UV Curable Polysiloxane-acrylic Hybrid Resins

Koji Uemura, Takashi Mukai, Teruki Kiyohara

DIC Corporation Sakai plant

1-3, Takasago, Takaishi city, Osaka, Japan

1. Introduction

Plastics have been used in a wide range of products including architectural materials and exterior and/or interior automotive parts. Plastics can offer excellent impact resistance and clarity attractively, they allow for design freedom and thus allow for some very aesthetically appealing appearances that were once inconceivable. However, they have a major drawback in that they don't always provide the desired degree of chemical, scratch and weather resistance. To overcome this problem, a new development work has been done in the coating area. We previously reported the inorganic-organic hybrid non UV curable resin which shows high weather resistance[1-2].

In this paper, we report a novel synthetic method of the UV curable polysiloxane-acrylic hybrid resin applicable to plastic coatings and demonstrate the cured film provides an excellent property by UV-thermal dual curing system.

2. Experimentals & Concepts

2-1. Procedure for the synthesis of the resins

UV curable inorganic-organic hybrid resin was prepared by condensation reaction between polysiloxane having UV curable double bond and acrylic polymer having alkoxysilyl groups as shown in Fig.1. The synthetic methods of the hybrid resin consist of two steps.

At first, we prepared polysiloxane segments, having UV curable groups and alkoxysilyl groups by the sol-gel reaction in the presence of acid catalyst (e.g. phosphoester). Organoalkoxysilane was used as the primary silane monomer and as the source of UV curable double bond.

Secondly, we hybridized the polysiloxane segments with acrylic polymer having both alkoxysilyl functional groups and hydroxyl groups in organic solvent in the presence of pure water and acid catalyst through the hydrolysis and the condensation reaction. Hydroxyl groups in the hybrid resins can crosslink with polyisocyanate to form a cured film.

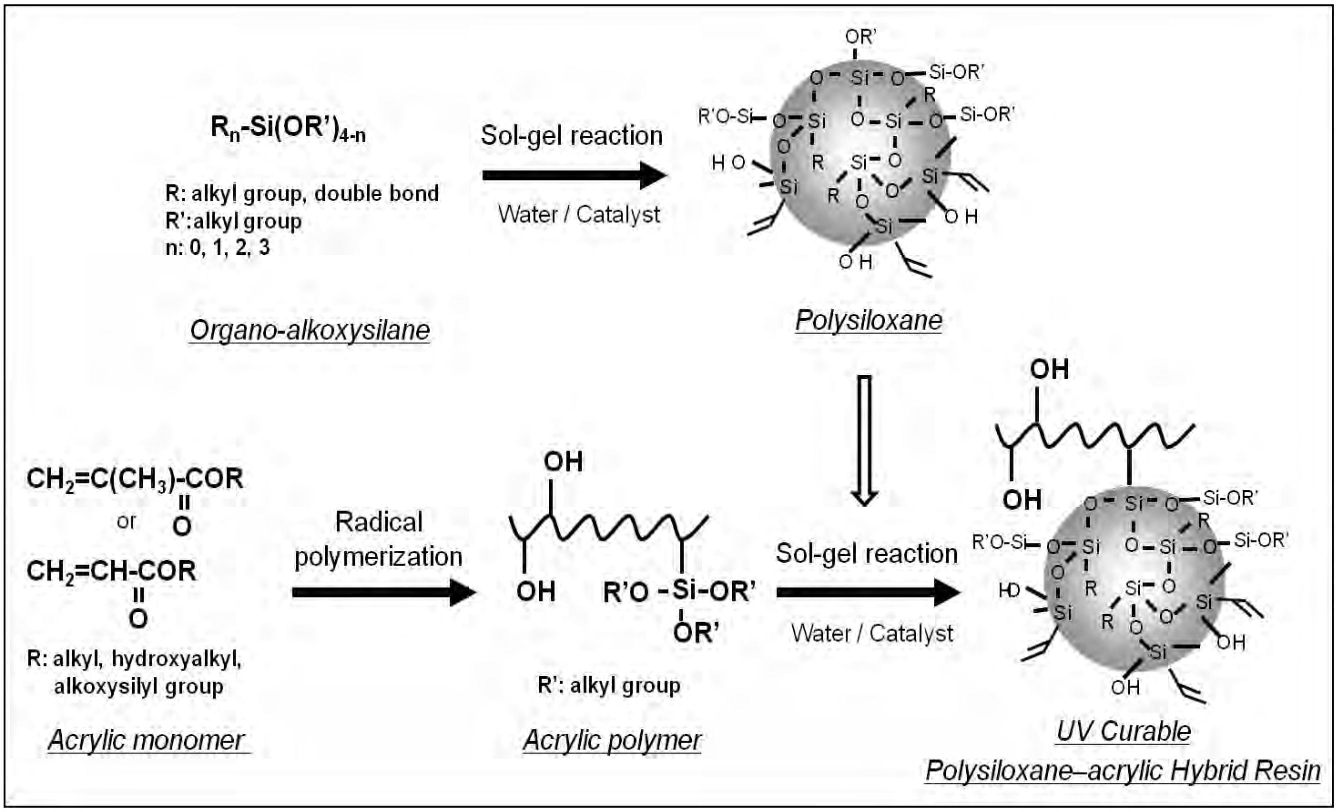


Fig.1 Hybridization of acrylic polymer and polysiloxane.

In this work, we could prepare several types of UV curable inorganic-organic hybrid resins in the ratio of 25 to 90 wt% of polysiloxane without issue of gel.

2-2 The concept of hybrid curing system

Fig.2. shows the concept of cross-linking of the hybrid resin[3-4]. The resin is designed for dual-curing system by introducing double bond and hydroxyl group into the polymer that gives UV curable reaction and urethane reaction, respectively. The hybrid resin certainly shows excellent weather and scratch resistance even by only UV curing system; however, it has drawback such as brittleness and/or poor adhesive property of the cured film.

We will report the performances of the inorganic-organic hybrid resin in UV curing and polyisocyanate curing system in our presentation.

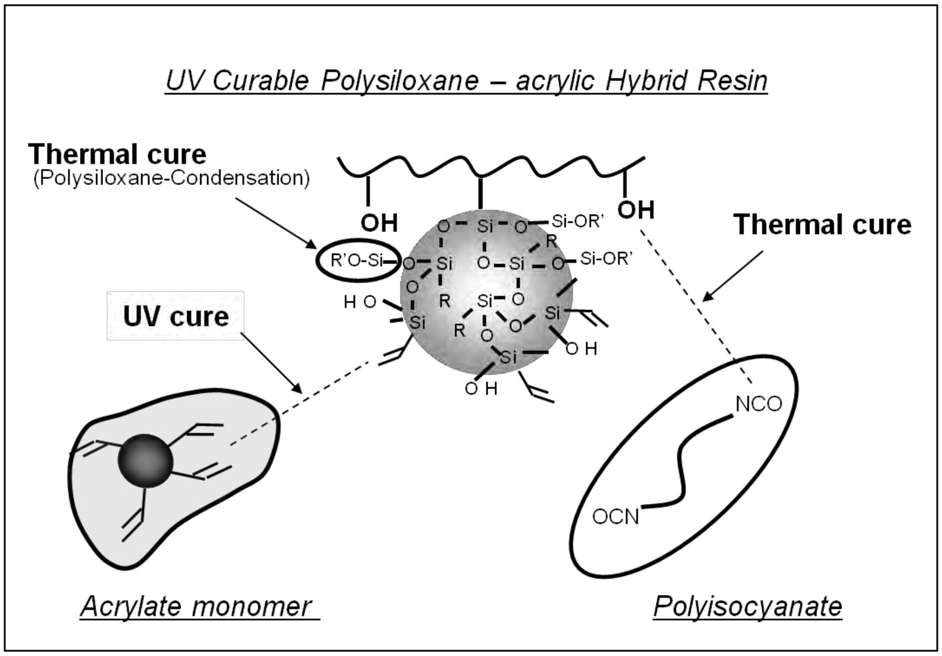


Fig.2 Cross-linking system of the hybrid resin coating

2-3 Coating formulation

Coating composition was formulated by the UV curable inorganic-organic hybrid resin, multifunctional acrylates, photoinitiator, UV absorber, light stabilizer. The composition was designed to contain 35 wt% polysiloxane in order to give not only good weather resistance, but also good scratch resistance. Furthermore, we added polyisocyanate as hardener before UV irradiation.

2-4. Preparation of UV cured films

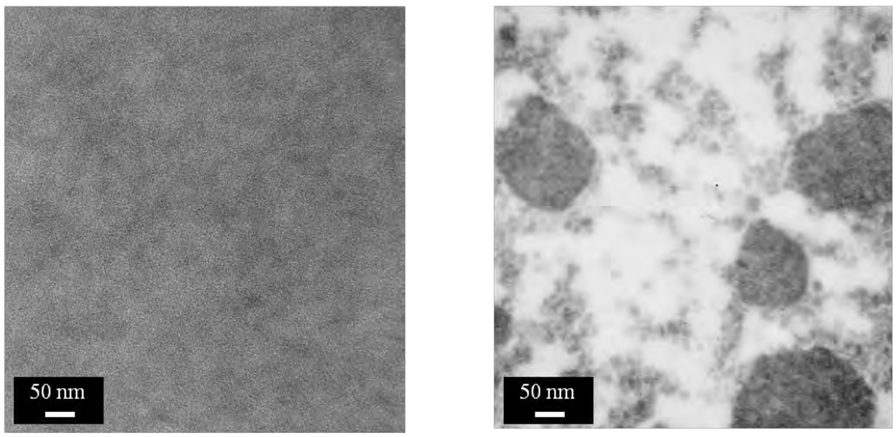
The film of 20 µm thickness was prepared on the various substrates through flash off at 80℃ for 4 minutes and UV dose of 1000 mJ/cm^{2,} , and it was stayed for 3 days at 60℃.

3. Results and Discussions

3-1. Characterization of UV cured films

We researched the characterization of UV cured film of the composition containing 30 wt% of polysiloxane. Fig.3A shows the cross-section photo of polysiloxane-acrylic hybrid resin coat measured by TEM, and Fig.3B shows the photo of silica/acrylic-polymer blended resin as a reference so that we can compare our hybrid resin with the conventional blend material. Silica material in general is observed in black and acrylic material in white in case of polymer just blended due to the difference of the refractive index.

Since the cured film in Fig.3A has uniform matrix in black compared with 3B, we can recognize polysiloxane domain is well dispersed in nano size in polysiloxane-acrylic hybrid resin coat. Therefore it is expected the morphology remarkably reflects the cured film in a high durability performance such as weather and chemical resistance.



A. Polysiloxane–acrylic Hybrid resin coat B. Silica/acrylic-polymer blended resin coat

Fig.3 Film morphology of the clear coating measured by TEM

3-2. Weather resistance

Weather durability of polysiloxane-acrylic hybrid resin coat was evaluated by comparing 3 types of resins, these are Fluoro-olefin coat, Acrylic-polymer coat, and UV-oligomer coat as a reference. Fig.4 shows the results employed in accelerated sunshine weather-o-meter in 4 kinds of the resins. Gloss retention of UV cured coating abruptly dropped after 1000 hours and, many micro cracks at the film surface were observed. ⊿E of UV coating gradually increased from the beginning of around 500 hrs. Acrylic-polymer coat maintained high gloss retention until 3000 hrs while it lost the gloss retention over around 3300 hrs as well as ⊿E change. On the other hand polysiloxane-acrylic hybrid resin coat did not show significant changes in gloss retention as well as Fluoro-olefin coat. Same trend was observed in the behavior of ⊿E. Surprisingly polysiloxane-acrylic hybrid resin coat provided less yellowing property than fluoro-olefin coat even if after 5,000 hours exposure.

Field exposure test was done, and polysiloxane-acrylic hybrid resin coat also showed a similar result. 60-degree gloss retention after exposure for three years in Okinawa, Japan exhibited a higher value more than 85 %, and this was comparable to weather resistance of Fluoro-olefin coat.

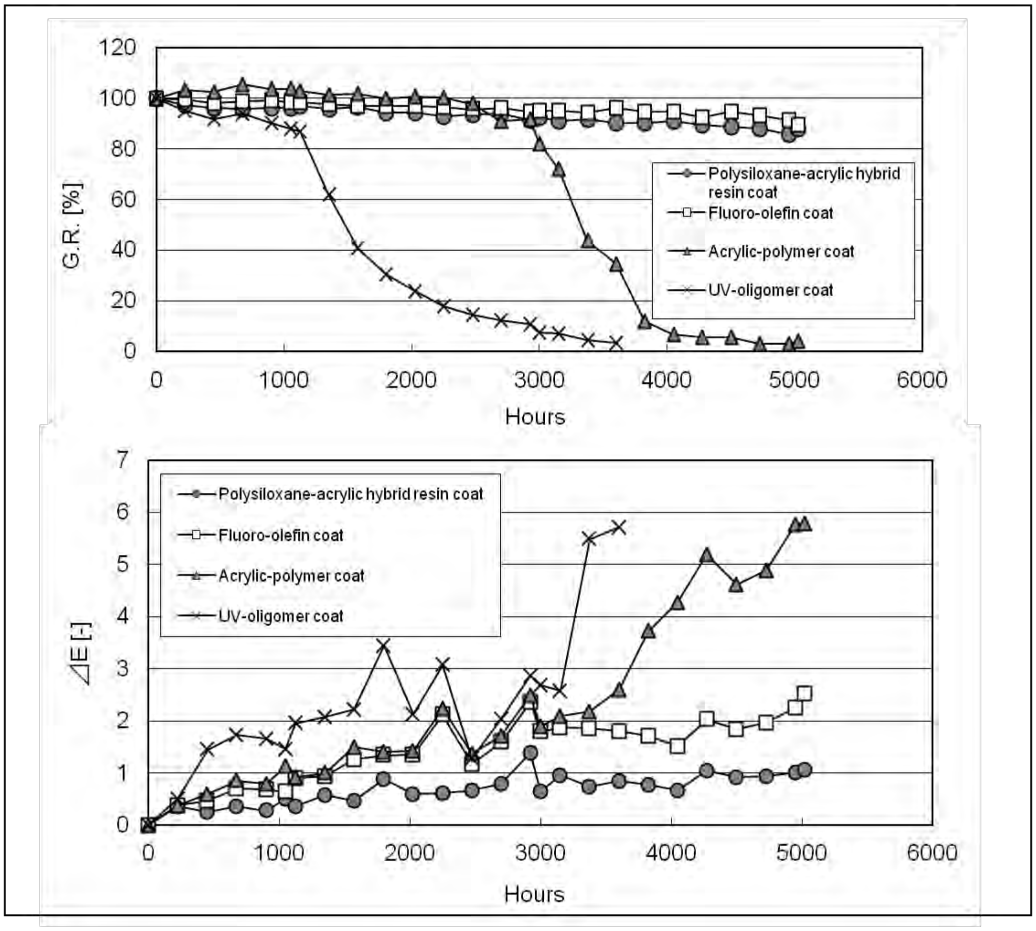


Fig.4 60-degree gloss retention and ⊿E in sunshine weather-o-meter test

3-3. Self-cleaning effect

Fig.5 shows the results of the stain resistance test of polysiloxane-acrylic hybrid resin coat film after exposure for 1 year in Osaka, Japan. The left graph shows the index of stain level and color change among 3 kinds of the coatings, and water contact angle of the coating surface during 12 months on the right graph. The coating surfaces were smeared with dusts and stains so on as Acrylic-polymer coat and Fluoro-olefin coat got dirty after 12 months, but polysiloxane-acrylic hybrid resin coat showed keeping same or less ⊿E.

Based on fact that the surface of polysiloxane-acrylic hybrid resin coat decreased water contact angle during exposure time, we could figure out the surface gradually become hydrophilic. It is suggested that Si-OH concentration in polysiloxane segment increased on the film surface, and it allowed the film to show the self-cleaning effect.

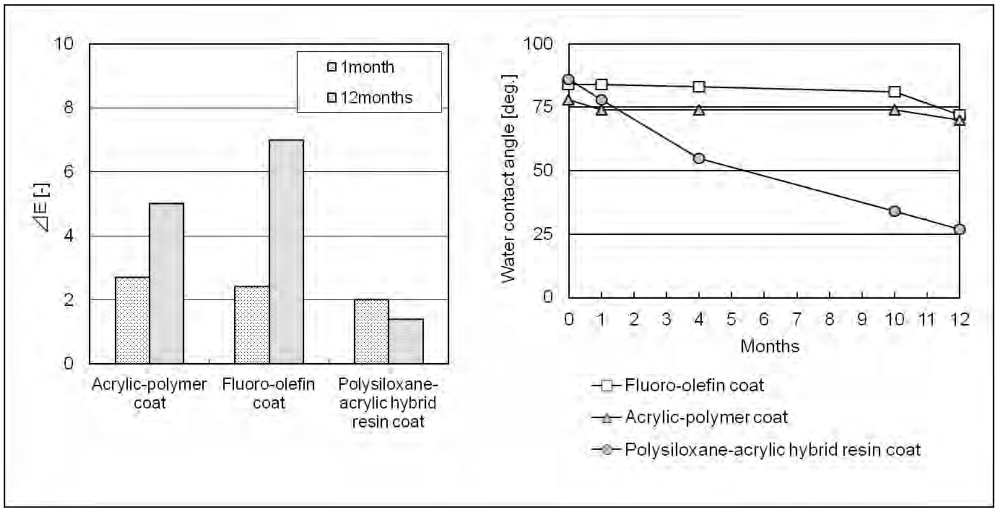


Fig.5 Field exposure test in Osaka, Japan

4. Waterborne polysiloxane-acrylic hybrid resin

From an environmental standpoint, waterborne type hybrid resin dispersion is our next challenge. As shown in Fig.6, introducing hydrophilic segments into acrylic resin part lead us to obtain a stable waterborne hybrid dispersion. The particle size distribution and the appearance of the dispersion are shown in Fig.7. The film property obtained from this dispersion is under investigation (e.g. adhesion, weather resistance and self-cleaning effect).

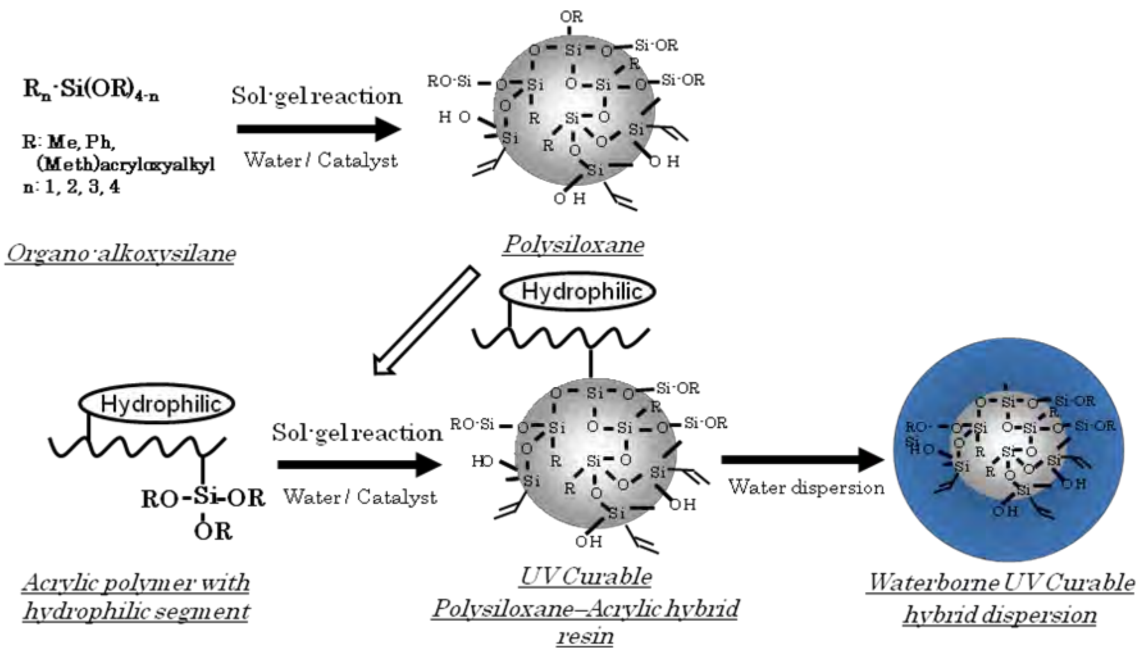


Fig.6 Waterborne UV curable hybrid dispersion

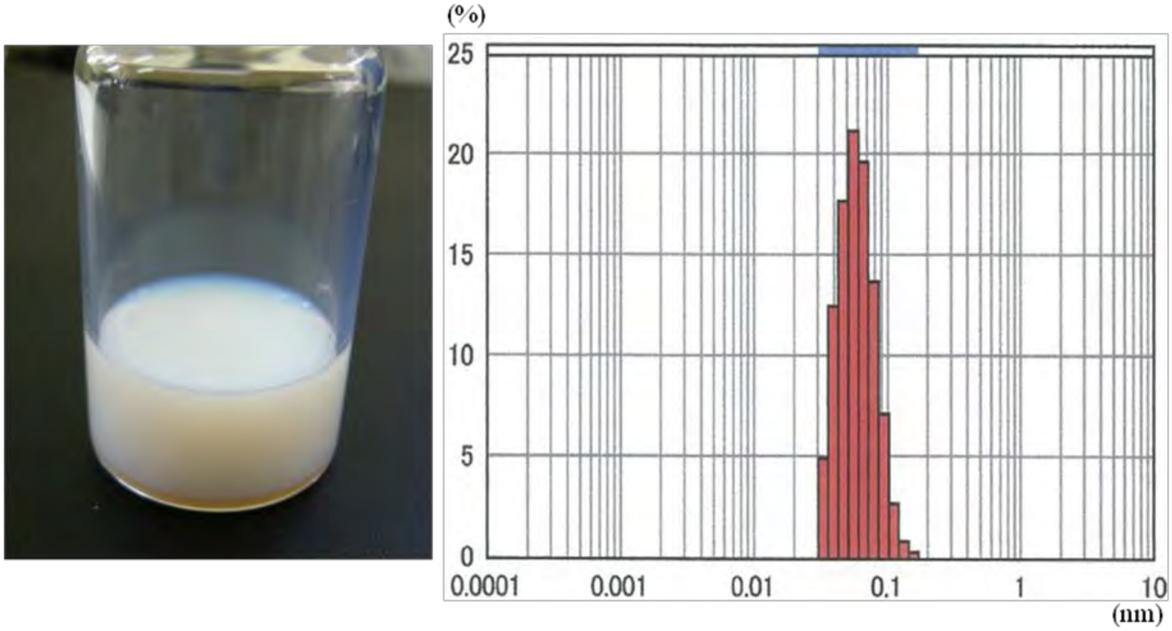


Fig.7 Appearance of the dispersion and particle size distribution.

5. Conclusions

We established a novel synthesis method specially designed by combining polysiloxane and acrylic polymer. By using this method, we obtained several types of UV curable inorganic-organic hybrid resins in the ratio of 25 wt% to 90 wt% of polysiloxane content. It enables us to develop a new durable coating resin in the application of not only plastics also inorganic materials.

References

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