

Mechanical Properties of Alkoxy Type Silicone Sealants

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Abstract: Alkoxy type silicone sealants were prepared with various PDMS (polydimethylsiloxane) viscosities. In addition, effect of plasticizer, crosslinkers, and catalyst on sealant performance made by mixture of PDMS viscosities of 20000 and 80000 was investigated. Tensile strength and elongation at break using dumbbell specimens were measured. S-S curve slope was decreased as PDMS viscosity and plasticizer content increased. As PDMS viscosity and plasticizer content increased, elongation at break was increased whereas tensile strength was decreased. As crosslinker content increased, tensile strength was increased and elongation at break was decreased. And, as catalyst content increased, tensile strength and elongation at break were decreased.

Keywords: silicone sealant, alkoxy type, polymer viscosity, crosslinker, plasticizer, catalyst

Introduction

Structural glazing has become a popular method of finishing building exteriors. The technique consists of fastening glass, aluminum or other materials to the building frame using sealants. Thus the sealants play an integral part of the structural glazing, and they are identified as structural sealants [1].

Silicone sealants are important for structural glazing applications. The market growth has been rapid because they have many unique advantages and proven performance in building construction. Silicone sealants cure at room temperature due to the action of atmospheric moisture that forms crosslinked, rubbery compounds and have good rheological and physical properties. Also, they have better environmental stability [2,3].

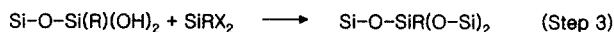
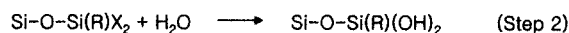
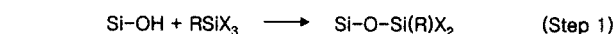
Silicone sealants are based on mixtures of silicone polymers, crosslinker, fillers, and catalysts [4]. They are distinguished into as acetoxy, oxime, or alkoxy types according to the crosslinkers. Alkoxy type sealant has been recently developed, but because of environmental advantages, the use of alkoxy type sealants increased. It releases methanol as a by-product, which is non-

corrosive to most substrates and is not particularly offensive in odor. However, reactions are relatively slow, and sealants used as a crosslinker require high concentrations of a special catalyst to hasten the cure. Thus, proper catalyst systems are required and the types and compositions of components affect sealant performance [5,6].

In general, sealants are distinguished into one-part- and two-part system. The curing of a two-part sealant occurs on mixing two components, the base polymer and a curing agent. Although, one-part sealants rely upon atmospheric moisture/oxygen to initiate cure reactions, which begin when the sealant is exposed to the atmosphere [7].

Curing mechanism of one part silicone sealant is shown in Figure 1. In one-part systems, the silanol terminated PDMS is prereacted with crosslinker (step 1). Excess crosslinker is generally used to avoid multiple reactions of PDMS chains with a single crosslinker molecule, which would lead to premature gelling and also provide the compounded sealant with a certain degree of protection from adventitious moisture. On exposure to atmospheric moisture during cure, hydrolysis of the terminal functional groups releases silanol groups (step 2), which then condense to form the final network structure (step 3) [6].

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R = methyl or ethyl,
 alkoxy type : X = OMe
 acetoxy type : X = AcO
 oxime type : X = CH₃(C₂H₅)CNO

Figure 1. Schematic curing mechanism of one-part silicone sealants [6].

Proebster [8] and Wakabayashi [9] studied the performance of sealants based on MS-Polymer (silane modified polymer). The cross-linking of MS-polymers occurs according to well-known mechanisms from the chemistry of alkoxy-curing silicones in a two-step reaction starting with the hydrolysis of the silane groups and subsequent condensation. Organic tin-catalysts can be used to boost the reaction [8].

In recent, modified silicone sealants were studied and developed by Kang and coworkers [10-13]. They studied the preparation and properties of α, ω -trimethoxysilyl polyurethane modified with polyorganosiloxane sealant. Also, they reported that TUMPS sealant exhibited more stable rheological and sealant properties than those of TUMPS hybrid elastomer.

In previous study [14], we investigated the effects of component types and ratios on alkoxy type silicone sealant preparation and adhesion properties. This paper discusses the effects of composition variances on mechanical properties (tensile strength and elongation) of silicone sealants.

Experimental

Materials

One part room temperature curable alkoxy type silicone sealants were prepared with various compositions. Component type and ratios were similar with those of our previous study [14].

The silicone polymer was silanol terminated PDMS (polydimethylsiloxane) with viscosities of 20000, 50000, and 80000 cps (Shinetsu Co.), respectively. The molecular weights (M_w) of PDMS were 61500, 106000, and 120500 with viscosities of 20000 (20 k), 50000 (50 k), and 80000 (80 k) cps, respectively.

The crosslinker was TSL-8113 (Thoshiba Co.), alkytriacetoxysilane with 2, 4, 6, and 8 wt.% based on PDMS. The plasticizer was KF-96 (Shinetsu Co.), silicone plasticizer with 5, 10, 15, and 20 wt.% based on PDMS. The catalyst was Tilkom (Tioxide specialties LTD.), titanate type catalyst with 1.5, 1.9, 2.3, and 2.7 wt.% based on PDMS and crosslinker. In addition,

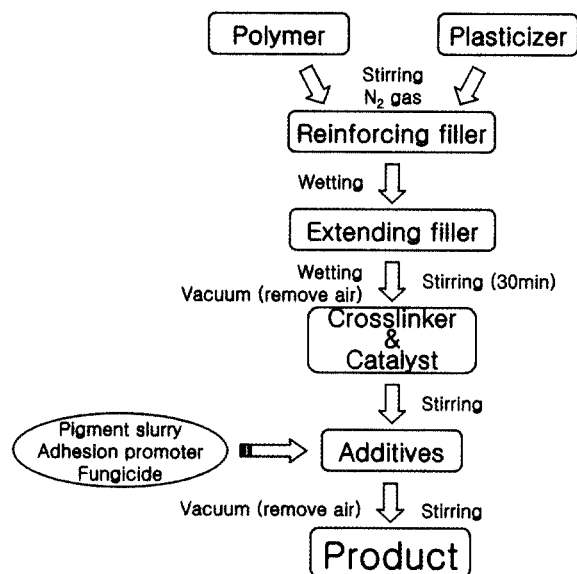


Figure 2. Method of silicone sealant blending.

filler and additives (chain extender, adhesion promoter, pigment slurry, fungicide) were used.

Preparation of Alkoxy Type Sealants

Alkoxy type silicone sealants were prepared in Hermann Linden LPMD10, high disperser mixer with cooling apparatus. The preparation procedure of silicone sealants is shown in Figure 2.

In the alkoxy type silicone sealants preparation, stable reaction can be achieved by adjusting composition variance ratio in the sealant mixture of below 40°C. Above 45°C of reaction temperature, gelation of sealant mixture was observed. Cooling system with cooling water can be used to prevent gelation. The results were discussed in our previous study [14].

FT-IR Spectra of Alkoxy Type Sealants

Basic chemical structure was analyzed by ATR (Attenuated Total Reflectance) FT-IR spectroscopy (Bio-RAD Digilab FTS-60 with microscope UMA-250). A 2 mm thick specimen of the sealant (with 5% of plasticizer, 6% of crosslinker and 2.3% of catalyst) was prepared. The specimen was cured at 25°C, 50% RH for two weeks. FT-IR (ATR) spectra of alkoxy type silicone sealant are shown in Figure 3.

The peak at 2962 cm⁻¹ represents C-H stretching vibrations of the methyl group absorbs in the normal region. The band at 1258 cm⁻¹ is due to the CH₃ rocking. The peak at 1083 and 1012 cm⁻¹ represents Si-O-Si stretching vibrations [15].

May and Love [16] studied FT-IR spectra of Dow Corning 888 silicone joint sealant coated on KBr disk. In the paper, They reported that peaks of FT-IR spectra were observed at 2964 cm⁻¹, 1260 cm⁻¹, and the

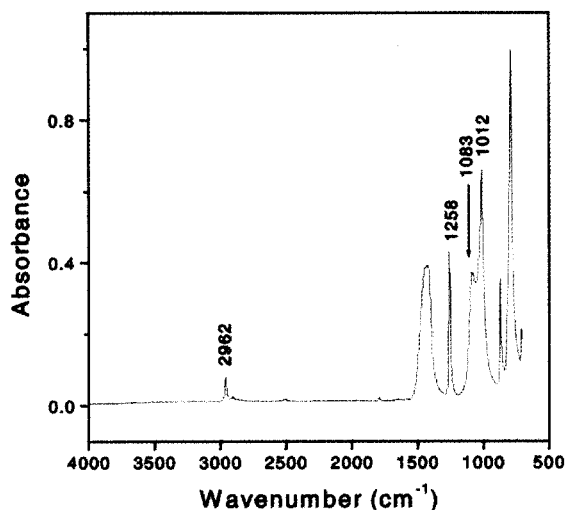


Figure 3. FT-IR spectra of alkoxy type silicone sealant.

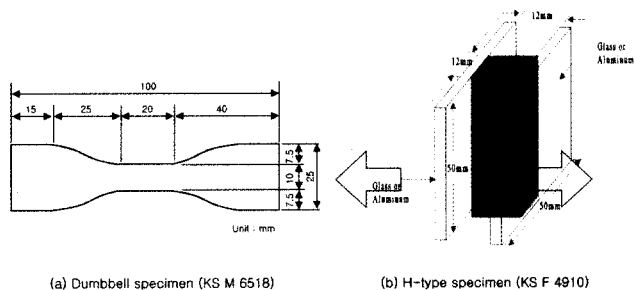


Figure 4. Comparison of dumbbell specimen and H-type specimen.

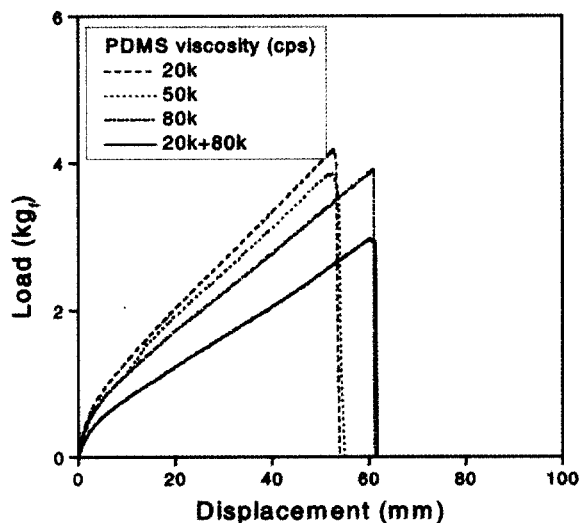


Figure 5. Stress-strain curves as a function of PDMS viscosity.

fingerprint region between 850-1100 cm^{-1} and 800-880 cm^{-1} . Their results are similar with those of our study.

Mechanical Properties

In our previous study, adhesion properties were measured

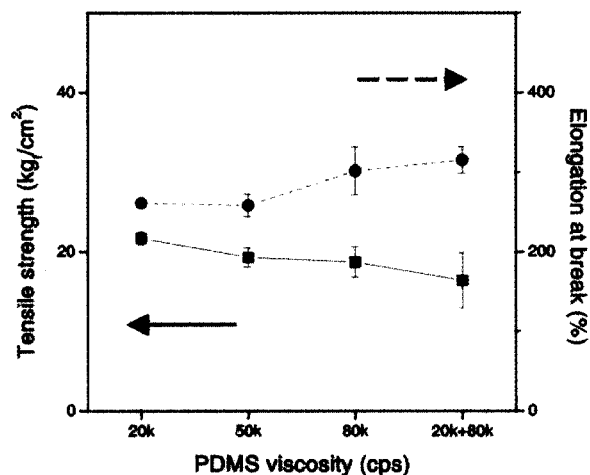


Figure 6. Tensile strength and elongation at break as a function of PDMS viscosity.

Table 1. Tensile Strength at 50 (TS₅₀) and 100 (TS₁₀₀) Elongation Values of Silicone Sealant by PDMS Viscosity

PDMS viscosity(cps)	TS ₅₀ (kgf/cm ²)	TS ₁₀₀ (kgf/cm ²)
20k	6.5	10.2
50k	5.9	9.3
80k	5.3	8.1
20k+80k ^{*1}	4.3	6.7

^{*1}; 50:50 wt% of mixture

by H-type specimens according to KS F 4910 (Figure 4, b). The substrates used in adhesion test were glass, aluminum, and specimens of glass/sealant/glass, glass/sealant/aluminum, aluminum/sealant/aluminum were prepared.

In this study, mechanical properties (tensile strength, elongation at break) were measured by dumbbell specimens according to KS M 6518 (Figure 4, a). Dumbbell specimens used in this study were No. 2 type, with a thickness of 2 mm. The specimens were cured at 25°C, 50% RH for two weeks. The crosshead speed during the tensile strength and elongation measurement was 200 mm/min using UTM (Zwick Z100, NICEM at Seoul National University). The tensile strength and elongation at break point and special elongation (eg, 100% of elongation) were measured.

Results and Discussion

Mechanical Properties as a Function of PDMS Viscosity

The stress-strain curves of alkoxy type silicone sealant dumbbell specimens as a function of PDMS viscosity are shown in Figure 5. Tensile strength and elongation at break are shown in Figure 6, and tensile strengths at 50% (TS₅₀) and 100% (TS₁₀₀) elongation values are listed in Table 1.

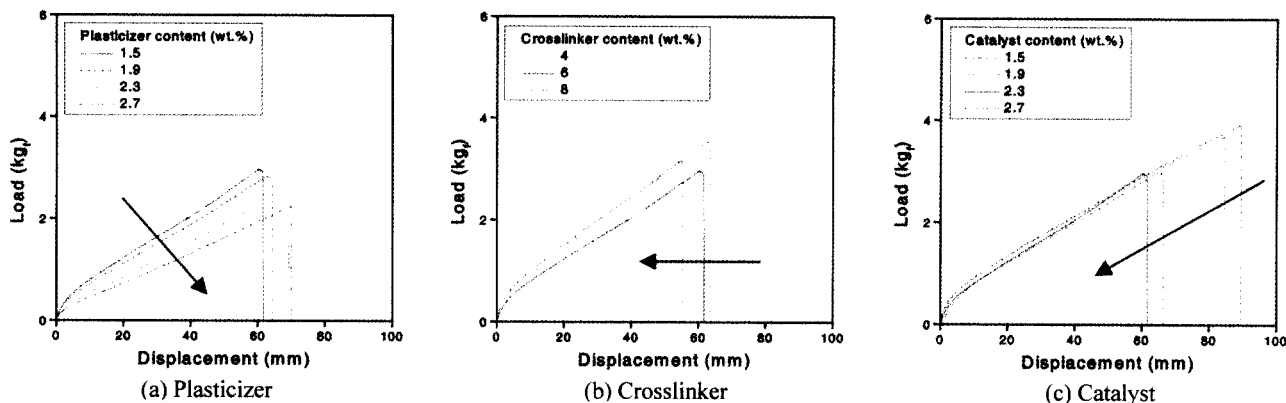


Figure 7. Effects of composition variances on stress-strain curves.

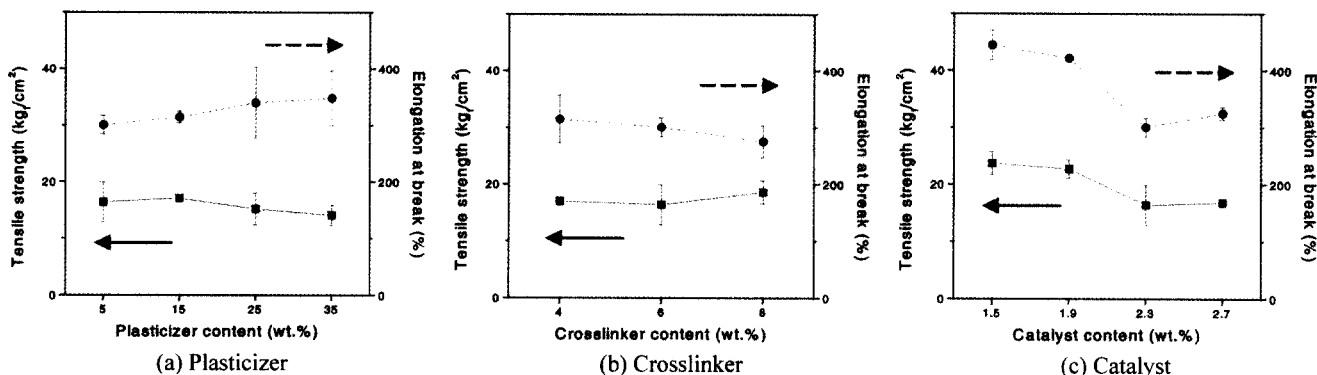


Figure 8. Effects of composition variances on tensile strength and elongation at break.

As shown in Figure 5, S-S curve slope was decreased as PDMS viscosity increased. In the previous study, adhesion properties were measured using H-type specimens with various substrate systems [14]. S-S curve slope for H-type specimens was also decreased as polymer viscosity increased (e.g., polymer weight increased).

As polymer viscosity increased, elongation at break was increased and tensile strength was decreased, as shown in Figure 5. And also, TS_{50} and TS_{100} were decreased as PDMS viscosity increased as shown in Table 1.

According to earlier studies, the increase in viscosity of PDMS associated with an increase in molecular weight of PDMS causes the uncured sealant to become thicker [6]. However, the molecular weight of a polymer chosen for a sealant tends to influence the tensile and elongation (stress and strain) characteristics of the sealant. Therefore, sealant formulator can match polymer molecular weight to the stress-strain performance value [5]. In general, an increase in molecular weight causes a decrease in the modulus of the cured sealant, and a corresponding increase in the ultimate elongation [3,5,6].

Mechanical Properties as a Function of Composition Variances Change

The effects of plasticizer, crosslinkers, and catalyst on

Table 2. Tensile Strength at 50 (TS_{50}) and 100 (TS_{100}) Elongation Values of Silicone Sealant by Plasticizer

Plasticizer content*1 (wt%)	$TS_{50}(kg/cm^2)$	$TS_{100}(kg/cm^2)$
5	4.3	6.7
15	4.3	6.5
25	2.8	4.6
35	3.3	5.2

*1 ; Weight fraction based on PDMS

mechanical properties of sealant made by mixture of PDMS viscosities of 20000 and 80000 were investigated and are shown in Figure 8, and Tables 2, 3 and 4. The stress-strain curves of sealant dumbbell specimens by composition variance are shown in Figure 7.

As shown in Figure 7, S-S curve slope was decreased as plasticizer content increased. In crosslinker and catalyst content change, S-S curve slopes are similar in all range except for 6% of crosslinker content. However, the load of break point was decreased as crosslinker and catalyst content increased. In our previous study using H-type specimens [14], similar results were obtained.

Due to the plasticizer, tensile strength was decreased but elongation at break was increased as plasticizer content increased up to 25%, as shown in Figure 8. TS_{50} and TS_{100} were decreased as plasticizer content increased

Table 3. Tensile Strength at 50 (TS₅₀) and 100 (TS₁₀₀) Elongation Values of Silicone Sealant by Crosslinker

Crosslinker content* ¹ (wt%)	TS ₅₀ (kgf/cm ²)	TS ₁₀₀ (kgf/cm ²)
4	4.6	6.8
6	4.3	6.7
8	5.7	8.7

*¹ ; Weight fraction based on PDMS

Table 4. Tensile Strength at 50 (TS₅₀) and 100 (TS₁₀₀) Elongation Values of Silicone Sealant by Catalyst

Catalyst content* ¹ (wt%)	TS ₅₀ (kgf/cm ²)	TS ₁₀₀ (kgf/cm ²)
1.5	5.5	8.1
1.9	5.5	8.0
2.3	4.3	6.7
2.7	4.5	6.8

*¹ ; Weight fraction based on PMDS and crosslinker

up to 25%, as listed in Table 2. These results are similar with those of previous study using H-type specimens [14].

Plasticizers are typically added to silicone sealant compositions in order to adjust rheology of the paste, and to make it easier for the polymer chains to slide over when the cured material is elongated or compressed in its real-life joint configuration [17]. Plasticizer increases ultimate elongation and reduces hardness in the cured sealant. It modifies the rheology of uncured sealant. The use of a low viscosity plasticizer will make the sealant more mobile and easier to extrude although at high loadings the yield point could be reduced to the point where the material begins to flow [6].

Due to the crosslinker, tensile strength was increased but elongation at break was decreased as crosslinker content increased up to 8%, as shown in Figure 8. Also, TS₅₀ and TS₁₀₀ were similar between 4% and 6% of crosslinker content, but increased at 8%. In the previous study where H-type specimens were used [14], adhesion failure of 70% and 40% occurred in aluminum/aluminum and glass/aluminum systems above up to 8% of crosslinker content. In the study, proper adhesive properties were obtained in the range from 4% to 6% of crosslinker content.

According to earlier studies, the degree of crosslinking in elastomers is directly related to the modulus of material. Low-modulus materials tend to be slightly crosslinked, while higher-modulus materials have greater crosslink densities in their structures. The crosslink density for a rubbery material can be estimated from stress-strain measurements in tension or compression [18]. Generally, the chemistry of elastic sealant is characterized by the fact that a flexible polymer component is crosslinked to form a three-dimensional structure [17]. The crosslink density is dependent on crosslinker functionality and concentration. The crosslink

density of a sealant system is often modified to achieve desired stress-strain performance profile. Alkoxy type crosslinker has relatively slow reaction rate, and sealants used as a crosslinker require high concentrations of a special catalyst to hasten cure [5]. Thus, it is important to find a proper crosslinker content.

Due to the catalyst, tensile strength and elongation at break were decreased as catalyst content increased up to 2.3%, as shown in Figure 8. And also, TS₅₀ and TS₁₀₀ were decreased as catalyst content increased up to 2.3%. These results differ from those of previous study using H-type specimens [14]. In this study, strength and elongation were increased as catalyst content increased up to 2.3%. It seems that catalyst influences adhesion between the substrate and sealant.

The curing of one-part sealant systems is generally slow, as the curing reactions need an external agent for it to diffuse through the body of the sealant to initiate the process of cure [7]. In sealant preparation, catalysts are, in general, not true catalysts because they are consumed or transformed during the curing process. They are rather designated accelerators [6]. Increasing the catalyst concentration increases the reaction rate, but there are limits unique to each catalyst. Above these concentration limits, the intrinsic stability of the silicone sealant, and especially the thermal stability, is lessened. Catalysts provide an effective means of controlling cure rate, but they must be used judiciously [5].

Conclusion

Mechanical properties of alkoxy type silicone sealants were measured using dumbbell specimens. S-S curve slope was decreased as PDMS viscosity and plasticizer content increased. In crosslinker and catalyst content change, S-S curve slopes are similar in all range except for 6% of crosslinker content. However, the load of break point was decreased as crosslinker and catalyst content increased. As PDMS viscosity and plasticizer content increased, elongation at break was increased whereas tensile strength was decreased. As crosslinker content increased, tensile strength was increased and elongation at break was decreased. And, as catalyst content increased, tensile strength and elongation at break were decreased.

References

1. C. V. G. Vallabhan, M. Zülfü Asik, and K. Kandil, *Computers & Structures*, **65**, 231 (1997).
2. P. Descamps, J. Inker, and A. T. Wolf, *Construction and Building Materials*, **10**, 527 (1996).
3. M. D. Beers and J. M. Klosowski, in *Adhesives and*

- Sealants*, H. F. Brinson, Ed., pp. 215-222, ASM International Handbook Committee (1992).
4. E. M. Petrie, *Handbook of Adhesives and Sealants*, p. 451, McGraw-Hill, New York (2000).
 5. J. M. Klosowski and G. A. L. Gant, in *ACS Symposium Series 113*, pp. 113-126, American Chemical Society, Washington DC (1979).
 6. R. D. Grant, in *Polymeric Materials Encyclopedia*, J. C. Salamone Ed, pp. 7699-7705, CRC Press (1996).
 7. K. W. Allen, A. R. Hutchinson, and A. Pagliuca, *Int. J. Adhesion and Adhesives*, **14**, 117 (1994).
 8. M. Proebster, in *Proc. 2001 Beijing Bonding Technology Symposium*, Daoyou Luo Ed., Beijing, PR China (2001).
 9. H. Wakabayashi, in *Proc. 2001 Beijing Bonding Technology Symposium*, Daoyou Luo Ed., Beijing, PR China (2001).
 10. D. W. Kang and Y. M. Lim, *J. Ind. Eng. Chem.*, **5**, 280 (1999).
 11. D. W. Kang, B. J. Kim, and D. S. Shim, *J. Ind. Eng. Chem.*, **6**, 270 (2000).
 12. D. W. Kang, M. S. Han, H. J. Kang, S. M. Lee, and Y. M. Kim, *Korean Ind. Eng. Chem.*, **12**, 205 (2000).
 13. D. W. Kang, M. S. Han, H. J. Kang, S. M. Lee, and Y. M. Kim, *J. Ind. Eng. Chem.*, **7**, 223 (2001).
 14. D.-J. Kim, Y.-J. Park, H.-J. Kim, B. W. Lee, and J. C. Han, *Adhesion & Interface*, **2**(4), 1 (2001).
 15. The Infrared Spectroscopy Committee of the Chicago Society for Coatings Technology, in *An Infrared spectroscopy ATLAS for the Coatings Industry*, p. 35, Federation of Societies for Coatings Technology (1980).
 16. R. J. May and B. J. Love, Center for Adhesive and Sealant Science, Virginia Tech, CASS/MATE-95-1 (1995).
 17. K. Ramesh and R. W. Tock, *Polym.-Plast. Technol. Eng.*, **33**, 537 (1994).
 18. F. Buyl, *Int. J. of Adhesion & Adhesives*, **21**, 411 (2001).