

Effect of TRITON™ X-based Dispersants Bearing a Carboxylic Terminal Group on Rheological Properties of BAM/Ethyl Cellulose/Terpineol Paste

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Received 21 August 2006; accepted 14 January 2007

DOI 10.1002/app.26297

Published online 2 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, we attempted to use TRITON™ X (or octyl phenol ethoxylate (OPE) of different oxyethylene units (i.e., $n = 2, 5,$ and 10))-based dispersants containing a carboxylic group in the oxyethylene chain end for the formulation of BAM phosphor paste. Thus, a three-component system employing OPE-COOH as a dispersant, terpineol as a solvent, and ethyl cellulose as a binder was compounded with BAM particles, and the rheological properties of the paste were investigated in detail. Among three

acidic TRITON X-based compounds we tested (i.e., [OPE2-COOH], [OPE5-COOH], and [OPE10-COOH]), OPE10-COOH containing the highest number of oxyethylene units in the backbone was found to be the dispersant showing the lowest viscosity of BAM paste under identical conditions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2012–2019, 2007

Key words: powder processing; oxides; block copolymers; polymer blends; rheology

INTRODUCTION

Luminescent materials, also called phosphors, can be found in a broad range of display applications.^{1–3} One of the important technical issues for large-area displays involving phosphors is low cost processing, such as screen printing,^{4–6} ink jet printing, and tape casting.^{2–4} To achieve the cheap processing successfully, the preparation of homogeneous luminescent paste (or suspension) with the dispersion stability of phosphor particles is required. Thus, it is important to develop novel dispersants that give proper rheological properties to a phosphor paste for low cost processing.

TRITON™ X-based surfactants manufactured by Dow Chemical, i.e., octyl phenol ethoxylates (OPEs, Scheme 1) are versatile nonionic surfactants, which are widely used in various applications such as detergency, cosmetics, and enhanced oil recovery.^{7–10} OPEs are also recognized for pigment wetting and stabilization in coatings, and are offered in a range of HLB to match specific wetting and dispersing requirements.¹⁰ OPEs contain two main molecular regions: the oligoether moiety which is a hydrophilic chain, and the

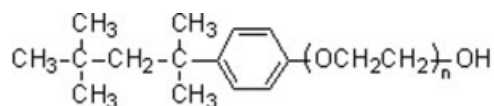
alkyl moiety which is hydrophobic (Scheme 1). OPEs are similar in structure to alcohol polyethers. However, OPEs contain a benzene ring situated between the two regions found in alcohol polyethers.^{9,10} In general, in nonaqueous systems, the anchoring oxyethylene chain of OPEs adsorbs at polar sites of the target particle surface, causing the tail (alkyl chains of OPEs) to extend into the liquid phase. It is also known that oxyethylene groups elevate van der Waals forces between the target particle and OPE, and they play an important role in the dispersions of nanoparticles.¹¹

We previously reported the synthesis and characterization of a series of TRITON X (or OPE)-based dispersants containing a carboxylic group in the oxyethylene chain end.¹² Three acidic TRITON X-based surfactants, e.g., [OPE2-COOH], [OPE5-COOH], and [OPE10-COOH], were prepared from commercially available OPEs of different oxyethylene units and ethyl bromoacetate via a simple etherification reaction followed by saponification reaction. From thermal analyses of these dispersants, it was found that TRITON X-based acidic dispersants are easily burned out at relatively low temperatures, and especially that of 10 oxyethylene units show no char under air condition. Thus, it is postulated that the use of TRITON X-based acidic dispersants can be a means of dispersing particles of relatively basic particles such as BAM and a route to the paste formulation of enhanced stability.

In this study, we attempted to use TRITON X-based dispersants with a carboxylic end group for the formulation of [BAM/ethyl cellulose/terpineol] paste.

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Contract grant sponsor: Samsung Advanced Institute of Technology (Korea).



Scheme 1 A typical structure of octyl phenol ethoxylates (OPEs, $n = 2, 5,$ and 10).

To evaluate the dispersion effectiveness of the acidic dispersants we synthesized and other commercially available dispersants, various rheological characterizations of the pastes such as viscosity, viscoelasticity, and thixotropy were performed. The effect of the oxyethylene chain length of the acidic TRITON X-based dispersants on rheological properties of BAM paste was investigated in detail.

EXPERIMENTAL

Materials

The phosphor employed in this study, BAM ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}, \text{Mn}^{2+}$), was purchased from Kasei Optonix, Japan. The BAM powder has a nominal particle diameter of $3.81 \mu\text{m}$. To remove any physically adsorbed water and volatile organics on the powder surface, BAM was vacuum-dried at 130°C for 24 h before use. α -Terpineol (Kanto Chemical, Japan) and butyl carbitol acetate (Kanto Chemical) were used as suspending media (Table I). Ethyl cellulose (Ethocel, standard 45, Dow Chemical, USA) with 48.0–49.5% ethoxy contents was used as a binder (Table I). KD-9 and KD-15 (Uniqema), BYK111 (BKY-Chemie, Germany), RE610 (TOHO, Japan), oleic acid (Aldrich), and oleoyl sarcosine (Aldrich) were used as commercial dispersants. TRITON™ X-based surfactants containing a carboxylic group in the oxyethylene chain end, i.e., [OPE2-COOH], [OPE5-COOH], and [OPE10-COOH], were prepared from OPEs of different oxyethylene units ($n = 2, 5,$ and 10) and ethyl bromoac-

tate via an etherification reaction followed by saponification.¹²

The dispersants we synthesized are coded for example OPE10-COOH. The codes of OPE10 and COOH represent OPE with 10 oxyethylene units and terminal carboxylic acid, respectively, (Table II).

Instruments

The particle size and zeta potential of the BAM powder were determined by electrophoretic light scattering spectrophotometer (ELS-8000, Photal, Otsuka Electronics, Japan). The rheological behaviors of the BAM pastes were monitored using 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: $54 \mu\text{m}$).

Formulation of BAM pastes

Formulation process of the pastes is shown in Scheme 2. First, ethyl cellulose binder solution was prepared by dissolving ethyl cellulose (10 wt %) in α -terpineol at 70°C in the 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 adding a dispersant into the ethyl cellulose binder solution followed by adding a certain amount of BAM powder. The paste was milled with yttria-stabilized zirconia ball for 12 h to ensure a thorough and uniform adsorption of the dispersant on the particles.

RESULTS AND DISCUSSION

This research was performed toward the development of well-dispersed BAM paste by applying improved dispersion chemistry, focusing on the newly synthe-

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

	Ethyl cellulose	α -Terpineol	BCA
Synonym	EC-STD45, Ethocel®	–	Butyl diglycol acetate
M.W.	10,000–20,000	154.25	204.27
Structure			
Density (g/mL)	1.14	0.93	0.978
Boiling point	–	217°C	245°C
Supplier	Dow Chemical	Aldrich	Aldrich
Comment	48–49.5% ethoxy content	–	–

TABLE II
Codes for Various TRITON™ X-Based Dispersants Used in This Study

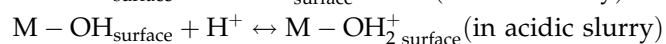
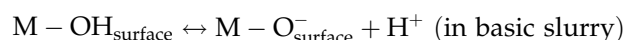
Code	Chemical structure
OPE2-COOH	
OPE5-COOH	
OPE10-COOH	
NPE10-NH2	
NPE10-imidazole	

sized carboxylic acid-containing dispersants. Thus, three novel TRITON X-based dispersants prepared from OPEs of various oxyethylene units and ethyl bromoacetate via a simple etherification reaction followed by hydrolysis¹² (i.e., [OPE2-COOH], [OPE5-COOH], and [OPE10-COOH]) were used as carboxylic acid-containing dispersants. The other two basic TRITON X-based dispersants, we synthesized previously,¹² were also used in this study for comparison (i.e., amine and imidazole-terminated nonyl phenol ethoxylates, NPEs). The chemical structures of the TRITON X-based dispersants containing hydroxyl, carboxylic acid, or amine functionality are shown in Scheme 1 and Table II.

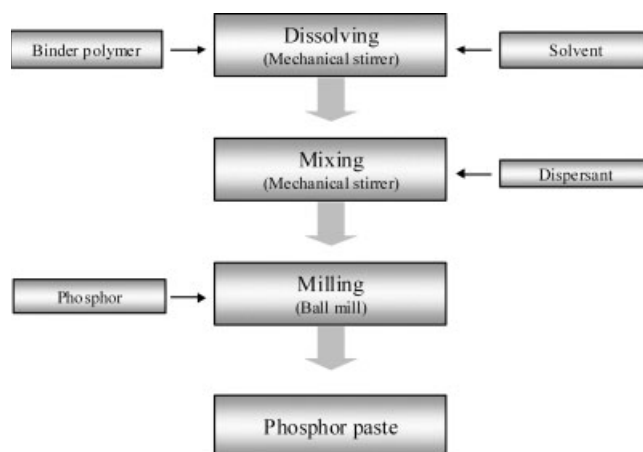
Characterization of BAM particle surface

The state of dispersion of particles in slurry (or paste) is directly dependent on the zeta potential (ζ) of the particles. The higher this potential with the same polarity, the more the electrostatic repulsion between particles. On the other hand, when close to the isoelectric point (IEP, $\zeta = 0$), the particles tend to flocculate. For a given slurry, the zeta potential is directly dependent on the pH. When dispersing oxide particles in water, there is a surface reaction leading to the for-

mation of M—OH type hydroxide groups that can dissociate as weak acid or base:



The pH of slurries is determinant on the electrostatic charges on the surface of oxide particles and



Scheme 2 Formulation process of the BAM phosphor pastes.

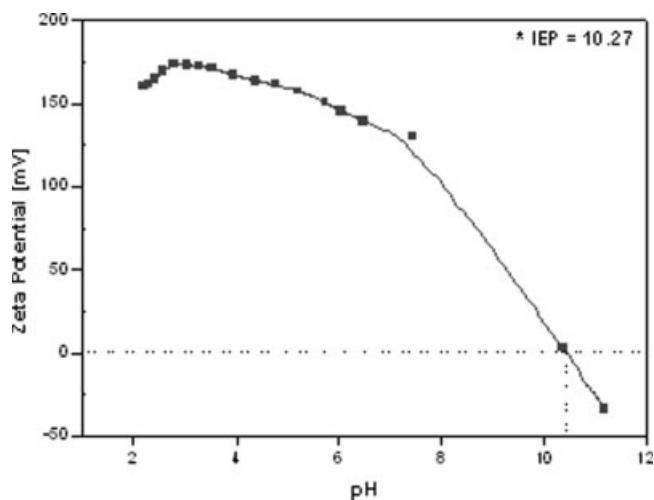


Figure 1 Zeta potential value of BaMgAl₁₀O₁₇:Eu²⁺, Mn²⁺ phosphor (36.4 g) in DI water (230 mL).

therefore on the zeta potential value, hence, on their dispersion state.

In our experiment, we placed BAM (36.4 g) in DI water (230 mL) to prepare 4 vol % BAM slurry. And then we measured the zeta potential as an index of dispersion/aggregation of BAM particles using ELS spectrophotometer. IEP of BAM phosphor is 10.27 (Fig. 1). And in the course of the acidic titration, BAM phosphor shows the increase of zeta potential value. Therefore, it is considered that BAM phosphor particles are stable in acidic water because it has basic surfaces.

Rheological characterization of BAM pastes using various dispersants

The route to BAM paste formulation is shown in Scheme 2. For example, a dispersant (0.11 g) was added to the premade ethyl cellulose binder solution (9.143 g, 10 mL). The mixture solution was stirred for 30 min. And then BAM (10.72 g) was added, and the slurry was milled with yttria-stabilized zirconia ball (20 g) for 12 h to yield BAM paste of a volume fraction of 22% solids in the binder solution.

The rheological, viscoelastic, and thixotropic behaviors of the pastes were monitored using a stress- and strain-controlled rheometer. The viscosity and thixotropy tests were performed as a function of shear rate. The oscillatory experiments were carried out as a function of angular frequency.

Optimization of the amount of dispersants in BAM pastes

First, the viscosity of a BAM paste at a fixed volume fraction of 22% solids was measured as a function of dispersant concentration to determine the optimum

amount of dispersant in BAM pastes. Figure 2 shows the effect of the amount of OPE10-COOH as a dispersant on the viscosity of the BAM paste (22 vol % or 54 wt %) when subjected to constant shear rate of 5 s⁻¹. It can be seen that the viscosity decreases sharply until the dispersant percentage of about 1 wt %. It then becomes constant and increases slightly beyond 1 wt %. The viscosity drop may result from the increase in the rate of dispersant adsorption on the particle surface, as the amount of OPE10-COOH in the paste increases. Beyond 1 wt % for high dispersant concentrations, the slight viscosity increase could be due to the attraction between the excess nonadsorbed dispersants. It was found that the amount of 1 wt % of the OPE10-COOH dispersant corresponds roughly to the quantity necessary to cover the total surface of the BAM particles. The optimum amount of OPE10-COOH for the coverage of phosphor surfaces could be estimated by the following calculation. If the thickness (*t*) of surfactant is 70 Å, (which could be easily speculated by molecular weight of OPE10-COOH), as it is attached on the phosphor particle surfaces,

$$\begin{aligned} \text{Optimum amount of OPE10 - COOH(\%)} &= t\sigma\rho \\ &= 7 \times 100^{-10} \text{ cm} \times 2.005 \times 10^6 \text{ cm}^2/\text{g} \times 1.16 \text{ g/cm}^3 \\ f &= 1.6\% \end{aligned}$$

where σ = the surface area of phosphor (2.005 m²/g), ρ = the density of OPE10-COOH (1.16 g/cm³).

From Figure 2, the minimum paste viscosity is attained at a lower dispersant concentration than that of its theoretical calculations. This discrepancy is attributed to either incomplete dispersion of phosphor

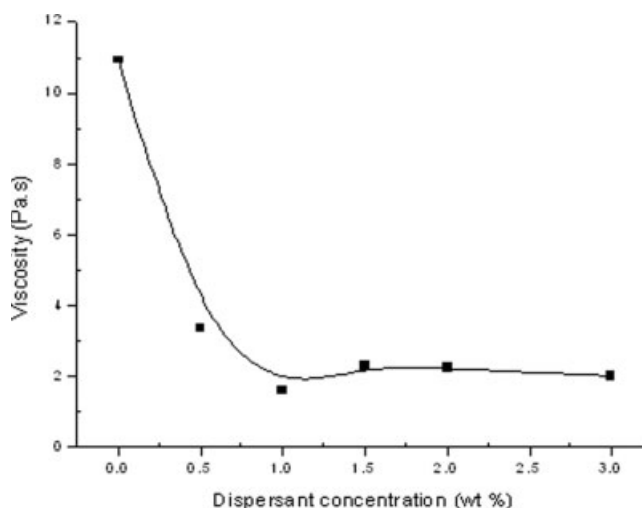


Figure 2 Apparent viscosity of BAM paste (22 vol % solid loading) as a function of OPE10-COOH concentration at shear rate of 5 s⁻¹.

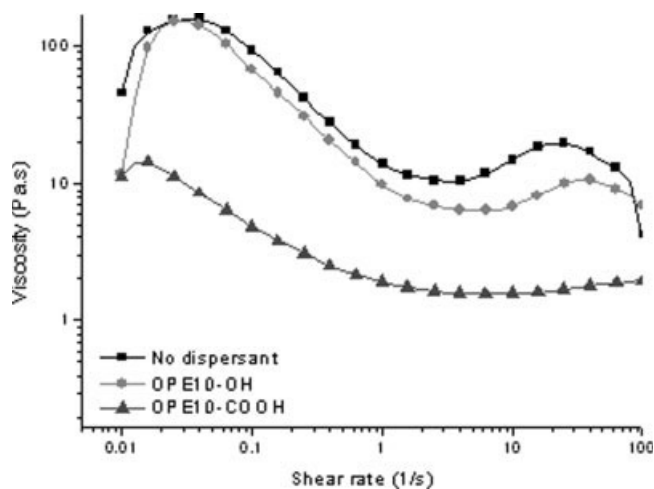


Figure 3 Apparent viscosity of BAM pastes (22 vol % solid loading) employing OPE10-OH and OPE10-COOH, respectively, as a function of shear rate.

particles during the ball milling or mass action between surfactant molecules and organic solutions.¹³

Effect of terminal groups of OPEs: Hydroxyl versus carboxylic acid

The state of dispersion of particles in slurry is highly related to its viscosity. Nondispersed and flocculated particle slurries have higher viscosities. On contrary, well-dispersed stable and deflocculated slurries have lower viscosities. Thus, various viscosity studies were carried out with 22 vol % of solid content and 1 wt % of dispersant content.

Figure 3 shows viscosities of BAM pastes using OPE10-OH and OPE10-COOH, respectively. The rheology of the paste without dispersant shows shear thinning properties at low shear rates, but the viscosity increases as the shear rate increases (dilatancy) after the onset point. First of all, for both no dispersant and OPE10-OH containing BAM paste at 22 vol %, the suspensions showed the “onset of dilatancy.”¹⁴ Dilatancy started at the shear rate at which the apparent viscosity begins to increase. In other words, in this onset of dilatancy, the suspensions showed a shear thinning property at shear rate below the “onset,” and then at the shear rate above this point, they showed a shear thickening or dilatant property. The onset of dilatancy is a function of the solid loading, particle size distribution of the powder,¹⁵ and the type of additives. When further increasing shear rate ($>20 \text{ s}^{-1}$), the paste viscosity is rapidly decreased due to slippage.¹³ This behavior indicates that the particles are severely agglomerated in the BAM paste of 22 vol % solid loading. With OPE10-OH this trend is also found, although slight reduction in viscosity is observed. However, the paste with OPE10-COOH shows the lowest viscosity implying the least agglomerates

and the most stable dispersion state. Therefore, the anchoring effect of OPEs toward BAM particles can be significantly enhanced by replacing the hydroxyl group with the carboxylic acid group in the oxyethylene chain end. From Figures 3–7, the “onset points” of 22 vol % BAM phosphor-loaded ethyl cellulose slips are shown for pastes containing as-received, hydroxyl, and amine head group dispersants, respectively.

By a comparison with the paste with no dispersant, it is evident that TRITON X-based acidic dispersant helps the dispersion of the BAM particles because of its good wettability toward BAM particles. It can be inferred that this effect is due to the enhanced adsorption of the acidic dispersant onto the basic particle surfaces (i.e., acid-base interaction, *vide supra*).

Effect of oxyethylene length of OPE-COOH

Figure 4 shows the results of viscosity measurements employing three acidic TRITON X-based dispersants of different number of oxyethylene units (i.e., OPE2-COOH, OPE5-COOH, and OPE10-COOH). OPE10-COOH shows the lowest viscosity among the acidic dispersants. It is considered that the dispersant having more oxyethylene groups is better adsorbed on polar sites of the BAM surface, causing the tail (alkyl chains of OPE-COOH) to extend into the binder solution phase. It is also likely that the stability of the adsorbed dispersant layer can be modulated by the length of the oxyethylene unit: the longer the oxyethylene unit, the higher the steric effect.

Another plausible explanation is that the longer the oxyethylene chain length, the better the solubility of the OPE-COOH in ethyl cellulose binder solution due to hydrogen bonding.

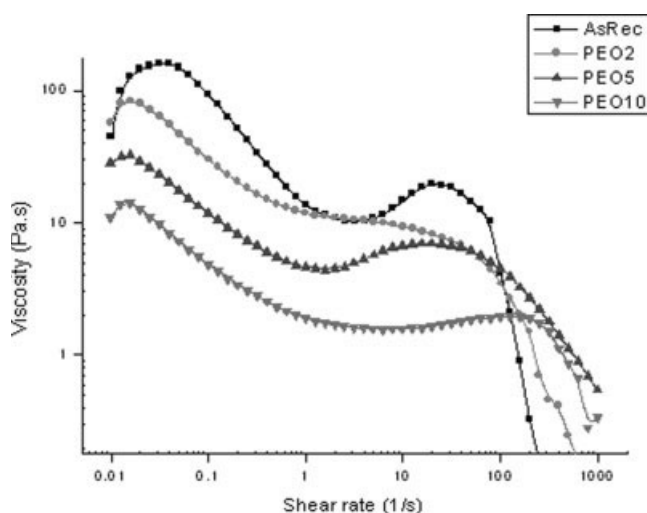


Figure 4 Apparent viscosity of BAM pastes employing OPE-COOH of different oxyethylene units as a function of shear rate.

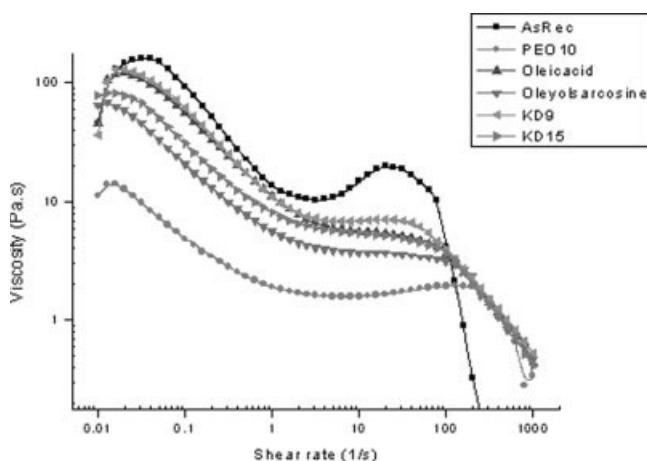


Figure 5 Apparent viscosity of BAM pastes employing OPE10-COOH and other commercial acidic dispersants, respectively, as a function of shear rate.

Comparison of OPE10-COOH with other commercial dispersants

Figure 5 shows viscosities of BAM pastes (22 vol % of solid loading) as a function of shear rate using 1 wt % of various acidic dispersants. The dispersants were commercially available products, except OPE10-COOH. All dispersants having the same carboxylic head group with different tail structures are likely to be well anchored on the BAM particles. However, it was found that KD-9, KD-15, oleic acid, and oleoyl sarcosine are less effective in dispersing BAM particles than does OPE10-COOH in the BAM/EC/terpineol system.

Since OPE10-COOH shows the lowest viscosity among the carboxylic acid-containing dispersants used in this experiment, it is likely that the structures of oxyethylene units and octyl phenol moiety of OPE10-COOH play a significant role in the anchoring of the BAM. The presence of more polar oxyethylene groups next to the carboxylic acid group may result in the enhanced physical adsorption of the dispersant onto the particle surface. In addition, OPE10-COOH is likely to have a molecular structure with polarity gradient to give well-stretched conformation in the paste. That is, OPE10-COOH has a well-extended hydrophobic tail, which may result in the superior steric stabilization compared to other commercial dispersants. The rigid benzene ring moiety of OPE10-COOH may also elevate this steric effect.

Next, this data was compared with those for other commercially available phosphoric acid-based surfactants (i.e., RE610 and BYK111; their exact chemical structures are not reported in literatures, but both are well recognized as surfactants for high-temperature purposes in industry) (Fig. 6). It can be seen that compared with the dispersants with phosphoric acid group as an anchoring group, OPE10-COOH shows more enhanced dispersion capability.

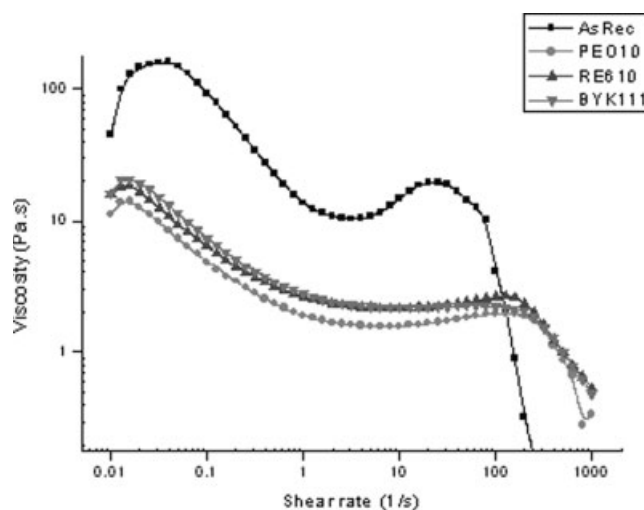


Figure 6 Apparent viscosity of BAM pastes employing OPE10-COOH and other commercial phosphoric acid-based dispersants, respectively, as a function of shear rate.

When compared with two basic TRITON X-derivatives (i.e., NPE10-NH₂ and NPE10-imidazole), OPE10-COOH also shows more enhanced dispersion capability (Fig. 7). Although both NPE10-NH₂ and NPE10-imidazole have the almost same alkyl phenol ethoxylate structure as OPE10-COOH, they are less effective in dispersing BAM particles in our system probably due to the presence of basic amino terminal groups, resulting in poor anchoring onto the basic BAM surface.

Viscoelasticity of BAM pastes

Concentrated colloidal suspensions commonly display viscoelastic behaviors, which can be characterized by dynamic rheological measurements (or oscilla-

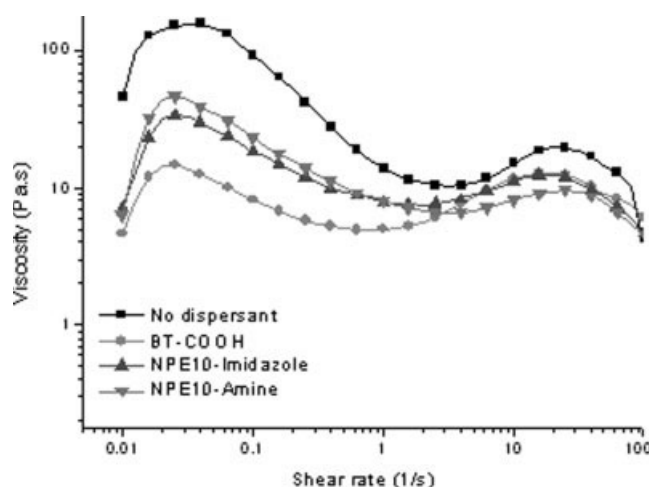


Figure 7 Apparent viscosity of BAM pastes employing BT-COOH, NPE10-imidazole, and NPE10-amine, respectively, as a function of shear rate.

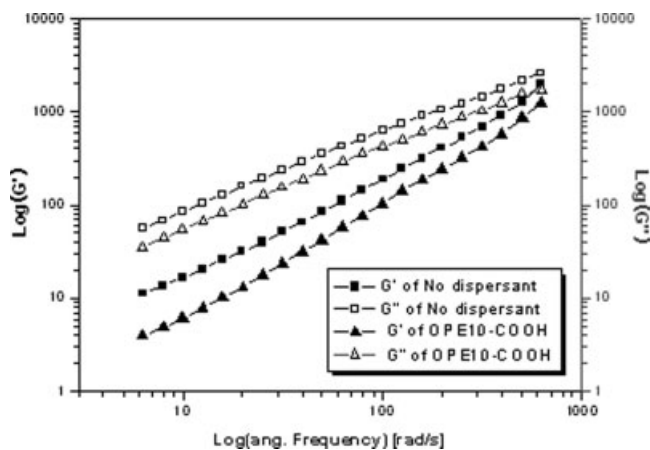


Figure 8 G' and G'' of BAM pastes with or without OPE10-COOH.

tory techniques). To clarify the dispersion stability of the BAM paste using OPE10-COOH, oscillatory shear measurements were carried out. The effect of angular frequency amplitude on the storage modulus (G') and loss modulus (G'') of BAM pastes in the absence and presence of OPE10-COOH is shown in Figure 8. Liquid-like responses ($G'' > G'$ and $0 < \delta < 90$) are observed in both cases. This viscoelastic response is common in suspensions and pastes. Figure 9 shows that the BAM paste containing OPE10-COOH (1 wt %) has a higher $\tan \delta$ ($= G''/G'$) at low frequency levels, which indicates that it is more like liquid and better dispersed than the paste without OPE10-COOH.

Thixotropy of BAM pastes

Shear stress (τ) versus shear rate ($\dot{\gamma}$) curves for the BAM paste without dispersant and the one with 1 wt % of OPE10-COOH are shown in Figure 10, in which the

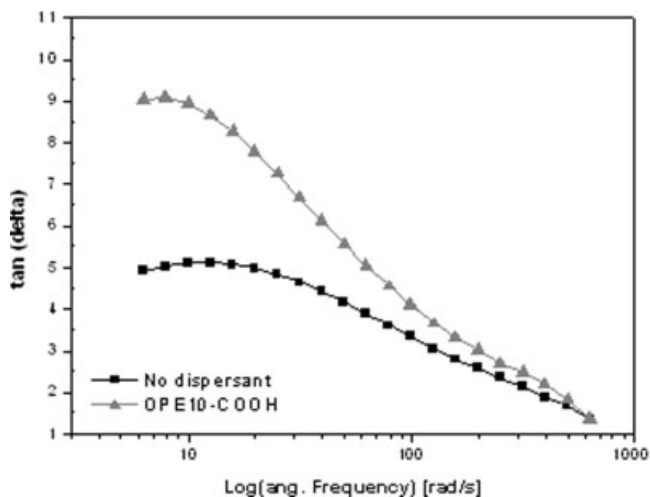


Figure 9 $\tan \delta$ values of BAM pastes with or without OPE10-COOH.

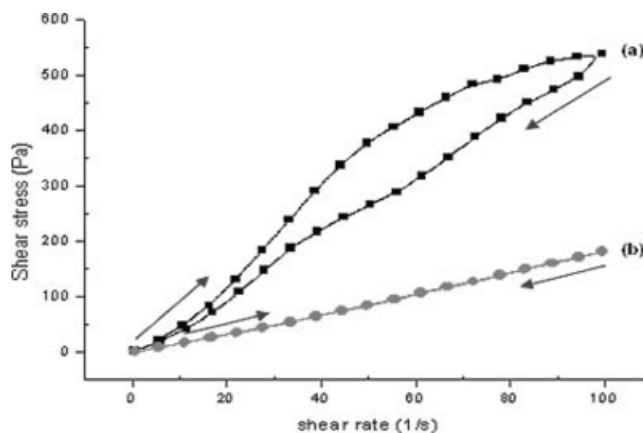


Figure 10 Shear stress versus shear rate diagrams of BAM pastes (a) with no dispersant and (b) with 1 wt % of OPE10-COOH.

effect of OPE10-COOH on the rheology is clearly seen. In case of the paste with no dispersant, the BAM particles are aggregated, and non-Newtonian behavior is observed. On the other hand, the paste with OPE10-COOH shows Newtonian flow behavior, indicating well-dispersed particle suspension.

The rheological properties of concentrated colloidal suspensions are often time-dependent. Thixotropic systems exhibit an apparent viscosity that decreases with time under shear, but recovers to its original viscosity when flow ceases. Thus, thixotropy is defined as viscosity changes with time due to particle flocculation in liquid and described by the area of curves formed during the cyclic shear flow [Fig. 10(a)]. By adding the OPE10-COOH dispersant into the BAM paste without dispersant, the thixotropic behavior of the paste is significantly reduced [Fig. 10(b)].

CONCLUSIONS

TRITON X-based dispersants that are composed of a OPE (or NPE) backbone and a terminal carboxylic acid (or amine) as an anchoring group were employed in the formulation of [BAM/ethyl cellulose/terpineol] pastes. The addition of TRITON X-based acidic dispersants (i.e., OPE2-COOH, OPE5-COOH, and OPE10-COOH) regulated the rheological behavior of the paste enormously. The results showed that the introduction of the acidic dispersants into the paste greatly reduced the apparent viscosity of the pastes. The addition of TRITON X-based basic dispersants (i.e., NPE10-NH₂ and NPE10-imidazole) into the paste could regulate the rheological behavior of the paste to a much small extent. It was concluded that OPE10-COOH having an amphiphilic 10 oxyethylene units and a carboxylic acid head showed the better dispersion ability for the BAM phosphor powder than any

other various type dispersants used in this study. Therefore, it is expected that the OPE10-COOH dispersant is most suitable to the display industry.

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