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UV-curable organic–inorganic hybrid hard coatings for metal sheets

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Abstract A new type of UV-curable organic–inorganic hybrid oligomer was synthesized from vinyltrimethoxysilane (VTMS), tetraethylorthosilicate, and colloidal silica (CS) using a sol–gel method. UV-curable hybrid hard coating formulations were then prepared by mixing the organic–inorganic hybrid oligomer and acrylic monomers, trimethylolpropane triacrylate and tetrahydrofurfuryl acrylate, with a levelling agent and a photoinitiator. The oligomer was hydrolyzed and condensed from alkoxysilane and CS to obtain the UV-cured hybrid films. The hybrid oligomer and resulting hybrid films were characterized by Fourier transform infrared spectroscopy, ^{29}Si nuclear magnetic resonance spectroscopy, scanning electron microscopy, and ultraviolet–visible spectrophotometry to confirm the chemical functionality, oxo-silicon signal, cross-sectional morphology, and transparency, respectively. When the concentration of the CS/VTMS mixture in the organic–inorganic hybrid oligomer was 0.50 mol, remarkable pencil hardness (up to 5H) with excellent transparency was observed. The hardness and transparency of the UV-cured hybrid coating films were improved significantly by increasing the CS content in the organic–inorganic hybrid oligomer.

Keywords UV-curable coatings, Organic–inorganic hybrid oligomer, Hard coating, Pre-coated metal

Introduction

Organic–inorganic hybrid materials have attracted considerable research interest for a wide variety of applications, such as energy, environmental, and biological applications.[1,2] This is due mainly to the combination of organic and inorganic components in a single material, which enhance the final properties of the material.[3] Currently, organic–inorganic hybrids have attracted attention in the coating industry because they can enhance the properties, such as transparency, mechanical, chemical and thermal stability, abrasion resistance, surface adhesion, and hardness.[4] Various techniques are used to coat the prepared organic–inorganic nanohybrids on a substrate, such as dip coating, spray coating, spin-coating, brush-coating, and electrospraying.[5] These coating techniques allow the easy deposition of thin layers of organic–inorganic hybrid materials on a substrate for desirable applications. On the other hand, volatile organic compounds (VOCs) used in the organic–inorganic hybrid coating material may be carcinogenic and environmentally hazardous.[6] These hazards can be overcome using solvent-free or water-based coating techniques. Recently, a solvent-free ultraviolet–visible (UV) light curable coating system has attracted interest in the coating industry because of the easy curable approach under UV light.[7] The UV-curable coating system has been used in a range of substrates, such as glass, fabrics, aluminum, steel, and other metal substrates depending on the applications.[8]

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Pre-coated metal sheets (PCMs) are generally referred to as metal sheets that have been covered by painting or coating with a coating material. PCMs are manufactured in a sheet or coil coating line, processed, and assembled in factories to make household electrical appliances, building materials, and products without a painting process.[9–11] Scheme 1 presents a schematic diagram of a UV-curable PCM coating line. The forming technology of PCMs is well developed for applications to various industrial uses. To expand their applications, there is increasing demand for functionalized PCMs. On the other hand, most coatings for PCMs have limited applications because of their surfaces with low hardness, which can be scratched easily by friction or abrasion.[12] Similarly, organic solvents are generally used with organic–inorganic hybrid materials to coat the PCM sheet. Solvent-type coatings are affordable and have superb properties, but the great deal of VOCs generated during the manufacturing process causes environmental problems. Therefore, a coating material for PCMs requires good hardness and needs to be produced using a solvent-free method.

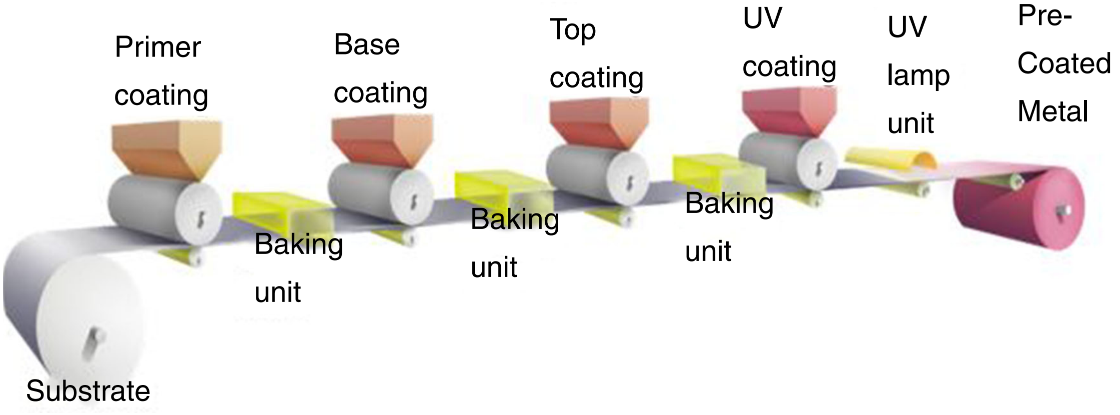
In general, two types of hard coating systems are used: thermally curable polysiloxane-based and acrylate-based UV-curable organic–inorganic hybrid systems. Among them, the UV-curable hybrid coating system is a representative eco-friendly coating method owing to its solvent-free approach.[13] The use of organo-functional silanes can improve the mechanical properties, hardness, thermal stability, and adhesion to specific organic coating systems compared to sol–gel materials based on non-functional organo-silanes.[14,15] In particular, the inorganic content of organic–inorganic hybrid coating formulations must be adjusted in organic components to overcome their rigidity, which causes cracking when the materials are cured by UV light. The sol–gel process is generally used to ensure an optimal hybrid coating on PCMs.

In this study, a novel UV-curable organic–inorganic hybrid oligomer, acrylate-modified colloidal silica, was produced by a sol–gel reaction. The modified colloidal silica was mixed with a multifunctional oligomer and mono-functional acrylate, which act as a curing agent and viscosity controller, respectively. The resulting UV-curable organic–inorganic hybrid coatings on a steel sheet were cured by UV irradiation, and the chemical and physical properties of the coated PCM substrates were investigated.

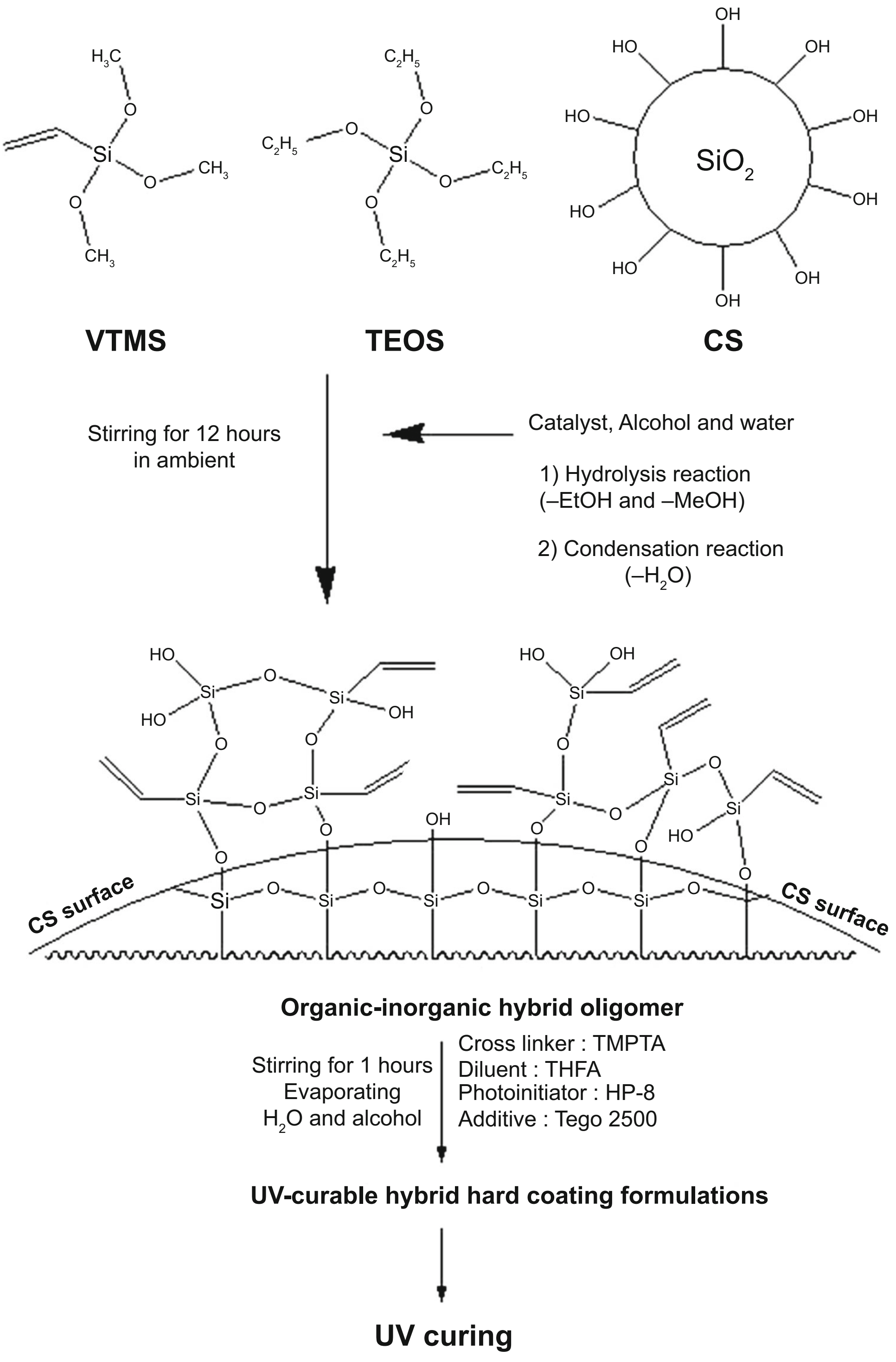
Method

Tetraethylorthosilicate (TEOS) and vinyltrimethoxysilane (VTMS) were purchased from Dow Corning. Colloidal silica (CS, Ludox HS30, 12 nm mean particle diameter), trimethylolpropane triacrylate (TMPTA, Miwon Commercial, Korea), tetrahydrofurfuryl acrylate (THFA, Miwon Commercial, Korea), hydroxyl dimethyl acetophenone (Micure HP-8, Miwon Specialty Chemical, Korea), a levelling agent (TEGO-2500, Evonik), isopropyl alcohol (IPA), and anhydrous ethanol (Samchun Chemical, Korea) were obtained from the respective companies and used without purification. Galvanized steel sheet (Dongkuk Steel, Korea) with a thickness of 0.5 mm was used as the substrate.

Scheme 2 presents the preparation procedure of the UV-curable hybrid coatings. First, the organic–inorganic hybrid oligomers were prepared under an ambient atmosphere by stirring with a mixture of IPA, ethanol, and formic acid as the catalyst, and distilled water with the following mole ratio: VTMS/TEOS/CS/IPA/ethanol/formic acid/H_2O = 1:0.025:x:1:3:0.01:4.5 for 12 h. The variation factor 'x' was 0.0, 0.2, 0.3, 0.4, and 0.5, as listed in Table 1. Second, the UV-curable organic–inorganic hybrid oligomers were obtained by mixing the reactive TEOS, VTMS, and CS, followed by modifying with mono and multifunctional acrylates (THFA and TMPTA) by stirring at 25°C for 1 h. The composition of 3-functional acrylate (TMPTA) in the coating formulations was fixed to 30 wt% based on the total inorganic components due to the proper curing speed and rigidity. The mixtures were then evaporated



Scheme 1: Schematic diagram of the UV-curable PCM coating line



Scheme 2: Synthetic scheme of UV-curable hybrid coating formulations

to eliminate the alcohol and water in a rotary vacuum evaporator. The photoinitiator (HP-8) and levelling agent (TEGO-2500) were added to this evaporated oligomer for the UV-curable coating. Finally, UV-curable hybrid coatings were obtained after 2 h of an evaporation process. The curable coatings were cast onto a glass plate at room temperature and cured in a conveyor belt type UV curing machine equipped with a mercury lamp (160 W/cm, main wavelength: 365 nm, UV dose: 2000 mJ/cm^2, arc system). To measure the discoloration during the UV resistance tests, a bar coater (No. 20) was used to coat each UV-curable

Table 1: UV-curable hybrid coating formulations with different amounts of CS

Formulations	Mol ratio of the inorganic components			Relative intensity of T^3/T^2 in the ^{29}Si-NMR spectra
	VTMS	TEOS	CS	
(a)	1	0.025	0.0	1.6
(b)	1	0.025	0.2	2.5
(c)	1	0.025	0.3	3.0
(d)	1	0.025	0.4	3.2
(e)	1	0.025	0.5	3.9

For the final coating formulations, 60 wt% of the inorganic components and 40 wt% of organic components (30 wt% TMPTA and 10 wt% of THFA) were used unless noted otherwise. The contents of HP-8 (a photoinitiator) and TEGO (a leveling agent) were fixed to 5 and 0.5 phr based on the total weight of the organic–inorganic hybrid oligomer

coating formulation on a white-colored steel sheet. The thickness of the obtained films was approximately 20 μm.

The viscosities of the organic–inorganic hybrid oligomers with different CS contents were evaluated by pouring the organic–inorganic hybrid oligomers into 50-mL cylinders using a Brookfield viscometer with an S62 spindle at a rotation speed of 100 rpm and 15°C. The chemical bonding and functionality of the samples were investigated by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Clarus 500). ^{29}Si liquid state nuclear magnetic resonance (NMR, Bruker Avance III HD 400, 400 MHz) spectroscopy was performed at room temperature (20°C) with a Bruker BBO probe. Chloroform-d ($CDCl_3$ with 0.01% tetramethylsilane (TMS, Aldrich) was used as the solvent of organic–inorganic hybrid oligomer and chromium(III) acetyl acetonate was used as the spin relaxation agent. The optical transmission spectrum of the hybrid coating films was obtained on a UV–Vis spectrometer against bare soda-lime glass. Scanning electron microscopy (SEM, JEOL 840) was used to view the cross sections and microstructures. The samples were coated with gold prior to the measurement. The alkali resistance of the UV-cured films was also estimated after immersion in a 10% aqueous NaOH solution for 24 h at room temperature (JIS K-5400). The other measurements were conducted using ASTM and JIS standards, such as the pendulum hardness (ASTM D-4366), pencil hardness (ASTM D-3363), cross cut test (ASTM D-3359), boiling resistance (JIS K-5400) and UV light resistance (JIS K-5400).

Results and discussion

Viscosity

Table 2 lists the viscosity, torque, and hybrid solid content of the organic–inorganic hybrid oligomers. Their solid contents were calculated after vacuum evaporation. All values for the oligomers increased with increasing CS content. On the other hand, an oligomer with a controlled viscosity has an advantage in forming a well-levelled film. All hybrid oligomers were found to be suitable for the bar coating process in this experiment. A CS content of up to 0.5 wt% was used for the experiment. At higher concentrations, the films were extremely brittle and could not be used for these measurements.

FTIR spectra

The change in the chemical structure before and after UV curing was analyzed by FTIR spectroscopy (Fig. 1). The hybrid coating formulation showed typical peaks of C–H asymmetric and symmetric stretching bands (2940 and 2890 cm^{-1}), acrylate functional group (1636 and 810 cm^{-1}), and stronger Si–O–Si (1075 cm^{-1}) bands before UV curing. The acrylate peaks at 1636 and 810 cm^{-1}, which were assigned to the C=C and =CH bonds, respectively, almost disappeared after UV exposure. This suggests that the reaction had occurred successfully in the C=C bonds of the acrylates.

NMR spectra

^{29}Si-NMR spectroscopy is a useful method to analyze the internal structure of silicone species. The Si chemical shift is linked directly to the close environment of the Si atom. In the case of trifunctional alkoxysilanes, R-Si(OR′)$_3$, the chemical shifts of silicon vary from $\delta = -30$ to -70 ppm. In this range, four groups, corresponding to the different environments of silicon, are observed. The conventional T^n notation, where T represents a silicon atom and n is the number of bridging oxygen atoms, is used to describe the inorganic network of hydrolyzed and condensed monomers. According to this notation, T^0, T^1, T^2, and T^3 represents monomeric groups, end groups of chains, middle groups in chains or cycles, and fully branched sites, respectively. Liquid state NMR spectroscopy has been implemented to investigate the structure of the UV-curable hybrid material subsequent to UV curing of VTMS. The different environ-

Table 2: Viscosity of organic–inorganic hybrid oligomers with different contents of CS

Formulations	Viscosity (cp)	Torque (%)	Solid content (%)
(a)	111.3	37.1	48.65
(b)	184.5	61.5	49.27
(c)	213.0	71.0	49.74
(d)	232.7	78.6	50.16
(e)	238.1	79.4	50.28

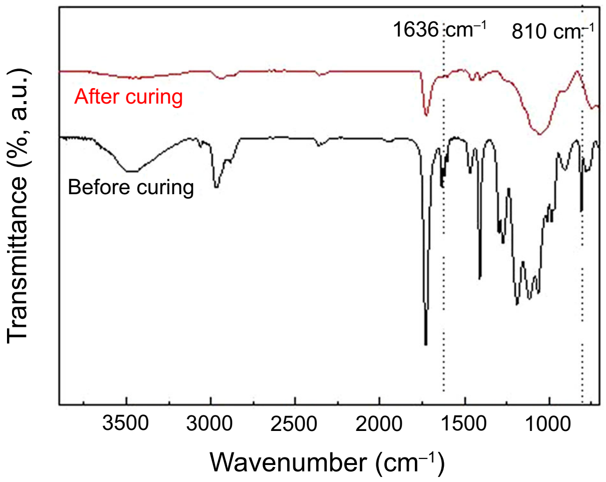


Fig. 1: FTIR spectra of UV-curable hybrid coating formulation before and after UV curing

ments at the silicon center (T^n) depend on the degree of condensation. For trialkoxysilane precursors, T^n indicates the fraction of units with one siloxane bond –O–Si– attached to the central silicon.[16,17]

Figure 2 shows the ^{29}Si-NMR spectra of UV-curable hybrid coating formulations in the liquid state. The Q^1 signal represents a type of silanol (Si–OH) structure stretched on a Si atom, e.g., Si–O–Si–$(OH)_3$. The T^1 signal was observed in sample (a) only and not in the other samples (Fig. 2a). This signal means that the hydrolysis of sample (a) was not sufficient because of its chemical composition design. For example, a lack of catalyst, water, or solvent can cause imperfect hydrolysis. On increasing the CS contents, however, the ratio of the T^3 to other T^n signals, including in particular T^2, was increased as shown in Figs. 2b–2e and Table 1. This means that alkoxysilane had been well-absorbed on the CS surface at higher CS contents, so that the sample could reach an oxo-silicon (–O–Si–O–) rich state by the increasing degree of condensation between VTMS or TEOS on CS, making the film harder.

SEM images

SEM was used to observe the adhesion morphology, film thickness, and cracking phenomenon in cross sections of the UV-cured hybrid coating films. Figure 3 shows a cross-sectional view of the hybrid layers coated on the substrate. The structure of the raw substrate consisted of an organic coating layer (clear coating layer, base coating layer, and primer coating layer), galvanized layer, and body. The organic coating layers were made of a polyester-melamine-based polymer. The thickness of the hybrid films on the coated substrate were approximately 20 μm. SEM showed that all the coating formulations were coated uniformly on the PCM substrates at CS contents of up to 5 wt%, even though the surface roughness increased with increasing CS content due to the higher inorganic component in the hybrid material (Figs. 2a–2e). The optimal mole ratio of the CS/VTMS mixture for a better surface coating and performance of organic–inorganic hybrid oligomers on the coated substrate was found to be < 0.5. The substrate became brittle above the optimal level due to higher content of inorganic particles on the substrate, which reduced the adhesion strength between the materials and substrate.

UV–visible transmission spectroscopy

The optical transmission of the UV-cured hybrid coating films was measured using a UV–Vis spectrophotometer. The soda-lime glass substrate showed a transparency of 93% at a wavelength of 400 nm, whereas the transparency was reduced further in the visible wavelength range. The transparency of the hybrid-coated soda-lime glass substrates showed enhanced transparency, regardless of the CS content (Fig. 4). The coating films prepared with the maximum CS content showed excellent transparency, approximately 100%, compared to the films with a low CS content due to the homogeneous distribution of reactive functional materials on the coated substrates.[18] This is not surprising if one considers that average particle size of CS in the film is 20–25 nm, and thus, the CS nanoparticles can reduce the reflection of the coated surface in the visible wavelength region.[19]

Mechanical and other properties

Figure 5 presents the pendulum hardness of the UV-cured hybrid coating films. The hardness of the samples

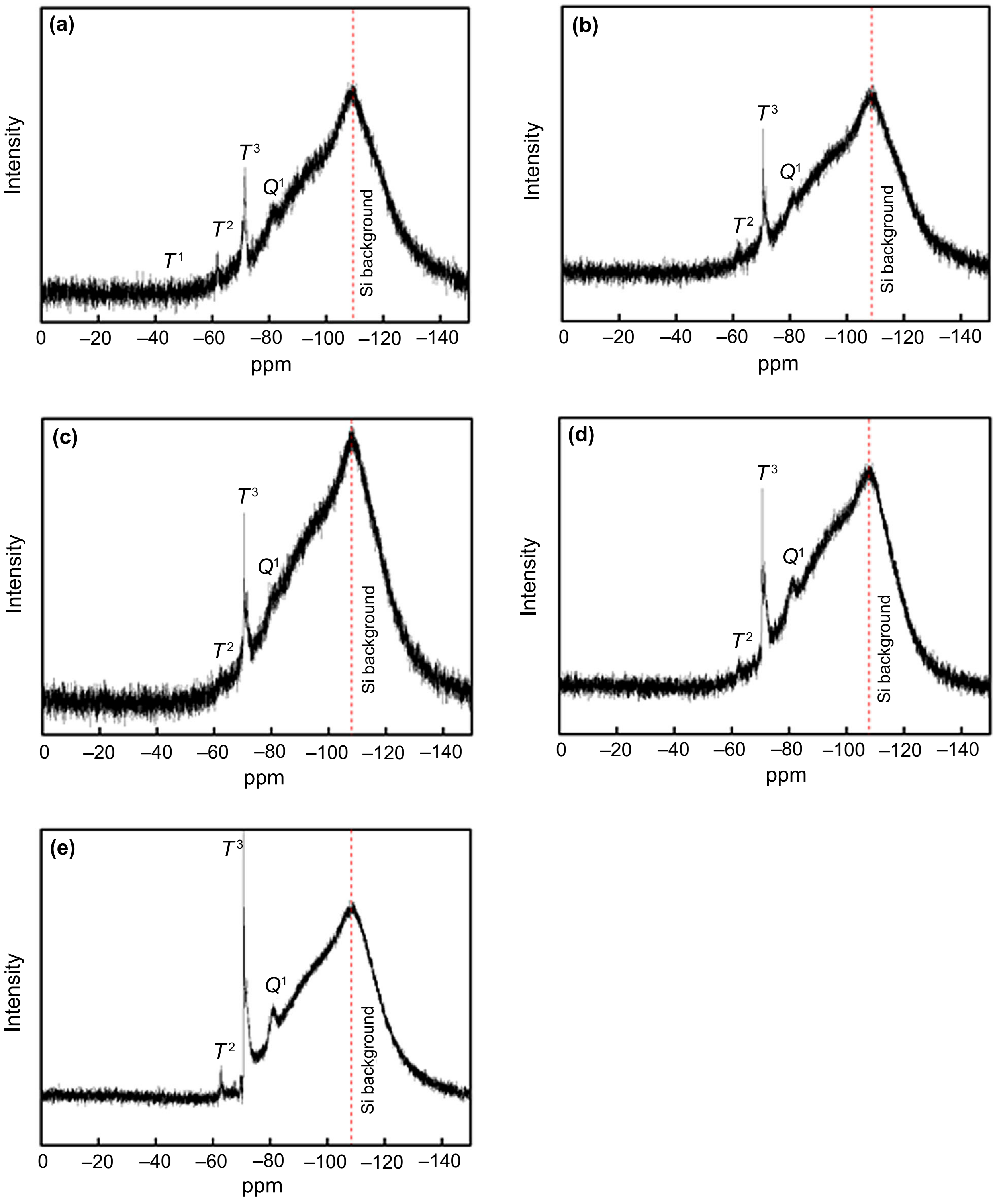
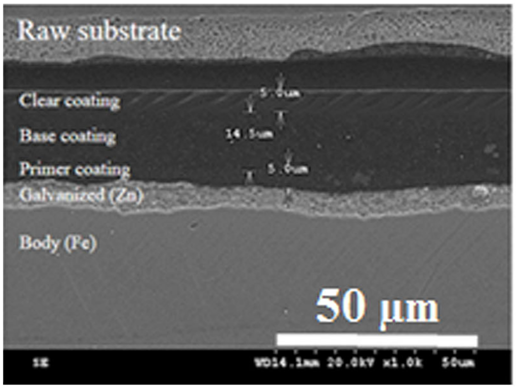


Fig. 2: ^{29}Si NMR spectra of UV-curable hybrid coating formulations (a–e) in the liquid state. The coating formulations are listed in Table 2

showed relatively constant values at a UV dose > 2000 mJ/cm^2, regardless of CS content. Based on this result, the UV dose for curing was then fixed for further UV curing throughout the experiments to measure the properties of the coating films. The pendulum hardness increased linearly with increasing CS contents due to the better adhesion and formation of the rigid structure of the organic–inorganic hybrid



Layers of raw substrate	Thickness (µm)
Clear coating	5.0–8.5
Base coating	13.0–15.0
Primer coating	4.5–5.0
Galvanized (Zn)	5–8
Body (Fe)	500±15

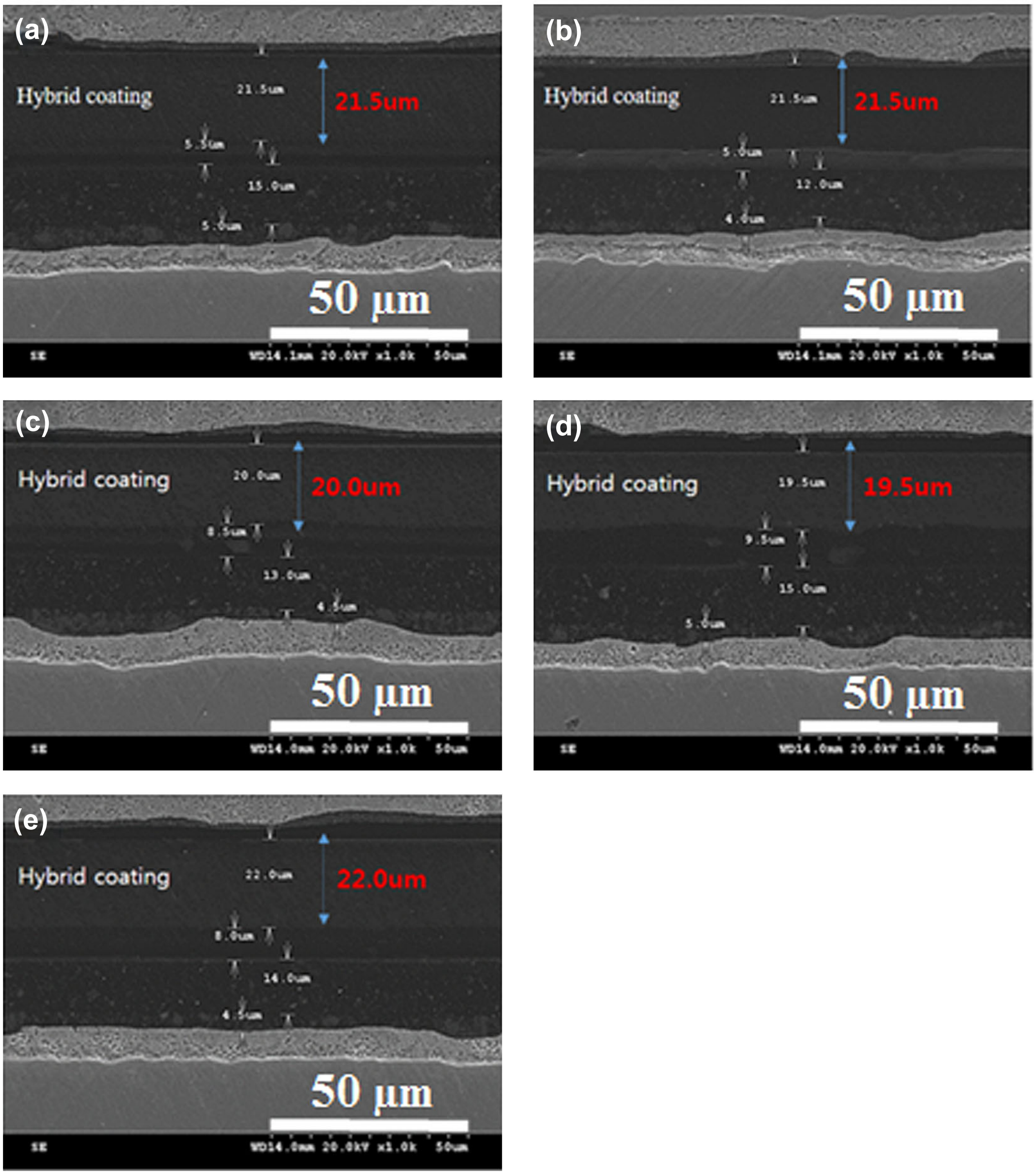


Fig. 3: Cross-sectional SEM images of UV-cured hybrid PCMs (a–e). The coating formulations are listed in Table 2

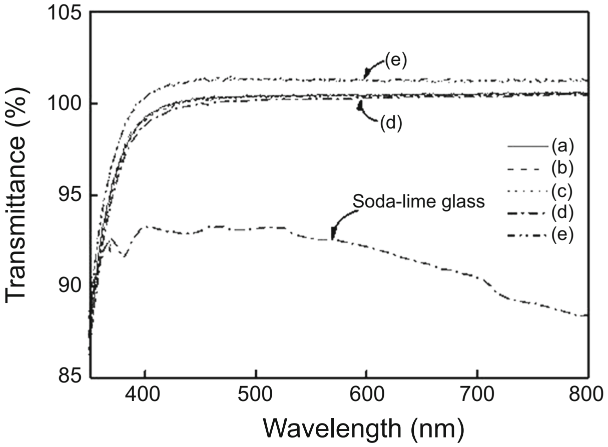


Fig. 4: UV-Visible transmission spectra of UV-cured hybrid coating films (a–e) on soda-lime glass. The coating formulations are listed in Table 2

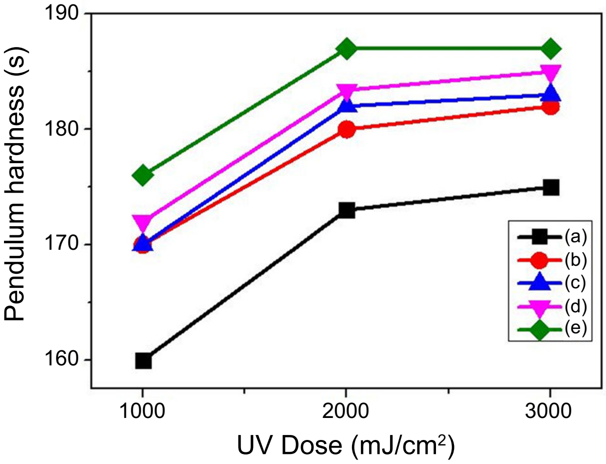


Fig. 5: Pendulum hardness of UV-cured hybrid coating films. The coating formulations are listed in Table 2

oligomer on the coated substrate. Similar phenomena were also observed for the pencil hardness test. Higher hardness was predicted with a higher CS content in the coating materials. The hybrid coating films were strengthened by increasing the inorganic component due to its rigid property. It should be noted here that though our preliminary T-bend tests for all the coating formulations showed some cracks this was not a concern, since the coatings in this study were for applications in a high hardness sheet type which might not need flexibility. This is why PCMs with high hardness, which usually show poor processibility and flexibility, can apply to sheet-typed forms, interior material, refrigerator door, TV back panel, and so on.

The stability of the UV-cured hybrid layer to UV exposure is quite important for outdoor applications. The UV resistance of the coated substrate was checked using Konica Minolta Color Systems (CR-400). The UV lamp was composed of UV-B radiation (wavelength: 313 nm with an optical power of 15 W/m^2; distance between a sample and the light source of 20 cm, for 3 days) and the test was carried out by placing the samples (a–e) at 20 cm away from the lamp. The yellowing index (ΔYI) of the coating films was measured as a function of the UV exposure time. ΔYI is used widely as a semi-quantitative expression in UV resistance; a small ΔYI indicates good UV resistance.[20] Figure 6 shows the yellowing index values of the different hybrid coating films. The yellowing indices of the cured samples decreased with increasing CS contents, meaning that the UV resistance of the cured samples increased with increasing CS contents. In general, oxo-silicon may be too strong for UV radiation due to their strong metal-oxygen bonding. The organic acrylates in the hybrid coatings may be a major factor influencing the yellowing index values.

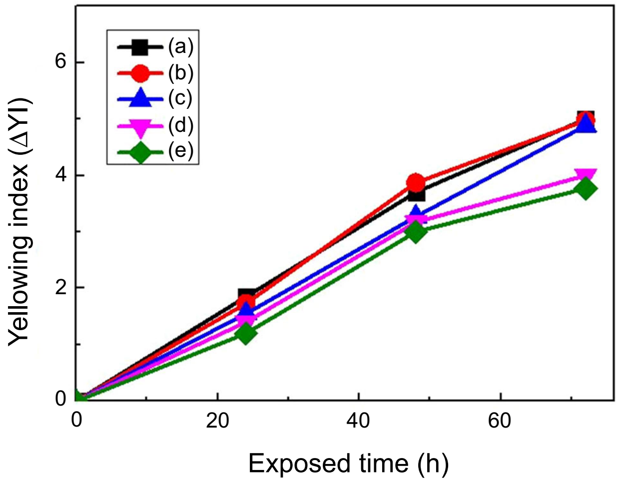


Fig. 6: UV resistance (UV-B) of UV-cured hybrid coating films. The coating formulations are listed in Table 2

The alkali resistance and cross cutter test (CCT) of the UV-cured hybrid coating films were also evaluated according to proper national standards mentioned in the characterization section.

Figure 7 shows that all prepared films were unaffected by exposure to a 10% NaOH solution for 24 h at room temperature. In this study, the CS content did not influence alkali resistance of the coated films in 24 h. The results mean good chemical resistance of the organic–inorganic hybrid oligomer, which suggests the potential use of the coating formulations on steel and other substrates for prevention from corrosion.

A CCT test is used to evaluate the adhesive property between the base material and coating films. According to the ASTM D-3359 standard, after processing each coated test specimen, 100 squares with a 1 mm length and width were prepared using a cross hatch cutter. After adhesive tape was pressed and stuck to the squares, the tape was detached rapidly, and the number of undetached squares remaining was then counted and marked. The mean value of five measurements was calculated. All the prepared coating films perfectly

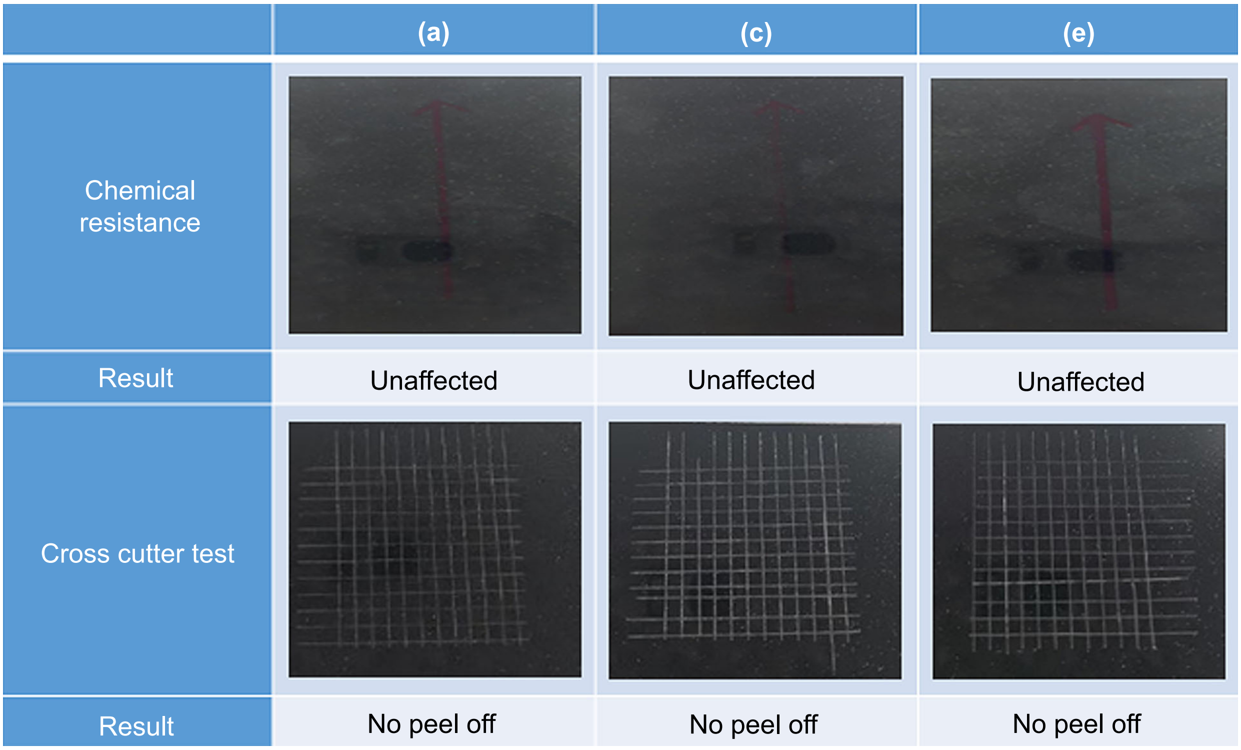


Fig. 7: Alkali resistance for a 10% NaOH solution and CCT results of UV-cured hybrid coating films. The coating formulations (a, c and e) are listed in Table 2

Table 3: The performance of UV-cured hybrid coating films

Formulations	Pendulum hardness (s)	CCT (ea)	Alkali resistance (10% NaOH)	Pencil hardness (H)	Yellowing index (UV-B)	Crack* (0 or 1)
(a)	173	100/100	Unaffected	1	+ 5.04	0
(b)	180	100/100	Unaffected	3	+ 4.97	0
(c)	182	100/100	Unaffected	3	+ 4.88	0
(d)	183.4	100/100	Unaffected	4	+ 4.37	0
(e)	187	100/100	Unaffected	5	+ 3.77	0

*Crack (0: no crack observed on the film/1: crack observed on the film)

passed the CCT (100 ea passed/100 squares). The CCT test showed excellent adhesion of the cured hybrid coating films to the substrate. Table 3 lists the overall performance of the UV-cured hybrid coating films on the PCM sheet. In a previous study,[21] a UV-curable cycloaliphatic polyester polyol-based (PUPCL) coating film was developed for the coating of PCMs. Although the PUPCL film exhibited good CCT property (100/100) and water resistance, it showed lower pendulum hardness (120 s), poorer UV resistance (yellowing index: +7.41), and lower hardness (HB) than the hybrid coating films in the present work. The alkali resistance under 10% NaOH of the hybrid coating film was superior to that of the previous PUPCL film because the PUPCL film was affected when exposed to 10% NaOH as well as 5% NaOH for 5 days.

In terms of commercial applications, these tests have been used to estimate the standard of PCMs. In particular, the pendulum hardness, UV resistance, and alkali resistance were discussed with regard to the effects of the CS contents. The results suggest that excellent stability can be achieved using the prepared organic–inorganic hybrid oligomer with the optimal CS content.

Conclusion

UV-curable hybrid hard coating materials were synthesized by a sol–gel process with acrylates (TMPTA and THFA) for applications as hard coatings of PCMs. Chemical bonding, microstructure of cross section, and oxo-crosslinking were studied by FTIR spectroscopy, SEM, and ^{29}Si-NMR spectroscopy, respectively. The transmittance of the hybrid coatings was excellent compared to that of soda-lime glass. No cracks were observed in any of the coated samples. The maximum pencil hardness of the UV-curable hybrid coating film on PCMs was 5 H when the composition of CS/VTMS was 0.5. In conclusion, these UV-curable hybrid hard coating films showed excellent performance compared to that of commercial PCMs in terms of UV resistance, chemical resistance, cross cutter test, and surface hardness. In this study, a hard coating on PCMs with hybrid coatings can be a new candidate material for indoor/outdoor use.

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References

1. Chujo, Y, "Organic–Inorganic Hybrid Materials." *Curr. Opin. Solid State Mater. Sci.*, **1** 806–811 (1996)
2. Wen, J, Wilkes, GL, "Organic/Inorganic Hybrid Network Materials by the Sol−Gel Approach." *Chem. Mater.*, **8** 1667–1681 (1996)
3. Ha, CS, Nagappan, S, *Hydrophobic and Superhydrophobic Organic–Inorganic Nano Hybrids*, pp. 3–4. Pan Stanford Publishing, Singapore (2018)
4. Faustini, M, Nicole, L, Ruiz-Hitzky, E, Sanchez, C, "History of Organic–Inorganic Hybrid Materials: Prehistory, Art, Science, and Advanced Applications." *Adv. Funct. Mater.*, **28** 1–30 (2018)
5. Malucelli, G, "Hybrid Organic/Inorganic Coatings Through Dual-Cure Processes: State of the Art and Perspectives." *Coatings*, **6** 101 (2016)
6. Chang, YM, Hu, WH, Fang, WB, Chen, SS, Chang, CT, Ching, HW, "A Study on Dynamic Volatile Organic Compound Emission Characterization of Water-Based Paints." *J. Air Waste Manage. Assoc.*, **61** 35–45 (2016)
7. Bretterbauer, K, Holzmann, C, Rubatscher, E, Schwarzinger, C, Roessler, A, Paulik, C, "UV-Curable Coatings of Highly Crosslinked Trimethylmelamine Based Acrylates and Methacrylates." *Eur. Polym. J.*, **49** 4141–4148 (2013)
8. Çakır, M, "Investigation of Coating Performance of UV-Curable Hybrid Polymers Containing 1H,1H,2H,2H-Perfluorooctyltriethoxysilane Coated on Aluminum Substrates." *Coatings*, **7** 37 (2017)
9. Ueda, K, Kanai, H, Suzuki, T, Amari, T, "Effects of Mechanical Properties of Paint Film on the Forming of Pre-painted Steel Sheets." *Prog. Org. Coat.*, **43** 233–242 (2001)
10. Moon, JI, Lee, YH, Kim, HJ, Schwartz, S, Rafailovich, M, Sokolov, J, "Investigation of the Peel Test for Measuring Self-Cleanable Characteristic of Fluorine-Modified Coatings." *Polym. Test.*, **31** 433–438 (2012)
11. Dzunuzovic, E, Tasic, S, Bozic, B, Babic, D, Dunjic, B, "UV-Curable Hyperbranched Urethane Acrylate Oligomers Containing Soybean Fatty Acids." *Prog. Org. Coat.*, **52** 136–143 (2005)
12. Wang, F, Hu, JQ, Tu, WP, "Study on Microstructure of UV-Curable Polyurethane Acrylate Films." *Prog. Org. Coat.*, **62** 245–250 (2008)
13. Bao, F, Shi, W, "Synthesis and Properties of Hyperbranched Polyurethane Acrylate Used for UV Curing Coatings." *Prog. Org. Coat.*, **68** 334–339 (2010)
14. Schwalm, R, Häußling, L, Reich, W, Beck, E, Enenkel, P, Menzel, K, "Tuning the Mechanical Properties of UV Coatings Towards Hard and Flexible Systems." *Prog. Org. Coat.*, **32** 191–196 (1997)
15. He, J, Nebioglu, A, Zong, Z, Soucek, MD, Wollyung, KM, Wesdemiotis, C, "Preparation of a Siloxane Acrylic Functional Siloxane Colloid for UV-Curable Organic–Inorganic Hybrid Films." *Macromol. Chem. Phys.*, **206** 732–743 (2005)
16. Derouet, D, Forgeard, S, Brosse, JC, Emery, J, Buzare, JY, "Application of Solid-State NMR (13C and 29Si CP/MAS NMR) Spectroscopy to the Characterization of Alkenyltrialkoxysilane and Trialkoxysilyl-Terminated Polyisoprene Grafting Onto Silica Microparticles." *J. Polym. Sci. Part A Polym. Chem.*, **36** 437–453 (1998)
17. Mauger, M, Dubault, A, Halary, JL, "Synthesis and Physico-Chemical Characterization of Networks Based on Methacryloxypropyl-Grafted Nano-Silica and Methyl Methacrylate." *Polym. Int.*, **53** 378–385 (2004)
18. Mahadik, SA, Mahadik, DB, Parale, VG, Wagh, PB, Gupta, S, Rao, AV, "Recoverable and Thermally Stable Superhydrophobic Silica Coating." *J. Sol-Gel Sci. Technol.*, **62** 490–494 (2012)
19. Hwang, Y, "High-Transmittance Films From Silica Colloidal Nanoparticles." *J. Korea Ceram. Soc.*, **41** (10) 766–770 (2004)
20. Ha, CS, Jung, SJ, Kim, ES, Kim, WS, Lee, SJ, Cho, WJ, "Properties of UV-Curable Polyurethane Acrylates Using Nonyellowing Polyisocyanate for Floor Coating." *J. Appl. Polym. Sci.*, **62** 1011–1021 (1996)
21. Choi, WC, Lee, WK, Ha, CS, "Synthesis and Properties of UV-Curable Polyurethane Acrylates Based on Different Polyols for Coating of Metal Sheets." *Mol. Cryst. Liq. Cryst.*, **660** 104–109 (2018)