

UV curable acrylic dispersion for the cationic electro-deposition coating

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Summary

The vinyl group containing polymer was synthesized via radical polymerization of acrylic monomers followed by reaction with methacrylic oxyethyl isocyanate(MOI). Stable dispersions of the vinyl group containing polymer, pentaerythritol triacrylate(PETA) and photo initiator were prepared by neutralization of the above synthesized polymer with lactic acid. Electro-deposition process was introduced to apply UV-curable acrylic dispersion into the nickel-plated plastic substrate. The prepared dispersion containing PETA has higher particle size and higher deposition yield than those of the dispersion without PETA. The electro-deposited film was cross-linked by UV radiation after 10 minutes flash-off stage at 80 °C. The kinetic study by real-time FT-IR revealed that the cross-linked films containing PETA gave higher conversion than those without PETA resulting in harder film.

Introduction

The growing concern in the environment friendly coating industry has led to the development of solvent-free formulations, which can be cured at ambient temperature by short exposure to UV-light or electron-beam.¹ Water-borne UV curable resins have started to gain commercial significance over the past few years.² A new development in water-based UV curable resins results in a wide variety of technical approach for industrial applications. They are classified into the aqueous emulsion and the aqueous dispersion. Both resins should have vinyl groups for UV curing and hydrophilic groups for stabilization in water. The main drawback of water-borne UV curable resins is that the curing behavior is significantly dependent on the water content of the applied film. To overcome this problem, it is necessary to reduce the water content of wet film before UV curing, such as flash off process. The water flash-off stage, however, requires energy, space and time, as well as changes of design in coating line.³

On the other hand, electro-deposition process of the water-borne resin can electrophoresis, penetrate, and deposit to form a uniform film even on the surface of the recessed and shielded area where other coating methods cannot be applied.⁴ Moreover the electro-deposition film can be reduced to 5 wt% of the water content by the electro-osmosis.⁵

In this study, electro-deposition process was introduced to the UV curable acrylic dispersion. We prepared acrylic dispersions containing vinyl groups to investigate the electro-deposition, curing and film properties of UV-curable coating.

Experimental

Methacryl oxyethyl isocyanate (MOI) was obtained from Showa Denko Corporation. The other methacrylic monomers, 2,2'-azobis(2-methylpropionitrile) (AIBN) and pentaerythritol triacrylate (PETA) were purchased from Aldrich, and were used without further purification. Photo-initiator, Darocure 1173 was obtained from Ciba-Geigy Co.. All solvents were dried over molecular sieves.

Vinyl group containing polymer was prepared as follows: 32.56g of butyl methacrylate, 138.4g of methyl methacrylate, 57.0g of 2-hydroxy ethyl methacrylate, 18.0g of 2-(dimethylamino)ethyl methacrylate and 8.0g of AIBN were slowly added to 207.0g of methyl ethyl ketone(MEK) at 90 °C for 2 hours. After additional 2 hours, 1g of hydroquinone, 0.20g of dibuthyltin dilaurate and 54.3g of MOI were added to acrylic polymer solution (1) and maintained at 60 °C for 2 hours. The resulting polymer(2) was characterized by ¹H NMR, δ 5.6 and 6.1 ppm (CH₂=) and 2.3 ppm

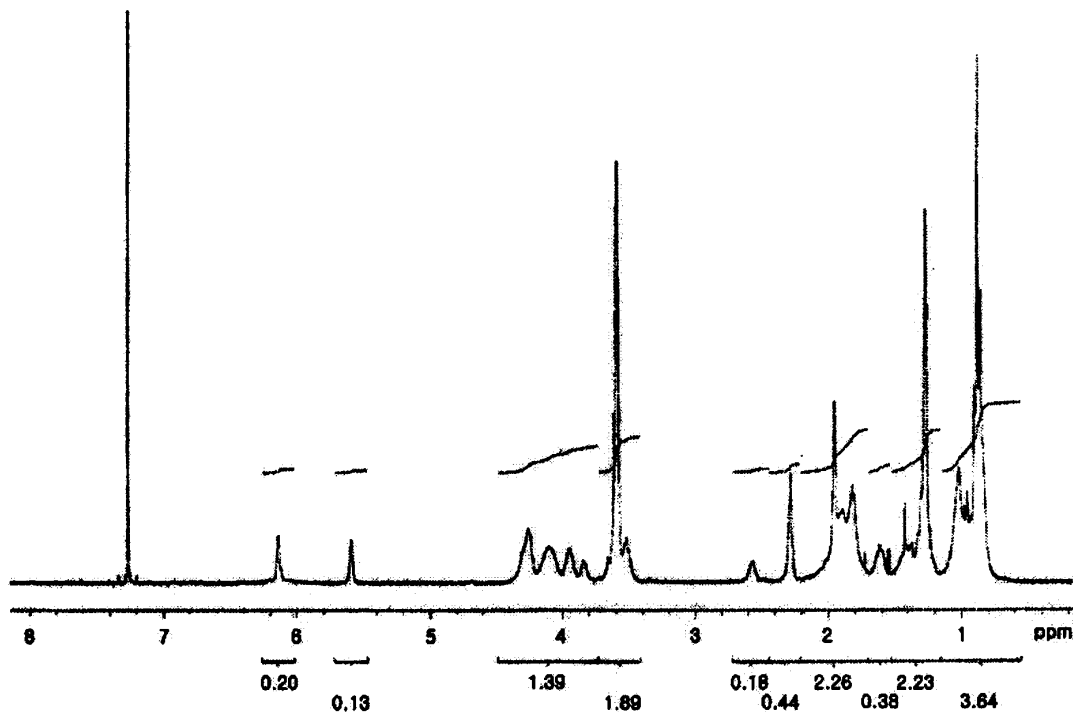


Figure 1. ¹H NMR Spectrum of Polymer (2).

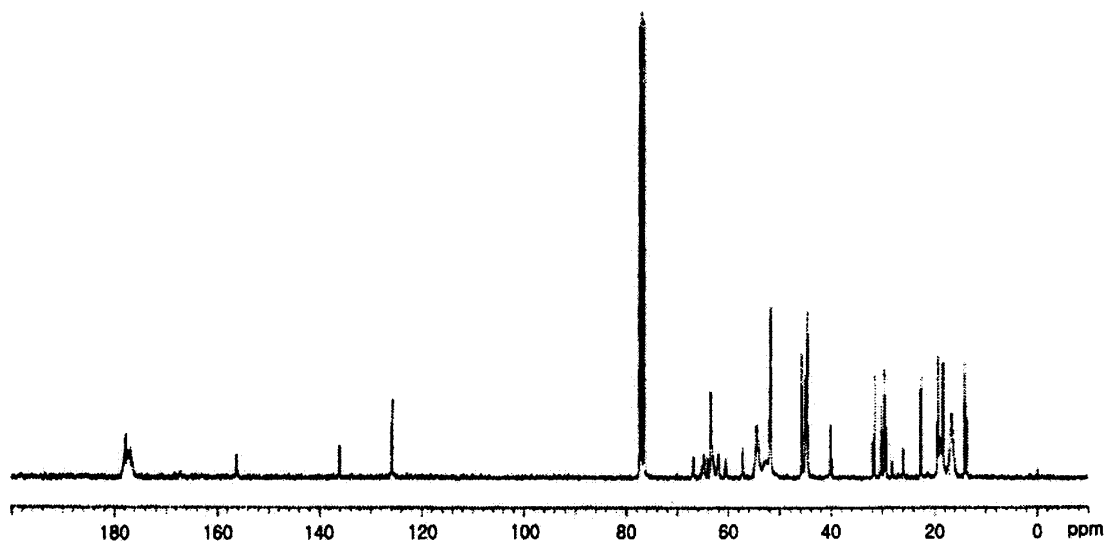


Figure 2. ^{13}C NMR Spectrum of Polymer (2).

$((\text{CH}_3)_2\text{N}-)$ as shown in Figure 1 and by ^{13}C NMR, δ 177.7 ppm ($-\text{CO}_2-$), δ 156.4 ppm ($-\text{NHCOO}$), δ 136.1 ppm ($=\text{C}(\text{CH}_3)-$) and δ 126.8 ppm ($\text{CH}_2=$) as shown in Figure 2.

Three hundred grams of the polymer (2) (60 w% in MEK), 15g of PETA and 4.5g of Darocure 1173 were charged to a reactor equipped with an electrical stirrer and neutralized with 0.6 g of lactic acid, one thousand grams of deionized water was added into the mixture slowly and agitated violently to disperse the polymer into a water phase to form a stable emulsion, having a resin concentration of 14.5 wt% by total weight.

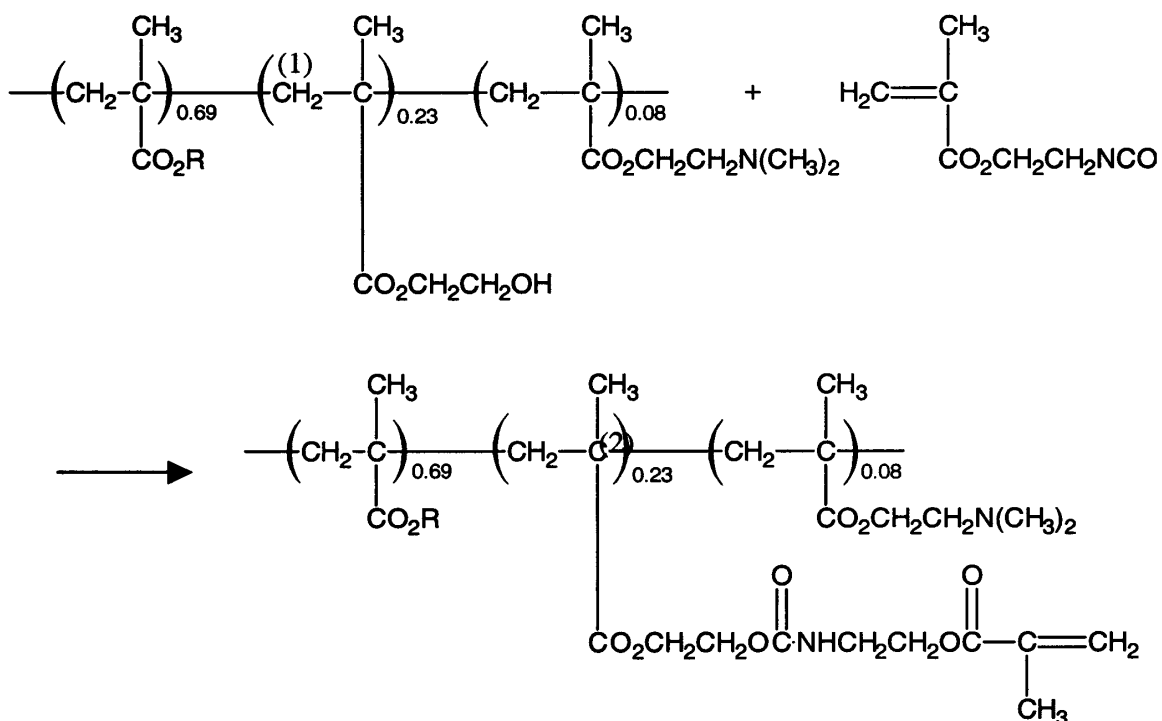
The cathode panels were cut out nickel plated poly(ethyleneterephthalate)(PET) film and had an area of 130 cm^2 , while the area of the stainless steel counter electrode (anode) was 100 cm^2 . Cathode-to-anode distance was 10 cm. The bath was moderately stirred by mechanical means. After deposition, the coating was rinsed with distilled water and exposed to the radiation of a 200 W/inch medium pressure mercury lamp, in the presence of air, at a passing speed of 60 m/min (light intensity: 500 mWcm^{-2})

The hardness of the cured film was measured by using graphite pencils of increasing hardness as described in ASTM D 3363-74. The photopolymerization of polymer (2) and mixture of polymer (2)/PETA was studied by using real-time FT-IR/ATR spectroscopy (ATS-1000 from ASI Applied Systems). The samples were continuously irradiated with 80 W/cm^2 from a mercury lamp. In particular, the decrease of the peak centered at 811 cm^{-1} (C-H deformation mode of acryl group) was monitored.

Results and Discussion

Synthesis

The radical polymerization of 2-(dimethylamino)ethyl methacrylate, 2-hydroxyethyl methacrylate and alkyl methacrylates with AIBN was carried out in methyl ethyl ketone at 90 °C. Hydroxy group containing polymer (1) further reacted with MOI producing vinyl group containing polymer(2) as shown in Scheme 1.



Scheme 1. Synthesis of Polymer (2) containing vinyl group.

Particle Size Control

Stable dispersions were obtained by the neutralization of dimethylamino group of polymer (2) with lactic acid. Darocure 1173(Ciba-Geigy) as a liquid type photoinitiator was used. The neutralized polymer (2) solution containing Darocure 1173 could be dispersed into stable dispersion without any phase separation of photoinitiator. The greater of the concentration of salt groups in the resin, the greater the tendency of the organic phase to disperse. As shown in Figure 3, particle size of the polymer dispersion is decreased with the concentration of salt groups in the polymer. Particle size of polymer dispersion containing PETA is larger than that of without PETA in the same concentration of salt groups.

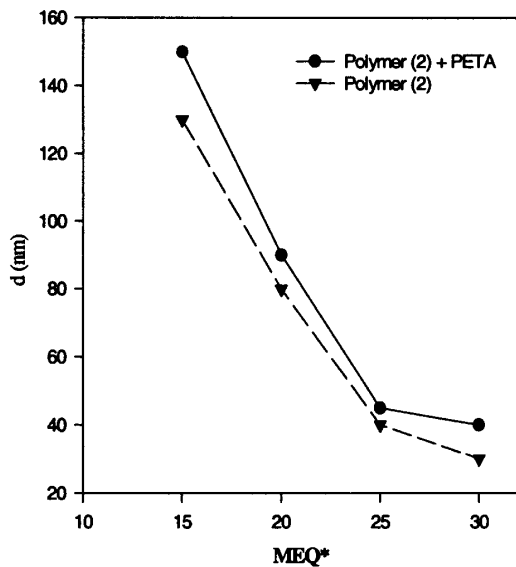


Figure 3. Dispersion particle control on the degree of neutralization; ▼: polymer (2), ●: polymer (2) containing 10 wt% PETA, measured by a Coulter N4M sub-micron particle analyzer

*MEQ : milliequivalents of salt/100g of solid resin

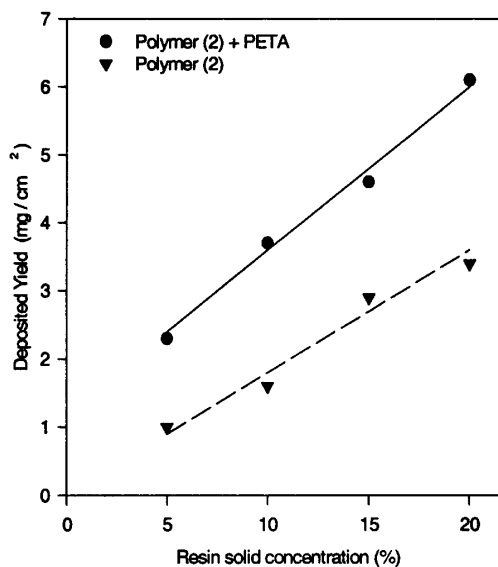


Figure 4. Effects of resin solid concentration of dispersion on deposited yield; ▼: polymer (2), ●: polymer (2) containing 10 wt% PETA.

Curing Properties of UV cured Films

Water content of electrodeposited film measured by Karl Fisher titration was 4.5 wt%. This 4.5 wt% of water with MEK, which was used in radical polymerization, was evaporated during 10 minutes flash-off process at 80 °C. The electro-deposited film was cross-linked by UV radiation after the flash-off stage. The kinetics of the radiation-induced cross-linking of the electro-deposited film was studied by real time FT-IR spectroscopy, by monitoring the decrease of the absorption bands characteristics of the acrylate double bond at 811 cm⁻¹ upon UV exposure.⁵

The typical real-time FT-IR/ATR spectra of UV exposed polymer (2) containing 10wt% PETA are shown in Figure 5. The spectra are highlighted by the disappearance of the 811 cm⁻¹ band characteristic of the C-H deformation modes of the acryl group. The cure profile of polymer (2) was compared to the polymer (2) containing 10 wt% PETA. Figure 6 shows the conversion curves of photopolymerization for polymer (2) and polymer (2) containing 10wt% PETA, respectively. The conversion was calculated at various intervals using the following equation:

$$\text{Conversion (\%)} = ([I_{811}]_0 - [I_{811}]_t) / [I_{811}]_0 \times 100$$

Where $[I_{811}]_0$ and $[I_{811}]_t$ are the sample absorbance intensity at 811 cm^{-1} , before and after UV exposure, respectively. As shown in Figure 6, the overall reaction rate as well as final conversion of polymer (2) containing 10 wt% PETA are higher than those of polymer (2), presumably because the reaction is more highly diffusion controlled in triacrylate polymerization. Pencil hardness of film was found to increase with the addition of UV curable acrylic PETA into dispersion from 1H to 2H. It is believed that the addition of PETA in dispersion raised the conversion by increasing the mobility of the acrylic double bond and acting as a bridge during cross-linking, leading to harder films.

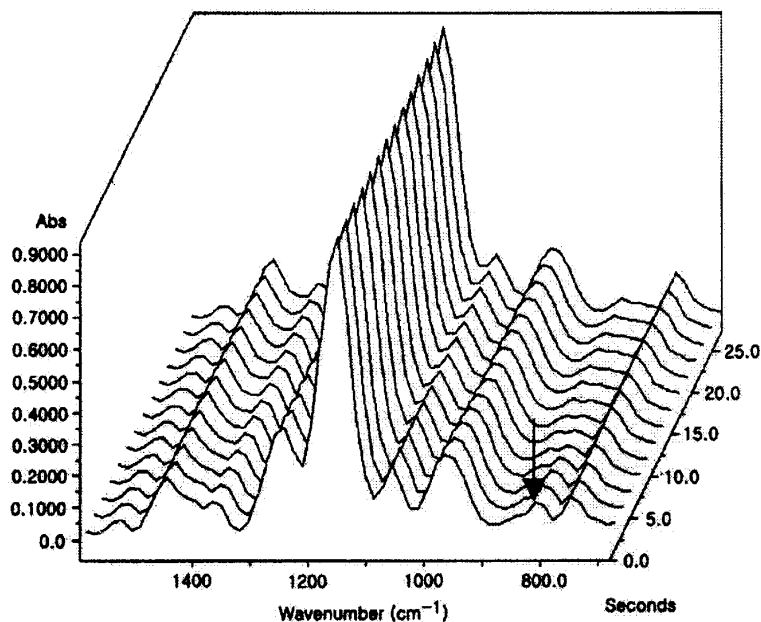


Figure 5. Real-Time FT-IR/ATR spectra of UV exposed sample: polymer (2) containing 10 wt% PETA.

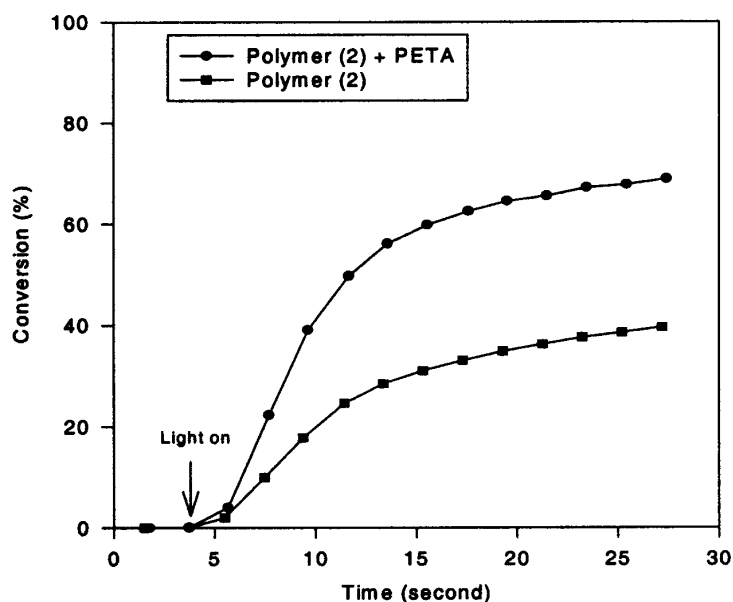


Figure 6. Conversion vs reaction time for polymer (2) and polymer (2) containing 10 wt% PETA.

Conclusion

It is notable that combination of cationic electrodeposition and UV curable acrylic dispersion makes ambient curing possible after relatively short flash-off process, which is comparable with the conventional UV coating system. UV curable acrylic dispersion containing vinyl group for electro-deposition coating was prepared by radical polymerization of acrylic monomer and neutralization with organic acid. The PETA containing dispersion has higher particle size and higher deposition yield than those of the dispersion without PETA. The UV cross-linking of cationic electrodeposition coatings is an efficient method to produce ambient curing film with reasonable coating properties.

References

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