Surface Modification of Carbon Fiber and the Mechanical Properties of the Silicone Rubber/Carbon Fiber Composites

Eung Soo Kim, Tae Hwa Lee, Eun Jeong Kim, Jin-San Yoon

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea

ABSTRACT: Effects of the incorporation of the PAN-based carbon fiber (CF) into a room temperature vulcanized silicone rubber (RTV), poly(dimethylsiloxane) (PDMS) containing terminal silanol groups, on the thermal stability and mechanical properties were explored. CF was modified with nitric acid to introduce hydroxyl and carboxyl groups on the CF surface. These functional groups were then treated with an isocyanato silane compound, 3-isocyanatopropyltriethoxysiane (IPTS) to incorporate trialkoxy groups to the acid-treated CF to prepare IPTS grafted CF (I-CF). The alkoxy groups on the surface of I-CF may undergo the condensation reaction with the silanol groups of RTV to enhance the interfacial interaction between I-CF and RTV. Morphology of the fractured surface of RTV/CF composites was examined by scanning electron microscopy (SEM). The mechanical properties and thermal stability of the composites were analyzed and rationalized by the increase in the degree of curing of RTV and the enhanced interfacial interaction. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: fiber; silicones; reinforcement; surface modification

INTRODUCTION

Silicone rubber is one of the most important inorganic polymers because of its high thermal stability, low surface tension, and outstanding dielectric properties.[1–4] Polydimethylsiloxane (PDMS) is the most prevalent rubber of this class. However, most applications require that PDMS be reinforced by solid fillers.[5–7] The reinforcement is considered to be very important in the elastomer technology because the mechanical strength in the unfilled silicone rubber is very poor.[4,8] The most widely used fillers for reinforcing PDMS are silica, carbon black, and fibrous fillers.

Carbon fiber (CF) is an attractive reinforcing material due to its superior specific strength and specific modulus. Also, CF has a low linear coefficient of thermal expansion.[9,10] Moreover, CF is more resistant to stress corrosion or stress rupture failures at room temperature than the other competing fillers such as glass and organic polymer fibers.[11] Because of the decrease in the CF production cost and the increasing demand of structural materials with advanced properties, CF composites are becoming a greater priority.[11,12]

CF composites are suitable for applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical necessities.[11–13] However, usually the interfacial interaction between CF and the polymer matrix is not strong enough, which means that the incorporation of CF could form defects in the composites[14,15] to cause easy failure. Therefore, surface-treatment of CF is required to raise the mechanical properties through the interfacial interaction enhancement. The failure mechanisms of CF-reinforced composites were analyzed by Larson et al.[16]

Various methods have been developed for the treatment of CF, for instance, oxidation,[17,18] coating,[19,20] grafting,[21–22] hot NaOH solution treatment,[23] and plasma.[24,25] CF can also be treated by ozone or silane to improve the surface wettability.[26–28]

The surface modification with silane compounds has most often been used for glass fibers to prepare high performance glass fiber-reinforced composites.[29–32] However, the similar techniques have been employed far less frequently for the modification of CF due to the relatively inert nature of the CF surface.

In this study, following our previous research,[33] silicone rubber composites were prepared with a room temperature vulcanized (RTV) type silicone rubber, carbon black, and CF. CF was modified by treating with nitric acid followed by grafting of the silane compound containing isocyanato group to the CF surface to enhance the interfacial interaction

TABLE I
Recipe for the Preparation of the RTV Composites. (Unit: wt %)

	CF	CB		Silane		Catalyst	
	CF	I-CF	N774	MA100	APTES	TPOS	Tin
RTV	–	–	–	–	2	10	0.1
RTV/N774	–	–	2	–	2	10	0.1
RTV/MA100	–	–	–	2	2	10	0.1
RTV/N774/CF	3.5	–	2	–	2	10	0.1
RTV/N774/I-CF	–	3.5	2	–	2	10	0.1
RTV/MA100/CF	3.5	–	–	2	2	10	0.1
RTV/MA100/I-CF	–	3.5	–	2	2	10	0.1

between CF and the RTV matrix. The effects of the surface modification of CF on the mechanical and thermal properties were explored for the RTV/CF composites.

EXPERIMENTAL

Materials

Hydroxyl-terminated poly(dimethylsiloxane) (PDMS) was purchased from Dong Yang Silicone (Korea). Tetrapropoxysilane (TPOS), γ-aminopropyltriethoxy-silane (APTES), and 3-isocyanatopropyltriethoxy-siane (IPTS) were purchased from Aldrich (St. Louis, MO). Two kinds of carbon black, N774 (N700 series, semi reinforcing furnace grade) and MA100 (N200 series, intermediate super abrasion furnace grade), were supplied by OCI (Korea) and Mitsubishi Chemicals (Japan), respectively. N774 and MA100 have different particle size with about 61–100 and 10–20 nm in diameter, respectively. The carbon black was premixed with low viscosity silicone oil (200 cps PDMS oil) to prepare a master batch, which was then intermixed with PDMS to obtain a well dispersed mixture. The PAN-based CF was obtained from Toho Tenax (Japan, grade: HT C413 6 mm) and was chopped into staples of 6 mm in length. The sized CF was burnt in a furnace with an air flow for 2 h at 400°C to remove the coating chemicals from the CF. The resulting CF was compounded with the PDMS/carbon black mixture.

Modification of CF

CF (5 g) was added to 90 mL of 60% HNO_3 aqueous solution. The mixture was subjected to ultrasonication for 30 min and stirred for 12 h with reflux,[34] followed by vacuum-filtering through a polytetrafluo-roethylene (PTFE) membrane filter. The sludge residue was washed with distilled water until pH of the filtrate became neutral. The strong acid treated CF (Acid-CF) was prepared by drying the sludge under vacuum for 2 h at 60°C. Hydroxyl groups and carboxyl groups might form on the surface of Acid-CF.[35,36] Grafting of IPTS onto the Acid-CF surface

was proceeded typically as follows: Acid-CF (2.0 g) was introduced into a 150 mL round-bottomed flask and then 50 mL of benzene and 20 mL of IPTS were added. Then two to three drops of dibutyltin dilaurate were added as a catalyst into the flask. The mixture was stirred at 80°C for 4 h under a gentle nitrogen flow. The mixture was filtered through a PTFE membrane and thoroughly washed with benzene to remove the solvent and unreacted reactants followed by drying at 60°C for 24 h under vacuum to obtain IPTS-grafted CF (I-CF).

Preparation of the RTV/CF composites

The RTV/CF composites were prepared by mixing hydroxyl-terminated PDMS, TPOS, APTES, and each of the two kinds of carbon black master batch (CBM) in a bulk state, using a dibutyl tin dilaurate as a catalyst. The recipe for the RTV/CF composites is summarized in Table I. The mixture was mixed with a paste mixer for 10 min and for another 3 min to remove the formed bubbles from the mixture. It was then cured at 60°C for 48 h in a convection oven.

Measurements

Fourier-Transform-Infra-Red (FTIR) spectra were recoded with VERTEX 80V (Bruker Optics, Germany) at a wave number range of 4000–400 cm^{-1}. The composition of the CF surface was analyzed by an electron spectroscopy for chemical analysis (ESCA, Thermo Fisher Science, K-Alpha, England). The Mg Kα X-ray gun was operated at 15 kV and 10 mA and the analyzer chamber was kept under a high vacuum state. The cross-section morphology of the RTV/CF composites was observed by using a scanning electron microscopy (SEM, Hitachi, S-4300, Japan). The composites were fractured cryogenically. The thermal stability of the composites was observed by thermo-gravimetric analyses (TGA, TA Instruments Q50, USA). The samples were heated at 20°C/min from 25°C to 800°C under dry nitrogen flow at 90 mL/min. The thermal properties of CF and I-CF were analyzed by Differential Thermal
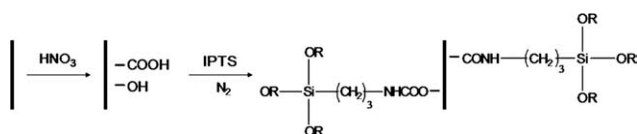
Scheme 1   The CF surface modification process.

Analysis-Thermal Gravimetric Analyzer (DTA-TGA, NETZSCH, STA 409 PC/PG, Germany) at 5°C/min of heating rate from 50 to 1400°C under a dry nitrogen flow at 40 mL/min. The degree of cross-linking was guessed by measuring the swelling ratio of the RTV composites in toluene. Tensile properties of the composites were measured using a universal testing machine (UTM, Hounsfield H 10KS-0061, UK). The specimens were prepared according to KSM 6518. The cross-head speed was 500 mm/min. The results of the five measurements were averaged.

RESULTS AND DISCUSSION

Surface modification of CF

CF containing hydroxyl and carboxyl groups (Acid-CF) was prepared by treating neat CF with nitric acid under nitrogen flow.[35–37] The surface of Acid-CF was then grafted with IPTS by having the isocyanate group of IPTS reacted with the hydroxyl and carboxyl groups of Acid-CF as schematized in Scheme 1. Reaction between the carboxyl group and the isocyanate one may yield an unstable bond which is stabilized by transforming subsequently to amide bond as displayed in Scheme 2(a).[34] The IPTS grafted CF was named as I-CF.
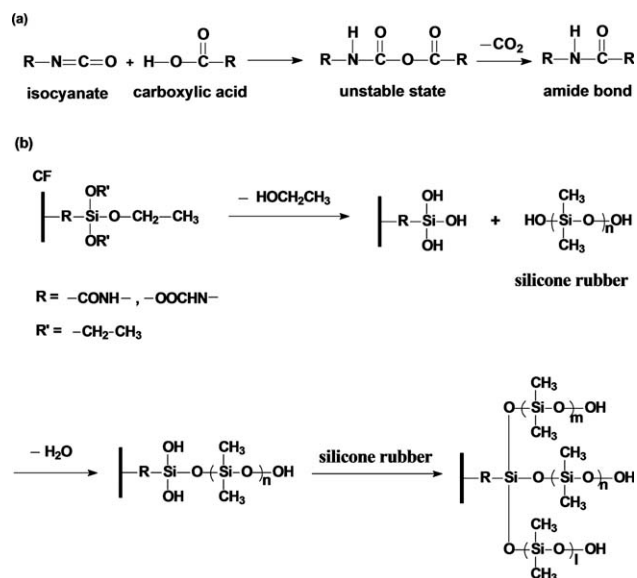
Scheme 2   (a) Reaction between carboxylic acid and isocyanate groups and (b) reaction between RTV and I-CF.

Condensation reaction between the alkoxy groups of I-CF and the silanol groups of RTV is feasible as depicted in Scheme 2(b) so that the RTV molecules grafted to I-CF should increase the interaction between the RTV silicone rubber and I-CF.

Figure 1(a) shows the FTIR spectra of CF, Acid-CF, and I-CF. The FTIR peaks at 1650–1600 cm^{-1} and 3000–2830 cm^{-1} in the FTIR spectrum of CF are due to the conjugated aryl and aliphatic chains, respectively.[38,39]

The FTIR peaks of Acid-CF at 1740–1700 cm^{-1} and 1150–1040 cm^{-1} correspond to the saturated aliphatic carboxylic acid groups and tertiary hydroxyl bonds, respectively.[39,40] This confirms that hydroxyl and carboxyl groups were formed on Acid-CF as a result of the treatment with nitric acid. As for I-CF, which is Acid-CF modified with IPTS, the peaks appearing at 610–590 cm^{-1} correspond to the bending motion of the amide (R_1—CH_2—CO—NH—R_2) bond, while the peaks at 1480–1430 cm^{-1} are due
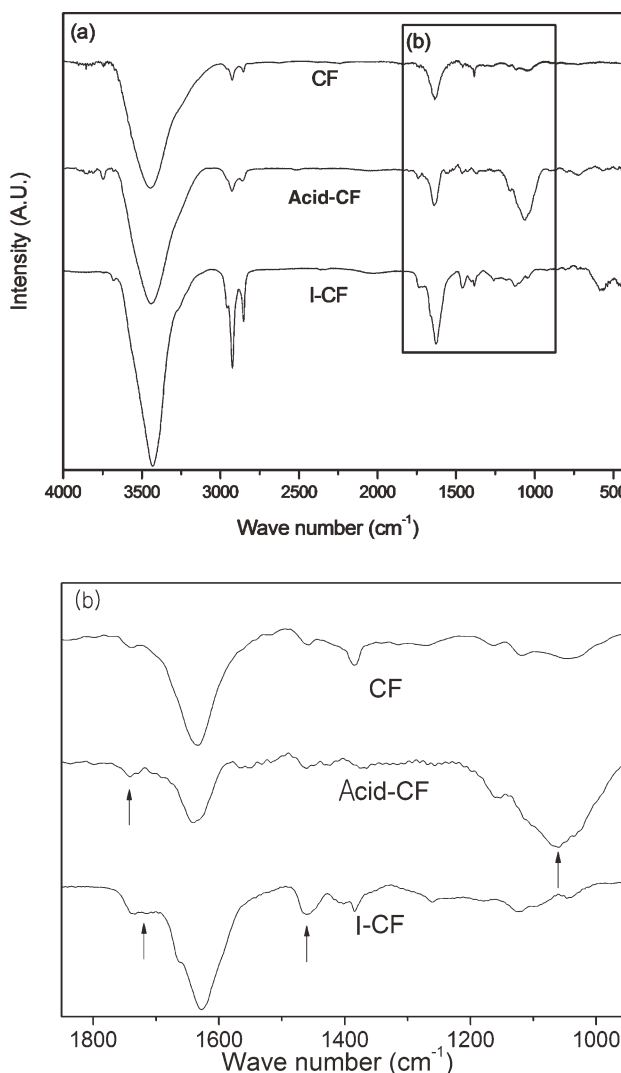

Figure 1   FTIR spectra of (a) CF, Acid-CF, and I-CF and (b) Magnified image of the FTIR spectra.
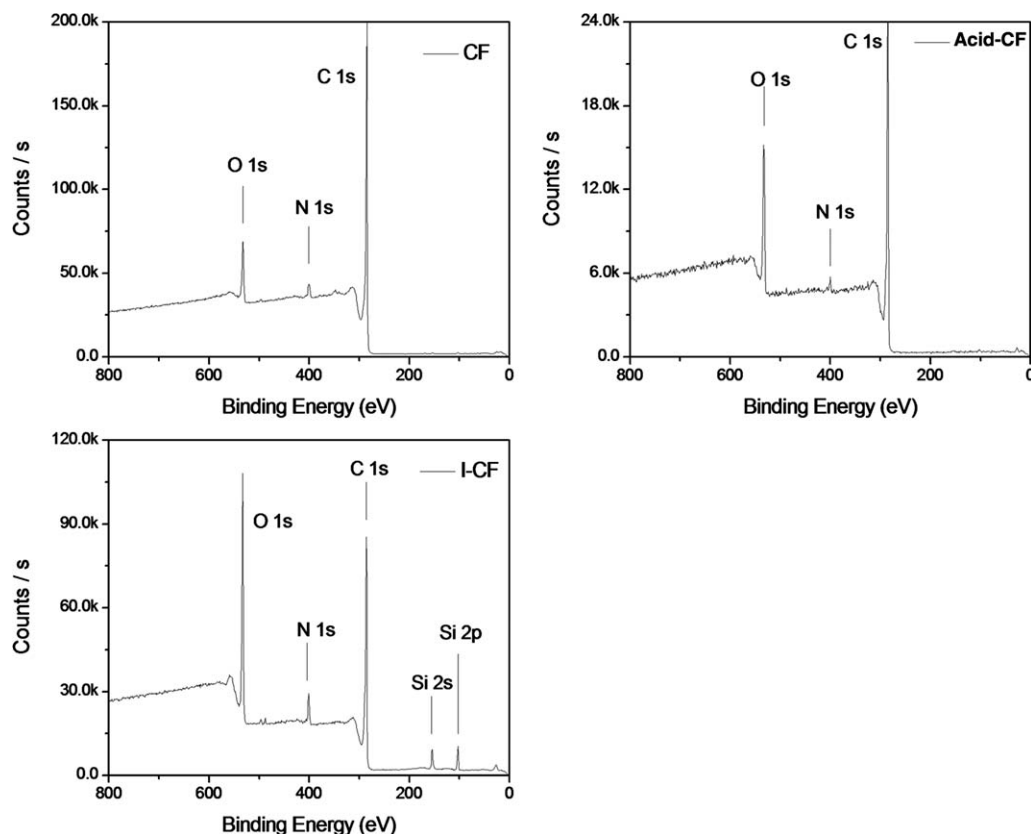
Figure 2 ESCA profiles of CF, Acid-CF, and I-CF.

to the secondary amide bond.[41] In addition, the carbonyl stretching vibration peak appearing at 1740–1680 cm^{-1} comes from the urethane bond.[34]

ESCA analysis of the modified CF

Figure 2 displays the ESCA profiles of CF, Acid-CF, and I-CF. The peaks corresponding to C, O, and N atoms are observed, but Si atom peak is missing in the ESCA profiles of the CF and Acid-CF. In contrast, in the ESCA profile of I-CF, the s and p orbital peaks of Si atom appear at 150 and 100 eV, respectively. Each atom is labelled at the corresponding specific binding energy (BE) in Figure 2. The surface of the different CF fibers was composed mainly of C atom as can be confirmed by the C1s peak at around 284 eV. All the fibers exhibited the s orbital peak of O atom at 532 eV too.

The atomic contents determined from the ESCA measurements are listed in Table II. The C atom contents of CF, Acid-CF, and I-CF were 86.8, 82.0, and 60.6%, respectively. The decrease in the C content in the written order came from the fact that the atoms other than C such as O, N, and Si were formed as a result of the treatment of CF with nitric acid and IPTS. The O atom content increased from 9.4 to 16.4% as a result of the acid treatment of CF due to the formation of hydroxyl and carboxyl groups.

Obviously, I-CF has higher oxygen and nitrogen content than Acid-CF due to the IPTS residue grafted to Acid-CF. Moreover unlike CF and Acid-CF, I-CF contained 9.86% of Si atom, again confirming that IPTS was successfully grafted onto Acid-CF. Since the ESCA detects the atomic contents of the specimens less than 10 nm deep from the surface,[9] the results in Table II do not correspond to the bulk composition but to the surface composition of the different fibers.

Figure 3 displays the core region spectra of CF and the modified CF fitted to different number of peaks. The main C1s peak showed at around 284.6–285.1 eV, which was assigned to the graphitic linkage of CF. In addition, some small peaks appearing at the higher binding energy positions correspond to different oxygen-containing groups or linkages.[26]

The assignments and contents of the separated peaks are listed in Table III. Different structural

TABLE II
ESCA Elemental Analyses Results of CF, Acid-CF, and I-CF

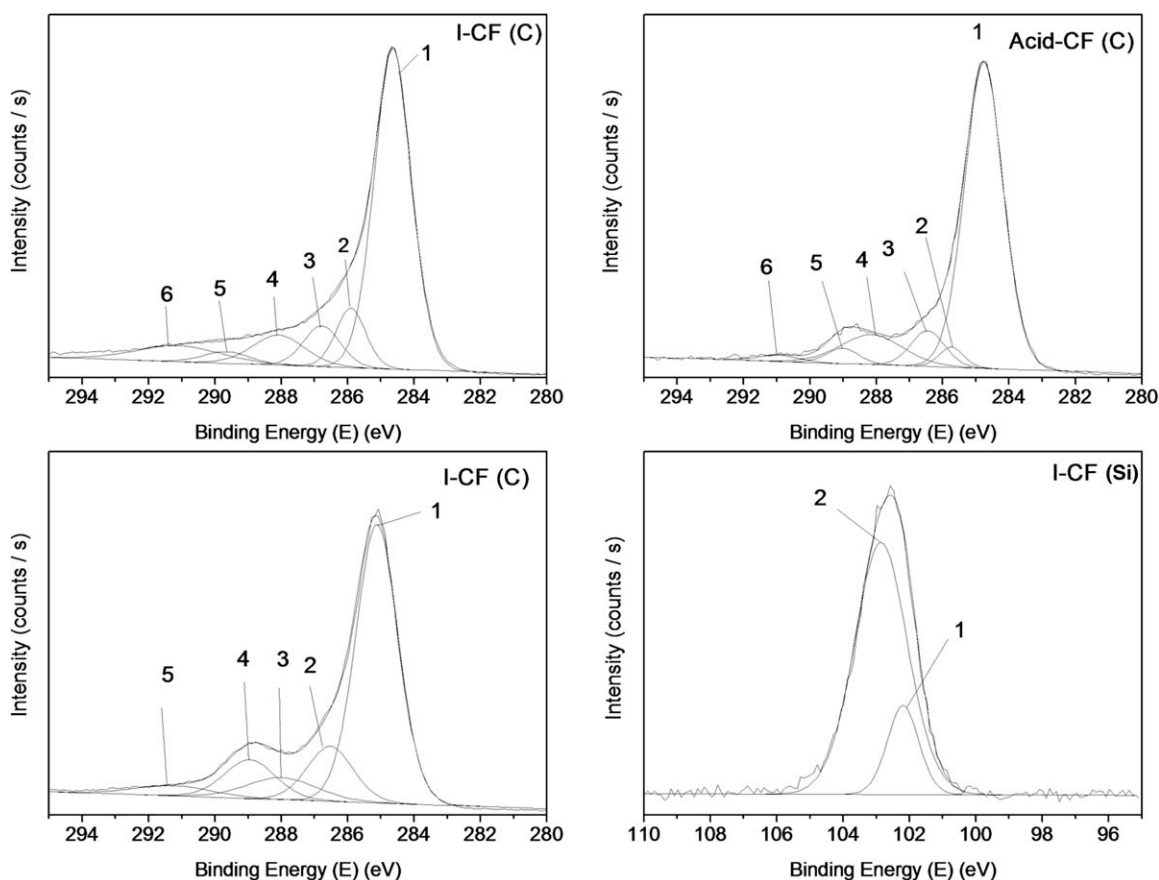| Sample name	Surface composition, atomic (%)			
	Carbon	Oxygen	Nitrogen	Silicon
CF	86.82	9.43	3.75	–
Acid-CF	81.95	16.41	1.64	–
I-CF	60.63	23.71	5.8	9.86

**Figure 3** High-resolution ESCA spectra of CF and the modified CF.

components of the oxygen-containing carbon linkages (OCL) of CF and the modified CF can be seen in Table III. The change of OCL content ratio represents the change of the chemical linkage on the fiber surface. The β-C and π-π* come from the β carbon of bridged structure and the shake-up satellites.[42] The β-C bond was induced between the carbonyl and hydroxyl groups as shown in Scheme 3(a). However, the β-C peak was absent in the spectra of I-CF. It might be due to the fact that lots of hydroxyl groups were exhausted by the reaction with IPTS and

thereby the hydroxyl groups next to the carbonyl groups became scarce in I-CF. The oxidation of CF during the treatment with nitric acid raised the content of OCL such as carbonyl (R—C=O) and carboxyl (R—COOH) groups compared with neat CF. I-CF had higher content of carbonyl (R—C=O) groups than CF and Acid-CF so that it increased from 7.43 to 18.93%. However, it is curious that the content of C—O groups in the O assignment decreased as a result of the nitric acid treatment of CF. However, the slightly lower content of C—O

TABLE III
Binding Energies (eV) of CF and the Modified CF

Atom	Assignment[a]	Peak BE			Atomic %			Reference
		CF	Acid-CF	I-CF	CF	Acid-CF	I-CF	
C	1. C-C	284.64	284.79	285.12	63.86	76.01	64.53	39
	2. β-C	285.91	285.75	–	9.49	0.56	–	
	3. R-C-O	286.78	286.45	286.53	8.02	7.43	7.94	
	4. R-C=O	288.08	288.14	287.99	8.46	11.4	18.93	
	5. R-COOH	289.65	289.01	288.95	2.89	3.02	4.61	
	6. π-π*	291.1	290.97	291.25	7.27	1.58	3.99	
Si	1. —SiO(OH)$_2$	–	–	102.19	–	–	17.39	43
	2. —SiO$_2$(OH)	–	–	102.86	–	–	82.61	

[a] The assigned numbers correspond to the numbers in Figure 3.
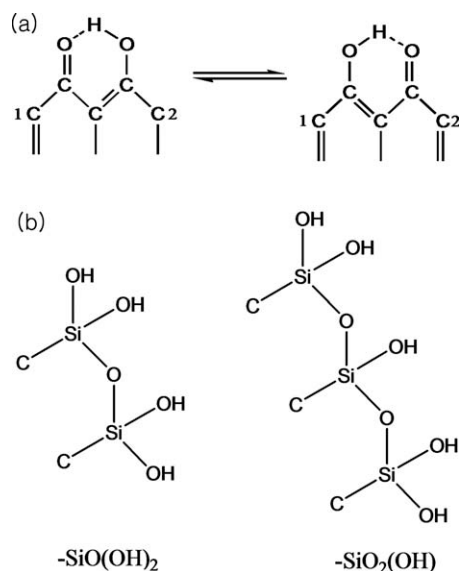
Scheme 3 The structure of the β—C bond and silane-coupling agents on CF.

spectrum of I-CF in Si core region can be resolved into two peaks at 102.19 and 102.86 eV as can be seen in Figure 3 and Table III. The two assignments of Si indicate the hydrolyzed structure of the silanes.[43] The peaks at 102.19 and 102.86 (eV) can be assignable to -SiO(OH)$_2$ and -SiO$_2$(OH), respectively [Scheme 3(b)].

Morphology of the RTV/CF composites

Chopped CF is usually supplied in bundles through the surface coating with organic matters because uncoated CF provokes dust scattering problems during storage and handling. Therefore, the coating agent needs to be removed from the CF surface in order to well disperse the chopped fiber in the rubber matrix. Since part of CF may be broken down to be shorter during the compounding, special care should be taken to disperse it in the polymer matrix without damages.

groups of I-CF compared with that of Acid-CF may be due to the transformation of carboxyl groups into amide groups as shown in Scheme 2(a).

The observed unsymmetrical binding energy peak at 100–105 eV for Si core region is the proof of the existence of more than one Si core state. The

The cross section morphologies of the RTV/CF composites are displayed in Figure 4. The CF fibers in the RTV/CF composite exhibit a comparatively clean surface. On the other hand, I-CF in the RTV/I-CF composite is blotted with RTV debris as shown in Figure 4(b,d), indicating that the wettability of I-CF to the RTV matrix was greatly enhanced. This
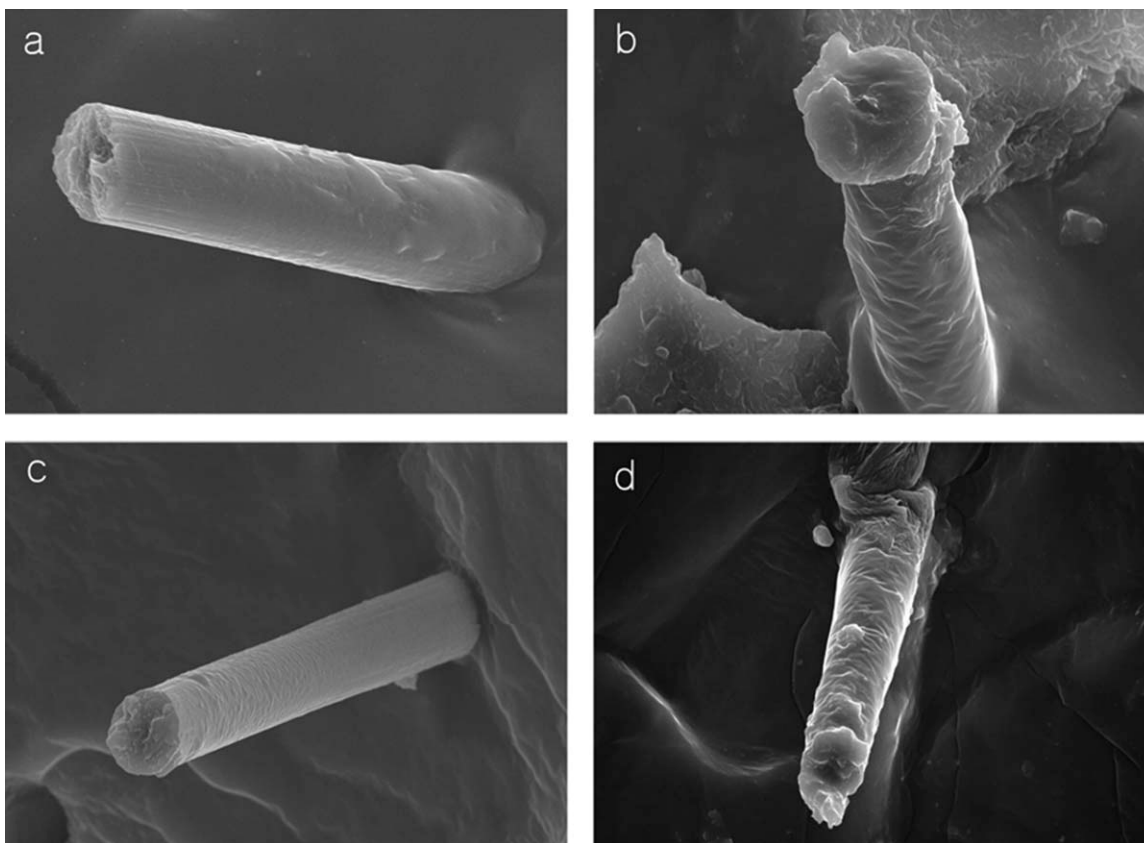

Figure 4 SEM image of the fractured surface of (a) RTV/N774/CF (b) RTV/N774/I-CF (c) RTV/MA100/CF (d) RTV/MA100/I-CF.
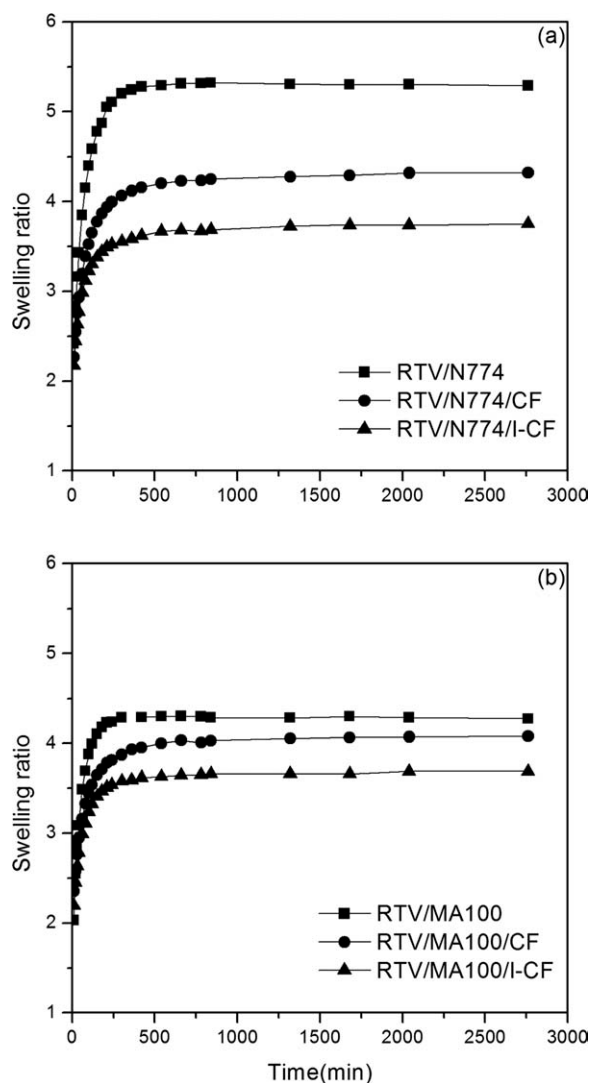
Figure 5 Swelling ratio of the RTV composites in toluene as a function of impregnation time.

is because CF does not have any functional groups to interact strongly with the RTV matrix, while the silanol groups of I-CF underwent the condensation reaction with the RTV during the preparation of the RTV/I-CF composite to raise the compatibility between the two components. However, the cross section morphologies were not affected by the addition of carbon black, neither N774 nor MA100.

Swelling ratio of the RTV/CF composites

The degree of cross-linking of RTV/CF and RTV/I-CF composites was estimated from the swelling properties of the composites in toluene. The swelling ratio (S_R) of the composites was determined by using Eq. (1).[44]

$$S_R = \frac{[m_s - (\alpha_{\text{filler}} m_d)]}{(\alpha_{\text{pol}} m_d)} \quad (1)$$

where, m_s is the weight of the swollen sample at equilibrium, m_d is the weight of the dried sample. α_{filler} and α_{pol} are the weight fractions of the filler and RTV, respectively. S_R is plotted as a function of time as exhibited in Figure 5. The equilibrium swelling ratio of RTV/carbon black/CF composites was lower than that of RTV/carbon black composites. The RTV/carbon black/I-CF composites exhibited the lowest equilibrium swelling ratio, confirming the occurrence of the extra curing of RTV by I-CF.

Thermal properties of RTV/CF composites

Figure 6 demonstrates the TGA profile of CF and I-CF. I-CF began to lose weight faster than CF and the temperature corresponding to 10% of weight loss, T_{10}, of I-CF was 160°C lower than that of CF. Moreover, the residual weight of CF at 1200°C was heavier (95.0%) than that of I-CF at the same temperature (89.2%). The decomposition of the IPTS residue on the surface of I-CF and the defect of I-CF caused by the treatment with nitric acid followed by IPTS are also responsible for the faster and larger weight loss of I-CF compared with that of CF.

Figure 7 demonstrates the TGA profile of the RTV/CF composites. The addition of CF to the composites lowered the thermal stability of RTV in that the onset temperature of significant weight loss went down. RTV/carbon black/CF composites again lost weight faster than RTV/carbon black composites. All the TGA curves show a one-step degradation profile. The value of T_{10} and T_{50}, the temperatures corresponding to 10 and 50% of weight loss, respectively, are summarized in Table IV.

T_{10} of RTV/N774 (508°C) was higher than that of RTV/N774/CF (498°C). In contrast, T_{10} of RTV/N774/I-CF (520°C) was higher than that of RTV/N774. T_{50} exhibited the same trend as T_{10} did.
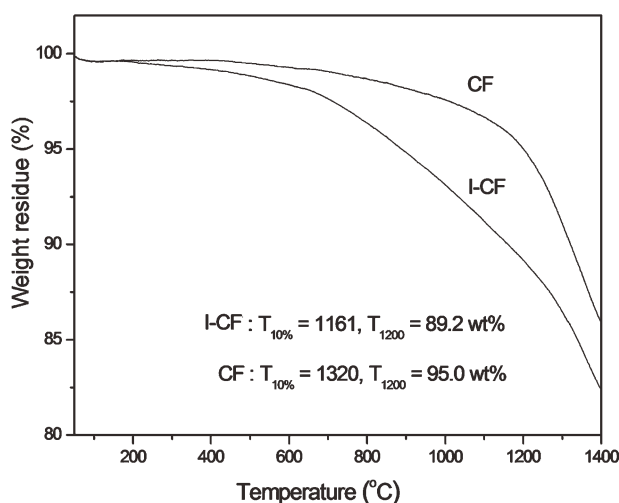

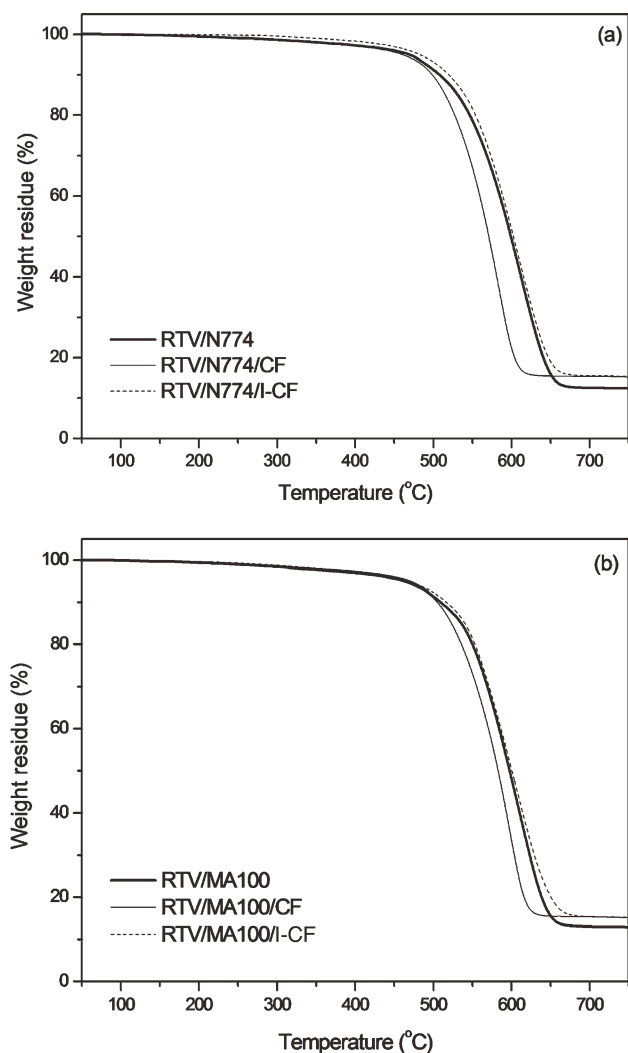**Figure 6** TGA profiles of CF and I-CF.

Figure 7 TGA profiles of the RTV/CF composites.

TABLE V
Tensile Properties of the RTV/CF Composites

	Tensile strength (MPa)	Elongation (%)
RTV/N774	1.6	245
RTV/N774/CF	1.6	63
RTV/N774/I-CF	4.1	18
RTV/MA100	1.4	118
RTV/MA100/CF	1.7	41
RTV/MA100/I-CF	4.3	15

trast, since I-CF is coated with organic layer, its thermal conductivity should be lower than that of CF. The enhanced thermal stability of the RTV composites due to the incorporation of I-CF was attributed to the extra curing of RTV by the silanol groups attached to I-CF and to the enhanced interfacial interaction between RTV and I-CF.

Mechanical properties of RTV/CF composites

The tensile properties of the RTV composites are summarized in Table V. The typical stress–strain curve of the RTV composites is drawn in Figure 8.

The addition of CF to RTV/N774 did not raise the tensile strength, and also the tensile strength of RTV/MA100/CF was marginally higher than that of RTV/MA100.

CF is expected to influence on the mechanical properties of the RTV composites in two different ways. CF can play a role like the steel reinforcing rod inside the concrete to enhance the mechanical properties. On the contrary, defects may exist between CF and the RTV matrix due to the poor interfacial interaction to initiate failure during the tensile tests.

However, the thermal stability of the RTV composites with MA100 was similar to those with N774.

It is to be noted that incorporation of CF and I-CF to RTV/N774 reduced T_{10} and T_{50}, while, on the contrary, addition of I-CF to RTV/N774 raised T_{10} and T_{50}. We do not have a clear answer why CF and I-CF exerted effect opposite to each other on the thermal stability of RTV/N774. This may be partly due to the fact that the increase in the thermal conductivity as a result of the CF incorporation facilitated the heat transfer into the composite.[45,46] In con-

TABLE IV
Temperatures Corresponding to 10 and 50% Weight Loss

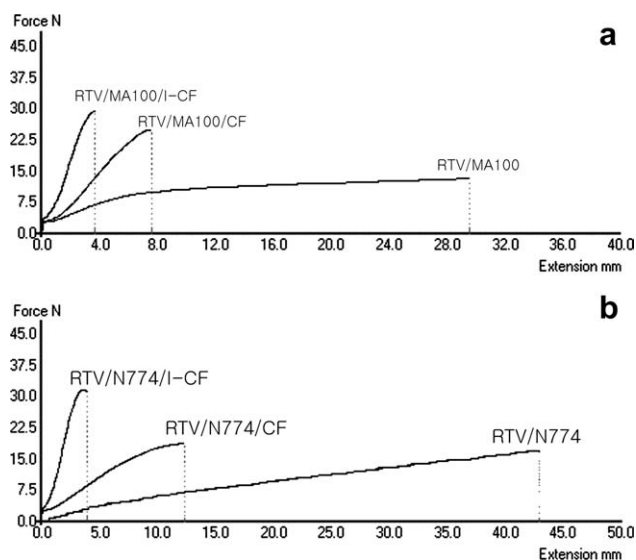|	T_{10} (°C)	T_{50} (°C)
RTV/N774	508	599
RTV/N774/CF	498	571
RTV/N774/I-CF	520	602
RTV/MA100	509	598
RTV/MA100/CF	505	583
RTV/MA100/I-CF	516	601

Figure 8 The typical stress-strain curve of RTV/MA100, RTV/MA100/CF, and RTV/MA100/I-CF

Incorporation of I-CF to RTV/N774 and RTV/MA100 enhanced considerably the tensile strength of the respective composites. Moreover, the decrease in elongation at break of the composites was more significant when I-CF was incorporated into the composites instead of CF. These results confirm again the occurrence of the extra curing of RTV due to I-CF and the enhanced interfacial interaction.

CONCLUSIONS

Silicone rubber/CF composites were prepared by compounding PDMS with TPOS, CBM, and CF. I-CF was synthesized by the nitric acid treatment of CF followed by grafting of IPTS. CFs devoid of any blots were observed on the fractured surface of the RTV/CF composites, while some RTV debris were glued onto the surface of I-CF in the RTV/I-CF composites, indicating that the interaction between CF and RTV was greatly enhanced when I-CF was incorporated into RTV instead of CF due to the plausible chemical reaction between RTV and I-CF. The tensile strength and thermal stability of RTV were improved significantly due to the incorporation of I-CF. Not only the enhanced interaction but also the increased degree of curing was responsible for the improved tensile strength and thermal stability of RTV/carbon black/I-CF composites compared to those of RTV/carbon black and/RTV/carbon black/CF composites.

References

1. Mark, J. E.; Ngai, K.; Graessley, W.; Mandelkern, L.; Samulski, E.; Koenig, J. et al, Physical Properties of Polymers, 3rd ed.; Cambridge University Press: Cambridge, 2003.
2. Mark, J. E.; Allcock, H. R.; West, R. Inorganic Polymers, 2nd ed.; Oxford University Press: New York, NY, 2005.
3. Clarson, S. J.; Semlyen, J. A. Siloxane Polymers; Prentice Hall: Englewood Cliffs, NJ, 1993.
4. Rochow, E. An Introduction Chemistry of the Silicones; Macnutt Press: New York, 2008.
5. Peignot, P.; Rhodes, K. Med Dev Technol 2004, 15, 22.
6. Morton, M. Rubber Technology, 3rd ed.; Van nostrand reinhold Company: New York, 1987.
7. Kraus, G.; Medalia, A. I. In Science and Technology of Rubber, 3rd ed.; Mark, J. E.; Erman; Eirich, F. R.; EdsAcademic Press, CA, 2005; p 387.
8. Erman, B.; Mark, J. E. Structures and Properties of Rubber-Like Networks; Oxford University Press: New York, 1997.
9. Choi, M. H.; Jeon, B. H.; Chung, I. J. Polymer 2000, 41, 3243.
10. Issi, J. P.; Nysten, B. In Carbon Fibers, 3rd ed.; Donnet, J. B.; Wang, T. K.; Peng, J. C. M.; Rebouillat, S., Eds.; Marcel Dekker: New York, 1998; p 371.
11. Peebles, L. H.; Yanovsky, Y. G.; Sirota, A. G.; Bogdanov, V. V.; Levit, P. M. In Carbon Fibers, 3rd ed.; Donnet, J. B.; Wang, T.

K.; Peng, J. C. M.; Rebouillat, S.; Marcel Dekker: New York, 1998; p 311.
12. Morgan, P. Carbon Fibers and Their Composites; Boca Raton, Taylor & Francis: UK, 2005.
13. Chand, S. J. Mater Sci 2000, 35, 1303.
14. Mandell, J. F.; Huang, D. D.; Mcgarry, F. J. Polym Compos 1981, 2, 137.
15. Lang, R. W.; Manson, J. A.; Hertzberg, R. W. Polym Eng Sci 1982, 22, 982.
16. Larson, B. K.; Drzal, L. T.; Sorousian, P. Composites 1990, 21, 205.
17. Rashkovan, I. A.; Korabelnikov, Y. G. Compos Sci Technol 1997, 57, 1017.
18. Dilsiz, N.; Ebert, E.; Weisweiler, W.; Akovali, G. J Colloid Interf Sci 1995, 170, 241.
19. Yue, Z. R.; Jiang, W.; Wang, L.; Gardner, S. D.; Pittman, C. U. Carbon 1999, 37, 1785.
20. Pamula, E.; Rouxhet, P. G. Carbon 2003, 41, 1905.
21. Fjeldly, A.; Olsen, T.; Rysjedal, J. H.; Berg, J. E. Compos A 2001, 32, 373.
22. Varelidis, P. C.; Mccullough, R. L.; Papaspyrides, C. D. Compos Sci Technol 1999, 59, 1813.
23. Sugama, T.; Kukacka, L. E.; Carciello, N.; Galen, B. Cem Concr Res 1988, 18, 290.
24. Paredes, J. I.; Martínez-Alonso, A.; Tascón, J. M. D. J Colloid Interf Sci 2003, 258, 276.
25. Bismarck, A.; Kumru, M. E.; Springer, J. J Colloid Interf Sci 1999, 210, 60.
26. Xu, Y.; Chung, D. D. L. Carbon 2001, 39, 1995.
27. Fu, X.; Lu, W.; Chung, D. D. L. Cem Concr Res 1996, 26, 1007.
28. He, J. M.; Huang, Y. D. J Appl Polym Sci 2007, 106, 2231.
29. Ishida, H.; Low, H. Y. J Appl Polym Sci 1998, 69, 2559.
30. Ishak, Z. A. M.; Ariffin, A.; Senawi, R. Eur Polym J 2001, 37, 1635.
31. Laura, D. M.; Keskkula, H.; Barlow, J. W.; Paul, D. R. Polymer 2002, 43, 4673.
32. Ozkoc, G.; Bayram, G.; Bayramli, E. Polymer 2004, 45, 8957.
33. Kim, E. S.; Kim, H. S.; Jung, S. H.; Yoon, J. S. J Appl Polym Sci 2007, 103, 2782.
34. Zhang, Z. Z.; Song, H. J.; Mena, X. H.; Luoa, Z. Z. Wear 2008, 264, 599.
35. Pittman, C. U.; Jr.Wu, Z.; Jiang, W.; He, G. R.; Wu, B.; Li, W.; et al. Carbon 1997, 35, 929.
36. Pittman, C. U.; Jr.He, G. R.; Wu, B.; Gardner, S. D. Carbon 1997, 35, 317.
37. Zhang, Z. Z.; Songa, H. J.; Mena, X. H.; Luoa, Z. Z. Wear 2008, 264, 599.
38. Wenzhong, S.; Wang, H.; Guan, R.; Li, Z. Colloid Surface Physicochem Eng Aspect 2008, 331, 263.
39. Cecen, V.; Seki, Y.; Sarikanat, M.; Tavman, I. H. J Appl Polym Sci 2008, 108, 2163.
40. Lee, J. H.; Rhee, K. Y.; Park, S. J. Compos Part A-Appl S 2011, 42, 478.
41. SocratesG. Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd ed.; Wiley: New York, 2001.
42. Wang, Y. Q.; Zhang, F. Q.; Sherwood, P. M. A. Chem Mater 1999, 11, 2573.
43. Wang, Y.; Yu, Q.; Zhang, Y.; Guo, Z.; Gu, N.; Wesche, K. D. Appl Surf Sci 2004, 229, 377.
44. Kaneko, M. L. Q. A.; Yoshida, I. V. P. J Appl Polym Sci 2008, 108, 2587.
45. Shim, H. B.; Seo, M. K.; Park, S. J. J Mater Sci 2002, 37, 1881.
46. Wang, M.; Kang, Q.; Pan, N. Appl Therm Eng 2009, 29, 418.