

Temperature-dependent studies on catalytic hydrosilation of polyalkylsiloxane using NMR

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Abstract Polyalkylsiloxane has been spotlighted in pressure-sensitive adhesive (PSA) application due to excellent physical properties and good biocompatibility. Thermal behaviour of polyalkylsiloxane mixtures, such as thermal stability and heat flow, were studied using TG-DTA during catalytic hydrosilation. To understand reaction kinetics of cross-linking, catalytic hydrosilation of polyalkylsiloxane was monitored using variable temperature nuclear magnetic resonance (VT-NMR) as increased temperature. The formation of cross-linking bond Si-CH₂-CH₂-Si was directly observed using distortionless enhanced by polarization transfer (DEPT) technique. Successfully polyalkylsiloxane PSA samples exhibited excellent adhesion properties by cross-linking reaction.

Key words: VT-NMR, catalytic hydrosilation, cross-linking, polyalkylsiloxane, pressure-sensitive adhesive

1. Introduction

Polyalkylsiloxane is a macromolecule consisting of inorganic backbone and organic group with a broad range of application because of low surface tension, viscoelastic behavior, good biocompatibility, and excellent mechanical and thermal stability.¹⁻⁵ In particular, many studies have been made to use polyalkylsiloxane as a pressure-sensitive adhesive (PSA).^{2,3} For example, Silicone, polydimethylsiloxanes (PDMS), has been studied medical PSA applications such as medical dressing,¹ drug delivery material for controlled release² and elastic tube for blood

transfusion.⁴

PSA refers to a substance which can be attached to a material with little pressure without thermal or solvent process.^{6,7} When PSA contacts with a material, the material surface is wetted by the adhesive through formation of temporary bonds due to the molecular interaction, so-called van der Waals force. The most important feature of PSA is low adhesion without destroying interface. Thus, it can be removable and reusable because there is no residue on the material surface. There are various kinds of PSA such as rubber-, acrylic-, and polyalkylsiloxane-base adhesives.⁷ Rubber-base PSA has been widely used

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at low prices but has poor weatherability, durability and chemical resistance. Acrylic-base PSA has better physical properties than rubber-type PSA but is not suitable for use exposed to moisture. Polyalkylsiloxane-base PSA has several benefits such as moisture resistance, weatherability, chemical resistance and durability.^{6,7}

Much effort has been devoted to improving the physical properties of polyalkylsiloxane because polyalkylsiloxane has low glass transition temperature due to high flexibility of main chain.^{2-5,8} For example, linear-type PDMS is liquid state at room temperature regardless of molecular weight.⁵ The cross-linking reaction by catalytic hydrosilation gives polyalkylsiloxane advanced properties including rubber elasticity and viscoelasticity.⁵⁻⁹

Nuclear magnetic resonance (NMR) has been a widely used tool for studying molecular structures and chemical reactions.⁹⁻¹² Monitoring chemical reactions provides a solution not only to understand the mechanism and kinetics of chemical reactions but also to help optimizing reaction conditions such as temperature and reactant ratio. For the reaction activated by thermal energy, variable temperature NMR enables *in-situ* measurement to observe formation of cross-linking bonds and intermediates.⁹⁻¹¹

In this paper, we have attempted to study reaction about catalytic hydrosilation on three different reaction sites in polymers using *in-situ* VT-NMR and TG-DTA. The bond formation by cross-linking was confirmed by ¹³C NMR with DEPT technique. Cross-linked polyalkylsiloxane network was evaluated whether it had sufficient adhesion performance for PSA applications.

2. Experiment

2.1. Chemicals and reagents

Vinyl terminated polydimethylsiloxane (PMC500T), hydride terminated polydimethylsiloxane (CL1050T), trimethylsilyl terminated polymethyl hydrosiloxane (CL1950SH), trimethylsiloxane terminated (3-4% methylhydrosiloxane) dimethylsiloxane copolymer (CL1950SC), platinum divinyltetramethyldisiloxane

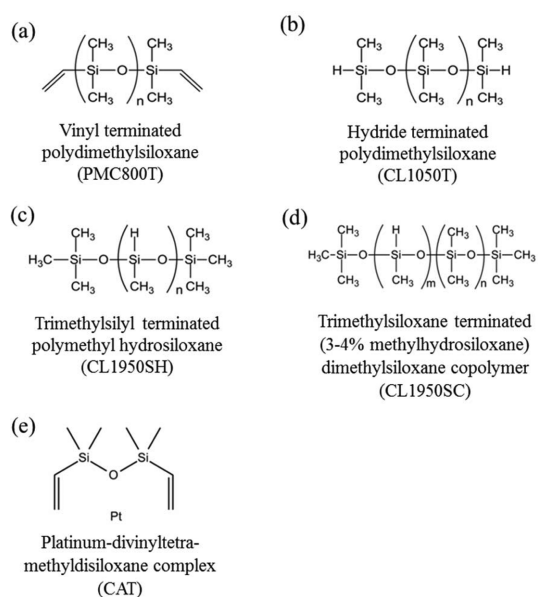


Fig. 1. The chemical structures of polyalkylsiloxanes and catalyst.

complex (CAT) were purchased from Gelest (USA) and used without further purification. The reagents are shown in Fig. 1. Toluene-*d*₈ as a solvent for VT-NMR analysis was purchased from Euriso-top (France) and used without further purification.

2.2. Analytical instrument

TG-DTA results were recorded using Thermo plus EVO II TG8120 (Rigaku, Japan). The ¹H NMR and ¹³C NMR spectra were acquired using AVANCE 500 (Bruker, Germany) operating at 500 MHz resonance frequency. The magnetic field was about 11.75 Tesla and 5 mm Broad Band Probe (BBO) (Bruker, Germany) was installed. The NMR tube in a 5 mm diameter (Wilmad, USA) was used. The VT-NMR spectra were analyzed using Bruker Topspin 3.1.1 software and MestReNova 6.0.2. The results of adhesion force were obtained from the 180° peel tests using AGS-10kNXD (Shimadzu, Japan).

2.3. Sample preparation

For catalytic hydrosilation, a mixture of PMC800T and cross-linker was sufficiently prepared at a molar ratio of 1:1.2 with respect to the number of

Table 1. Characteristics of polyalkylsiloxane mixture

Mixture abbreviation	Composition	Polymer contents (mg)	Catalyst amount (μL)
PMC800T-CL1050T	PMC800T, CL1050T, CAT	22.25:5.37	0.68
PMC800T-CL1950SH	PMC800T, CL1950SH, CAT	22.41:36.78	0.68
PMC800T-CL1950SC	PMC800T, CL1950SC, CAT	22.28:116.90	0.68

functional groups and added to Pt catalyst (0.05 mol %) in sequence. The detailed information of mixtures are listed in Table 1. A mixture solution for NMR measurement was dissolved in toluene- d_8 to prepare the total volume of 1 mL.

2.4. Experiments

The thermal analytical results were measured with TG-DTA using Al_2O_3 as a standard material. Temperature was raised from 25 °C to 300 °C at a rate of 10 °C/min in N_2 gas at a flow rate 300 ml/min. The sample in toluene- d_8 were monitored by *in-situ* VT-NMR at appropriate temperature intervals. As temperature increasing from 25 °C to 100 °C at a rate of 1.25 °C/min, each spectrum was recorded every 5 °C and collected for a minute. The holding time was set to 4 minutes so that sample temperature reached equilibrium with the ambient temperature of the probe during the measurement. Upper limit of measuring temperature was determined to be 100 °C to prevent damage to the NMR probe due to boiling toluene solvent. All VT-NMR experiments were measured with a state of homogeneous solution.

3. Results and Discussion

3.1. Thermal analysis

Fig. 2 shows TGA curves of polyalkylsiloxane mixtures at a heating rate of 10 °C/min under nitrogen gas. There is no weight loss such as evaporation and thermal degradation of mixtures during the heating process. Polyalkylsiloxanes are stable up to 300 °C and the their weight changes during thermal cross-linking reactions can be negligible.

Thermal cross-linking behavior of polyalkylsiloxanes was characterized by DTA as can be seen Fig. 3. PMC800T - CL1050T shows a sharp peak observed

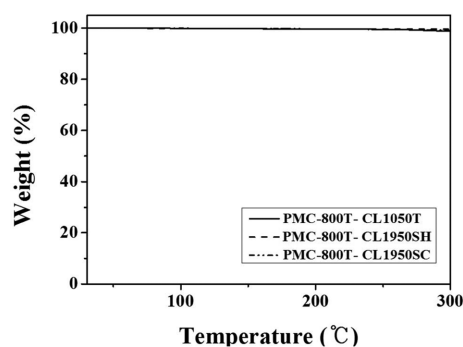


Fig. 2. TG curves of PMC800T - crosslinker mixtures; temperature was raised from 25 °C to 300 °C at a rate of 10 °C/min in N_2 gas at a flow rate 300 ml/min.

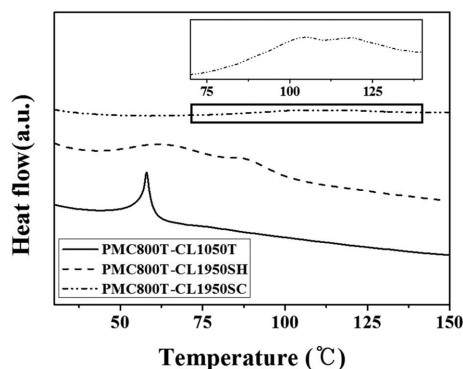


Fig. 3. DTA curves of PMC800T - crosslinker mixtures; temperature raised from 25 °C to 300 °C at a rate of 10 °C/min in N_2 gas at a flow rate 300 ml/min. Inset shows enlarged TG curve of PMC800T-CL1950SC.

at 60.5 °C due to heat flow of the cross-linking reaction between terminal vinyl groups and Si-H groups of PDMSs. PMC800T - CL1950SH shows two broad peaks observed at 67.0 °C and 92.6 °C due to heat flow of the cross-linking reaction between terminal vinyl groups of PDMS and Si-H groups of polymethylhydrosiloxane (PMHS). This broader shape and higher-shifted position of two peaks can be considered as effects of molecular weight and steric

hindrance of PMHS. PMC800T - CL1950SC shows two weak and broad peaks located at 104.2 °C and 118.7 °C caused by heat flow of the cross-linking reaction between terminal vinyl groups of PDMS and Si-H groups of PDMS-co-PMHS. The extreme change in the shape and location of PMC800T - CL1950SC is mainly due to the limitation of reactions in the mobility of polymer molecules at high viscosity condition.

3.2. NMR measurements

Fig. 4 shows full-range ^1H NMR spectra of three polyalkylsiloxane solutions at room temperature. There

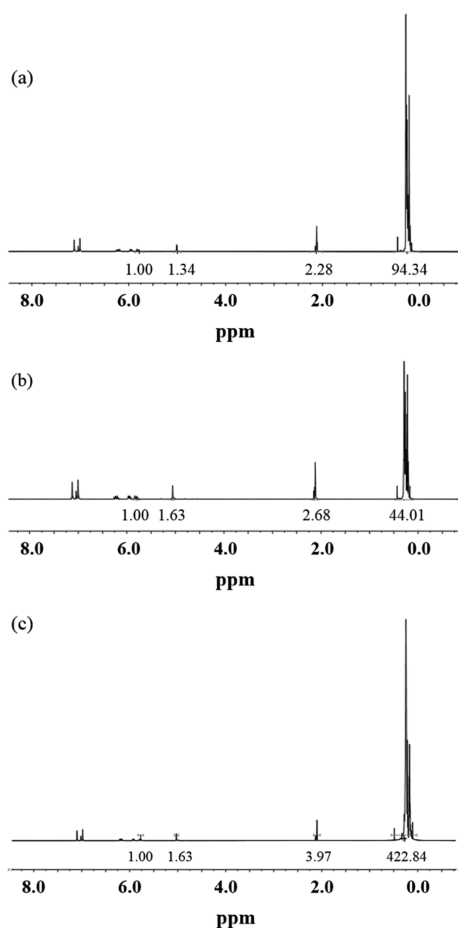


Fig. 4. ^1H NMR spectra of toluene- d_8 solutions of (a) PMC800T - CL1050T, (b) PMC800T - CL1950SH, and (c) PMC800T - CL1950SC at 25 °C. Signals detected at 5.7 - 6.2 ppm and 4.9 - 5.1 ppm can be assigned to vinyl and Si-H group, respectively.

are representative ^1H NMR peaks that can be assigned to be methyl groups (0.0 - 0.5 ppm), vinyl groups (5.8 - 6.2 ppm) and Si-H groups (4.9 - 5.1 ppm), respectively. The proportion of protons participated in catalytic hydrosilation can be determined by integrated ratio of Si-H groups to overall functional groups. The relative ratio of initial protons can be sorted in sequence of PMC800T - CL1950SH, PMC800T - CL1050T and PMC800T - CL1950SC because of reaction probability.¹³

In-situ variable temperature ^1H NMR studies were performed to monitor chemical bond formation by catalytic hydrosilation in polyalkylsiloxane solutions. Fig. 5(a) shows VT-NMR spectra of PMC800T -

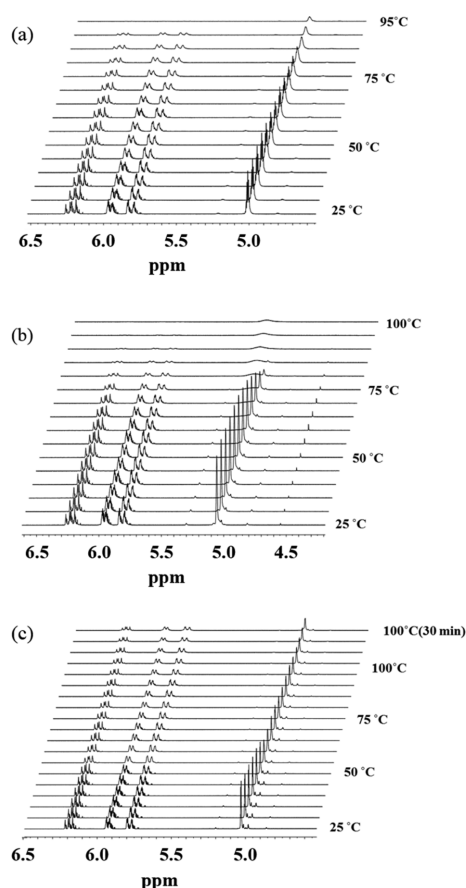


Fig. 5. *in-situ* VT-NMR spectra of toluene- d_8 solutions of (a) PMC800T - CL1050T, (b) PMC800T - CL1950SH, and (c) PMC800T - CL1950SC. Signals detected at 5.7 - 6.2 ppm and 4.9 - 5.1 ppm can be assigned to the vinyl and Si-H group, respectively.

CL1050T at the temperature range from 25 °C to 95 °C. As the temperature increases, the NMR peaks of the vinyl group gradually decreases and disappears at 95 °C. Fig. 5(b) shows VT-NMR spectra of PMC800T - CL1950SH as increased the temperature from 25 °C to 100 °C. During the heating process, the NMR peaks of the vinyl group gradually decreases and disappears at 100 °C. In contrast to the TGA result, the trend of cross-linking reaction is similar to that of PMC800T - CL1050T except the shift of termination temperature. It can be explained to increase molecular free motion in solution state. Here, new peak appears at about 4.55 ppm. It can be considered that an intermediate formed by Pt catalyst and Si-H group was detected.⁵ The formation of intermediates is fast and stable but formation of crosslinking bonds is relative slow due to steric hindrance. Fig. 5(c) shows VT-NMR spectra of PMC800T - CL1950SC as increased the temperature to 100 °C and maintained at final temperature for 30 min. At 100 °C, the signal intensity of the vinyl groups is weaker than the intensity at 25 °C but still remains after 30 minutes. Not only the cross-linking reaction was not completed but also its rate is gradually decreased. The cross-linking reaction of PMC800T - CL1950SC can be explained by diffusion limitation of reactive molecules in non-reactive PDMS moieties.

To monitor the degree of conversion from vinyl groups to cross-linked bonds, integrations of peak areas for vinyl groups are executed and plot the

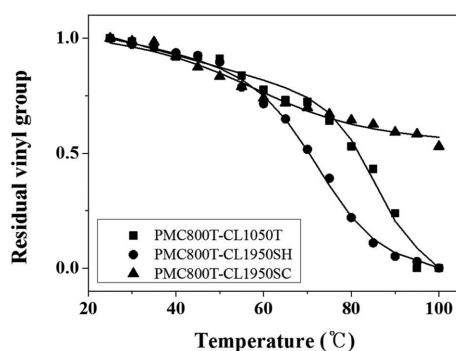


Fig. 6. Plot for the conversion of vinyl group against temperature.

conversion of vinyl group against temperature as can be seen Fig. 6. The reaction rate of catalytic hydrosilation in viscous solution is fast in order of PMC800T - CL1950SH, PMC800T - CL1050T and PMC800T - CL1950SC. Compared with DTA results, the fastest reaction in viscous solution is PMC800T - CL1950SH even though the slope of the conversion of PMC800T - CL1050T is steeper than that of PMC800T - CL1950SH. At initial state of catalytic hydrosilation at around 50 °C, the activation energy is not enough and reaction of cross-linking is limited. At middle state of cross-linking reaction above the activation energy, the reaction rate depends on diffusion distance to encounter vinyl groups with Si-H groups. In the final state of catalytic hydrosilation above 85 °C, the reaction rate is strongly dependent on the molecular

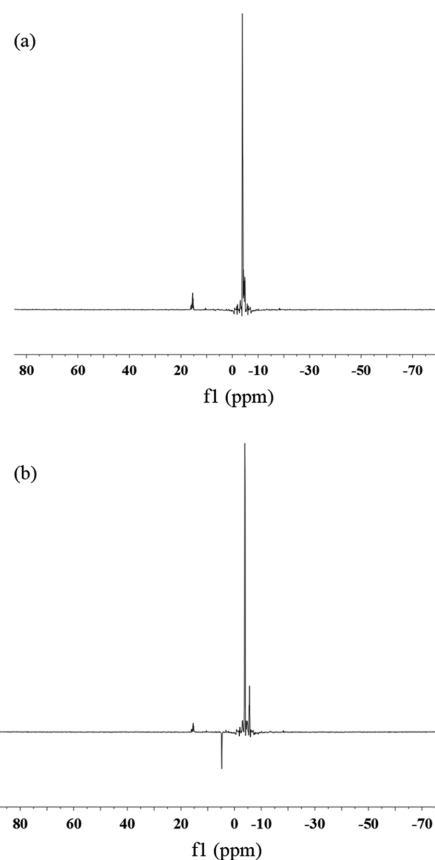


Fig. 7. DEPT spectra of PMC800T - CL1050T (a) before and (b) after cross-linking. The signal of cross-linking bond, Si-CH₂-CH₂-Si, can be assigned to be at around 5 ppm.

motion of limitation parameters such as steric hindrance of the joint formation, longer molecular length of a polymer chain and higher viscosity.

To confirm the formation of cross-linked bonds, ^{13}C NMR measurements were performed with distortionless enhancement polarization transfer (DEPT) technique¹² before and after the chemical reaction. The DEPT technique is a very useful tool to adopt the specific pulse sequence in ^{13}C spectroscopy to measure the number of hydrogen bonds connected to carbon atom. The DEPT135 can recognize all types of protonated carbons and provide positive intensities for CH and CH_3 and negative intensity for CH_2 . The cross-linked bonds, $\text{Si-CH}_2\text{-CH}_2\text{-Si}$, were characterized by DEPT135 before and after thermal cross-linking reaction of PMC800T - CL1050T. (Fig. 7) Before catalytic hydrosilation, there is no signal of CH_2 groups detected at around 5 ppm about CH_2 in Fig. 7(a). However, after catalytic hydrosilation, a signal of CH_2 groups with a negative intensity is detected at around 5 ppm and infers that vinyl groups and Si-H groups were successfully cross-linked each other.

3.3. Industrial PSA product analysis

Industrial PSA samples were analyzed by *in-situ* VT-NMR to understand relationship between physical properties and cross-linking reaction. The industrial samples from a chemical company, sample α and β , were supplied as mixtures consisting of vinyl-terminated PDMS, polyalkylsiloxane containing Si-H groups and PT catalyst. For the NMR sample preparation sample α and β were dissolved in toluene- d_6 and mixed moderately.

In-situ VT-NMR measurements for sample α and β were execute to observe cross-linking formation as temperature increased to 90 °C and sustained for 10 minute. Fig. 8 shows the representative VT-NMR spectra of sample α and β during heating process. At 25 °C, representative ^1H NMR signals of vinyl groups and Si-H groups are located at 5.7 - 6.2 ppm and 4.9 - 5.1 ppm, respectively. As temperature increased, vinyl groups and Si-H groups were consumed to form cross-linking bonds and the NMR signals about vinyl groups in both sample solutions almost

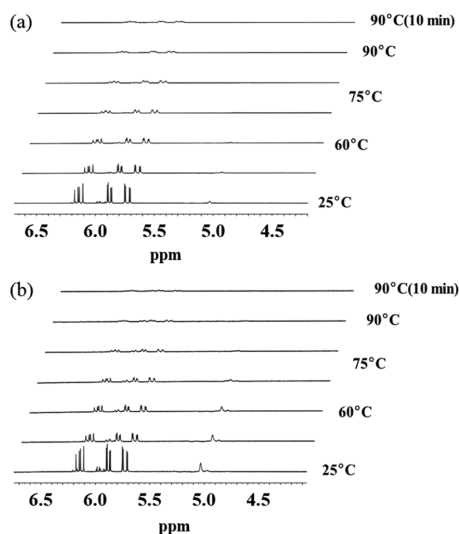


Fig. 8. *in-situ* VT-NMR spectra of (a) sample α and (b) sample β . Signals detected at 5.7 - 6.2 ppm and 4.9 - 5.1 ppm can be assigned to the vinyl and Si-H group, respectively.

disappeared at the end of measurements.

The adhesion tests were conducted to understand physical properties and cross-linking reaction of PSA samples. The cross-linked PSA samples were placed between two aluminum foils to measure adhesion force. The PSA-aluminum samples were stored in the air for 1 day to remove interfacial defects between PSA and aluminum foil. The adhesion forces of sample α and β measured by 180 ° peel test were 309 and 287 mN/50 mm, respectively. The cross-linked PSA samples exhibits good adhesion performance and reveal the relationship of adhesion and degree of cross-linking.

4. Conclusions

Catalytic hydrosilation of polyalkylsiloxane was studied using TG-DTA, *in-situ* VT-NMR and ^{13}C NMR with DEPT-135 to understand cross-linking reactions according to the reaction site effect. At TG-DTA analysis, the reaction rates were strongly affected by mobility of polymer molecules and the positions of reactive sites. At NMR analysis, consumption of vinyl and Si-H groups and formation of cross-linking bond were successfully monitored by *in-situ* VT-

NMR and ^{13}C NMR with DEPT135. The cross-linking reaction represented multi-step reaction behavior due to steric hindrance of branched sites, larger molecular size and higher viscosity environment. Industrial PSA samples exhibited excellent adhesion properties by cross-linking reaction and its result indicated strong correlation between adhesion properties and degree of cross-linking reaction.

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