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Test method

Investigation of the peel test for measuring self-cleanable characteristic of fluorine-modified coatings

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ABSTRACT

The self-cleanable ability of coatings is important to prevent or remove polluting fingerprints, dust, water and oils for a number of applications. Fluorocarbon polymers have been used to provide self-cleanable ability due to their low surface energy. The efficiency of fluorine-modified coatings has been evaluated by measuring surface free energy using a contact angle measurement. However, this method is not sufficient to define the polluting-preventive ability or removability of fluorine-modified coatings due to the amount of fluorine content.

A peel test can be used to determine the self-cleanable characteristics of fluorine-modified coatings by evaluating adhesion between the coating surface and pressure sensitive adhesives (PSAs). In addition, adhesion can be used to predict the amount of polluting-preventive ability or removability of coatings by comparing the peel strength of commercial PSAs. We designed fluorine-modified acrylic resins with different fluorine contents for a new testing method. Comparing the contact angle measurement with the peel test results, the peel test for the self-cleanable characteristic of coatings was more suitable than the contact angle measurement to predict the polluting-preventive ability and removability of coatings.

1. Introduction

The self-cleanable ability of coatings is important to prevent or remove pollution due to fingerprints, dust, water and oils for a number of applications such as eye glasses, automotive coatings and electric devices (monitors, cellular phones and portable displays, etc.). Fluorocarbon polymers have been used to provide self-cleanable ability due to their low surface energy created by the small polarization effect of the C–F bond. Therefore, commercial use of fluorocarbon polymers for many applications has sharply increased [1–9].

The efficiency of fluorine-modified coatings has been evaluated by measuring surface free energy using a contact angle measurement to determine the angle size of a water droplet on the coating surface. However, this method is not sufficient to define the polluting-preventive ability or removability of fluorine-modified coatings due to the amount of fluorine content. In addition, surface free energy is not an adequate parameter for measuring the force needed to remove pollutants on a coating surface.

For this reason, we investigated a new method to define the polluting-preventive ability and removability of fluorine-modified coatings using a peel test. The peel test is a common

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method used to measure the adhesion of pressure sensitive adhesives (PSAs) when the coated film is removed from substrates. This method can be applied to determine the self-cleanable characteristic of fluorine-modified coatings by evaluating adhesion between the coating surface and PSAs. With decreasing surface free energy, the adhesion between different surfaces is decreased. Fig. 1 shows the concept of measuring the self-cleanable characteristic using a peel test [10]. In addition, adhesion can be used to predict the polluting-preventive ability or removability of coatings by comparing the peel strength of commercial PSAs.

In this study, we designed fluorine-modified acrylic resins with different fluorine contents for a new testing method. The fluorine-modified coatings were synthesized for application as a self-cleanable automotive clear coat with physical properties similar to those of a conventional acrylic clear coat, for evaluating self-cleanable characteristics under realistic conditions. Acrylic is widely used in surface coating applications. This can be attributed to the particular chemical structure of the polyacrylics, because the polymer backbone is composed of chemically stable carbon–carbon bonds that are resistant to hydrolysis. The polymer structure of acrylic resins can be easily designed to include monomers which have a C=C double bond [8]. For these reasons, we chose a fluorine-contained acrylate (1H,1H,2H,2H-perfluorodecyl acrylate) which has a long perfluoroalkyl side chain for the self-cleanable characteristic, and designed a hydroxyl-functional acrylic resin to form a crosslinked network. In a previous study, a fluorine-modified acrylate is reported where the perfluoroalkyl portions of the side chains caused the formation of highly ordered surfaces with an increased concentration of $-CF_3$ groups in the top layer [9]. Surface analysis was conducted and physical properties were measured to determine what part of the effects were due to the perfluoroalkyl portions of the side chains. The contact angle measurement was used determine any correlation with a peel test for the self-cleanable ability.

2. Experimental

2.1. Materials

1H,1H,2H,2H-perfluorodecyl acrylate (Aldrich) was prepared for measuring its self-cleanable ability. 2-hydroxylethyl acrylate (Samchun chemical) was used with a curing agent. Methyl methacrylate (Samchun chemical) was used to control the surface hardness and scratch resistance. Butyl acrylate (Samchun chemical) and 2-ethylhexyl acrylate (Samchun chemical) were prepared without further purification. Butyl acetate (Samchun chemical) was prepared as a solvent. Azoisobutyronitrile (Junsei Chemical, AIBN) and hexamethoxymethylmelamine (HMMM, Cytec) were used as free radical initiators and curing agents. An amine type curing catalyst (NACURE 5925) was supplied from KING industries. Table 1 lists the synthetic formulations of the acrylic resins.

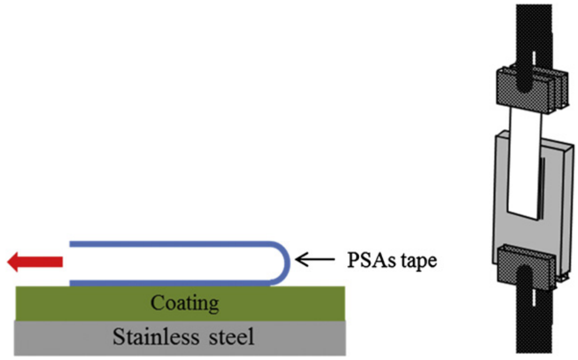


Fig. 1. The concept of a peel test for measuring self-cleanable characteristic [10].

2.2. Synthesis of fluorine-modified acrylic resin

A 150 g batch of the resin was produced as a hydroxyl-functional acrylic resin by application of a solution polymerization technique using a free radical initiator, AIBN (1% based on total monomer weight). A 60 g aliquot of butyl acetate was placed in a 250 mL 4-neck round type reactor fitted with a temperature controller, a heating mantle, N_2 purge, a condenser and an impeller. The reactor was heated to 120 °C, and the mixture of 1H,1H,2H,2H-perfluorodecyl acrylate, 2-hydroxylethyl acrylate, methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate and 1 wt% AIBN was added dropwise into the reactor using a dropping funnel over a 4-h period. During the synthesis, the progress of the free radical reaction was followed using FT-IR by monitoring the disappearance of C=C double bonds in all raw materials. Afterwards, the initiator was quenched by hydroquinone monoethylether (MEHQ) containing 30 g butyl acetate. Scheme 1 shows the process for synthesis of fluorine-modified acrylic resins.

2.3. Preparation of fluorine-modified acrylic coating

The fluorine-modified acrylic coatings were prepared by blending the synthesized acrylic resins with the HMMM catalyst at a ratio of 8:2. The blended mixture was coated (40 μm thickness) on a stainless steel substrate using a bar applicator and then dried at 80 °C for 5 min. After the drying process, the coating was cured at 150 °C for 30 min in an oven.

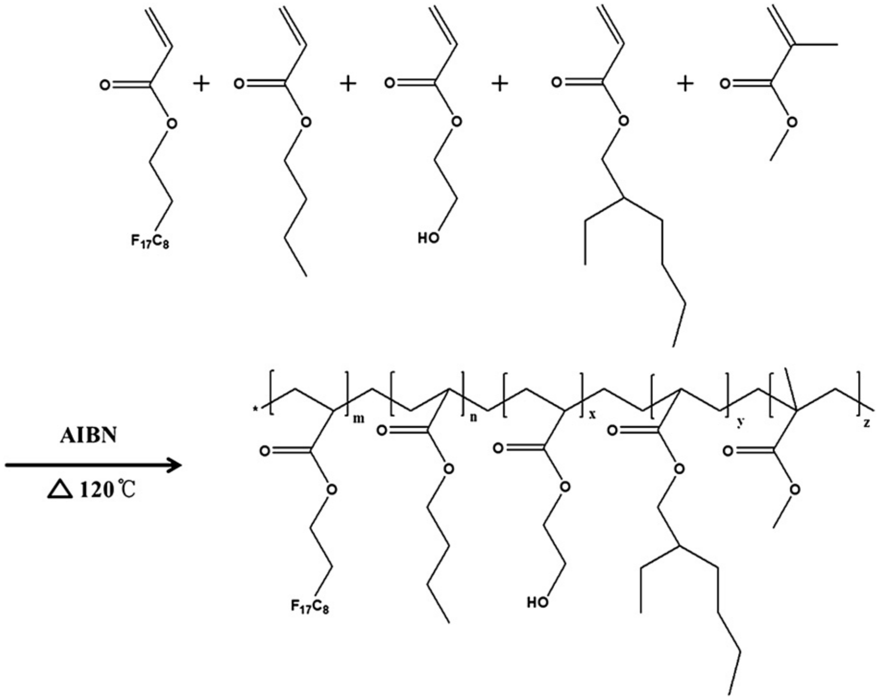
2.4. Methods

2.4.1. Characterization of the fluorine-modified coatings

The IR spectra were measured to detect the increasing fluorine content using a JASCO FT/IR-6100 (Jasco, Japan)

Table 1
Formulation of the fluorine-modified acrylic resins. (unit: mole of monomer).

Contents	FA-0	FA-10	FA-20	FA-30
1H,1H,2H,2H-perfluorodecyl acrylate	0	1	2	4
Methyl methacrylate	8	7	6	4
Butyl acrylate	4	4	4	4
2-hydroxyethyl acrylate	10	10	10	10
2-ethylhexyl acrylate	2	2	2	2



Scheme 1. Synthesis process of the fluorine-modified acrylic resins.

equipped with a Miracle accessory and attenuated total reflectance (ATR). The ATR crystal was made from diamond with a refractive index of 2.4 at 8500–2500 and 1700-300 cm^{-1}. The spectra range was from 4000–650 cm^{-1} and the resolution was 4 cm^{-1} as shown in Fig. 2.

Chemical analysis was performed on the surface of cured coatings with an X-ray photoelectron spectrometer (XPS, Sigma Probe, Thermo Scientific., U.S.A), equipped with spherical sector analyzer. The XPS spectra of the regions are presented in Fig. 3, and correspond to 0–1200 eV. The signals of fluorine, oxygen, and carbon were observed at 689, 532, and 291 eV, respectively. The fluorine content at the surface of each coating is listed in Table 4 [11].

2.4.2. Physical properties

To evaluate the change in the surface hardness of each cured coating, the pendulum hardness of the coatings was measured by a pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd.) according to the König method (ANS/ISO 1522) at 23 ± 1 °C and 50 ± 2%.

The scratch resistance was measured using a No. 553 pencil hardness tester (Yasuda Seiki Seisakusho Ltd.). The test was conducted in compliance with ISO 15184 [12]. The adhesion between the coating and the substrate was

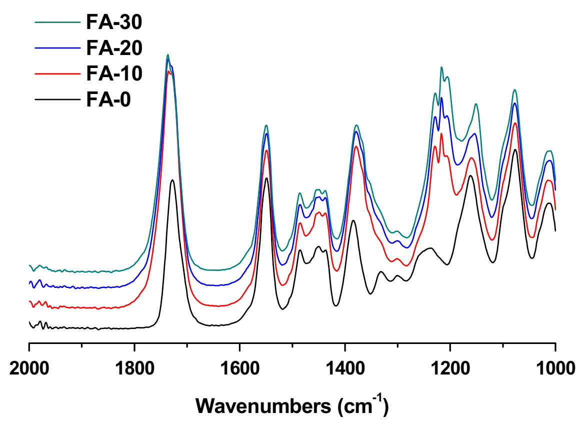


Fig. 2. IR spectra of the fluorine-modified coatings (1200–1230 cm^{-1}, 1150 cm^{-1}: C–F bonds).

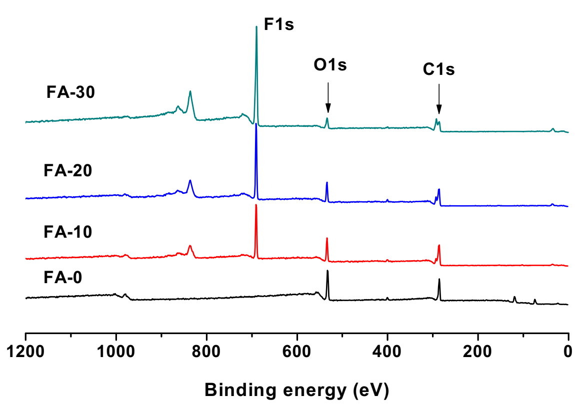


Fig. 3. XPS curves of the fluorine-modified coatings.

evaluated using a cross-cut tester according to the guidelines in ISO 2409. The distance between cuts was 1 mm, as measured by a cutting guide. An adhesion test result is classified as 0B when >65% flaking of the crosscut area occurs, and 5B when no flaking is observed. A degree of 1-4B was determined in a test range between 0B and 5B [13,14].

2.4.3. Contact angle measurement

The self-cleanable ability was determined from the contact angle of water drops at the surface using a contact angle analyzer (DSA100, KRÜSS GmbH., Germany). The analysis conditions were 23 ± 2 °C and 50 ± 2% R.H. [15].

2.4.4. Peel test

The peel strength was measured using a Stable Micro Systems TA-XT2i Texture Analyzer (UK). SCOTCH No. 810 tape, (3 M Company) was used to evaluate the self-cleanable ability of coatings. The PSA tape, (width of 18 mm) was attached and a 2 kg rubber roller was rolled over it 2 times on the coating surface. The testing was conducted at a speed of 300 mm/min at 20 °C, based on guidance in ISO 8510-2. The peel strength unit was recalculated from g/18 mm to g/25 mm [10,16]. Data of peel strength units were used to evaluate the self-cleanable characteristic of coatings by using the pressure-sensitive adhesive classification concept lists in Table 4 [17]. For pressure sensitive adhesives a higher peel strength unit is preferred for permanent performance and a lower peel strength unit is preferred for removable adhesion. In our case, a lower peel strength unit means a higher self-cleanable ability of coatings.

3. Results & discussion

3.1. Characterization of the fluorine-modified coatings

Fluorine-modified acrylic resins containing fluorine were designed to have self-cleanable characteristics. As can be seen in Fig. 2, the intensity of the C–F stretching vibration peaks (1200–1230 and 1150 cm^{-1}) increased considerably with increasing contents of fluorine-contained acrylate. To analyze the amount of the fluorine component, XPS was used to detect F, O and C atoms on the cured coating surface. As shown in Fig. 3, the fluorine peak sharply increased with fluorine content. In the synthesized resins, fluorine contents were 0, 10.3, 18.2, and 29.4 wt%. However, the fluorine contents at the surface of the coatings were 0, 18, 25.5, and 42.4%, as shown in Table 2. The result proves that the perfluoroalkyl groups migrate to the surface of cured coatings [9].

Table 2
The fluorine content at the surface of acrylic coatings.

Sample	Perfluorodecyl acrylate content in resin (mole)	Fluorine content in resin (wt%)	Fluorine content at the surface (%)
FA-0	0	0	0
FA-10	1	10.3	18
FA-20	2	18.2	25.5
FA-30	4	29.4	42.4

Table 3
Physical properties of the fluorine-modified acrylic coatings.

Resins	Physical properties		
	Pendulum hardness (ASTM D4366-95)	Pencil hardness (ASTM D3363-74)	Cross-hatch adhesion (ASTM D3359-83)
FA-0	199.5	3H	5B[a]
FA-10	189.5	2H	5B
FA-20	176.9	H	5B
FA-30	163.1	HB	5B

[a] 5B: when no flaking is observed after a cross-hatch adhesion test.

3.2. Physical properties

Table 3 shows the results of the pendulum hardness test, pencil hardness test and cross-cut adhesion test of cured coatings conducted on a stainless steel substrate. The pendulum hardness was in order of FA-0 > FA-10 > FA-20 > FA-30. The maximum pendulum hardness was around 200 s, and this value is similar to the surface hardness of glass. The minimum pendulum hardness was 163.1 s at the maximum content of perfluorodecyl acrylate. In terms of scratch hardness as determined using a pencil hardness test, the hardness value also depended on the perfluorodecyl acrylate content (3H > 2H > 1H > HB). As shown by these results, methyl methacrylate is a harder monomer than perfluorodecyl acrylate in the polymer chain. According to the adhesion test, the adhesion between the coating and the steel substrate was 5B, indicating that no flaking was observed.

3.3. Self-cleanable ability

Figs. 4 and 5 show the results of contact angle measurements on the coating surface. FA-0 contained 0 wt % fluorine content and the other samples contained fluorine in the order: 10.3, 18.2, and 29.4 wt%. The contact angle

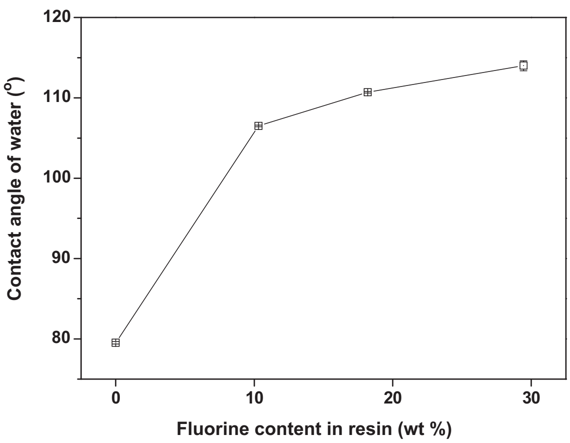


Fig. 4. Contact angle of water on the fluorine-modified coatings with fluorine content in resin (wt%).

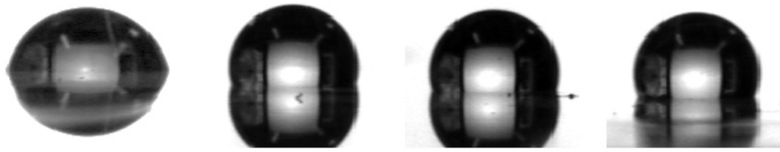
Photograph				
Fluorine Content (wt %)	0	10.3	18.2	29.4
Contact angle (°)	79.5	106.5	110.7	114

Fig. 5. The images of water droplet on the fluorine-modified coatings with fluorine content in resin (wt%).

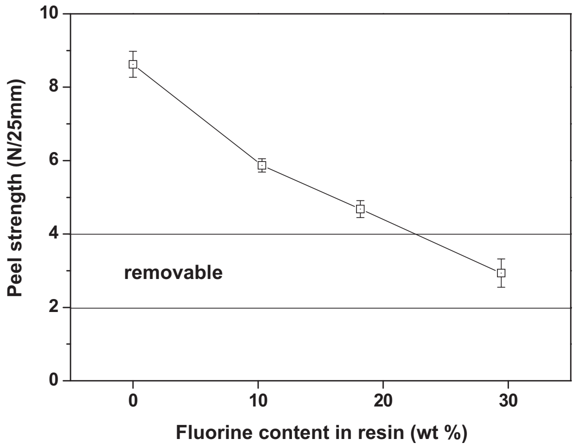


Fig. 6. Peel strength on the fluorine-modified acrylic coatings as a function of fluorine content in resin (wt%).

of water increased with increasing fluorine content, but the efficiency of fluorine was decreased at a content of >20 wt %. The peel test results for evaluation of the self-cleanable characteristic in a resin with a perfluoroalkyl group are shown in Fig. 6. The maximum strength was 8.63 N/25 mm in the FA-0 sample. In the case of FA-30, the value was <3 N/25 mm, and FA-30 had a similar peel adhesion of removal PSAs as listed in Table 4 [17]. Peel strength definitely showed a decreasing tendency with increasing fluorine content. Regarding the efficiency of fluorine, the peel test result was not similar to that of the contact angle measurement. According to results of contact angle measurement, the efficiency of fluorine was limited at a content of >20 wt%. However, the peel strength test results steadily decreased with fluorine contents ranging from 0 wt% to 30 wt%. The tendency shows that the correlation between the surface free energy and the self-cleanable ability is not perfect under realistic conditions. The results suggest that the investigated method of comparing the peel strengths of removable PSAs for predicting the self-cleanable and polluting-preventive characteristics of coatings is more suitable than using the contact angle measurement.

Table 4
Classification of pressure-sensitive adhesive vs. peel adhesion [17].

Kind of PSA	Adhesion of PSA [N/25 mm] (180° peel test)
Excellent permanent	>14
Permanent	10–14
Semi-removable	6–8
Removable	2–4
Excellent removable	<1

4. Conclusions

A peel test was investigated to define the polluting-preventive ability and removability characteristics of fluorine-modified coatings. We designed fluorine-modified acrylic resins with different fluorine contents for the new testing method. Surface analysis was conducted and physical properties were measured to determine the effects of the perfluoroalkyl portion of the side chains. The contact angle measurement was used to measure the angle of a water droplet on the coating surface to determine any correlation with the peel test for the self-cleanable ability.

Regarding the characterization of fluorine-modified coatings, the intensities of the C–F stretching vibration peaks (1200–1230 and 1150 cm^{-1}) in the FT-IR results and the amount of fluorine atoms in XPS results increased with increasing fluorine-containing acrylate content.

Regarding surface hardness as determined by pendulum hardness and pencil hardness, the hardness value was in an order which depended on perfluorodecyl acrylate content (FA-0 > FA-10 > FA-20 > FA-30). In the case of adhesion, all cured coatings were evaluated as grade 5B, indicating that no surface flaking was observed. Regarding the self-cleanable ability of coatings, the contact angle of water decreased with fluorine content and the efficiency of fluorine was limited to a content of >20 wt%. However, the peel strength steady decreased at fluorine contents between 0 wt% and 30 wt%. These results showed that the correlation between the surface free energy and the self-cleanable ability is not perfectly correct under real conditions, and that the investigated method for the self-cleanable ability of coatings is more suitable than the contact angle measurement.

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References

[1] F.A.- Khonsari, M. Tatoulian, Advanced Plasma Technology, Wiley–VCH, 2007.
[2] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, Super-hydrophobic surfaces: from natural to artificial, Adv. Mater. 14 (2002) 1857.
[3] W. Chen, A.Y. Fadeev, M.C. Hsieh, D. Oner, J. Youngblood, T.J. McCarthy, Ultrahydrophobic and ultralyophobic surfaces: some comments and examples, Langmuir 15 (1999) 3395.
[4] C.J. Drumond, Z.R. Vasic, N. Geddes, M.C. Jurich, R.C. Chatelier, T.R. Gengenbach, H.J. Griesser, Hydrophobic radiofrequency plasma-deposited polymer films: dielectric properties and surface forces, Colloids Surf. A Physicochem. Eng. Asp. 117 (1997) 129.
[5] C.M.G. Carlsson, G. Strom, Reduction and oxidation of cellulose surfaces by means of cold plasma, Langmuir 7 (1991) 2492.
[6] F. Denes, Z.Q. Hua, E. Barrios, R.A. Young, J. Evans, Influence of RF-Cold plasma treatment on the surface properties of paper, J. Macromol. Sci. Pure Appl. Chem. 32 (1995) 1405.
[7] H.T. Sahin, S. Manolache, R.A. Young, F. Denes, Surface fluorination of paper in CF4-RF plasma environments, Cellulose 9 (2002) 171.
[8] H.J. Streitberger, K.F. Dossel, Automotive Paints and Coatings, WILEY-VCH, 2008.
[9] V.C. Malshe, N.S. Sangaj, Fluorinated acrylic copolymers: part I: study of clear coatings, Prog. Org. Coat. 53 (2005) 207.
[10] D. Satas, Handbook of Pressure Sensitive Adhesive Technology and Application, Satas & Associates Warwick, 2002.
[11] H. Miao, L. Cheng, W. Shi, Fluorinated hyperbranched polyester acrylate used as an additive for UV curing coatings, Prog. Org. Coat. 65 (2009) 71.
[12] J.H. Choi, J. H-. Kim, Three hardness test methods and their relationship on UV-curable epoxy acrylate coatings for wooden flooring systems, J. Ind. Eng. Chem. 12 (2006) 412.
[13] H.K. Yasuda, Y.-S. Lin, Q.S. Yu, Durable bonding characteristics of thermoplastic olefins plasma-treated by low-temperature cascade arc torches, Prog. Org. Coat. 42 (2001) 236.
[14] Paints and Vanishes – Cross-Cut Test, ISO. (2007) 2409.
[15] B.H. Lee, H.-J. Kim, Curing behaviors of Korean dendropanax lacquer determined by chemical and physical measures, J. Appl. Polym. Sci. 92 (2004) 625.
[16] Y.J. Park, D.H. Lim, H.-J. Kim, Curing behavior and adhesion performance of UV-curable styrene–isoprene–styrene-based pressure-sensitive adhesives, J. Adhes. Sci. Technol. 22 (2008) 1401.
[17] Z. Czech, Solvent-based pressure-sensitive adhesives for removable products, Int. J. Adhes. Adhes. 26 (2006) 414.