Silicone Resin Synthesized by Tetraethoxysilane and Chlorotrimethylsilane Through Hydrolysis–Condensation Reaction

Chung-Feng Jeffrey Kuo,[1] Jiong-Bo Chen,[1] Chung-Yang Shih,[2] Chao-Yang Huang[3,4]

[1]National Taiwan University of Science and Technology, Department of Materials Science & Engineering, Taipei 106, Taiwan
[2]Department of Materials Engineering, Kun Shan University, Tainan 710, Taiwan
[3]Green Energy & Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 310, Taiwan
[4]Department of Mechanical Engineering, National Chiao Tung University, Hsinchu 310, Taiwan
Correspondence to: C. -F. J. Kuo (E-mail: jeffreykuo@mail.ntust.edu.tw)

ABSTRACT: Silicone pressure-sensitive adhesives compositions contain a polydimethylsiloxane and a silicone resin, which can enhance the instant bonding ability and bonding strength of the adhesive. In this study, silicone resin was designed to have a low molecular weight and a highly nonpolar chemical structure. The silicone resin was applied to silicone pressure-sensitive adhesives. The molecular structure of silicone resin was characterized by FT-IR, GPC, ^{1}H-NMR, and ^{29}Si-NMR spectroscopic techniques. Properties such as thermal stability, solubility, hydrophobic, and transparent properties were researched and compared. When the chlorotrimethylsilane increased, it appeared that the amount of silanol groups, molecular weight and thermal stability decreased, while the hydrophobic and transparent properties increased. The silicone resin was completely soluble in toluene and xylene. It was also applied to silicone pressure-sensitive adhesives, resulting in good peel adhesion. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40317.

INTRODUCTION

Pressure-sensitive adhesives are inherently and permanently soft, sticky materials that exhibit instant adhesion or tack with minimal pressure to surfaces to which they are applied. They generally have a high cohesive strength and can often be removed from substrates without leaving any residue. The wide range of applications include tapes, labels, decals, medical products, and others.[1–3] Silicone pressure-sensitive adhesives have traditionally been made by compounding a resinous silicone resin of M unit (monofunctional silane) and Q unit (tetrafunctional silane) with a high molecular weight polydimethylsiloxane gum at a selected resin-to-gum ratio.[4] Silicone resin has a low molecular weight.[5–7] Basic principles for the hydrolysis and condensation of alkoxysilanes have been known.[8,9] In the past, silicone resin was synthesized from sodium silicate, hexamethyldisiloxane, and alcohol, while using large amounts of acid in the process. The waste liquid was difficult to be recovered, causing environmental pollution.[5] In the early process for the preparation of silicone resin, sodium silicate, and HMDS were used as starting materials.[10] Sodium silicate was acidified to silica sol, which was capped by the M units to produce silicone resins. Although the starting materials were inexpensive, structure control of the resin product was difficult. Gels were easily produced. In addition, it was also difficult to control the M/Q molar

ratio of silicone resin synthesized by sodium silicate with a broad molecular weight distribution.[6] Therefore, the molar ratio of the M/Q was of the utmost importance. In this study, we synthesized silicone resin of a low molecular weight by the tetra-ethoxysilane and chlorotrimethylsilane reaction. The tetra-ethoxysilane was the source of the Q unit and the chlorotrimethylsilane was the source of the M unit. The tetra-ethoxysilane was less reactive than sodium silicate, therefore, when tetra-ethoxysilane was used as the starting material. The M/Q molar ratio of silicone resin could be controlled easily and the chlorotrimethylsilane contained a chlorine group, which produced hydrochloric acid after hydrolysis, for use as a catalyst.[6] The aim of this study was to investigate the effect of M unit content on the chemical structure, thermal stability, hydrophobic, and light transmittance property of silicone resin. Finally, the silicone resin was applied as a tackifier resin to silicone pressure-sensitive adhesives. A discussion was made on the effect of silicone resin molecular weight on the peel strength and rolling ball tack property of silicone pressure-sensitive adhesives.

EXPERIMENTAL

Materials

Tetra-ethoxysilane (TEOS) was purchased from Seedchem Company Propriety Limited, Australia. Chlorotrimethylsilane (TMCS),
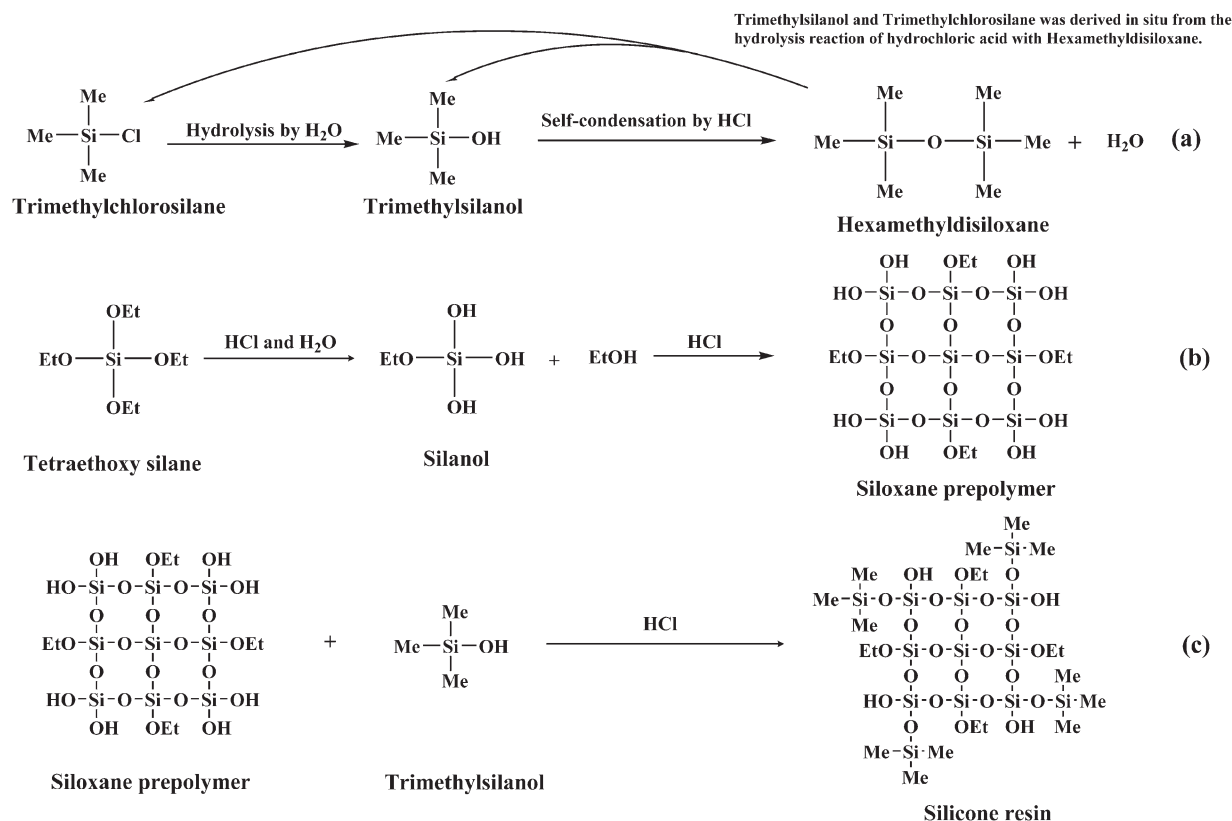
Figure 1. Synthesis reaction equation of silicone resins.

(3-Aminopropyl) triethoxysilane (APTES), and Tetrabutyl titanate (TBT) were purchased from Acros organics, USA. Toluene was industrial grade and was purchased from Echo Chemical Corporation Limited, Taiwan. Polydimethylsiloxane (PDMS) were purchased from Chi Giz Technology & Consultant Corporation Limited, Taiwan. Both copper and polyvinyl fluoride (PVF) film were obtained from Forest Lai Enterprise Corporation Limited, Taiwan.

Hydrolytic Condensation Catalyzed by Acid
In the synthesis, hydrolytic condensation of a mixture of TEOS and TMCS was inhomogeneous at the beginning. The Synthesis reaction equation of silicone resins was shown in Figure 1. TEOS was the source of the tetrafunctional silane and TMCS was the source of the monofunctional silane. The trimethylsilanol and hydrochloric acid were produced by hydrolysis of TMCS. During the hydrolysis of TMCS, the trimethylsilanol not only reacted and condensed with the siloxane prepolymer, but also self-condensed to form hexamethyldisiloxane (HMDS). The trimethylsilanol and TMCS was derived *in situ* from the reaction of hydrochloric acid with HMDS.[11] The TMCS could continuously produce trimethylsilanol in the cycle, as seen in Figure 1(a). Next, TEOS was dripped into the system after a few minutes, and the system turned transparent because ethanol was formed in reaction.[12] The siloxane chain formation after hydrolysis of TEOS was as shown in Figure 1(b). The silicone resin with a highly cross-linking density structure was formed with trimethylsilanol condensation end-capping as shown in Figure 1(c).

Synthesis of Silicone Resin
Typical process for preparation of silicone resins was as follows. An appropriate amount of deionized water was added to a

three-necked flask and the temperature was held constant at 30°C. A mixture of TMCS and toluene was quickly added into the flask with vigorous agitation, and was then heated to 70°C. Appropriate amounts of TEOS were dripped (90 min) into the flask, and the temperature was raised to 70°C and held for 2 hours. After cooling to room temperature, the mixtures were washed repeatedly with deionized water to neutral pH. After filtration and removing toluene and water by evaporation, the silicone resins were obtained. Detailed experimental conditions were listed in Table I.

Preparation of Silicone Pressure-Sensitive Adhesives
In a single-neck flask equipped with a stirrer, silicone resin (42 wt %), PDMS (28 wt %), APTES (1.5 wt %), TBT (0.5 wt %), and toluene (28 wt %) were proportionally added. The mixture was stirred for 20 min, and the reaction stopped. Finally, silicone pressure-sensitive adhesives solution was coated to copper

Table I. Components and their Quantities in the Synthesis of Silicone Resin

Code	M/Q molar ratio[a]	TEOS (g)	TMCS (g)	Toluene (g)	H_2O (g)
SR-A	0.6	208.3	65.4	50	82.8
SR-B	0.7	208.3	76.2	50	84.6
SR-C	0.8	208.3	87.1	50	86.4
SR-D	0.9	208.3	98.0	50	88.2

[a] Calculated from the molar ratio of the starting materials.
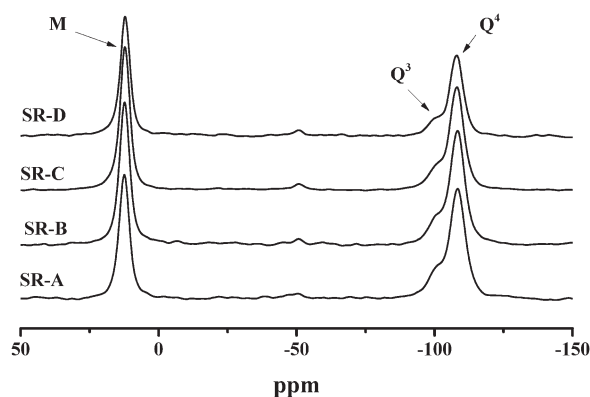
Figure 2. ^{29}Si-NMR spectrum of silicone resin.

Table II. ^{29}Si-NMR Analytical Data of Silicone Resin

Code	M/Q molar ratio[a]	Ratio of siloxane unit (%)	
		M unit	Q unit[b]
SR-A	0.66	39.84	60.16
SR-B	0.80	44.44	55.56
SR-C	0.90	47.39	52.61
SR-D	1.04	51.02	48.98

[a] Calculated from ^{29}Si-NMR spectra.
[b] $Q = Q^3 + Q^4$.

sheet with a thickness of 70 μm, cured at room temperature for 24 hours, and pasted onto the PVF film.

Characterization

Fourier Transform Infrared. Fourier transform infrared (FTIR) spectroscopy results were obtained using a FTS-1000 infrared spectrometer (Bio-Rad Digilab). The FTIR spectra were recorded in a wavenumber range of 4000–400 cm^{-1} in transmission mode.

^{1}Proton Nuclear Magnetic Resonance. ^{1}Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra were recorded using deuterated Deuterochloroform as a solvent on a Bruker AV400 NMR. The [EtO]/[M] and [OH]/[M] ratio of silicone resins was calculated according to the ^{1}H-NMR data.

^{29}Silicone Nuclear Magnetic Resonance (^{29}Si-NMR). ^{29}Silicone Nuclear Magnetic Resonance (^{29}Si-NMR) spectra were obtained on a Bruker AV600 NMR spectrometer. The relative ratio of siloxane for silicone resins was calculated according to the ^{29}Si-NMR data.

Thermogarvimetric Analysis. Thermal analyses of the silicone resin were performed with thermogravimetric analysis (TGA; TGA 1, Perkin-Elmer). The sample size was about 5 mg. The samples were heated at 20°C/min from 30°C to 600°C under a dry nitrogen flow at 20 mL/min.

Gel Permeation Chromatography. The molecular weight and its distribution of silicone resin were determined by Perkin-Elmer series 200 gel permeation chromatography (GPC) system, using THF as an eluent and polystyrene as the standard.

Ultraviolet–Visible. The Ultraviolet–visible (UV-vis) spectra were recorded on a Jasco V-530 Ultraviolet–visible spectrometer and scanned between 350 and 650 nm. The silicone resin solution was concentrated for 60 wt % at different wavelengths of 400, 500, and 600 nm, respectively, in order to study their transmittance properties.

Contact Angle Analysis. The contact angles (C.A.) were measured with deionized water on a film of silicone resin at room temperature. The water was poured as a drop by a syringe. Contact angles were measured by image analyzer software, and images were acquired by a camera. The sessile drop method was

used. All measured contact angles were the averages of three measurements.

Softening Point (S.P.). The softening point (S.P.) of silicone resin was checked using a S.P. tester at a speed of 5°C/min.

Peel Strength Analysis. The peel strength was measured at a peel rate of 254 mm/min at room temperature using a tensile testing machine (HT9501, Hung Ta Instrument) in accordance with ASTM D1876 (ASTM International Standards). All measured peel strength were the averages of five measurements.

Rolling Ball Tack Analysis. The rolling ball tack tester, meeting the standards of the pressure sensitive adhesive tape PSTC-6, was used for testing the tack of pressure-sensitive adhesives. Measure the distance from the point where the ball initially contacts the adhesive to where the ball stops. The average of the stopping distance measurements was reported in millimeters.

RESULTS AND DISCUSSION

^{29}Si-NMR Analyses

In Figure 2, the sharp signals at 12 ppm belonged to M unit. The signals ascribed to siloxane units Q^3 and Q^4, which denoted the unit structure Si(OSi)$_n$(RO)$_{4-n}$ ($n = 1$–4, R = Et), at -100 to -105 and -105 to -112 ppm, respectively.[13,14] The relative ratio of siloxane unit for silicone resin was summarized in Table II. The content of M unit increased and those of the Q unit decreased. This suggests that M unit was always in the end group
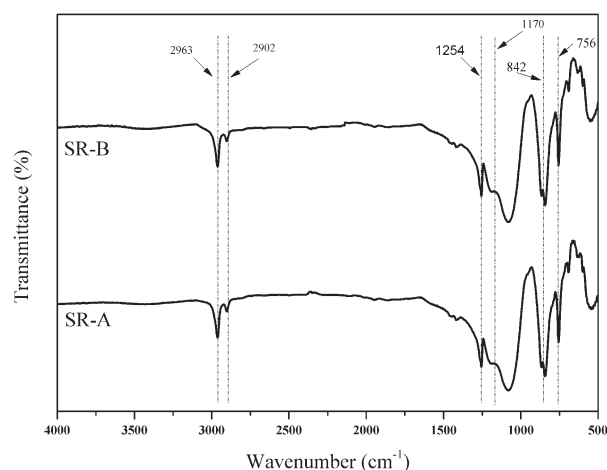

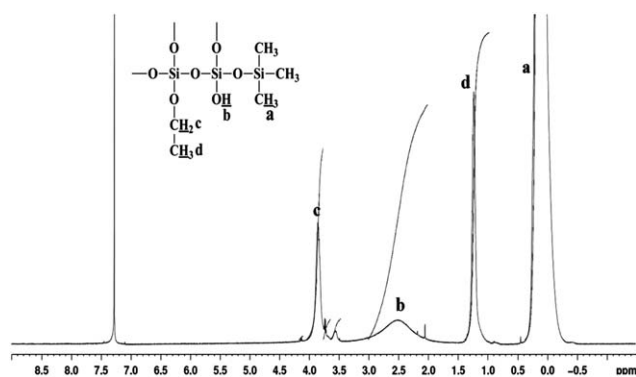**Figure 3.** FT-IR spectrum of silicone resin.

Table III. Assignments of Peaks Detected in FT-IR Spectrum of Silicone Resin

Wave number (cm^{-1})	Active bond	Mode	Reference
3100–3500	-OH	Stretching mode	15
2963	-CH$_3$	Symmetric stretching mode	16
2902	-C-H	Symmetric mode	16
1254	-Si-CH$_3$	Stretching bending mode	16
1170	-Si-OC	Asymmetric mode	17
1086	-Si-O-Si-	Stretching mode	18
842	-CH$_3$	Stretching bending mode	19
756	-Si-CH$_3$	Asymmetric mode	6

Table IV. ^{1}H-NMR Analytical Data of Silicone Resin

Code	[EtO]/[M] ratio	[OH]/[M] ratio
SR-A	0.053	0.030
SR-B	0.048	0.022
SR-C	0.045	0.014
SR-D	0.043	0.008

of each chain, and limits the crosslink of Q unit. Additionally, the molar ratio of the silicone resins found by ^{29}Si-NMR was close to that calculated from the ratio of the starting materials. For example, the molar ratio of SR-A calculated from the ratio of the starting materials was 0.60 and the molar ratio found by ^{29}Si-NMR was 0.66; the calculated unit ratio of SR-B was 0.80 and the molar ratio found by ^{29}Si-NMR was 0.90. Therefore, it was easy to produce silicone resins of different molar ratios by changing the composition of the feed.

FT-IR Analyses

The infrared spectra of the SR-A and SR-B were shown in Figure 3. The broad peak at 3100–3500 cm^{-1} was attributed to O-H stretching vibration of Si-OH. The sharp peak at 2963 and 2902 cm^{-1} was because of the symmetric -CH$_3$ and asymmetric C-H hydrocarbon portion of the spectra. The strong peak at 1086 cm^{-1} belongs to Si-O-Si groups. The peak at 1170 cm^{-1} belonged to the -Si-OEt. Moreover, the bands centered at 1170 cm^{-1} correspond to the ethoxy groups of TEOS, and permit the evaluation of the degree of hydrolysis and condensation of TEOS molecules. Peaks at 1000–1100 cm^{-1} suggested the presence of Si-O-Si. The characteristic absorption of M unit were 2963, 756, 842, and 1254 cm^{-1}. Additionally, the appearance of the wide peak at 3100–3500 cm^{-1} expressed an indication of hydrolysis of the ethoxy group of the TEOS, as well as the peak

at 1086 cm^{-1} and an indication of condensation of the hydroxyl groups of the TEOS and TMCS (Table III).

^{1}H-NMR Analyses

A ^{1}H-NMR spectrum with the assignment of the chemical shift for the silicone resin (SR-B) was shown in Figure 4. The ratio of [EtO]/[M] and [OH]/[M] for silicone resin was summarized in Table IV. The peak centered at 0.2 ppm was the resonance of the methyl protons in the M unit, and the peak centered at 3.80 and 1.20 ppm were the resonances of the methylene protons and methyl protons of the ethoxy groups, respectively.[5] Hydroxyl protons appeared as a broad peak at 1.7–3 ppm depending on their concentration. The content of M unit increased with the [EtO]/[M] and [OH]/[M] ratio decreased.[20] The reduced [OH]/[M] ratio indicated that the end-cap was nearly complete.[21]

GPC Analyses

A GPC curve of silicone resin was shown in Figure 5. Table V shows the variation of molecular weight for the silicone resin synthesized in the solvent of toluene as a relative amount of M unit. The content of the M unit increased, and the molecular weight of silicone resin decreased from 7713 to 1967 g/mol. It was interesting to indicate the change in the molecular weight distribution after the condensation reaction. The resin SR-D had a monomodal and narrow molecular weight distribution. Contrarily, the resin after condensation reaction (SRA, SR-B, and SR-C) showed a very broad distribution in the GPC chromatogram. This meant that the average molecular weight depends on the content of M units that came from the TMCS, which limited the growth of the resin molecule and decreased the amount of silanol groups. TMCS acted as chain-stoppers during the polymerization process: once attached to the chain,

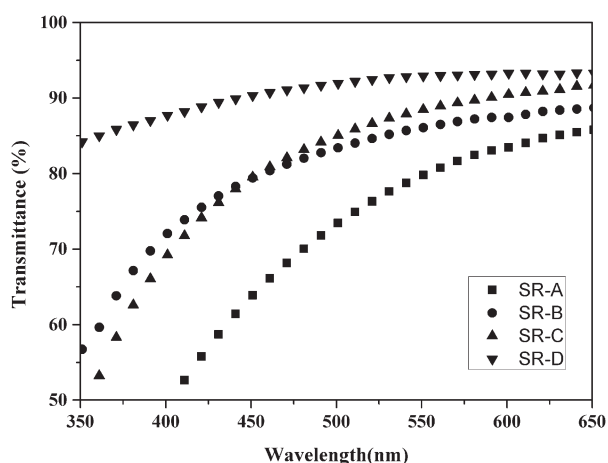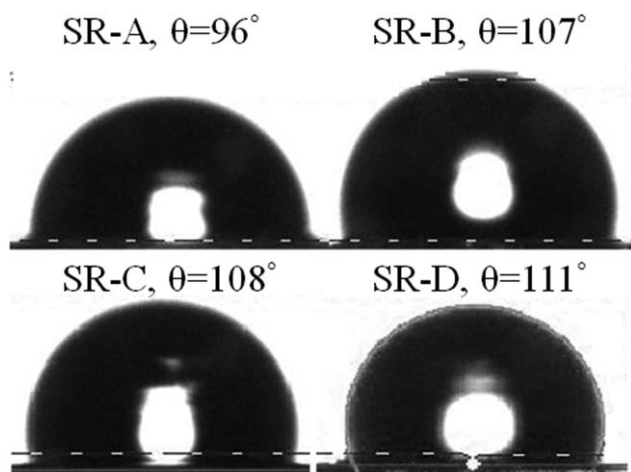**Figure 4.** ^{1}H-NMR spectrum of silicone resin (SR-B).
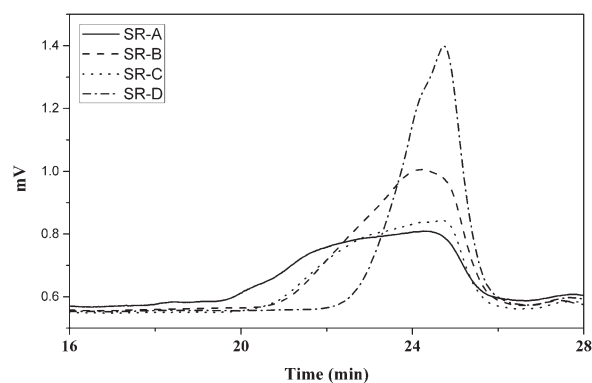
Figure 5. GPC for the silicone resin.

Table V. Molecular Weight of Silicone Resin

Code	M_w (g/mole)	M_n (g/mole)	M_w/M_n	Appearances	S.P. (°C)
SR-A	7713	2618	2.9	Transparent solid; melt while heating	180–190
SR-B	5358	2324	2.3	Transparent solid; melt while heating	140–150
SR-C	3997	2045	1.9	Transparent solid; melt while heating	130–140
SR-D	1967	1428	1.3	Transparent; semisolid	90–80

Table VI. Solubility and Transmittance Properties

Code	Solubility properties[a]				Transmittance properties		
	Methanol	Ethanol	Toluene	Xylene	600 nm	500 nm	400 nm
SR-A	–	–	+	+	83.3 %	73.2%	48.8%
SR-B	–	–	+	+	87.3%	83.2%	71.8%
SR-C	–	–	++	++	90.4%	84.9%	68.7%
SR-D	–	–	++	++	93.2%	91.9%	87.6%

[a] ++, easily soluble, +, soluble, –, insoluble.

Figure 6. UV-vis spectrum of silicone resin.

the chain could no longer grow on that particular side.[22] Lower molecular weight of silicone resin contained relatively great amounts of M unit functional end-groups with the molecular weight distribution range narrowed as the amount of M unit increased. This meant that TMCS could effectively inhibit self-condensation of TEOS, and resulted in homogeneity of the molecule segments of silicone resin. After removal of solvents, the silicone resin was obtained to be either transparent colorless viscous resins or white solids. The S.P. and molecular weight were also decreased as the content of M unit increased. Whereas a significant decreased in the molecular weight could be seen, the profound change in the structure was reflected in the S.P.[5]

Solubility and Transmittance Analyses

The solubility and hydrophobic properties of silicone resin was shown in Table VI. Solubility was evaluated as the volume of solvent to dissolve silicone resin of 6 g and solvent of 4 g. The silicone resin was very soluble, especially in the benzene solvent. Although solubility tended to decrease slightly as the molecular weight increased, all the samples were insoluble in methanol and ethanol, but were soluble in toluene and xylene. As far as

Figure 7. Contact angle of silicone resin film.
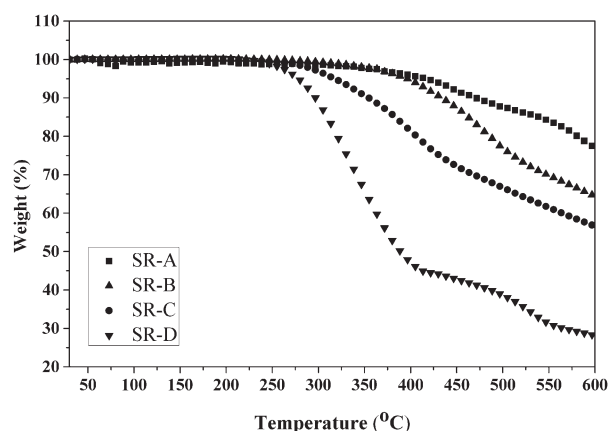
Figure 8. TGA curve diagram of silicone resin.

Table VII. Effect of M Unit Content on Thermal Behavior of Silicone Resin

| Code	T_5^a (°C)	T_{10}^b (°C)	T_{15}^c (°C)	MRD^d (%/°C)	Residual weight (%)
SR-A	418.7	470.3	539.6	−0.07	87.6
SR-B	396.7	433.7	462.3	−0.21	76.9
SR-C	317.3	354.3	383.0	−0.25	66.6
SR-D	278.0	296.7	309.3	−0.39	38.6

^{a} Temperature for 5% weight loss, ^{b} Temperature for 10% weight loss, ^{c} Temperature for 15% weight loss, ^{d} Maximum rate of decomposition.

the transmittance of resin solution was concerned, it increased in the order of SR-D > SR-C > SR-B > SR-A within the visible light range, as shown in Figure 6. The data in the three wavelength regions (400, 500, and 600 nm) were presented in Table VI. As seen, the transmittance of the resin solution was almost greater than 80%, but the others were between 68% and 80%. Contact angle measurements had traditionally provided a simple but powerful method for studying the wetting properties of surfaces, particularly their degree of hydrophobicity or hydrophilicity. The sphericity of a water drop on the resin surface was characterized by the contact angle (θ). According to the photograph of the contact angles, as shown in Figure 7, it was clear that the sphericity of the water droplet was increasing. It was observed that θ increased from 96° to 111° with an increased amount of M unit from 39.84 % to 51.02 %. This indicated that an increase in the hydrophobicity was because of the attachment of -Si-$(CH_3)_3$ groups by end-capping surface -OH groups from siloxane prepolymer. Moreover, the amount of non-polar CH_3 group increased and the siloxane prepolymer became highly hydrophobic.[23] The highest contact angle was 111°, suggesting that with a higher contact angle, the sphericity of the water drop on the hydrophobic surfaces was greater.

After observing the strong 12 ppm signal from the M unit on the silicone resin and the similar intensity of Q unit in ^{29}Si-NMR, obvious hydrophobicity of SR-D was indicated in ^{29}Si-NMR. The decrease in the hydrophobicity of SR-A was observed in ^{29}Si-NMR, as indicated by the decrease in the intensity of M unit signal and the increase in the amount of Q unit.

TGA Analyses

To investigate the influence of the M unit content on the thermal performance of silicone resin, the TGA curves of the four silicone resins were measured in an inert atmosphere. The results were presented in Figure 8. Values of T_5 and T_{10}, the temperature of the maximum rate of decomposition (MRD), and the ceramic yield at 500°C were calculated from the TGA curves. These were listed in Table VII. Each curve was divided into three regions. Region 1 (30–250°C) corresponded to the desorption of physically adsorbed water or perhaps residual solvent. Region 2 (250–550°C) was related primarily to the removal of organics (principal weight loss) accompanied by polymerization and structural relaxation. The transition from a polymeric material to an inorganic material occurred at 550–600°C. For all the samples over 45% M unit content, the weight loss in Region 1 was very small because -
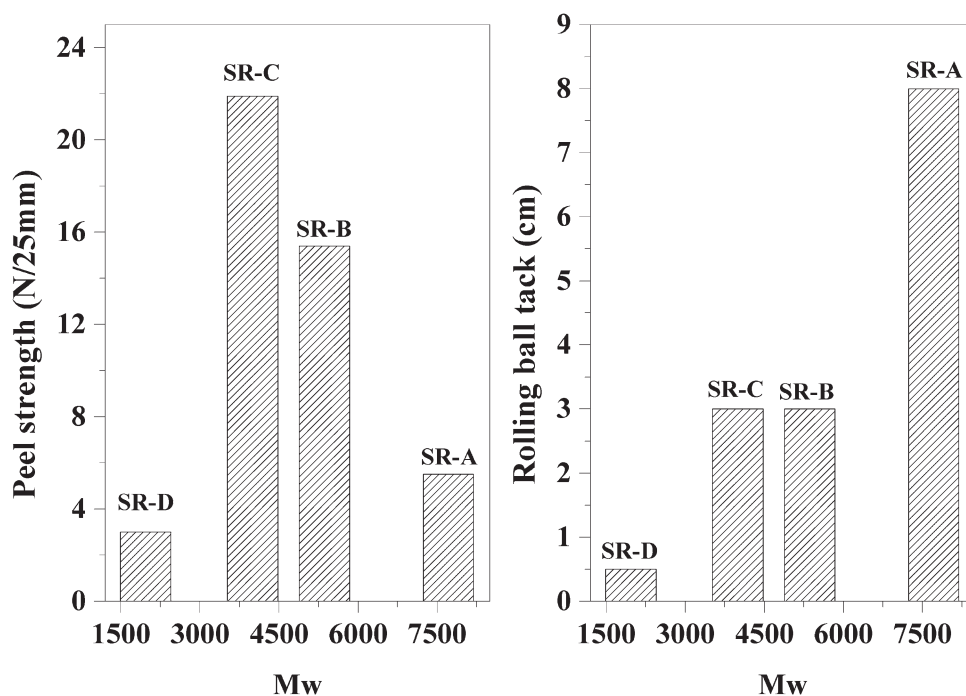
Figure 9. Rolling ball tack and peel strength of silicone pressure-sensitive adhesives.

CH$_3$ groups were hydrophobic and can prevent the adsorption of water.[20] Clearly, the values of T_5, T_{15}, and T_{10} for the four silicone resins generally increased with the decreased M unit content as the moieties of the organic groups in the silicone resins decreased at the same time. The residual weight at 500°C increased with the decreased M unit content. Meanwhile, the values of MRD decreased with the decreased M unit content. This indicated that the thermal decomposition rate of the silicone resin slowed down with the reduction of the size of the organic group moiety. In fact, as discussed above, some silanols could exist quite stably in silicone resins even when more severe experimental conditions were adopted. Therefore, in addition to the degradation reaction of silicone resin taking place in the TGA test at elevated temperatures, a cross-linking reaction also occurred at the same time. With the decrease in M unit content, there was a decrease in the amount of the end-capping groups attached to the surface of the silicone resin, thus causing more unterminated silanols to stay in the system. Under increased temperatures, these active silanols reacted and condense with each other, which leaded to the cross-linking of the silicone resins. The crosslinking density of the resins was highly dependent on the amount of residual silanols. As reported previously, the thermal stability of polysiloxane increased with the increase in the crosslinking density.[24–27] Therefore, with the increase in the amount of Q (SiO$_{4/2}$) segment, an improvement in the thermal stability of silicone resins was obtained. When the M unit content was larger than 50%, SR-D showed a greater total weight loss than did SR-A, B, and C. This implied that the silicone resin with the M units contained -Si-CH$_3$ bond in the end group of each chain, and decreased the crosslinking density. It was well known that the dissociation energy of Si-C bond (326.4 kJ/mol) was lower than that of the Si-O bond (460.5 kJ/mol).[18] The weight loss of SR-D was shown apparently in Region 2 because of the high content of -CH$_3$ groups. In the present study, when the M unit content decreased from 51.02% to 39.84%, the MRD values increased from −0.39 (%/°C) to −0.07 (%/°C), together with an increase in the residual weight at 500°C from 38.6% to 87.6%.

Silicone Pressure-Sensitive Adhesives Analyses

The rolling ball tack and peel strength of silicone pressure-sensitive adhesives according to the type of silicone resin was shown in Figure 9. The rolling ball tack depended on the M_w of silicone resin. The low M_w silicone resin, such as SR-D, has better tack property. Similar results were found in previous research.[1] In the region of silicone resin weight, the average molecular weight was less than ca. 2000, thus the peel strength was poor. At a low molecular weight, silicone resin showed cohesive failure upon the peel test. The cohesive failure was defined as the inability of an adhesive to resist internal separation. Because of cohesive failure, the adhesive sticks on both surfaces (copper and PVF film), but could not hold them together.[28] As the M_w approaches 3900, the peel strength rose sharply and appears to pass through a maximum. The peel strength increased with the molecular weight of silicone resin up to an optimum M_w of 3997 of SR-C.

This phenomenon was attributed to the combined effects of wettability and peel strength of silicone resin at the optimum molecular weight, and was ascribed to the maximum cohesive and adhesive strength during the peeling action. At the optimum silicone resin molecular weight, the adhesive layer could not easily be ruptured, hence showing maximum peel strength. Thus, at the optimum molecular weight of 3997 (g/mol), the optimum combination of cohesive and adhesive strength was achieved, and further contributes to the highest peel strength in this study. For silicone resin molecular weights > 5500 (g/mol), the silicone pressure-sensitive adhesives did not completely wet the test panel interface (PVF film). Probably because of the effect of entanglement, the entangled PDMS chain with silicone resin did not flow effectively to produce poor wettability on the test panel interface.

CONCLUSIONS

Silicone resins were synthesized through hydrolytic condensation of TEOS and TMCS. The content of M unit was increased, while the amount of silanol groups, molecular weight, and thermal stability decreased. The hydrophobic and transparent properties increased the silicone resin. The resin was completely soluble in solvents, such as toluene and xylene. Finally, the silicone resin was applied as a silicone resin to silicone pressure-sensitive adhesives. The silicone pressure-sensitive adhesives formulated various silicone resin, and the rolling ball tack and peel strength were measured. The peel strength increased with the molecular weight of silicone resin up to an optimum M_w of 3997 (g/mol) of SR-C. The silicone pressure-sensitive adhesives prepared from as-synthesized silicone resin have good tack and peel adhesion.

REFERENCES

1. Kong, W. k.; Ju, T. J.; Park, J. H.; Joo, S. R.; Yoon, H. G.; Lee, J. W. *Int. J. Adhes. Adhes.* **2012**, *38*, 38.

2. Fujita, M.; Kajiyama, M.; Takemura, A.; Ono, H.; Mizumachi, H. *J. Appl. Polym. Sci.* **1998**, *70*, 771.

3. Williams, J. A.; Kauzlarich, J. J. *Int. J. Adhes. Adhes.* **2008**, *28*, 192.

4. Lin, S. B. *J. Appl. Polym. Sci.* **1994**, *54*, 2135.

5. Huang, W.; Huang, Y.; Yu, Y. *J. Appl. Polym. Sci.* **1998**, *70*, 1753.

6. Sun, F.; Hu, Y.; Du, H. G. *J. Appl. Polym. Sci.* **2012**, *125*, 3532.

7. Mikrut, M.; Noordermeer, J. W. M.; Verbeek, G. *J. Appl. Polym. Sci.* **2009**, *114*, 1357.

8. Wang, C.; Lii, K. *J. Solid State Chem.* **2003**, *172*, 194.

9. Huang, S.; Shan, Y. *J. Solid State Chem.* **2000**, *152*, 229.

10. He, M.; Zhang, Q.; Guo, J. *Adv. Mater. Res.* **2011**, *306–307*, 1773.

11. Bains, R. S.; Kendrick, D. A.; Parsonage, J. R. *Polym. Int.* **1993**, *31*, 87.

12. Lentz, C. W. *Inorg. Chem.* **1964**, *3*, 574.

13. Gunji, T.; Hayashi, Y.; Komatsubara, A.; Arimitsua, K.; Abea, Y. *Appl. Organometal. Chem.* **2012**, *26*, 32.

14. Abe, Y.; Gunji, T. *Prog. Polym. Sci.* **2004**, *29*, 149.

15. Yang, Z.; Han, S.; Zhang, R.; Feng, S.; Zhang, C.; Zhang, S. *Polym. Degrad. Stab.* **2011**, *96*, 2145.

16. Montejo, M.; Partal Ureña, F.; Márquez, F.; Ignatyev, I. S.; López González, J. J. *Spectrochim. Acta A* **2005**, *62*, 293.

17. Elvira, M. R.; Mazo, M. A.; Tamayo, A.; Rubio, F.; Rubio, J.; Oteo, J. L. *J. Chem. Chem. Eng.* **2013**, *7*, 120.

18. Xu, X.; Wu, C.; Zhang, B.; Dong, H. *J. Appl. Polym. Sci.* **2013**, *128*, 4189.

19. Mahadik, D. B.; Venkateswara Rao, A.; Parvathy Rao, A.; Wagh, P. B.; Ingale, S. V.; Gupta, S. C. *J. Colloid Interface Sci.* **2011**, *356*, 298.

20. Mah, S. K.; Chung, I. J. *J. Non Cryst. Solids* **1995**, *183*, 252.

21. Sudo, Y. *J. Chromatogr. A* **1997**, *757*, 21.

22. Knoester, H. *Macromol. Theory Simul.* **2009**, *18*, 61.

23. Li, J.; Cao, J.; Yang, M.; Yin, W.; Yao, Y.; He, X. *J. Non Cryst. Solids* **2013**, *362*, 216.

24. Redondo, S. U. A.; Radovanovic, E.; Torriani, I. L.; Yoshida, I. V. P. *Polymer* **2001**, *42*, 1319.

25. José, N. M.; Prado, L. A. S. A.; Yoshida, I. V. P. *J. Polym. Sci. B Polym. Phys.* **2004**, *42*, 4281.

26. José, N. M.; Prado, L. A. S. A.; Schiavon, M. A.; Redondo, S. U. A.; Yoshida, I. V. P. *J. Polym. Sci. B Polym. Phys.* **2007**, *45*, 299.

27. Prado, L. A. S. A.; Sforça, M. L.; de Oliveira, A. G.; Yoshida, I. V. P. *Eur. Polym. J.* **2008**, *44*, 3080.

28. Krenceski, M. A.; Johnson, J. F. *Polym. Eng. Sci.* **1989**, *29*, 36.