

Mechanical Properties and Processibility of Glass-Fiber-, Wollastonite-, and Fluoro-Rubber-Reinforced Silicone Rubber Composites

Eun-Soo Park

Youngchang Silicone Company Limited, 481-7, Gasan-Dong, Kumchun-Gu, Seoul 153-803, Korea

Received 9 August 2006; accepted 6 December 2006

DOI 10.1002/app.26063

Published online 27 March 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The reinforcement of silicone rubber (SR) imparted by different types of fillers was investigated. Glass fiber (GF), wollastonite and fluoro rubber (FR) as nontraditional filler for rubber were compounded SR and mechanical properties of the prepared composites were evaluated. The addition of silane pretreated GF and wollastonite into SR, tensile strength, abrasion resistance and tear strength of the composites improved considerably. The improvement in the properties was assigned to an increased interaction between the filler and the polymer matrix. For the SR/FR composites system, the elongation at break was increase with increasing concentrations of FR due to sponge like structure resulting from poor compati-

bility between the two components. To investigate the production potential of extrusion processing method, prepared composites were extruded in a rod type sample. During the curing stage, GF, wollastonite and FR lead to the formation of void in the matrix resin. When GF and wollastonite were treated with silane, the void formations were reduced significantly. The silane treatment process improves not only mechanical strength but also processibility of SR composites in dry conditions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 460–468, 2007

Key words: composites; morphology; fillers; reinforcement; silicone rubber

INTRODUCTION

Silicone rubbers (SRs) are synthetic polymers with a giant backbone of alternating silicon and oxygen atoms. The strong silicon-oxygen chemical structure of silicone gives the elastomer its unique performance properties, including biocompatibility,¹ superior temperature and chemical resistance, radiation resistance and electrical properties.² SR perform exceptionally well in O-ring and sealing applications. Many types of wire and cable are insulated with these rubbers, which will burn to an ash yet still function as an insulator.³ However, SRs have relatively low tear strength, abrasion resistance, and tensile strength, and therefore, is generally not suited to dynamic applications. Therefore they are usually compounded with reinforcing fillers to improve their mechanical properties.⁴

The effectiveness of reinforcing filler depends on filler characteristics such as size and shape of the particles and, more significantly, on the strength of polymer filler interactions.^{5–10} These interactions increase the effective degree of crosslinking and such an effect is particularly strong if the particles

have some reactive surface groups. Silane derivatives are the most important and successful coupling agents to be used to treat mineral fibers. The general formula of an organosilane (R_nSiX_{4-n}) shows two classes of functionality. Silicon is the center of the silane molecule which contains an organic functional group such as vinyl, amino, epoxy and mercapto with a second functional group such as methoxy and ethoxy. The functional group will attach to an organic resin while the alkoxy group attaches to an inorganic material or substrate to achieve a coupling effect. The inorganic group of the silane molecule hydrolyzed to produce silanol, which forms a metal hydroxide or siloxane bond with the inorganic material. The organic group of the silane molecule reacted with the organic material to produce a covalent bond. A chemical bridge between the inorganic material and the polymer provides significantly improved electrical and mechanical properties. The improvement of mechanical strength is important in reducing production costs by increasing output, since complex parts can be removed from hot molds with reduced scrap rate.

GF and wollastonite are commonly used as functional fillers in thermoplastic. GF and wollastonite are used in composites to increase mechanical properties such as tensile, flexural, and impact strength. They are also used to increase dimensional stability

Correspondence to: E.-S. Park (t2phage@hitel.net).

and minimize distortion at elevated temperatures. In this study, glass fiber (GF), wollastonite, and fluoro rubber (FR) as nontraditional filler for rubber were compounded with SR and mechanical properties of prepared composite were evaluated. The effect of silane pretreatment of fiber and the applicability of prepared composites for molding and extrusion process were explored.

EXPERIMENTAL

Materials

Chopped GF [RCS03BM (GF01), RCS06BM (GF02), Hankuk Fiber, Korea], wollastonite [Kemolit A60 (untreated, WO01), Kemolit 1AF1 (3-aminopropyl triethoxysilane (APTS) treated, WO02), Chunghan Chem International, Korea], and silane coupling agent [HV 1860/023, allyltrimethoxysilane (ATMS), Dow Corning Corp.] were used as received. Fluoro rubber (FR, Aflas 100H, Asahi Glass), SR (GP60, Hae Ryong Silicone, Korea), and dicumyl peroxide (DCP, Hae Ryong Silicone) were used as received. 2,4-Dichlorobenzoyl peroxide (DCBP, DCLBP-50-PSI, 50% paste in silicone oil) was purchased by Akrochem (OH, USA). All fillers were predried in a convection oven for at least 12 h at 60°C to remove any moisture from the powders before processing. The characteristics of the reinforcement fillers used in this study were shown in Table I.

Instrumentation

Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S-4200 model. The fractured surfaces of the composites were prepared by using cryogenic fracturing in liquid nitrogen followed by a coating with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 10 kV.

Thermal stability of composites was determined by thermogravimetry (TG, Perkin-Elmer TGS-2, Norwalk, CT). The TG curves were obtained under an N₂ atmosphere at a flow rate of 4 mL min⁻¹ and a scanning from 20°C to 900°C with the heating rate of 20°C min⁻¹.

Hardness of the specimens was measured with a Shore A type hardness tester (GS-706, Teclock, Japan) and the readings averaged. Five locations were measured for each specimen and surface.

Silane treatment of glass fiber

GF01 and GF02 were heated in a convection oven at 400°C for 24 h to remove the adhesion binder from fiber surface. Thermally treated GF was immersed in silane solution for 1 h followed by GF was filtered and dried in an oven at 60°C for 6 h.

Compounding of SR composites

The silicone compound (95 g) and GF (5 g) was pre-mixed using a two-roll mill at room temperature for 10 min followed by curing agent (3 g, for compression molding composites: DCP, for extruding composites: DCBP) was slowly added to the flux roll. The compound band was then sheeted, folded and re-banded for mixing. This process was repeated 30 times to ensure thorough mixing.

Compression-molding of SR composites

The milled rubber sheet (180 × 180 × 2.5 mm) was fed into a compress mold cavity (200 × 200 × 2 mm). The molder was placed between two stainless-steel platens and heated in a 200°C hot press at a pressure of 10 atm for 10 min. When the curing process finished, the platens and molder were cooled to room temperature.

Extrusion of SR composites

All test specimens were extruded at a speed of 100 rpm using a single screw extruder equipped with a 3.0-mm-diameter die and a 1 : 10 compression ratio screw. Extruded samples were cured by passage through a heating box at 450°C with a rate of 50 m min⁻¹.

Tensile test procedure

Dumb-bell specimens for mechanical tests were prepared in accordance with ASTM D412 specification. The test specimens were preconditioned to 20% relative humidity and (20 ± 1)°C to standardize test

TABLE I
Characteristics of the Reinforcement Fillers

Properties	GF01	GF02	WO01	WO02	FR
Material	glass fiber	glass fiber	wollastonite	wollastonite	fluoro rubber
Particle size (μm)	3000	6000	75	75	10
Diameter (μm)	11	11	20	20	irregular
Specific gravity (25°C)	2.20	2.20	2.65	2.65	1.55

conditions. Tensile properties of samples were determined with a universal test machine (UTM, Model DECMC00, Dawha test machine, Korea) at a cross head speed of 250 mm min^{-1} according to ASTM D 412 at $(20 \pm 1)^\circ\text{C}$. The mean value of at least five specimens of each sample was taken, although specimens that broke in an unusual manner were disregarded. Tear strength was determined according to ASTM method D 624 using a die C specimen.

Abrasion test

Abrasion test was performed using an Abrasion Tester (Core Tech, Korea). The test pieces were $20 \times 20 \times 5 \text{ mm}^3$ in size and were prepared by compression-molding at 200°C . The travel distance of specimen was 10 mm at a speed of 60 cycles per minute and the test load was 5 N. The abrasive that was used was silicon carbide abrasive paper (no. 800, CC-800Cw; no. 120, AA-120; Daesung Abrasive, Korea). The percentage of abrasivity was calculated based on the weight loss after the test.

RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of GF and wollastonite. GF01 and GF02 are chopped GF strands having an average length of 3 and 6 mm. Wollastonite is calcium metasilicate. It is a naturally occurring pure white, acicular mineral. The aspect ratios of wollastonite are 15:1 and have a length $<75 \mu\text{m}$. The physical properties of the reinforcement fillers are summarized in Table I.

Premixed silicone compound and reinforcement fillers were mixed using a two-roll mill at room temperature and cured in a hot press at 200°C for 10 min. Table II records the mechanical properties of compression-molded SR/GF, SR/wollastonite, and SR/FR composites. The abbreviation of the sample code in Table II, SR/GF01-5.0ATMS, for example, means that the content of GF01 in the SR was 5.0 wt % and GF01 was treated with allyltrimethoxysilane. Elongation at break of compression-molded SR/GF and SR/wollastonite composites decreased with the presence of filler that indicates an interference¹¹ by the filler in the mobility¹² or deformability of the

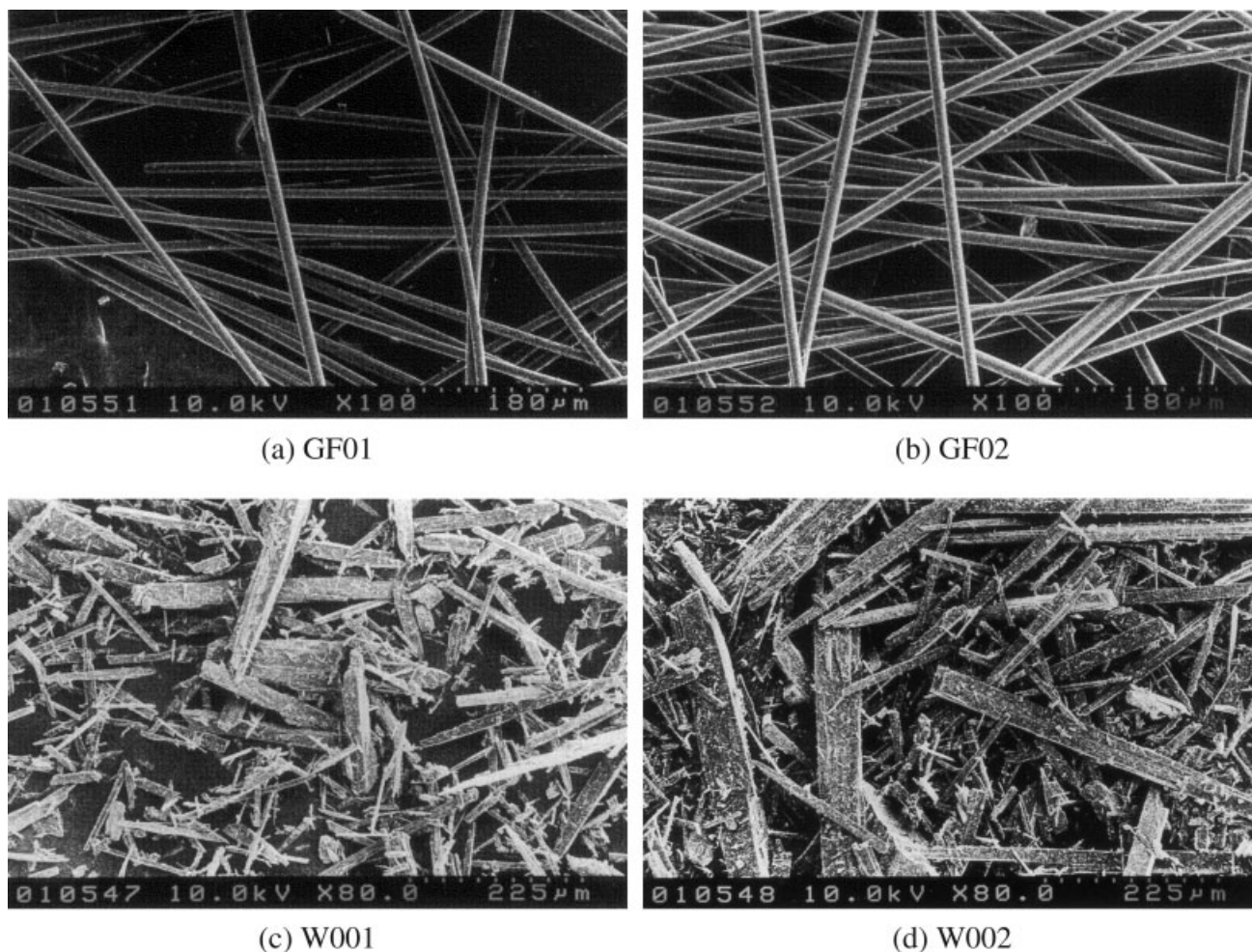


Figure 1 SEM micrographs of the GF and wollastonite.

TABLE II
Mechanical Properties of Compression-Molded SR/GF, SR/Wollastonite, and SR/FR Composites

Sample code	Composition (wt %)	Tensile properties				
		Maximum load (N)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN m^{-1})	Hardness (Shore A)
SR	100.0	84.1 ± 5.4	4.6 ± 0.3	220 ± 13	11.5 ± 0.8	65.8
SR/GF01-5.0ATMS	95.0/5.0	102.9 ± 15	9.0 ± 0.5	115 ± 9.8	16.1 ± 1.1	73.2
SR/GF01-10ATMS	90.0/10.0	128.4 ± 2.2	6.2 ± 0.1	43 ± 7.8	20.3 ± 0.8	76.0
SR/GF01-10	90.0/10.0	102.4 ± 11	5.5 ± 0.2	47 ± 5.6	18.3 ± 0.4	75.5
SR/GF02-2.5ATMS	97.5/2.5	100.0 ± 5.2	7.8 ± 5.2	134 ± 8.9	11.3 ± 0.8	72.0
SR/GF02-5.0ATMS	95.0/5.0	156.8 ± 5.9	7.6 ± 0.4	120 ± 7.4	12.5 ± 1.2	73.4
SR/GF02-10ATMS	90.0/10.0	137.2 ± 22	6.8 ± 1.0	98 ± 17	18.2 ± 2.5	75.8
SR/GF02-10	90.0/10.0	127.4 ± 16	5.8 ± 0.8	85 ± 22	13.2 ± 0.8	75.4
SR/GF02-20ATMS	80.0/20.0	76.4 ± 1.7	5.6 ± 0.6	14 ± 2.2	3.32 ± 0.2	89.2
SR/WO01-10	90.0/10.0	140.1 ± 12	4.8 ± 0.6	137 ± 3.7	15.6 ± 3.8	72.5
SR/WO01-10ATMS	90.0/10.0	143.4 ± 18	6.4 ± 0.7	128 ± 27	19.8 ± 1.5	72.5
SR/WO02-10APTS	90.0/10.0	164.4 ± 5.2	5.8 ± 0.4	99 ± 3.7	20.5 ± 2.0	72.8
SR/FR-10	90.0/10.0	147.0 ± 4.1	5.2 ± 0.7	107 ± 5.2	17.5 ± 1.0	68.6
SR/FR-20	80.0/20.0	92.3 ± 4.1	3.9 ± 0.2	372 ± 22	18.3 ± 1.0	54.6
SR/FR-30	70.0/30.0	36.1 ± 1.4	2.0 ± 0.1	624 ± 21	19.5 ± 1.2	40.2

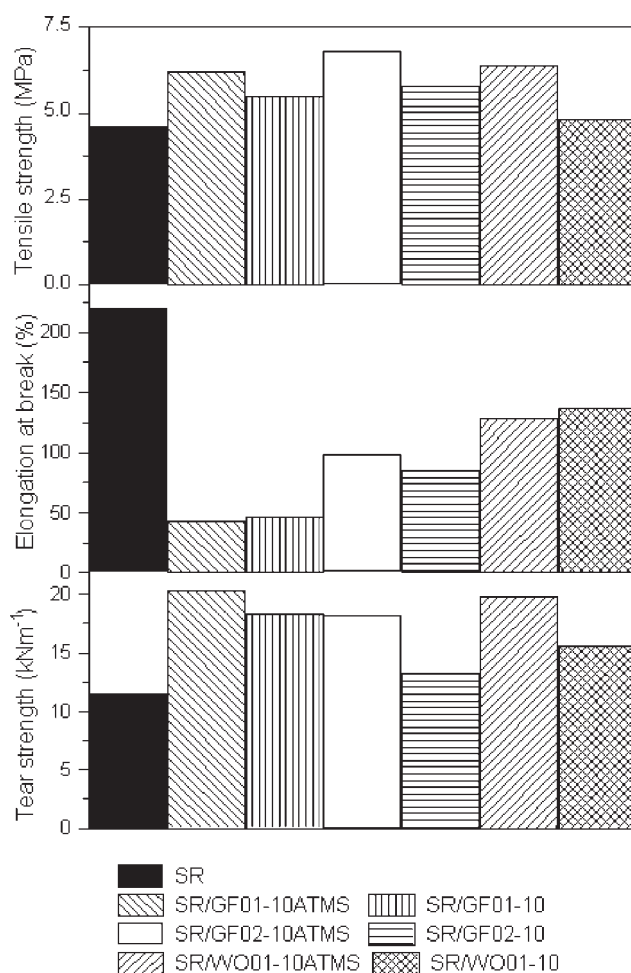


Figure 2 Tensile and tear test results of the compression-molded SR/GF and SR/wollastonite composites.

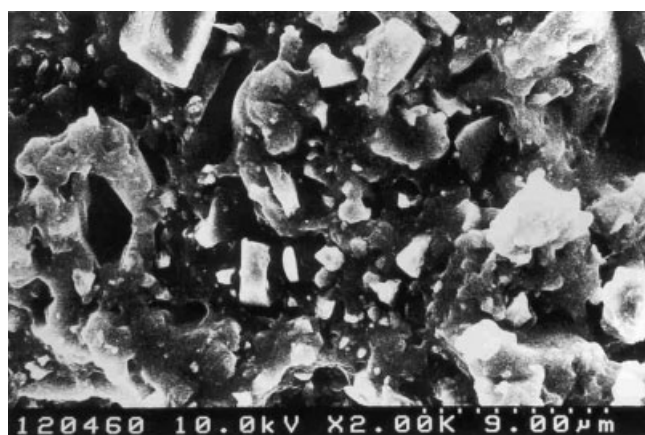
matrix. An increase in weight percentage of filler reduced the deformability of the matrix, and, in turn, reducing the ductility in the skin area so that the composite tended to form a weak structure. It is to be noted that the tensile strength for 10.0 wt % GF filler composite was higher compared to other two combinations. The addition of 10.0 wt % GF02 with length of 6 mm increased tensile strength by over 26% when compared with SR with no fiber additions. For SR/wollastonite composites, the addition of 10 wt % WO01 increased tensile strength by 4% when compared to SR. The SR/WO01-10 composite has lower values of tensile strength and higher values of elongation at break in comparison with the SR/GF01-10 and SR/GF02-10 composites, as a consequence of weaker adhesion.

In contrast, the silane treated GF and wollastonite composites developed higher tensile strength than untreated composites. An approximately 10% overall increase in the tensile strength from 5.8 to 6.8 MPa was observed pretreatment of the fibers with silane. There is also observed a significant improvement in tear strength of composite increase of silane treated GF and wollastonite contents (Fig. 2). Silane coupling agents are predominately used as mediators, binding organic materials to inorganic materials. These react with the silanols on the filler surface to give a strong bond, and also contain a functional group that bond to the rubber during vulcanization. The result is filler-polymer bonding that increases tensile strength and improves other compound properties.

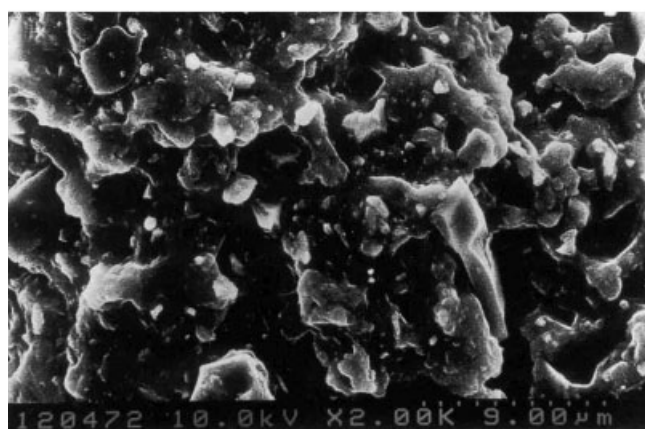
For SR/FR composites system, the elongation at break of composite was increase with increasing FR

contents whereas for the tensile strength proportionally decreased with increasing FR content. In practice, it is difficult to obtain uniform mixtures of SR and organic rubbers having polar groups through milling because of the poor compatibility between the two components. The interfacial bonding between constituent materials may not be strong due to void formation resulting from imperfect wetting and agglomeration (Fig. 3). This sponge-like structure leads to an extensive increase in the elongation at break of composites.

Figure 4 shows the results of the abrasion resistance test performed on compression-molded SR/GF, SR/wollastonite and SR/FR composites. There was a decreasing trend in weight loss with increasing hardness in all composites, and the percentage of abrasivity increased in the order SR/GF < SR/wollastonite < SR/FR. As abrasion resistance basically depends on the hardness of a material, most conventional abrasion-resistant composite achieve their hardness by adding mineral filler. The hardness of GF (Mohs scale hardness 5.5) is slightly larger than that of wol-



(a) SR/FR-10



(b) SR/FR-30

Figure 3 SEM micrographs of the compression-molded SR/FR-10 and SR/FR-30 composite.

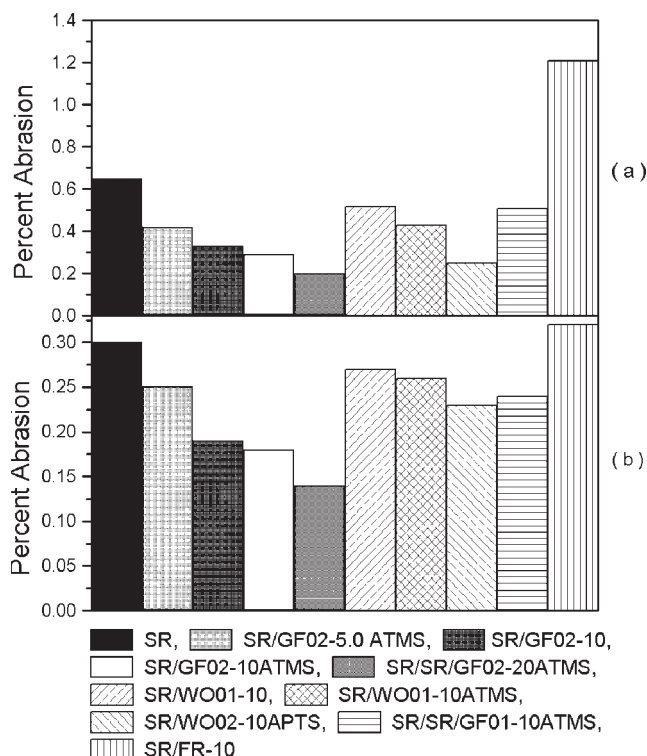


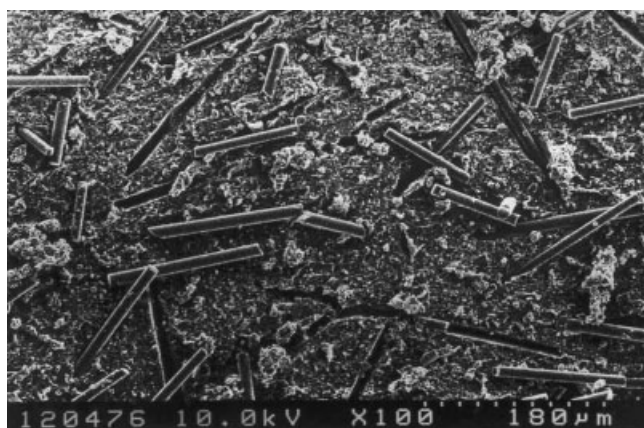
Figure 4 Abrasion resistance test results of compression-molded SR/GF, SR/wollastonite and SR/FR composites (a) CC-800Cw abrasive paper (no. 800); (b) AA-120 abrasive paper (no. 120).

lastonite (Mohs scale hardness 4.8), so it has a significant effect on abrasion resistance than wollastonite.

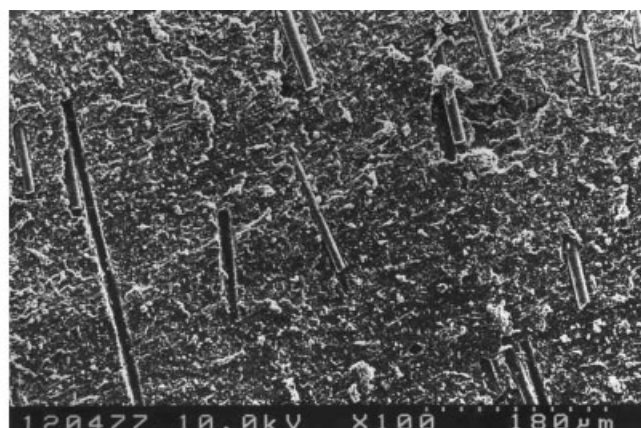
To investigate the production potential of extrusion processing method, SR/GF, SR/wollastonite and SR/FR composites were extruded in a rod type sample and cured at 450°C with a rate of 50 m min⁻¹. Table III compares the tensile properties of the extruded and postcured composites. It is found that the tensile strength of extruded composites was significantly lower than that of the compression-molded composites. In compression-molded SR/GF composites, the GF are randomly arranged in all three directions, approximately in random three-dimensional array [Fig. 5(a,c)]. This orientation effectively improves mechanical properties in the fiber direction and in the transverse direction. For extruded composite, fibers tend to align in the direction of extrusion flow and they are usually parallel to the stretching polymer chains [Fig. 5(b,d)]. Therefore, most of the fibers which comprise the skin are oriented in the flow direction and little reinforcement is imparted to the transverse direction. After postcuring, the effect of filler on the SR matrix is much more expressive. Organic peroxides undergo homolytic cleavage at elevated temperature. The peroxide decomposition reaction produces volatile byproducts such as short chain acids, aldehydes, ketones, and alcohols. Postcuring process drives off these residual materials from composites and increases the adhesion between matrix and filler.

TABLE III
Tensile Properties of Extruded SR/GF, SR/Wollastonite, and SR/FR Composites
Before and After Postcuring at 200°C for 2 h

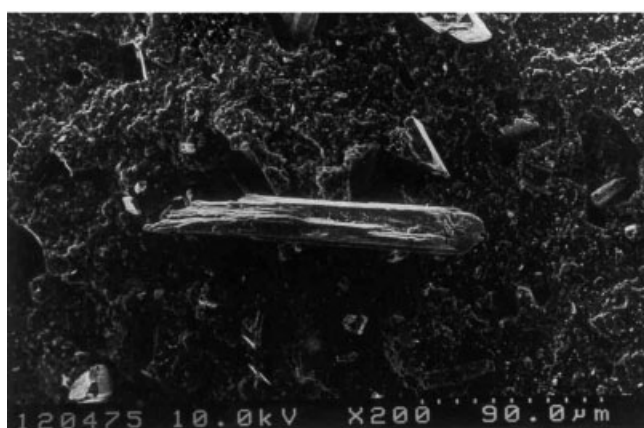
Sample code	Composite composition (wt %)	Tensile properties		
		Maximum load (N)	Tensile strength (MPa)	Elongation at break (%)
Extruded composites				
SR	100.0	40.1 ± 0.6	4.5 ± 0.1	206 ± 29
SR/GF01-10 ATMS	90.0/10.0	38.8 ± 4.3	5.1 ± 0.3	120 ± 37
SR/GF02-5.0 ATMS	95.0/5.0	45.5 ± 5.8	6.0 ± 0.8	176 ± 15
SR/GF02-10 ATMS	90.0/10.0	41.2 ± 0.8	6.3 ± 0.1	147 ± 4.3
SR/GF02-10	90.0/10.0	34.0 ± 1.2	4.5 ± 0.1	159 ± 6.8
SR/WO01-10	90.0/10.0	34.6 ± 0.6	4.6 ± 0.1	138 ± 25
SR/WO01-10 ATMS	90.0/10.0	40.0 ± 2.7	5.2 ± 0.4	123 ± 6.9
SR/WO02-10 APTS	90.0/10.0	37.3 ± 1.2	4.9 ± 0.1	128 ± 6.1
SR/FR-10	90.0/10.0	40.3 ± 3.2	4.6 ± 0.1	150 ± 20
Postcured composites				
SR	100.0	51.4 ± 1.5	4.9 ± 0.7	220 ± 18
SR/GF01-10 ATMS	90.0/10.0	44.8 ± 3.8	6.0 ± 0.5	122 ± 40
SR/GF02-5.0 ATMS	95.0/5.0	53.1 ± 4.1	7.1 ± 0.5	174 ± 22
SR/GF02-10 ATMS	90.0/10.0	42.3 ± 1.0	5.6 ± 1.2	153 ± 15
SR/GF02-10	90.0/10.0	39.1 ± 1.2	5.2 ± 0.1	173 ± 14
SR/WO01-10	90.0/10.0	35.2 ± 1.0	4.9 ± 0.1	142 ± 25
SR/WO01-10 ATMS	90.0/10.0	44.9 ± 1.4	6.0 ± 0.2	148 ± 12
SR/WO02-10 APTS	90.0/10.0	43.2 ± 2.0	5.7 ± 0.3	148 ± 16
SR/FR-10	90.0/10.0	45.2 ± 2.5	4.8 ± 0.3	159 ± 18



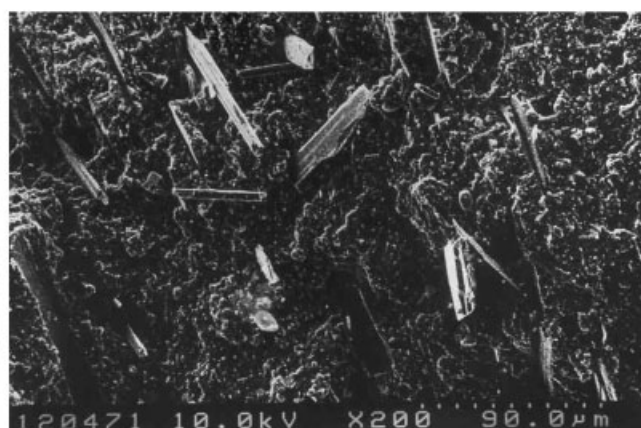
(a) Compression-molded SR/GF02-10 ATMS



(b) Extruded SR/GF02-10 ATMS



(c) Compression-molded WO01-10 ATMS



(d) Extruded WO01-10 ATMS

Figure 5 SEM micrographs of the compression-molded and extruded SR/GF and SR/wollastonite composites.

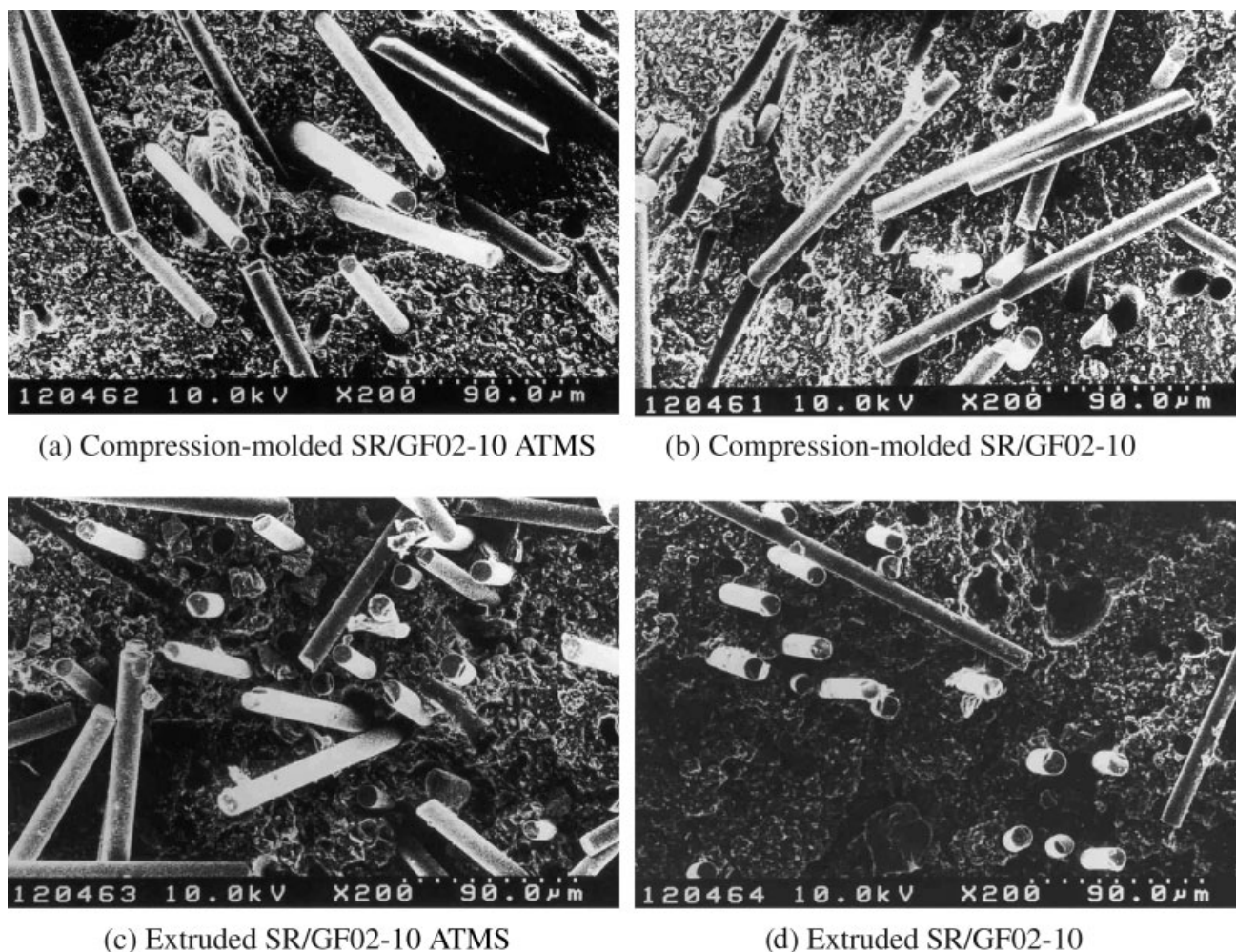


Figure 6 SEM micrographs of the SR/GF01-10ATMS and SR/GF01-10 composite after tensile test.

Figure 6 shows a fractured surface of compression-molded and extruded SR/GF composites after tensile test. In case of silane treated GF containing composite, adhesion with the matrix resin seems to be good through SEM observation as shown in Figure 6(a,c). On the entire fractured surface, broken fiber pieces can be seen abundantly. In the micrographs taken on the surface of the silane untreated GF containing specimens [Fig. 6(b,d)], many vacant holes in the matrix resin give evidence of fiber pull out during the fractured.

Figure 7 reveals optical microphotography of cross-section surfaces of extruded SR/GF, SR/wollastonite and SR/FR composites. SR/GF02-10, SR/WO01-10, and SR/FR-10 composites are covered with small bubbles (circled) that leave a bumpy texture on the surface. During the curing volatile molecules should be produced and this can lead to bubble and void formation depending on the filler. In contrast, silane treated composites did not show conspicuous voids or bubbles.

Thermal degradation of SR/GF and SR/wollastonite composites are shown in Figure 8. The TG traces show a significant shift of the weight loss towards higher temperature for both SR/GF and SR/wollastonite composites, with stabilization 50°C higher than the unfilled SR because inorganic fillers have high thermal stability. The pretreatment of silane on the filler surface resulted in a slight increase in thermal stability. This improvement is likely associated with the interaction increase between SR matrix and filler. However, SR/FR composite having a low compatibility did not increase in thermal stability as compared with SR.

CONCLUSIONS

GF, wollastonite, and FR were compounded with SR and prepared compounds were compression-molded and extruded. Test results for the compression-molded composites showed that with the addition of 10% of GF, tensile strength was increased by 26%

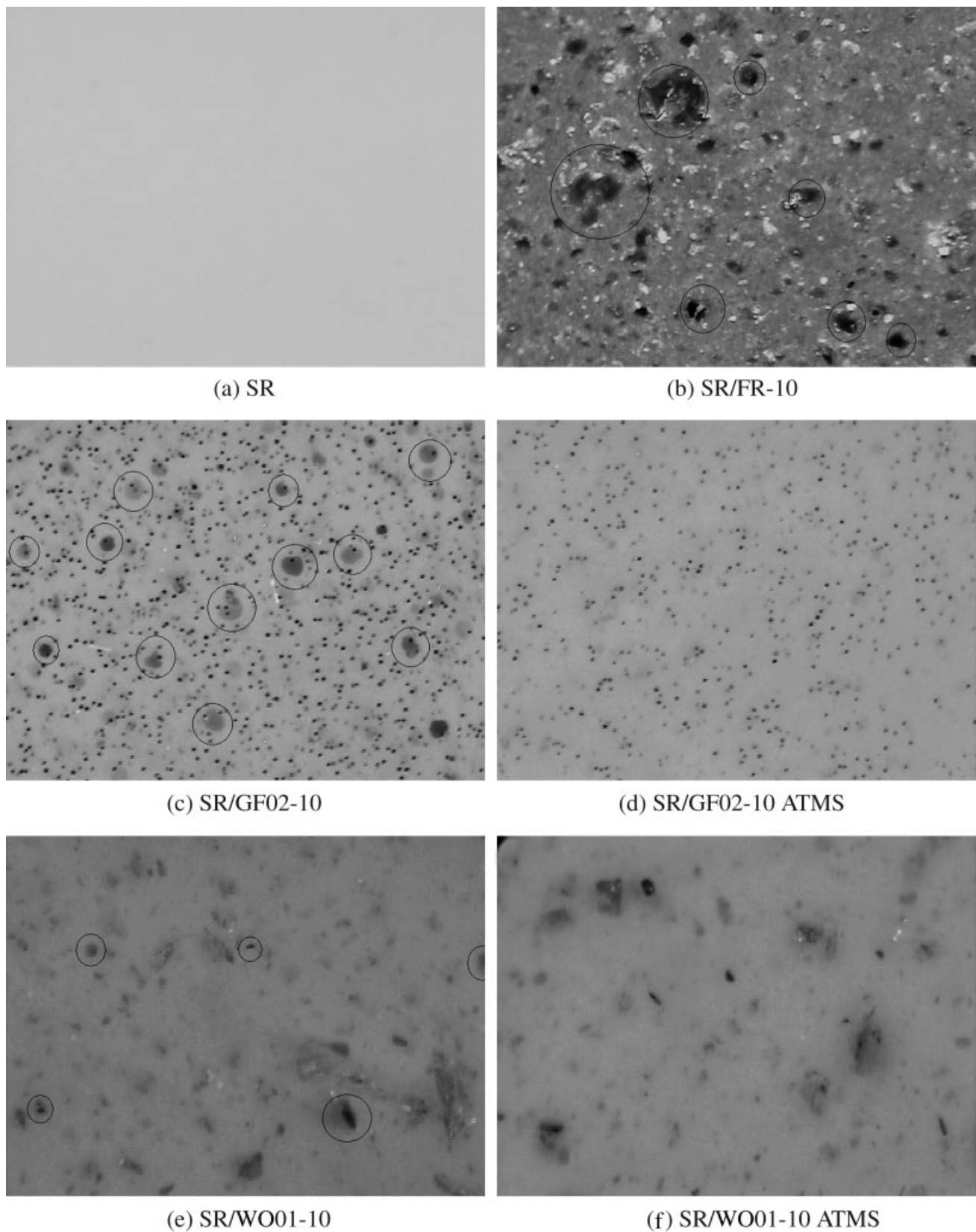


Figure 7 Microphotography ($\times 200$) of the extruded SR/GF, SR/wollastonite and SR/FR composites.

when compared to composite with no filler additions. The results demonstrate the potential value of GF as reinforcement filler to SR.

The silane-treated GF and wollastonite developed higher strength and abrasion resistance. An approximately 10% overall increase in the tensile

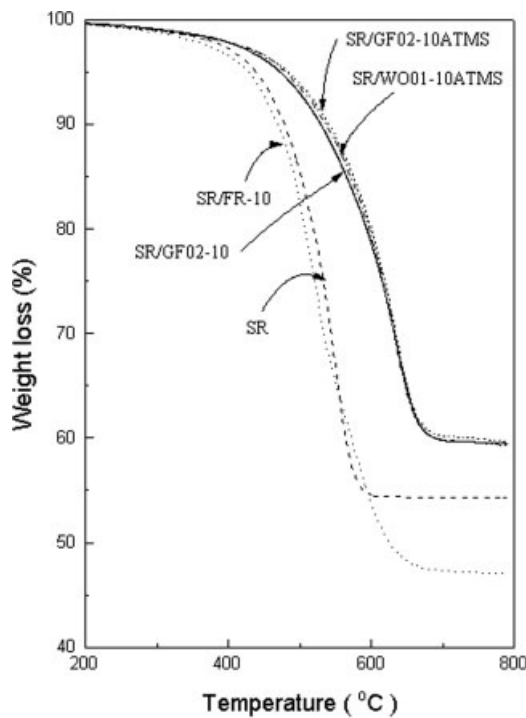


Figure 8 TG curves of the compression-molded SR/GF, SR/wollastonite and SR/FR composites.

strength and tear strength was observed using silane treated fibers. SEM revealed a visible gap between the fiber and matrix and clear regions of fiber pullout in silane untreated samples. In the composites formed with

silane treated fillers, SEM indicated improved fiber wetting through more complete adhesion of the fiber with matrix resin and less occurrence of fiber pullout.

During the extrusion process, silane pretreated method reduced the void formation in matrix resin significantly. This result indicated that silane treatment process improves the mechanical strength and processibility of SR composites in dry conditions.

References

1. Fallahi, D.; Mirzadeh, H.; Khorasani, M. T. *J Appl Polym Sci* 2003, 88, 2522.
2. Kricheldorf, H. R. *Silicon in Polymer Synthesis*; Springer: Berlin, 1996; Chapter 3.
3. Ehsani, M.; Borsi, H.; Gockenbach, E.; Bakhshandeh, G. R.; Morshedian, J. *Adv Polym Technol* 2005, 24, 51.
4. Maiti, S. N.; Lopez, B. H. *J Appl Polym Sci* 1992, 44, 353.
5. Bokobza, L. *Macromol Symp* 2001, 171, 163.
6. Bokobza, L.; Rapoport, O. *J Appl Polym Sci* 2002, 85, 2301.
7. Gupta, N.; Brar, B. S.; Woldesenbet E. *Bull Mater Sci* 2001, 24, 219.
8. Bose, S.; Mahanwar, P. A. *J Minerals Mater Charact Eng* 2004, 3, 23.
9. Anantharaman, M. R.; Malini, K. A.; Sindhu, S.; Mohammed, E. M.; Date, S. K.; Kulkarni, S. D.; Joy, P. A.; Kurian, P. *Bull Mater Sci* 2001, 24, 623.
10. Huang, H.; Tian, M.; Liu, L.; He, Z.; Chen, Z.; Zhang, L. *J Appl Polym Sci* 2006, 99, 3203.
11. Maazouz, A.; Sautereau, H.; Gerard, J. F. *J Appl Polym Sci* 1993, 49, 615.
12. Unal, H.; Findik, F. *J Appl Polym Sci* 2003, 88, 1694.