

Plasma Display Material Prepared from a New Blue Phosphor Dispersion

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ABSTRACT: An improved coating having a high concentration of blue phosphor powder was made with a modified Triton X-100 dispersant. The barium magnesium aluminate phosphor was very well dispersed in terpineol if the Triton (octyl phenol ethoxylate) had terminal carboxylic acid groups, which had been added to the Triton molecule by chemical synthesis. This improved dispersion was screen-

printed, dried, and then sintered. Because of the very tight packing of the phosphor particles, the photoluminescence intensity of the phosphor film in vacuum ultraviolet excitation was significantly increased up to 10.23%. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2571–2577, 2008

Key words: dispersions; additives; surfactants

INTRODUCTION

The particle packing and uniformity of phosphor films play important roles in improving the brightness of plasma display panels (PDPs). As the display resolution becomes higher, the unit cell volume of the PDP gets smaller. A more uniform phosphor film and improved particle packing (higher solid loading) within a unit cell are needed to maximize the output brightness, which depends on the number of phosphor particles interacting with a light source externally supplied. Also, a uniform phosphor film can minimize the light scattering. For these reasons, tightly packed phosphor films are required.^{1,2} In addition, after the temporary organic additives are burned out, a low-char residue is needed to maintain the usable life of the PDP [ceramists ordinarily do not like to use self-charring organic additives such as sulfonates, sulfates, or phosphates because they might leave uncontrolled sulfur (or phosphorous) compounds behind after burnout³]. A dispersant additive that can be burnt out below 500°C is desirable.

The screen-printable ink (paste) contains a binder and a dispersing agent in addition to the ceramic powder and the solvent. The dispersant is needed to ensure the stability of the suspension, especially with tightly packed phosphor particles, and proper rheological properties for low-cost processing. As ex-

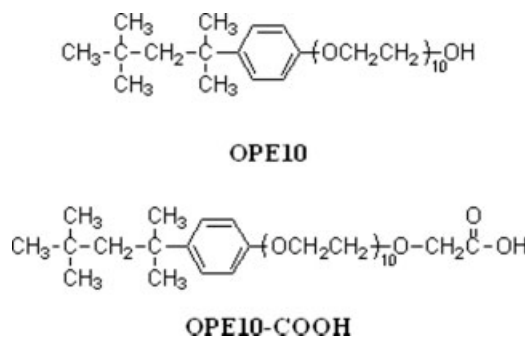
perimental dispersants for use in nonaqueous solvents such as terpineol, simple molecules such as long-chain carboxylic acids, glyceryl esters of carboxylic acids, and phosphate esters of long-chain alcohols and amines have been tried.^{4–6} On the other hand, inorganic films of complex lanthanide phosphors have been made from their aqueous dispersions with block copolymer emulsifiers.⁷

Generally, for a hydrophilic powder in a nonpolar solvent, a dispersant is a molecule with a hydrophilic polar functional group that is capable of anchoring itself to the particle surface. Also, there is usually a hydrophobic long hydrocarbon chain to provide steric stabilization.⁸ A group of versatile nonionic surfactants for hydrophilic powders in organic solvents includes the Triton X series (X-100, X-101, etc.) manufactured by Dow Chemical Co. These are hydroxyl-terminated octyl phenol ethoxylates (OPEs; see Scheme 1).^{5,8,9,10}

The synthesis and characterization of Triton X derivatives containing specially added acidic or basic moieties were reported earlier by our group.¹¹ We also demonstrated that a Triton X based compound with a terminal carboxylic acid (OPE-COOH) could be a better dispersant than others that have ester, phosphoric acid, or amino-functional groups.¹² The added carboxylic terminal group provides a strong interaction with the surface of a commonly used blue phosphor when dispersed in terpineol as a solvent. In addition, increasing the oxyethylene chain length was found to further decrease the flocculation of phosphor particles.¹²

In this work, a dense-structured film of phosphor particles was prepared by screen printing of the

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Scheme 1 Structures of OPE10 and OPE10-COOH.

phosphor-solvent paste followed by sintering heat treatments. The paste also contained dissolved dispersant and binder. The important effect of the dispersant on the particle packing (solid loading) was measured. The main dispersant in this study was acid-modified Triton X-100 with 10 oxyethylene units. The main solvent used was terpineol. Finally, we experimentally compared the surface uniformity and photoluminescence (PL) intensity of the phosphor films prepared with the modified dispersant and without the dispersant. The effects of other variations such as the viscosity and thermal degradation behavior are also reported here.

EXPERIMENTAL

Materials

The phosphor powder employed in this study was $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}, \text{Mn}^{2+}$ (BAM; 98%), which was purchased from Kasei Optonix, Ltd. (Odawara, Japan). The particle diameter of the BAM powder, reported by the supplier, was 3.8 μm . To remove any physically adsorbed water and volatile organics on the powder surface, the BAM powder was vacuum-dried at 130°C for 24 h before use. The liquids used as solvents (Table I) were α -terpineol (99%; Kanto Chemical Co., Isehara, Japan) and butyl carbitol acetate (BCA, 99%; Kanto Chemical). The binder was ethyl cellulose (Ethocel, Standard 45, Dow

Chemical Co., Midland, MI) with a 48.0–49.5% ethoxy content (Table I).

For comparison, a commercially available but proprietary dispersant was also tried (BYK111, a phosphate-based dispersant from BYK-Chemie, Berlin, Germany). Its exact chemical structure is not reported in the literature, but it is well recognized as a surfactant for high-temperature purposes in industry. The modified Triton X based dispersant containing a carboxylic group in the oxyethylene chain end, OPE10-COOH, was prepared from Triton X-100 (98%; Aldrich Co., St. Louis, MO) etherified with ethyl bromoacetate (99%) and then saponified.¹¹ The code OPE10-COOH represents OPE with 10 oxyethylene units and a terminal carboxylic acid (Scheme 1).

Instruments

The particle size and ζ potential of the BAM powder were determined with an electrophoretic light scattering spectrophotometer (ELS-8000, Photal, Otsuka Electronics, Kobe, Japan). The rheological behaviors of the BAM pastes were monitored with a stress- and strain-controlled rheometer (AR2000, TA Instruments). The experiments were carried out with a cone and plate geometry (diameter = 60 mm, angle = 2°, truncation = 54 μm). Thermogravimetric analyses (TGAs) were carried out in both nitrogen and air at a heating rate of 10°C/min with a TGA 2050 (TA Instruments, New Castle, DE). The flow rates for both cases were maintained at 10 and 90 cc/min for the balance part and for the furnace area, respectively. In each case, samples weighed ~ 100 mg. The microstructure of the sintered BAM film was observed by field emission scanning electron microscopy (SEM; S-4700, Hitachi, Tokyo, Japan). The thickness of the films was determined with a three-dimensional (3D) optical interferometer (NT-2000, Veeco, Inc., Woodbury, NY). The PL characteristics of the BAM films were evaluated with a spectrofluorometer (ISS PC1, ISS, Inc., London, UK). The PL spectra of the prepared films were obtained under

TABLE I
Binder and Solvents Employed in the Formulation of BAM Pastes

	Ethyl cellulose	α -Terpineol	BCA
Molecular weight	10,000–20,000	154.25	204.27
Structure	<p style="text-align: center;">R = H or $-\text{CH}_2\text{CH}_3$</p>		
Comment	48–49.5% ethoxy content	—	—

BCA, butyl carbitol acetate.

TABLE II
Typical Composition of the Phosphor Paste

Sample	Amount (g)
Ethyl cellulose	0.33
Terpineol	3.32
BCA	5.48
BAM	10.72
OPE10-COOH	0.11

BCA, butyl carbitol acetate.

the illumination of vacuum ultraviolet (VUV; 140 nm) emitted from a Kr₂ excimer lamp.

Formulation of BAM pastes

An ethyl cellulose binder solution was prepared by the dissolution of ethyl cellulose (10 wt %) in α -terpineol at 70°C in a silicone oil bath, and the solution was diluted with butyl carbitol acetate at a solvent weight ratio of 1 : 1.5. The BAM paste was prepared by the addition of a dispersant into the ethyl cellulose binder solution followed by the addition of a certain amount of BAM powder. The paste was ball-milled with yttria-stabilized zirconia grinding media for 12 h to ensure a thorough and uniform adsorption of the dispersant on the particles. A typical composition of the paste is given in Table II.

Formation of BAM films

The prepared BAM paste was coated onto a glass slide with a BYK Gardener film applicator (BYK-Chemie, Berlin, Germany). The layer was subsequently heated at 250°C for 30 min and sintered at 480°C for 30 min in air.

RESULTS AND DISCUSSION

BAM powders

Figure 1 shows SEM micrographs of the irregular and plate-type BAM powders employed in this work. From electrophoretic light scattering experi-

ments, it was found that the median particle size of the BAM powders is 4.43 μ m, and BAM has a relatively narrow particle size distribution (polydispersity = 1.3; Fig. 2).

The isoelectric point of BAM phosphor is 10.27.¹² In the course of the acidic titration, the ζ potential value of BAM phosphor increases (at pH = 2, the ζ potential is 162 mV). Therefore, it is thought that BAM phosphor particles have basic surfaces.

OPE10-COOH as a dispersant

The synthesized OPE10-COOH is a carboxylic group containing dispersant with 10 oxyethylene units.¹¹ The structure is given in Scheme 1. The terminal carboxylic group, which has an acidic nature, can interact strongly with the basic BAM surfaces.¹² In addition, the OPE backbone has a branched alkyl tail and polar oxyethylene units. Therefore, OPE10-COOH is an efficient dispersant for BAM in an apolar continuous phase.

BAM particles were introduced into an ethyl cellulose/terpineol system in which OPE10-COOH as a dispersant was predissolved. In an analysis with a rheometer, it was found that the introduction of OPE10-COOH into the BAM paste greatly reduced the apparent viscosity of the paste (Fig. 3). The paste viscosity minimum was achieved at an OPE10-COOH concentration of 1 wt % BAM.

High powder loading

A film with a high powder loading is desirable for getting a high sintered density. Films with different powder loadings could be obtained by the variation of the amount of BAM in the paste with or without a dispersant.

The apparent viscosity of the BAM pastes is shown in Figure 4 as a function of the powder loading. A high powder loading of up to 32 vol % (or 66.2 wt %) was achieved in the presence of 1 wt % OPE10-COOH when the paste viscosity was fixed at 20 Pa s. The inflection points, at which the viscosity increased

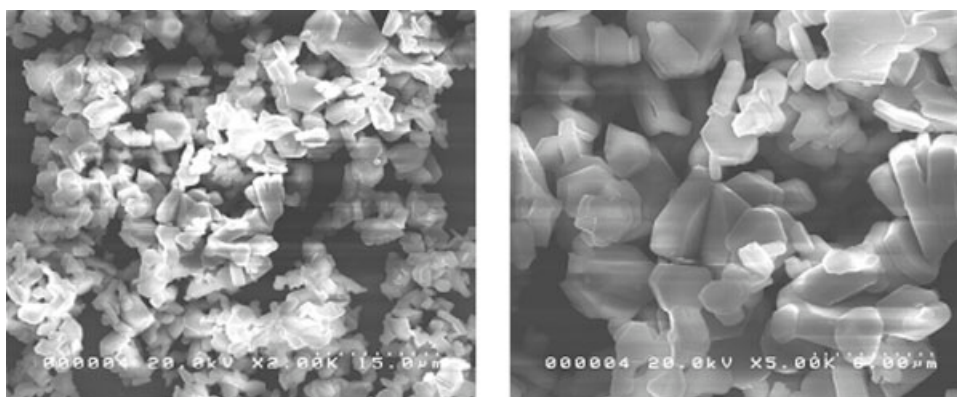


Figure 1 SEM micrographs of the BAM blue phosphor particles.

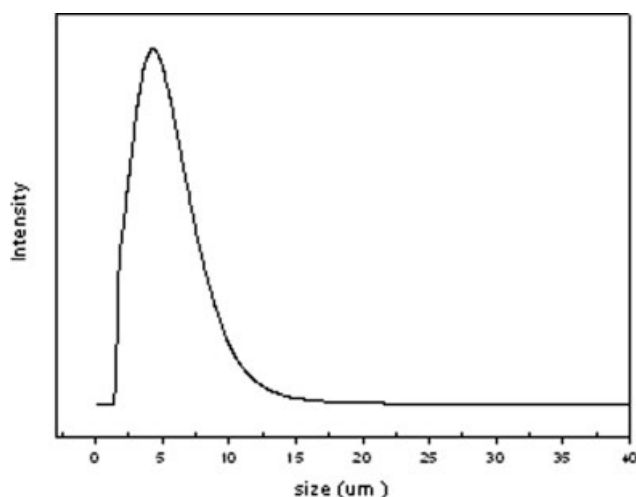


Figure 2 Particle size analysis of the BAM powders in ethanol.

abruptly, were in the range of 20–25% for the paste without dispersant and 30–35% for the paste with OPE10–COOH, respectively. We could load approximately 10 vol % more BAM powder into the ethyl cellulose/terpineol system in the presence of the OPE10–COOH dispersant. It is thought that this high powder loading effect is due to the reduced particle–particle interaction by the adsorption of acidic OPE10–COOH onto the basic particle surfaces.¹²

Paste preparation and film forming

To make a fine BAM film, a BAM paste with a high powder loading was prepared by the mixing of the BAM particles with the binder solution containing OPE10–COOH, in which the weight percentage of powder was 66.2%. Thereafter, the BAM film was built on a glass substrate by a screen-printing tech-

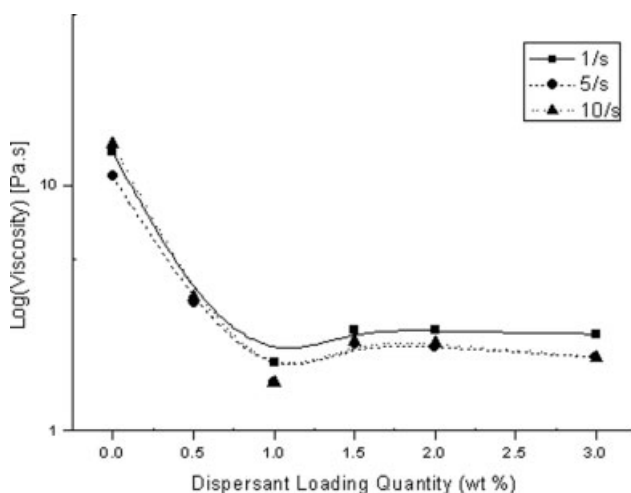


Figure 3 Effect of OPE10–COOH as a dispersant on the viscosity of BAM paste (22 vol %) in terpineol.

nique and fired at 480°C for 30 min under an air environment.

The bigger advantages of BAM film prepared from the paste with the OPE10–COOH dispersant lie in better film characteristics, as shown in Figure 5, which presents SEM photographs showing the surface of BAM film formed on a glass substrate. As shown in Figure 5(a), the BAM film made out of the paste with no dispersant (powder loading of 24 vol %) had a coarse structure, whereas the paste with OPE10–COOH (powder loading of 32 vol %) formed a fine and close-packed layer [Fig. 5(b)]. Figure 6 shows optical 3D profiles of the sintered BAM films from a white-light scanning interferometer. This indicates that the surface uniformity and particle density of the film prepared from the paste containing OPE10–COOH are much better than those of the film prepared from the paste containing no dispersant. The mean thickness values of the BAM films prepared from the paste without dispersant and the paste with OPE10–COOH are 77.861 and 79.340 μm , respectively.

These improved film characteristics (i.e., uniformity and highly packed phosphor layer) were found to be helpful for the PL characteristics of the BAM film under VUV excitation (discussed later).

PL of BAM films

Two kinds of BAM films, prepared with the paste without the dispersant (powder loading of 24 vol %) and with the paste with OPE10–COOH (powder loading of 32 vol %), were used in this experiment. The PL spectra under VUV (140 nm) excitation for the prepared BAM films are shown in Figure 7. In both film samples, BAM phosphors showed strong

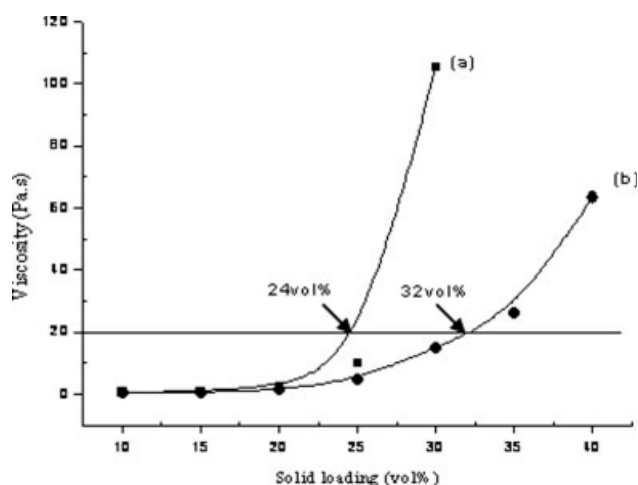


Figure 4 Apparent viscosity of BAM pastes as a function of the solid loading (volume percentage of the powder) at a shear rate of 5 s^{-1} : (a) without dispersant and (b) with OPE10–COOH.

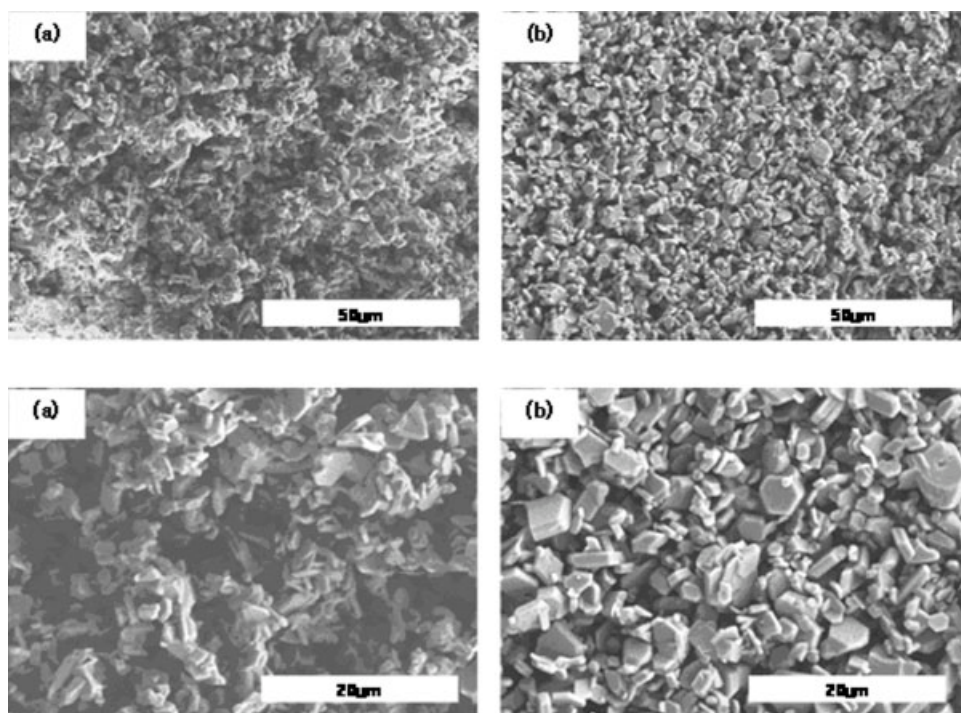


Figure 5 SEM photographs of the BAM films sintered at 480°C prepared from pastes with solid loadings of (a) 24 vol % (no dispersant used) and (b) 32 vol % (OPE10-COOH was used).

PL at 516 nm, which corresponded to the green emission of BAM. However, the PL intensity of the BAM film prepared from the paste with OPE10-COOH was 10.23% higher than that of the film pre-

pared from the paste with no dispersant (PL intensity: 9.20×10^6 versus 8.27×10^6).

It is also notable that the PL intensity of the film prepared from the paste with OPE10-COOH was

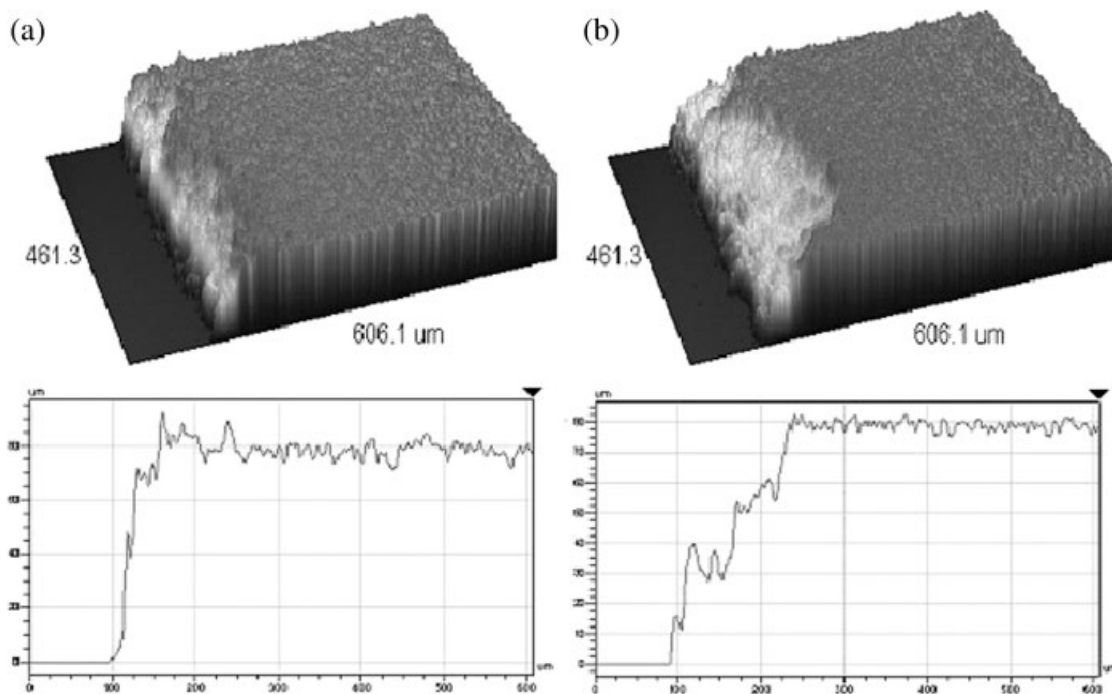


Figure 6 Optical 3D profiles of the BAM films prepared from pastes with solid loadings of (a) 24 vol % (mean thickness = 77.861 μm) and (b) 32 vol % (mean thickness = 79.340 μm).

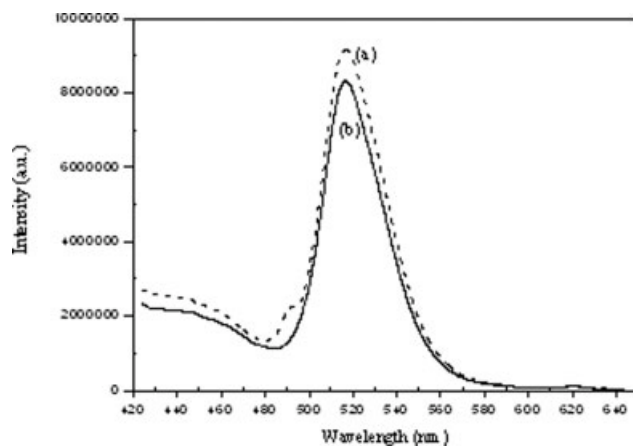


Figure 7 PL emission spectra of the BAM films under VUV (140-nm) excitation prepared from pastes with solid loadings of (a) 32 and (b) 24 vol %.

higher than that of the film prepared from the paste with BYK111 as a phosphoric acid based dispersant (Fig. 8).

Burnout property of neat OPE10-COOH

In ceramic processing, organic processing aids such as the binder and dispersant must be removed after sintering. Especially in the PDP manufacturing process, complete debinding of any organics is necessary to avoid harmful defects such as charred residues deposited on the phosphor surface. These kinds of defects caused by improper selection of organics are impossible to heal by subsequent sintering.¹³

Therefore, from the chemical aspects of the organic dispersants employed in the phosphor paste formulation, the burnout property of the dispersant plays an important role in the PL characteristics of phosphor films. The phosphor paste should retain a high percentage of the phosphor particle shoot, maintaining its luminescence after complete dispersant (and binder) burnout.^{14,15}

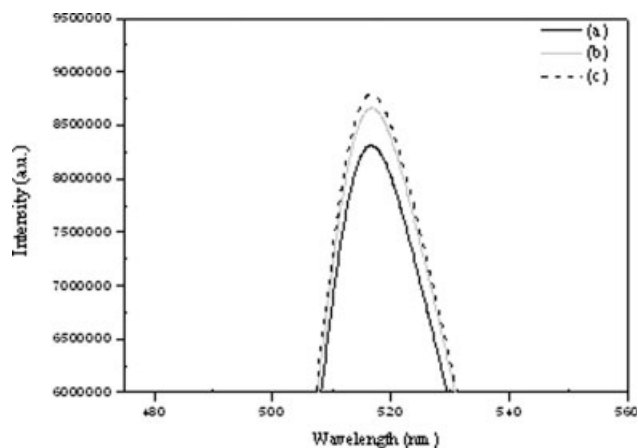
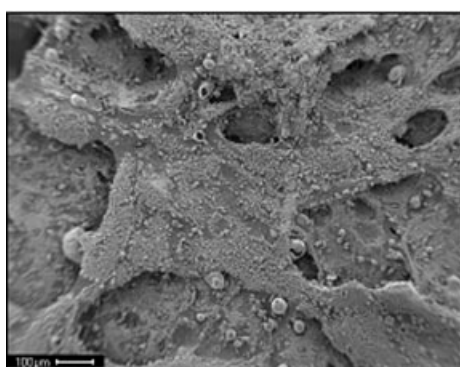


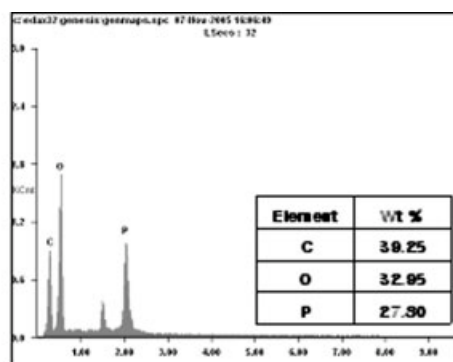
Figure 8 PL emission spectra of the BAM films under VUV (140-nm) excitation prepared from pastes with a solid loading of 24 vol % with (a) no dispersant, (b) BYK111, or (c) OPE10-COOH.

We previously reported that the BAM paste containing commercial BYK111, which has phosphoric acid as an anchoring group, shows rheological behaviors similar to those of the paste with OPE10-COOH.¹³ However, neat BYK111 produces 7.08 wt % residual char at high temperatures in air,¹² and this lowers the PL intensity of the corresponding BAM film compared to the film prepared from the paste with OPE10-COOH (Fig. 8). Figure 9 shows an SEM image and elemental analysis results of the residual char of BYK111. The char is composed of carbon (39.25 wt %), oxygen (32.95 wt %), and phosphorus (27.80 wt %), and this indicates that oxidative cross-linking in the condensed phase may account for the char formation. This charring effect of BYK111 is detrimental to the PL efficiency of the BAM phosphor.

Unlike BYK111, OPE10-COOH produces a very small amount of char in nitrogen (0.82 wt %), and in air, it is completely burned out at high temperatures (Fig. 10). In addition, the presence of oxygen affects



(a) SEM image



(b) EDS analysis

Figure 9 Field emission SEM/energy dispersive spectroscopy (EDS) analysis results of the charred residues of BYK111.

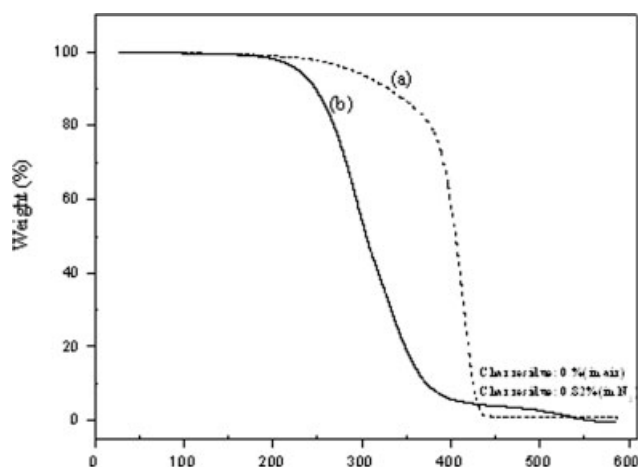


Figure 10 TGA thermograms for OPE10-COOH at a scanning rate of 10°C/min in (a) nitrogen and (b) air.

the initial thermal degradation temperature of OPE10-COOH significantly (200°C in air vs 260°C in nitrogen). Therefore, it can be concluded that relatively thermally stable OPE10-COOH can be expected to be suitable as a dispersant with a relatively long hydrophilic anchoring block for high-temperature purposes in which the dispersant should be burned out completely in air because it has a relatively low initial thermal degradation temperature and no char formation at high temperatures in air.

CONCLUSIONS

Triton X with a carboxylic terminal group (OPE10-COOH) as a dispersant was employed to prepare BAM phosphor films. It was found that simply introducing OPE10-COOH into the BAM/ethyl cellulose/terpineol paste was helpful in greatly increas-

ing the powder loading and made it possible to produce BAM films with higher surface uniformity and particle density after the sintering process. The best dispersion of BAM particles occurred at an OPE10-COOH concentration of 1 wt % with respect to BAM, and the powder loading increased from 24 (in the absence of the dispersant) to 32 vol % (in the presence of OPE10-COOH). As a result, the PL intensity of the densely structured BAM film under VUV excitation was significantly increased up to 10.23%. The OPE10-COOH dispersant showed no char formation after thermal decomposition in air.

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