Infrared Spectroscopy Evidence for the Hydrosilylation of Rubbers and Hydrogen-Containing Polysiloxane via Heat Processing

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ABSTRACT: The hydrosilylation reaction is very important in silicone-introducing reactions and in the crosslinking of silicone rubbers. In this study, through Fourier transform infrared spectroscopy, the hydrosilylation reaction between hydrogen-containing polysiloxane (H-PDMS) and several kinds of rubber, including styrene–butadiene rubber (SBR), nitrile–butadiene rubber (NBR), chloroprene rubber (CR), and natural rubber (NR), with heat processing was researched. The IR spectra of each compound film were determined after reaction with H-PDMS under 110°C for different times. Through the quantitative estimation of the progress of the hydrosilylation reaction in the course of the heat processing, we established a method for calculating the changes of the peak areas of the Si—H bond and vinyl groups of each sample at each reaction time and computed the ratio of the integral area of Si—H and C=C to that of each compound. The Si—H content decreased 85 and 30% in SBR–Si and NBR–Si, respectively. However, the ratio of the integral area of transmittance of Si—H in NR–Si and CR–Si changed very little during the whole process. The Si—H content decreased less than 20% in NR–Si and CR–Si. All ratios of the integral area of transmittance of the vinyl groups (R_{Vinyl}) of each compound decreased as the reaction time increased at 110°C; the decrease values were very small. The rates of all R_{Vinyl} decreases were slow, and the decreasing sequence was the same as the order of decreasing Si—H content. The hydrosilylation reaction between H-PDMS and SBR was quite smooth in the heat processing and better than that between H-PDMS and NBR. The hydrosilylation reactions of H-PDMS with NR and CR were less satisfying. The results show that polyolefin rubbers can be modified or crosslinked by H-PDMS via heat processing. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3000–3005, 2012

**Key words:** infrared spectroscopy; polysiloxanes; processing; rubber

INTRODUCTION

The modification of polymers with functional groups or components is an efficient strategy for generating new materials with enhanced or special physical and chemical properties.[1] The hydrosilylation reaction of unsaturated polymers offers an economical and convenient method for preparing silicone-modified polymers that might show potential application as rubber materials, adhesives, and drug-delivery agents.[2–4] Generally, the hydrosilylation reaction usually takes place in solution. The chemical environment in solution is relatively homogeneous as the reagents are mixed more easily. Actually, the hydrosilylation reaction can be traced by Fourier transform infrared (FTIR) spectroscopy, whether in solution or not. In the course of the hydrosilylation reaction, the weakening of the stretching vibrations of the silicone–hydrogen bond and vinyl groups can be used as a criterion for hydrosilylation reactions.

So far, almost all platinum-catalyzed hydrosilylation reactions occur in solution,[5,6] whereas reactions through heat processing are rarely reported besides those whose productions are addition-curable silicone rubbers.[7] Recently, an attempt to research polymer silicone functionalization by direct melt processing has been made. Polypropylene toughened by silane functionalized rubber has been obtained from extruders,[8] and the feasibility of grafting anhydride to molten polyethylene has been demonstrated.[9] This approach has obviously economical advantages because a functional polymer is produced without the necessary of constructing an entirely new facility, the process period is shortened, and the costs of solvent recovery are saved. Thus, we could obtain functionalization polymers simply through heat processing instead of through traditional synthesis in solution (Scheme 1).

More importantly, through the functionalization of rubber, we can obtain some new polymer materials. For example, Kim et al.[10] synthesized end-functionalized poly(styrene–butadine)s with poly(ethylene glycol)–polydimethylsiloxane (PDMS) by the termination reactions of the anionic living polymer of styrene and butadienes with PEG–PDMS containing an
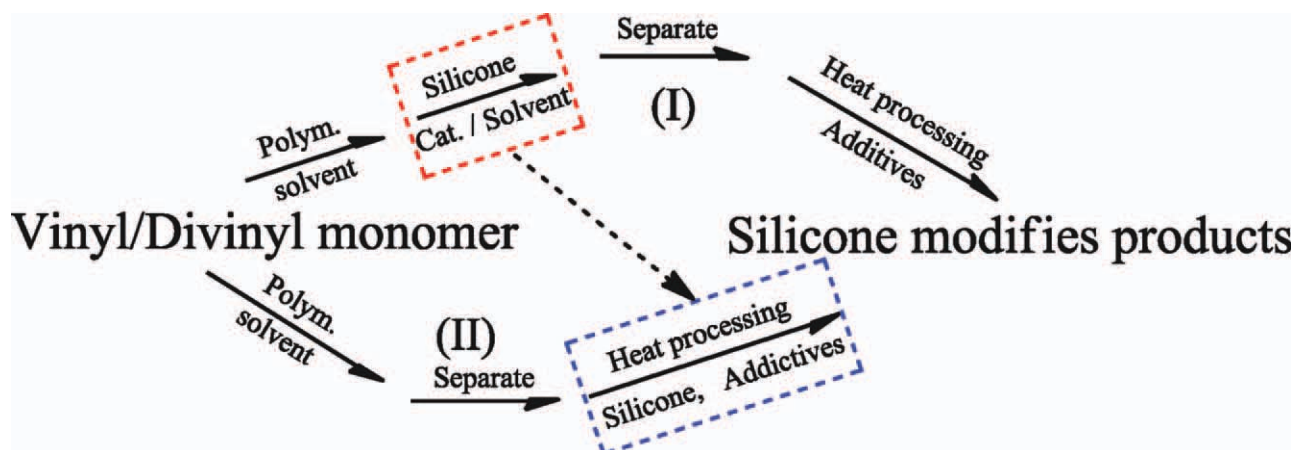
Scheme 1 Comparison of the heat processing (II) and the traditional synthesis route (I) to obtain a silicone modified polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

trichlorosilyl moiety. The composite of poly(ethylene glycol) and polydimethylsiloxane-terminated styrene–butadiene rubber (SBR-*t*-PEG–PDMS) with silica showed better silica particle dispersion compared to a dodecylsilyl- or tin-terminated styrene–butadiene rubber (SBR)/silica composite. Furthermore, the SBR-*t*-PEG–PDMS/silica composite showed improved thermomechanical properties.

In this article, we report our studies on hydrogen-containing polysiloxane (H-PDMS) polyolefin rubbers modified by a hydrosilylation reaction through heat processing. The polyolefin rubbers refer to SBR, nitrile–butadiene rubber (NBR), chloroprene rubber (CR), and natural rubber (NR). The structure of these butadiene and substituted butadiene chains included three types: trans-1,4-; cis-1,4-, and 1,2-, which is reactive to Si—H bonds in H-PDMS. We hoped the hydrosilylation reaction between Si—H and polyolefin rubber containing vinyl groups would both be capable of being carried out through heat processing instead of in solution and improve the properties of the polyolefin rubbers. To evaluate the reactivity of hydrosilylation in the course of heat processing, we used FTIR spectroscopy to measure each sample and established a method for calculating the peak area changes of the Si—H bond and vinyl groups of each sample at different reaction times. Our experimental results show that the reactivity of hydrosilylation in the SBR/H-PDMS system was quite satisfying. The stretching vibration of Si—H bond was weakened during the hydrosilylation reaction, and the rubber films had a good transparency and tenacity.

EXPERIMENTAL

Samples

Trimethylsilyl-terminated polymethylhydrosiloxane (H-PDMS) was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA); it's arithmetical-average

molecular weight was approximately 390, and its viscosity was 3 cSt. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (0.05M in vinyl-terminated PDMS) was supplied by Aldrich. Solution styrene–butadiene rubber (S-SBR) SOL 6450S, with 46 wt % vinyl and 34 wt % styrene groups, was provided by Korea KUMHO Petrochemical Co., Ltd. (Korea) NR (STR 5 L) was supplied by Shinhung Co., Ltd. (Korea). The copolymer of butadiene and acrylonitrile (NBR 6240) was polymerized at a low temperature with 34 wt % bound acrylonitrile content (manufactured by LG Chem, Ltd. (Korea)), and CR (grade neoprene WRT, ML (1+4) at 100°C, 41–51, manufactured by DuPont Performance Elastomers) was supplied by South Korea Pavco Industrial Co., Ltd. (Korea).

Methods and measurements

As the experimental formula used in this study, the amounts of each kind of rubber and H-PDMS were 50 and 2.0 g, respectively. All of the rubbers were cut into small pieces and masticated with Si—H containing silicone compounds in a two-roll mill: Made in Korea (No Model) for 15 min at 50°C. Thereafter, 0.01 g (ca. 4 drops) of platinum catalyst was added and masticated for another 10 min. After mixing, films of these compounds were prepared with a hydraulically operated hot press: Model 2699, Fred S. Carver, Inc. (Wabash, IN, USA) at 110°C, 15 MPa with a very thin mold. The thickness of these films was approximately 200 μm, as determined by a rubber thickness gauge. To keep the equality and persistence of these films' thicknesses, the samples were retained in a mold put in the hot press at 110°C and 2 MPa for different subsequent reaction times.

After a period of reaction time (every time interval was 0.5 h), the FTIR spectra of each sample were measured by a Nicolet IR200 instrument (Thermo

Nicolet): Nicolet IR200, Thermo Electron Corporation, U.S.A in dry air at room temperature. Spectra were taken within the range 4000–400 cm^{-1} in transmittance mode, and all of the calculations were based on Origin 7.0 software.

Theoretical calculation

The basis for the quantitative analysis of IR absorption spectrometry is the Bouguer–Beer–Lambert law, which is usually used when the light absorption of the homogeneous medium is not the solution, which is commonly called Lambert's law. For a more precise determination, an integral method of absorption should be used. For a compound in a uniform polymer film, the absorbency at any frequency is expressed as follows:

$$A = Kb = \log_{10} \frac{1}{T} = \int \log_{10} \frac{I_0}{I} d\nu$$

where A is the absorbance, K is the absorption coefficient, b is the thickness of the sample, t is the transmittance, I_0 is the incident light intensity, I is the emitted light intensity, and ν is the wave number.

Two methods could be taken into consideration when one wants to quantitatively calculate the group content changes in a chemical reaction:

1. Calculation of the integration area changes of the absorbency or transmittance of some groups in a certain range of wave numbers.
2. Calculation of the ratio of the integration area of the absorbency or transmittance of some groups in a certain range of wave numbers to that of compound in the range of all wave numbers.

The formula is shown as follows:

$$R = S_r/S = \int_{\nu_1}^{\nu_2} Td\nu / \int_{\nu_0}^{\nu_E} Td\nu$$

where R is the ratio of the integral area of transmittance of the selected group to that of the compound, S_r is the integral area of transmittance of the selected group, S is the integral area of transmittance of the compound, ν_1 is the wave number of the integral start of the selected group (cm^{-1}), ν_2 is the wave number of the integral end of the selected group (cm^{-1}), ν_0 is the wave number of the integral start of the compound (cm^{-1}), and ν_E is the wave number of the integral end of the compound (cm^{-1}).

To quantitatively estimate the progress of the hydrosilylation reaction through heat processing, we calculated the ratio of the integral area of Si—H and C=C to that of each of the compounds and then
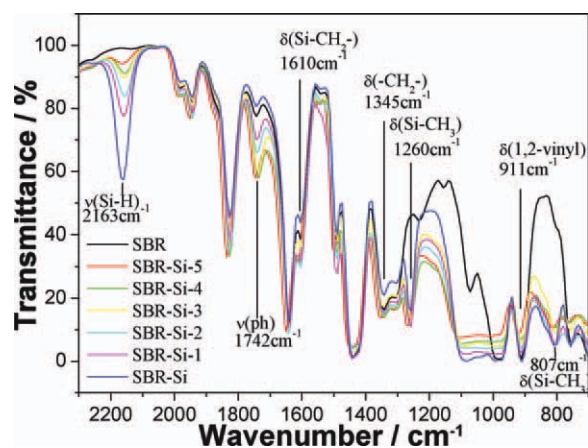
Figure 1 IR spectra of the SBR compounds reacted with H-PDMS at 110°C for different times: SBR–Si: after hot pressing, determined immediately; SBR–Si-1: under hot pressing, reacted for 0.5 h at 110°C; SBR–Si-2: under hot pressing, reacted 1.0 h at 110°C; SBR–Si-3: under hot pressing, reacted 1.5 h at 110°C; SBR–Si-4: under hot pressing, reacted 2.0 h at 110°C; and SBR–Si-5: under hot pressing, reacted 2.5 h at 110°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

made a curve from the plot with the x axis, which indicated the different reaction times; the y axis indicated the ratio of the integral area. Thus, the experimental results could be shown clearly.

RESULTS AND DISCUSSION

The four selected polyolefin rubbers, except NBR, were required to be nonplasticated. To prevent gelification, the mixing temperature was controlled below 50°C. The substituted groups of S-SBR were vinyl and phenyl, whereas those of NR were 2-isopropenyl groups. This fact led to a consequence that both S-SBR and NR had weak polar molecular chains. The compatibility between these two kinds of polymer and H-PDMS was very good; thus, they were very easily mixed by a two-roll mill. For NBR and CR, because the substituted side groups of these polymers were polar cyano groups and chlorine atoms, respectively; the polar molecules of these rubbers were very large. The compatibility between these polymers and H-PDMS was poor, and they were quite difficult to mix with the two-roll mill. However, all of the compounds used were easily moldable after uniform mixing by the hot press.

FTIR spectra

After the reaction of each polyolefin rubber with H-PDMS at 110°C for different times, the IR spectra of each compound film was determined. These rubber compound films were very easily deformed at 110°C at different times. For the infrared spectra determination from these rubber compound films, the maintenance
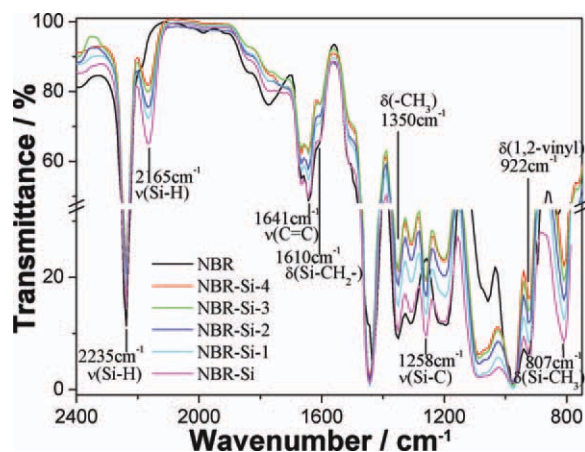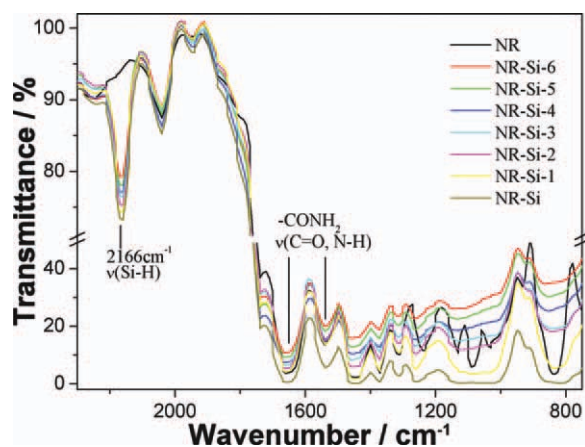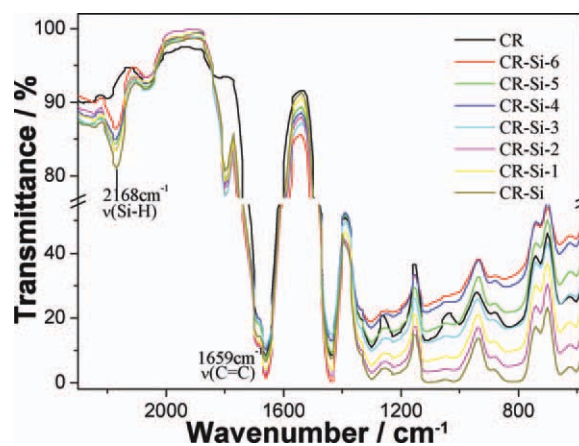
Figure 2 IR spectra of the NBR compounds reacted with H-PDMS at 110°C for different times: NBR–Si: after hot pressing, determined immediately; NBR–Si-1: under hot pressing, reacted for 0.5 h at 110°C; NBR–Si-2: under hot pressing, reacted for 1.0 h at 110°C; NBR–Si-3: under hot pressing, reacted for 1.5 h at 110°C; and NBR–Si-4: under hot pressing, reacted for 2.0 h at 110°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of these films' thickness was very important. The IR spectra of these mixed compounds are shown in Figures 1–4. Before mixture with H-PDMS, the vibrations of each of these vinyl groups and substituted vinyl groups in the IR spectra of every polyolefin rubber are summarized in Table I.

After the mixing and reacting, the infrared spectra of these compounds varied greatly. From the IR

Figure 3 IR spectra of the NR compounds reacted with H-PDMS at 110°C for different times: NR–Si: after hot pressing, determined immediately; NR–Si-1: under hot pressing, reacted for 0.5 h at 110°C; NR–Si-2: under hot pressing, reacted for 1.0 h at 110°C; NR–Si-3: under hot pressing, reacted for 1.5 h at 110°C; NR–Si-4: under hot pressing, reacted for 2.0 h at 110°C; NR–Si-5: under hot pressing, reacted for 2.5 h at 110°C; and NR–Si-6: under hot pressing, reacted for 3.0 h at 110°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 IR spectra of the CR compounds reacted with H-PDMS at 110°C for different times: CR–Si: after hot pressing, determined immediately; CR–Si-1: under hot pressing, reacted for 0.5 h at 110°C; CR–Si-2: under hot pressing, reacted for 1.0 h at 110°C; CR–Si-3: under hot pressing, reacted for 1.5 h at 110°C; CR–Si-4: under hot pressing, reacted for 2.0 h at 110°C; CR–Si-5: under hot pressing, reacted for 2.5 h at 110°C; and CR–Si-6: under hot pressing, reacted for 3.0 h at 110°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spectra of these polyolefin rubbers reacted with H-PDMS at 110°C for different times, the samples' IR spectra fell into two groups: compounds of SBR and NBR with H-PDMS (SBR–Si and NBR–Si) and compounds of NR and CR with H-PDMS separately (NR–Si and CR–Si). The IR spectra of SBR–Si and NBR–Si were obviously changed in the stretching vibration of the Si—H bond and C=C groups with the reaction at 110°C for different times, and their transmittance weakened gradually as the reaction time elapsed. However, in the IR spectra of NR–Si and CR–Si, almost all of the transmittances changed with the reaction at 110°C for different times. The main transmittances of all of these compounds changed at different wave numbers and are summarized in Table II.

According to the IR spectral changes of the variety of mixing compounds, it was possible to estimate the hydrosilylation reaction of H-PDMS with SBR and with NBR. However, with regard to that of H-PDMS with NR and CR, almost all of the vibration

TABLE I
IR Vibrations of Vinyl Groups and Substituted Vinyl Groups in the Four Polymers

Sample	Vibration (cm^{-1})			
	$\nu_{C=C}$	$\delta_{vinyl,1,4\text{-}trans}$	$\delta_{vinyl,1,2\text{-}}$	$\delta_{vinyl,1,4\text{-}cis}$
SBR	1640	980	910	756
NBR	1642	975	920	828
NR	1660	1030	900	837
CR	1654	1000	930	826

TABLE II
Samples' Main Transmittance as Changed at Different Wave Numbers

	Wave number						
Sample (cm^{-1})	~ 2160 cm^{-1} (ν_{Si-H})	~ 1650 cm^{-1} ($\nu_{C=C}$)	~ 1610 cm^{-1} (δ_{Si-CH_2})	~ 1345 cm^{-1} (δ_{-CH_2-})	~ 1260 cm^{-1} (δ_{Si-Me})	~ 911 cm^{-1} ($\delta_{1,2-vinyl}$)	~ 810 cm^{-1} (δ_{Si-C})
SBR–Si	○	⊘	○	○	⊗	○	○
NBR–Si	○	○	○	○	○	○	○
NR–Si	⊘	⊘	/	⊗	⊗	⊗	⊗
CR–Si	⊘	⊘	/	⊗	⊗	⊗	⊗

○, observably; ⊘, generally; ⊗, difficult to judge; /, seemed to be covered.

phenomenon of the Si—H bond and C=C groups changed during the reaction at 110°C for different times. In particular, all of the group vibrations of NR–Si and CR–Si decreased significantly with increasing reaction time at wave number of less than 1700 cm^{-1}. This made it difficult to evaluate whether the hydrosilylation reaction of H-PDMS with NR and CR happened directly by their IR spectra. An effective method for evaluating the reactivity of hydrosilylation of H-PDMS with NR and CR from such results is needed.

Quantitative calculation

To quantitatively estimate the progress of the hydrosilylation reaction in the course of heat processing, we calculated the ratio of the integral areas of Si—H and C=C to that of each compound according to the Theoretical Calculation section. To calculate the integral area of transmittance of the groups, Si—H, vinyl groups or substituted vinyl groups, which included trans-1,4-, cis-1,4-, and 1,2-, were selected. To calculate the integral area of vinyl groups or substituted vinyl groups, the calculation wave-number range should contain all three types. Fortunately, these types of vinyl groups or substituted vinyl groups are adjacent to each other in wave number. The calculated wave-number ranges of Si—H groups (S_{Si-H}) and vinyl groups and substituted vinyl groups (S_{Vinyl}) are displayed in Table III.

Where $S_1 = \int_{\nu_0}^{\nu_E} T d\nu$, $\nu_0 = 4000$, $\nu_E = 1700$ and $S_2 = \int_{\nu_0}^{\nu_E} T d\nu$, $\nu_0 = 1700$, $\nu_E = 400$. To calculate the ratio of the integral area of transmittance of Si—H ($R_{Si-H} = S_{Si-H}/S_1$) and the ratio of the integral area of transmittance of the vinyl groups (or substituted vinyl groups; $R_{Vinyl} = S_{Vinyl}/S_2$) of each compound accurately, we set ν_0 and ν_E of the integral start and end wave numbers in calculating S_1 and S_2 of each compounds to different amounts; the two scales varied from 4000 to 1700 and 1700 to 400 cm^{-1}, respectively. After calculating R_{Si-H} and R_{Vinyl}, we obtained that of the compound. Then, using the data calculated from the IR spectra of each compound, we plotted the relations of R and the reaction time (t) at 110°C, with R as ordinate and time as the abscissa (see Figs. 5 and 6).

R_{Si-H} and R_{Vinyl} of each compound could be regarded as the content of Si—H and C=C (1,4-trans, 1,2-, and 1,4-cis types) at 110°C at different times. The progress of the hydrosilylation reaction could be treated empirically by the changes in R_{Si-H} of these compounds, shown in Figure 5. The initial R_{Si-H} in SBR–Si and NBR–Si decreased as the reaction time elapsed, but the decreased rate of R_{Si-H} in SBR–Si was faster than that in NBR–Si. The Si—H content decreased 85 and 30% in SBR–Si and NBR–Si, respectively. However, R_{Si-H} in NR–Si and CR–Si

TABLE III
Calculated Wave-Number Ranges of the Si—H Groups and Vinyl Groups and Substituted Vinyl Groups

	Wave-number range	
Sample	ν_{Si-H} (cm^{-1})	δ_{vinyl} (cm^{-1})[a]
SBR–Si	2220–2080	980–730
NBR–Si	2200–2075	980–650
NR–Si	2210–2100	950–650
CR–Si	2210–2100	1000–740

[a] Vinyl types included 1,4-trans, 1,2-, and 1,4-cis.

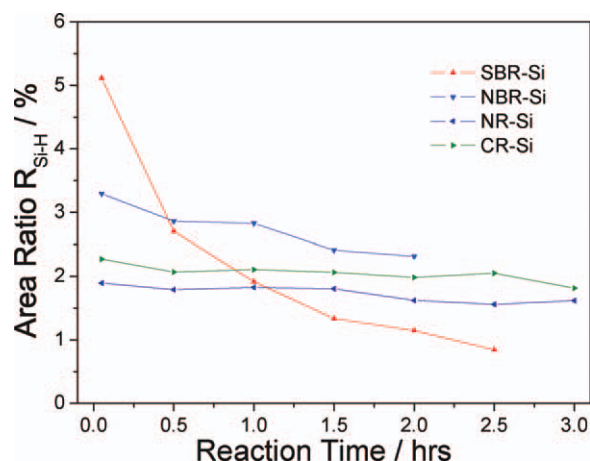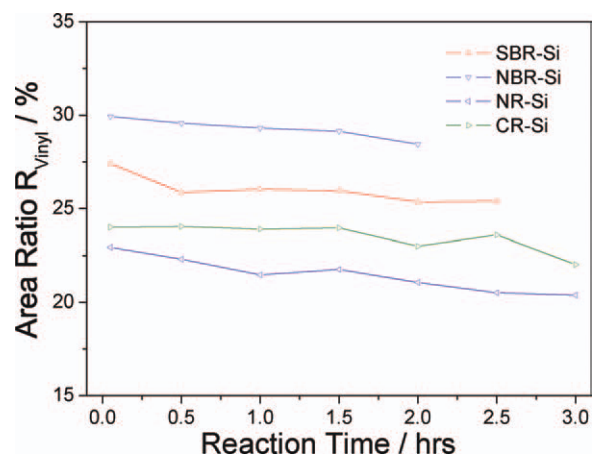**Figure 5** Relation of R_{Si-H} to the reaction time at 110°C in different compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Relation of R_{Vinyl} to the reaction time at 110°C in the different compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

changed very little during the whole process. The Si—H content decreased less than 20% in NR–Si and CR–Si, respectively. We obtained these results possibly because the compatibility of these polymers with H-PDMS decreased with the high-polarity groups, —CN and —Cl, as side groups in NBR and CR, and the steric effect of —CH$_3$ and —Cl as the substituted groups of the vinyl groups in the side groups of NR and CR.

Within the hydrosilylation reaction, the vinyl (or substituted vinyl) content decreased at the same time, and it was found from R_{Vinyl} of these compounds, which changed, as shown in Figure 6. All of the R_{Vinyl} values of each compound decreased as the reaction time elapsed at 110°C; the decrease in values was subtle, and the rates of all R_{Vinyl} decreases were slow. In fact, the hydrosilylation reactivity of vinyl, which grafted with polarity groups or with alkyl substituents, was poor. This was mainly because the vinyl content of all of the compounds was much higher than that of Si—H. However, the R_{Vinyl} decreases of the NR and CR compounds may have been induced by the thinner films, which were extended at 110°C. As far as we know, the thickness of sample was a parameter critical to the transmittance of the infrared spectrum. As the sample thickness increased, the transmittance decreased in the wavelength range 6–25 μm.[11] This phenomenon probably corresponded to the measurement results. All of the transmittance values of the NR–Si and CR–Si samples gradually increased; this may have been caused by the decrease in the sample thickness at wave numbers less than 1700 cm^{-1} (see Figs. 3 and 4).

CONCLUSIONS

We spectroscopically monitored the hydrosilylation reaction between polyolefin rubbers and H-PDMS through heat processing. From the determination of the hydrosilylation reactivity of these polyolefin rubbers in reaction with H-PDMS during heat processing, SBR presented a satisfying performance and one better than that of NBR, whereas the hydrosilylation reactivity was less satisfying in the reaction of H-PDMS with NR or CR. These results were mainly caused by the following:

1. The steric effect of vinyl groups debased the degree of hydrosilylation reaction in heat processing.
2. The compatibility of the polyolefin rubbers with H-PDMS was fatal for the hydrosilylation reaction in the course of heat processing.
3. In the presence of the steric effect, the polarity effects of the substituted vinyl groups became less important.

The results show that the hydrosilylation reaction could be carried out in the course of heat processing by the selection of the appropriate unsaturated polymers. The heat processing of rubbers is more economical and environmental friendly. More significantly, the experiment results provide a more convenient mechanism for the modification or crosslinking of polyolefin rubbers with silicone. As a new type of silicone-modified or crosslinked polyolefin rubber, these compounds may show good thermal performance or good compatibility with reinforced silica.

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