Effect of Core/Shell Acrylic Microgel on Rheological Properties and Orientation of Aluminium Flakes in Water–borne Metallic Basecoats

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Abstract

Core/shell acrylic microgels were synthesized by emulsion polymerization. The core is slightly crosslinked by a difunctional monomer and the shell contains a sufficient amount of carboxyl groups which are partially or fully neutralized by amines. After neutralization, sufficient pseudoplastic flow behavior due to the mutual interaction of the polymer particles at low solid contents below 20 w.t.\% in the final metallic basecoat paint can be achieved. As a results, the orientation of aluminium flakes with the extreme shrinkage of low solids metallic basecoat during flash-off time is parallel to the surface of substrate(flop effect). Dynamic rheological property was also found to influence the flop effect of metallic basecoats.

Introduction

Recently there has been an increasing demand to reduce the amount of volatile organic compound(VOC) causing atmospheric pollution in paint industry. Those demand has also brought new technologies such as high solids, powder and water–borne paints to the automotive paints. Especially, the introducing of water–borne paint was central to the metallic basecoat due to the low solid content for the best aluminium appearance. The only way of achieving such low solid content at application with a low VOC is to use a water–borne paints[1].

The various types of polymers used in waterborne paints has been studied from the point of view of the synthesis and their principal properties. Of the various polymers, microgel or crosslinked polymer microparticles has been of
more interest to automotive metallic basecoat because microgel can help to improve the quality of coatings such as rheological properties, tensile strength and solvent resistance[2-3]. More recently, the core/shell acrylic microgel of ICI company has been synthesized by nonaqueous dispersion(NAD) method and transferred to aqueous system[4]. This acrylic microgel has been reported to imparts to the paint sufficient pseudoplasticity or thixotropic properties, which are not much influenced by variation of temperature and humidity. Moreover water evaporates more rapidly, enabling short flash-off time, as the viscosity does not increased very much on evaporation of water. So the coating system in metallic basecoat shows good flop in the broad application windows (temperature and humidity).

In this study, we have synthesized core/shell acrylic microgel by emulsion polymerization to minimized VOC and simplify NAD processes. Finally, the properties of metallic basecoat containing acrylic microgel such as rheological behavior and the orientation of aluminium flakes are described.

**Experimental**

**preparation of microgel**

The acrylic microgel is synthesized by emulsion polymerization through the three steps of seed/core/shell. In the seed polymerization, a normal batch emulsion polymerization with two acrylic monomer mixture was carried out. For the preparation of crosslinked acrylic core, a difunctional monomer such as 1,6-hexanedioldiacrylate(1,6-HDDA) and the structural monomer mixture of seed polymerization stage were used. In the polymerization step of shell, the shell was prepared by polymerization of suitable acrylic monomers also containing (meth)acrylic acid to create the water solubilizing sites in the shell structure. Finally, the carboxylic groups of the product obtained was neutralized with dimethylamino ethanol(DMEA).

**preparation of silver metallic basecoat**

The main binder of the water-borne metallic basecoat was the core/shell acrylic microgel previously prepared. Other additives such as thickener(Hv-30), organic solvents(butoxy ethanol etc.), and inhibited aluminium flake(Korea chem. co. Ltd) were also used. Finally solvent-borne clearcoats was applied wet-on-wet on the basecoats.

**characterization of emulsion and its paint**
Particle size of microgels were measured by both a laser light scattering (LLS) method and a transmission electron microscopy (TEM). Rheological measurements of emulsion and its paints were made with Haake RS100 rheometer over shear rate of 1.0 sec\(^{-1}\) to 500 sec\(^{-1}\) at 25°C. The orientation of aluminium flakes of paints was investigated with by scanning electron microscopy (SEM).

**Results and discussion**

As the carboxylic groups of microgel is neutralized with DMEA, the shell size of particle and the viscosity of emulsion significantly increase. The viscosity behaviors were greatly changed with shear rate, being destroyed upon application of high shear stress and re-built when shearing stops. This concept is illustrated in Fig. 1.

![Fig. 1. Schematic illustration of the pseudoplasticity in core/shell microgel emulsion.](image)

The main factors that affect the rheological properties of the core/shell microgel is the hydrophilicity of the shell-forming copolymer in shell. But the viscosity of the microgel emulsion does not depend on \(T_g\) of the shell. The results obtained with respect to \(T_g\) and water solubility of the shell-forming copolymer were shown in Table 1.

In spite of extremely low solid content(17 to 19% b.w), the paint containing MG3 shows sufficient pseudoplasticity without a thickener. Fig. 2 (a) shows the rheological behavior of the silver metallic paint containing MG3. These pseudoplasticity endows the paint with good spray workability, sag resistance, and good storage stability. Due to the lower solid contents and faster drying time characteristics than solvent-borne counterparts, bigger shrinkage of the paint during flash-off time brings about good flop effect. Fig. 2 (b) shows
SEM micrograph of the cross section of paint film containing MG3. In this picture, the parallel orientation of the aluminium flakes is easily seen.

Table 1. Effect of shell-forming comonomer on rheological properties of microgel emulsions.\(^a\)

<table>
<thead>
<tr>
<th>Name</th>
<th>Shell-forming comonomer (16.7:83.3 w.t.%)</th>
<th>Calculated T_(\text{g}) of shell((^\circ)C)</th>
<th>Water solubility of the shell-forming comonomer (% at 25(^\circ)C)</th>
<th>Shell size (nm)</th>
<th>Viscosity (Poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG1</td>
<td>SM/BA</td>
<td>-18.6</td>
<td>0.17</td>
<td>87</td>
<td>181</td>
</tr>
<tr>
<td>MG2</td>
<td>MMA/BA</td>
<td>-18.3</td>
<td>0.42</td>
<td>86</td>
<td>273</td>
</tr>
<tr>
<td>MG3</td>
<td>MMA/EA</td>
<td>4.4</td>
<td>1.50</td>
<td>87</td>
<td>362</td>
</tr>
<tr>
<td>MG4</td>
<td>SM/EA</td>
<td>4.1</td>
<td>1.25</td>
<td>85</td>
<td>258</td>
</tr>
<tr>
<td>MG5</td>
<td>SM/2-EHA</td>
<td>-43.7</td>
<td>0.01</td>
<td>84</td>
<td>111</td>
</tr>
<tr>
<td>MG6</td>
<td>MMA/2-EHA</td>
<td>-43.5</td>
<td>0.26</td>
<td>85</td>
<td>153</td>
</tr>
</tbody>
</table>

\(^a\) : seed/core/shell w.t. ratio=4:73:23; seed composition SM/EA=50:50; core composition SM/EA/HDDA=34:64:2; Acid value by MAA is 20mg KOH/g and hydroxy value by 2-HEA is 20mg KOH/g; Butoxy ethanol is 7.5% of total weight. \(b\) : degrees of neutralization=100%

Fig. 2. Rheological property(a) and cross section of the silver metallic basecoat clear film(b) for the silver metallic paint of MG3.

Reference