light, and have high fluorescence emissions between 570 and 680 nm red light, especially at 600 and 630 nm. The emission spectra in the red-light region meet the requirements for plant growth. Furthermore, PLA/KCEu exhibits better luminous intensity than PLA/CEu at the same particle addition. This is mainly due to the better compatibility and dispersion of KCEu after modification with KH550.

Figure 2. Excitation spectra (λem = 600 nm) (A) and emission spectra (λex = 460 nm) (B) of the PLA/CEu and PLA/KCEu films.

The hot-pressed samples were also exposed under certain UV light. As shown in Figure 3, pure PLA showed no light conversion effect or color change under UV light. However, with the addition of CEu or KCEu, the PLA/CEu and PLA/KCEu changed to a brighter red color when exposed to 254 and 365 nm UV light, indicating their good light conversion from UV light to red light. Furthermore, the conversion effect increased with the additional amount of CEu in PLA/CEu and KCEu in PLA/KCEu films.

Figure 3. Images of PLA/CEu and PLA/KCEu films under 254 and 365 nm UV light, and visible light.
4. Conclusions

Biodegradable light conversion PLA agricultural film was successfully prepared. PLA/CEu and PLA/KCEu earth complexes films can emit red fluorescence under 254 and 365 nm ultraviolet light. After modification with KH550, KCEu showed a better effect in improving the films’ crystallinity and compatibility in comparison to CEu. Furthermore, the emission intensity performance of PLA/KCEu was also better than that of PLA/CEu films. This study can provide some insights into the preparation and application of biodegradable light conversion films.

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Conflicts of Interest: The authors declare no conflict of interest.

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