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Effects of two cellulose binders on the luminous properties of phosphor pastes

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Abstract

Two cellulose binders (ethylcellulose and nitrocellulose) were used to fabricate white-colored phosphor pastes prepared from the mixture of Y_2O_3:Eu (red), $LaPO_4$:Ce, Tb (green) and $BaMgAl_{10}O_{17}$:Eu (blue) for flat fluorescent lamps. The chemical composition of ethylcellulose and nitrocellulose vehicles was investigated by GPC (gel permeation chromatography) and FT-IR (Fourier transformation infrared spectroscopy) analysis, respectively, and the thermal properties of the binders were determined by TGA (thermogravimetric analysis) and DTA (differential thermal analysis). In addition, the residual carbon content of phosphor pastes calcined at 520 °C was measured by CS (carbon–sulfur determinator) analysis. After calcination at 400 °C, the residual carbon content of phosphor pastes fabricated from ethylcellulose and nitrocellulose was approximately 0.055 wt% and 0.028 wt%, respectively. The phosphor paste synthesized with nitrocellulose showed superior adhesion behavior, low residual carbon content and excellent luminescent properties.

Keywords: Flat fluorescent lamps; Cellulose binders; Phosphor; Residual carbon; Adhesion; Luminescence

1. Introduction

Recently, interest in the use of liquid crystal displays (LCDs) as flat panel displays (FPDs) has rapidly increased. LCDs are composed of a liquid crystal display panel, electrical circuits, and a back light unit (BLU). Recently, LCD panels have become larger and require wider, more efficient BLU modules for FPDs. BLU modules consist of an optical sheet and a fluorescent light source (lamp), such as a cold cathode fluorescent lamp (CCFL), external electrode fluorescent lamp (EEFL) or flat fluorescent lamp (FFL).

Generally, fluorescent lamps are made by laminating phosphor materials and filling the lamp socket with mercury or other inert gases. In the coating process, phosphor powders are synthesized from organic vehicles, which consist of binders and additives dissolved in a solvent. Organic binders, such as cellulose-based compounds, have been used to maintain the uniformity and adhesion of the phosphor screen on the glass substrate [1,2].

After the phosphor coating procedure, organic cellulose binders and solvents must be removed through a firing process to avoid abnormal lighting behavior, such as flickering caused by residual elements. Although organic compounds are easily removed from phosphor screens at high temperatures in an oxygen atmosphere, the luminescent properties or molecular structure of phosphor powders, such as $BaMgAl_{10}O_{17}$:Eu (BAM, blue phosphor), are deteriorated or significantly altered by annealing processes conducted at temperatures greater than 500 °C [3–5].

In $BaMgAl_{10}O_{17}$:Eu phosphor, the oxidation of Eu^{2+} to Eu^{3+} occurs at temperatures greater than 500 °C, and the migration of Eu^{2+} causes a shift in the *y*-value of the chromaticity graph at temperatures between 300 and 1100 °C [5]. The residue of organic vehicles causes problems during out-gassing procedures and degrades the luminescent properties of the material, producing black spots in the BLU. Therefore, organic species must be removed by firing under the proper conditions without damaging the phosphor powder.

Ethylcellulose (EC), which possesses CH_2CH_3 end-groups, has been used as a binder for phosphor pastes and glass powders [2,6]. Alternatively, nitrocellulose (NC), which contains

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O=N$^+$–O$^-$ end-groups, has been utilized in printing and coating inks due to its solubility in acetone and glycol. Nitrocellulose displays sharp exothermic behavior at 201 °C [7] and a lower decomposition temperature than that of other organic binder materials; thus, nitrocellulose can be fired at low temperatures.

In the present study, ethylcellulose and nitrocellulose were used as binders to fabricate phosphor pastes containing red (Y_2O_3:Eu), green ($LaPO_4$:Ce, Tb) and blue ($BaMgAl_{10}O_{17}$:Eu) powder. The residual carbon content of phosphor pastes fabricated with ethylcellulose and nitrocellulose were examined, and the adhesion and photoluminescence behavior of the pastes were investigated.

2. Experimental details

The exothermic behavior, weight loss and structural changes of ethylcellulose and nitrocellulose binders were examined using thermogravimetric analysis (TGA, TGA-Q5000, TA-Instrument, USA) and differential thermal analysis (DTA, DTG-60, Shimadzu, Japan). The molecular weight and chemical bonds of ethylcellulose and nitrocellulose binders were identified using gel permeation chromatography (GPC, Millenium32, Millipore, USA) and Fourier transformation infrared spectroscopy (FT-IR, UV-3600, Shimadzu, Japan).

The phosphor pastes were fabricated by mixing red (Y_2O_3:Eu), green ($LaPO_4$:Ce, Tb) and blue ($BaMgAl_{10}O_{17}$:Eu) phosphor powders (Kasei optix, Japan) with organic vehicles in a screen-printing process. The organic vehicles for phosphor pastes were prepared by combining the binder and the solvent. Ethylcellulose (EC, Junsei Co., Japan) and nitrocellulose (NC, CNC Co., Korea) were used as binders, and butyl carbitol acetate (BCA, diethyleneglycol monobutyletheracetate) was used as the solvent. EC and NC solutions were employed as organic vehicles during the fabrication of phosphor pastes. The phosphor powders were mixed according to the desired fraction of red (29.1 wt%), green (35.2 wt%) and blue (35.7 wt%) powders, and a white-colored ($x = 0.279$, $y = 0.281$) phosphor was produced. The phosphor powder mixture and organic vehicles were pre-mixed for 30 min using a paste mixer. Subsequently, the three-roll mill process was carried out to combine the phosphor powders with the organic vehicle. The residual carbon content of the phosphor pastes was measured with a carbon–sulfur determinator (CSD, Q8 Magellan, Bruker, Germany).

The phosphor pastes were printed onto soda lime glass. To remove organic solvent from the phosphor pastes, heat treatment was performed for 1 h at 110 °C in a dry oven under an atmosphere of air. Phosphor pastes printed on glass plates were fired at 520 °C in air to remove the organic binders. The photoluminescence behavior of the phosphor screen was analyzed with a spectrometer (PSI Co., Korea).

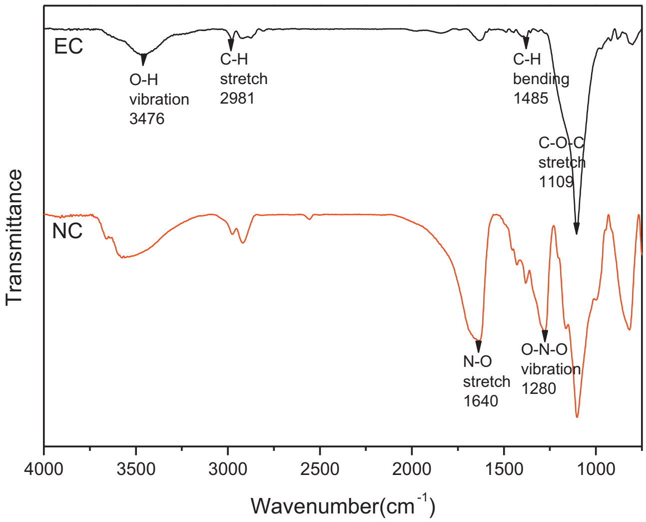

Fig. 1. FT-IR results of ethylcellulose (EC) and nitrocellulose (NC) vehicles.

3. Results and discussion

The viscosities of the organic binders and phosphor pastes, which are determined by the content (binder–solvent ratio) of ethylcellulose and nitrocellulose, are shown in Table 1. Although ethylcellulose (6 wt%) and nitrocellulose (2.5 wt%) binders were prepared from different weight ratios, the organic vehicles presented similar viscosities of 1540 cP and 1520 cP, respectively. Phosphor pastes prepared by mixing the organic vehicle and phosphor powder displayed similar viscosities (approximately 18,000 cP at 25 °C) [Table 1]. Thus, even small amounts of nitrocellulose binder controlled the viscosity of the pastes, and differences in the viscosities of the materials were attributed to the bonds present in the binders. In the FT-IR spectra shown in Fig. 1, the ethylcellulose binder displayed peaks corresponding to C–O–C and C–H bonds at 1109 cm^{-1} and 1485 cm^{-1}, respectively, and the nitrocellulose binder displayed peaks corresponding to O–N–O and N–O bonds at 1280 cm^{-1} and 1640 cm^{-1}, respectively. Compared to the C–H or C–O–C bonds of the ethylcellulose binder, the N–O and O–N–O bonds of the nitrocellulose binder can create a strong network, effectively increasing the viscosity of the material. Generally, nitrocellulose binders show explosive behavior due to their nitrogen content, as illustrated in the

Table 1
Composition and viscosity of vehicles (ethylcellulose and nitrocellulose) and white-colored phosphor paste prepared from three phosphor components.

	Vehicle composition & viscosity			Paste composition & viscosity		
	Binder	Solvent	Viscosity (DV-II)	[a]Phosphor	Vehicle	Viscosity
Ethyl cellulose content	6%	94% (Terpineol/BCA/BC)	1540 cP	72%	28%	18,0000 cP
Nitro cellulose content	2.5%	97.5% (BCA)	1520 cP	72%	28%	17,7000 cP

[a] The phosphor was prepared from the mixture of Y_2O_3:Eu (red, 29.1 wt%), $LaPO_4$:Ce, Tb (green, 35.2 wt%) and $BaMgAl_{10}O_{17}$:Eu (blue, 35.7 wt%).

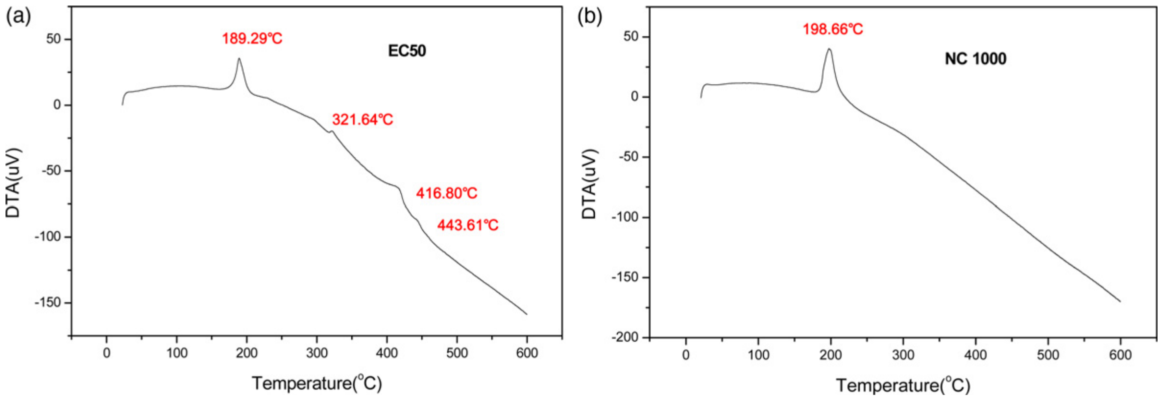

Fig. 2. DTA results of (a) ethylcellulose (EC) and (b) nitrocellulose vehicles (NC).

FT-IR spectra shown in Fig. 3. Thus, the content of the nitrocellulose binder was varied from 10.7 to 12.3 wt%.

Fig. 2 shows the DTA results of the ethylcellulose and nitrocellulose binders. The ethylcellulose binder showed exothermic peaks at 189 °C, 321 °C, 416 °C and 443 °C, and the nitrocellulose binder showed an exothermic peak at 198 °C. For both binders, the peaks observed at temperatures less than 200 °C represent the volatilization of BCA. In contrast, the exothermic peaks of the ethylcellulose binder at temperatures ranging from 300 °C to 450 °C represent the decomposition of the material.

Fig. 3 shows the TGA results of the ethylcellulose and nitrocellulose binders. The ethylcellulose binder showed significant weight loss at temperatures less than 200 °C and minor weight loss at temperatures ranging from 200 °C to 300 °C. The nitrocellulose binder presented significant weight loss at temperatures less than 200 °C, and weight loss peaks were not observed at temperatures greater than 200 °C. The DTA and TGA results indicated that the nitrocellulose binder decomposes at relatively low temperatures.

The molecular weights of the ethylcellulose and nitrocellulose binders, which were measured via GPC using a weight average method, were equal to 59,958 and 42,105, respectively. In BCA, the O–N–O and N–O bonds of the nitrocellulose binder display a stronger binding force than that of the C–O–C and C–H bonds of the ethylcellulose binder. Namely, the nitrogen atoms of nitrocellulose form stronger hydrogen bonds than the C–H groups of ethylcellulose. BCA (butyl carbitol

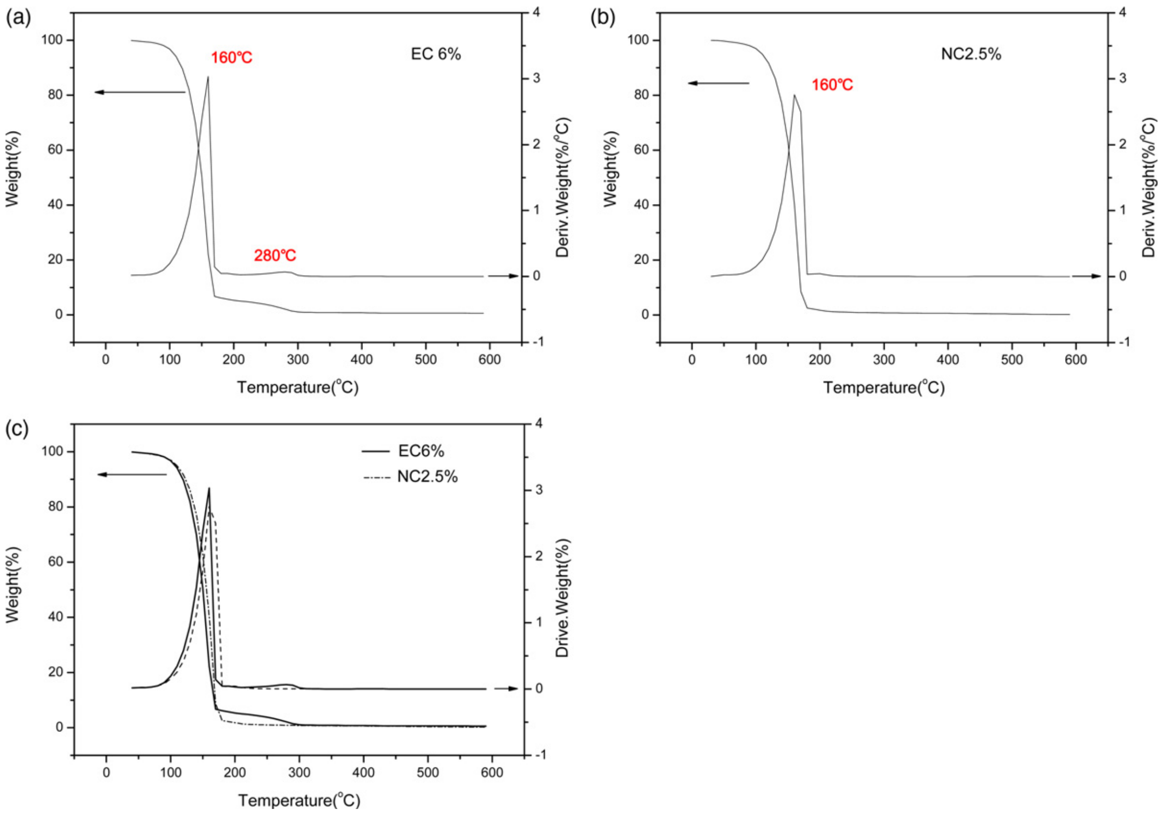

Fig. 3. TGA results of (a) ethylcellulose (EC), (b) nitrocellulose (NC) vehicles and (c) overlapped diagram of (a) and (b).

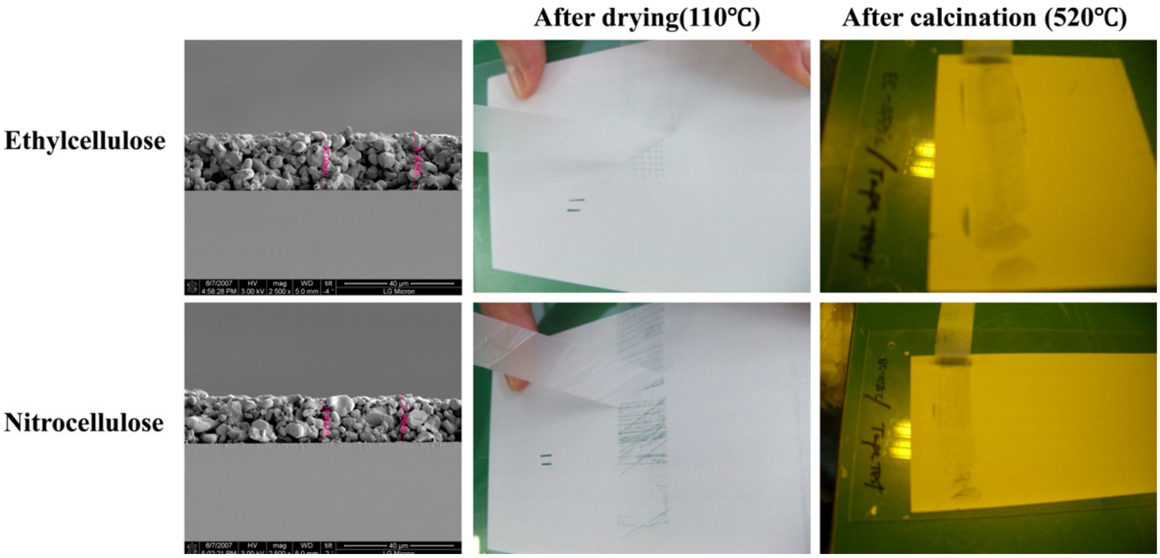

Fig. 4. Adhesion test after drying and calcination.

acetate) is widely used as a solvent for pastes, has a high boiling temperature and is not as toxic as terpineol, which is also used in pastes and possesses a high boiling temperature. To inhibit the blocking of mesh in the printing process, solvents with high boiling temperatures are often used as printing pastes.

Solvents with high solubilities can promote the dispersion of the organic binder, which affects the performance of the phosphor. Nitrocellulose is more soluble in BCA than ethylcellulose.

Fig. 4 shows the adhesion behavior of phosphor pastes fabricated from ethylcellulose and nitrocellulose binders on soda lime glass. After drying at 110 °C for 1 h, the phosphor paste fabricated with ethylcellulose showed stronger adhesion than the phosphor paste prepared with nitrocellulose; however, both phosphor screens displayed the same adhesion behavior after firing at 520 °C.

The residual carbon content of phosphor screens fired at 400 °C, 450 °C and 520 °C was calculated by CS analysis [Fig. 5]. After firing at 400 °C, phosphor screens fabricated with ethylcellulose and nitrocellulose binders showed a carbon content of 0.055 wt% and 0.028 wt%, respectively. However, after firing at 450 °C and 520 °C, phosphor screens prepared with ethylcellulose and nitrocellulose binders presented similar carbon contents.

The luminescence behavior shown in Fig. 6 indicates that shape and intensities are very similar for both the binders. Although a precise comparison of the luminescence efficiency require specific measurements, we note that the phosphor prepared from nitrocellulose binder displays a slightly higher luminescence in respect to the phosphor prepared from ethylcellulose binder [8]. Because the ethylcellulose binder showed a somewhat complex decomposition route at high temperatures, the phosphor screen fabricated with ethylcellulose binder likely possessed more residual carbon in its microstructure. It was inferred that the luminescence intensity of the phosphor screen is directly related to the residual carbon content after firing.

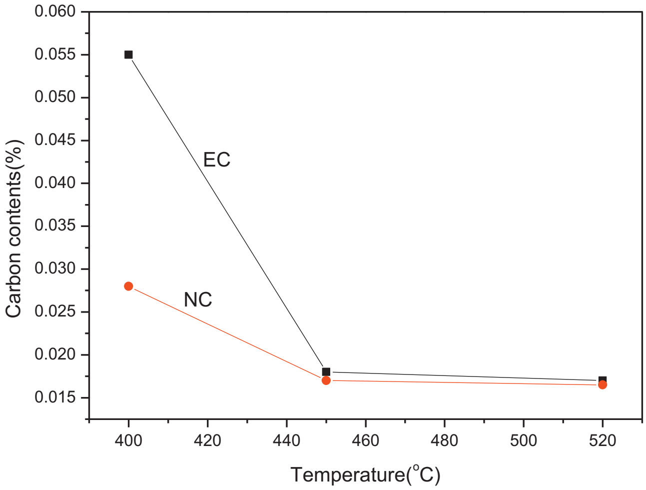

Fig. 5. Residual carbon contents of ethylcellulose (EC) and nitrocellulose (NC) with different temperatures.

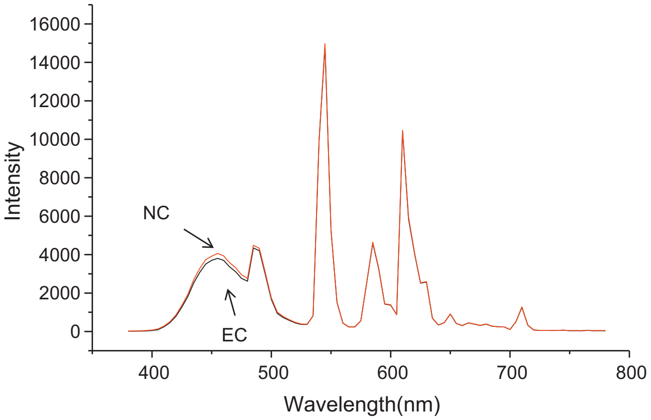

Fig. 6. Photoluminescence spectra of phosphors prepared with ethylcellulose (EC) and nitrocellulose (NC).

4. Conclusions

Phosphor screens were synthesized from two different organic binders. Phosphor screens prepared with nitrocellulose binder showed higher viscosity and lower residual carbon contents than phosphor screens prepared with ethylcellulose binder. After firing at 400 °C, 450 °C and 520 °C, phosphor screens prepared with nitrocellulose binder displayed lower carbon contents than phosphor screens prepared with ethylcellulose binder. Phosphor screens prepared with both the binders exhibit an effective luminescence. Phosphors prepared with nitrocellulose showed slightly higher luminescence intensity in the red, green, and blue color range.

Acknowledgement

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