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Effects of short-fiber shape on tensile properties of reinforced rubber

S. R. Ryu · D. J. Lee

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Abstract The tensile properties under various conditions were investigated to ascertain the optimum conditions to yield the best tensile properties. Fiber aspect ratio (AR: length of fiber/diameter of fiber), diameter ratio (DR: sphere diameter of dumbbell/diameter of fiber), interphase condition and fiber content were all considered as variables which impact the tensile strength, tensile moduli, pull-out force. In general, under good interphase conditions the tensile strength increased when the fiber aspect ratio was more than 20. The short-fiber reinforced SBR with a big end (DR = 3) did not show the dilution effect under interphase conditions when the fiber aspect ratio was more than 20. In case of short-fiber reinforced NR, when the specimen had DR = 3 and AR≥20, the dilution effect only showed up in the no-coated one. The tensile moduli were significantly improved due to the fiber aspect ratio, fiber content and good interphase at the same diameter ratio. The pull-out force increased with the diameter ratio, and keeping the diameter ratio the same, better interphase conditions also resulted in a higher pull-out force. Overall, it was found that the fiber aspect ratio, fiber diameter ratio, and interphase condition all have an important effect on tensile properties.

Introduction

Rubbers reinforced with continuous fibers are well known, but the applications of this composite are limited mainly to tires, belts and hoses. However, complex shape products cannot be easily made with continuous fiber reinforced rubber. On the other hand, the preparation of an intricate engineering component can be accomplished by using short fibers as the reinforcing material for the rubber. Such a process is used in extrusion and transfer molding techniques that are well-known in the rubber industry [1]. The properties of short-fiber reinforced rubber (SFRR) depend on the fiber aspect ratio, fiber content (V_f), fiber dispersion, fiber orientation and fiber–matrix adhesion [1–4]. The primary effects of short-fiber reinforcement on the mechanical properties of rubber include increased modulus, increased strength with good bonding for a high fiber content, decreased elongation at rupture, increased hardness even with relatively low fiber content, and possible improvements in resistance to cuts, tears and punctures. Compared to these properties, the tensile strength (σ_c) of SFRR shows the dilution effect. We define the dilution effect as the phenomenon when at low fiber content, increasing fiber content decreases σ_c [1, 3]. With low fiber content, σ_c was dominated by the rubber and reinforcing fibers that can be acted as material defects due to the fiber detachment from the rubber caused by large differences in their moduli. As a result, σ_c decreased with the fiber content until a critical fiber level was reached. With higher fiber contents, σ_c became the fiber-dominating property and increased with the fiber content. An initial drop of σ_c reaching a characteristic minimum around 10–20 phr was due to the dilution

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S. R. Ryu · D. J. Lee (✉)
School of Mechanical Engineering, Yeungnam University, 214-1, Daedong, Gyoungsan, Gyoungbuk 712-749, Korea
e-mail: djlee@yu.ac.kr

S. R. Ryu
e-mail: srryu@ynu.ac.kr

effect which weakened the reinforced rubber because its fiber content was not sufficient to sustain a significant fraction of the tensile load. We studied the effects of fiber aspect ratio and fiber content on tensile and tear properties and found the optimum fiber aspect ratio to be about 300 depending on the fiber content up to 30 phr [4]. Also, we investigated the effects of interphase conditions on the tensile and fatigue properties of SFRR [5]. To avoid the high stress concentration at the end of fiber that is the source of dilution effects, the dumbbell type of short rod is used. In previous works [6, 7], to improve the fracture toughness and tensile properties of fiber reinforced polyethylene composite, they has been studied the bridging capability of bone shaped short-fiber. However, they did not change the fiber length and shape since they made the PE short fibers using a torch to make a bead at the ends.

In this study, the fiber aspect ratio, fiber diameter ratio and interphase condition was modified to obtain the best tensile properties with no dilution effect using NR and SBR matrix. Also, the pull-out force was measured by the single fiber pull-out test.

Experimental procedure

The natural rubber (NR) and styrene butadiene rubber (SBR) polymers used in this study were SMR CV60 and SBR 1502. We also used carbon black (N550) and other ingredients of commercial grade quality as shown in Table 1. The tensile strength, tensile modulus, elongation and hardness were 12.7 MPa, 4.9 MPa, 360% and 56 Hs for NR, and 7.7 MPa, 5.1 MPa, 220% and 58 Hs for SBR, respectively. The dumbbell shaped short-fiber (DSF) was manufactured with TECHNYL® C216 V15 (Rhodia Polyamide Co., Ltd.) by the injection machine (LG. IDE 75EN). The body diameter of dumbbell shaped short fiber is 0.7 mm, and the end sphere is 1.05 (diameter ratio = 1.5) and 2.1 (diameter ratio = 3), respectively, as shown in Fig. 1. The tensile strength, tensile modulus, elongation and density were 120 MPa, 6,100 MPa, 4% and 1.22 g/cm^3. Table 2 shows the five kinds of reinforcing dumbbell shaped short-fiber (“**A**”–”**E**” type). The volume fraction (V_f) of short-fiber was 5 and 10%. We treated the fiber surface with a bonding agent (BA, Chemlok 402® of the UNIROYAL Co.) and a rubber solution by a dipping method at room temperature. The rubber solution (RS) means a solution of interphase rubber by the toluene. The abbreviation **NC** means no-coating; **402** indicates BA coated short-fiber; **RS** indicates BA and RS coated short-fiber as shown in Fig. 2. The hardness of interphase rubber was 85 Hs for NR and 87 Hs for SBR, respectively. To increase the interphase rubber hardness compared to matrix rubber, we just changed the carbon black content (90 phr) as shown in Table 1. The mixes were prepared in a two-roll laboratory model of a 14” open mixing mill at a nip of 1.5 mm. A square pre-formed cutting from the uncured sheet was marked in the direction of the mill grain and vulcanized at 170 °C in a hydraulic press heated platen at 1.5 times its respective optimum cure time (tc_{90}), based on data obtained from a rheometer.

Table 1 Formulation of rubber matrix

	NR		SBR	
	Ingredients	phr	Ingredients	phr
Polymer	SMR CV60	100	SBR 1502	100
Zinc oxide	←	5	←	5
Stearic acid	←	1	←	1
Carbon black	N550	28	←	28
Dispersive agent	WB16	2	←	2
Antioxidants	3P	1	←	1
	BLE	1	←	1
	Sunnoc	1	←	1
Accelerators	TBTD	0.6	←	0.6
	NOBS	1.4	←	1.4
Curing agent	Sulfur	2.5	←	2.5
Reinforcing fiber	C216 V15	a	←	a
Total	143.5 + a			

phr, parts per hundred parts of rubber

The tensile properties were measured using an Autograph (Model AG-5000E) of the Shimadzu

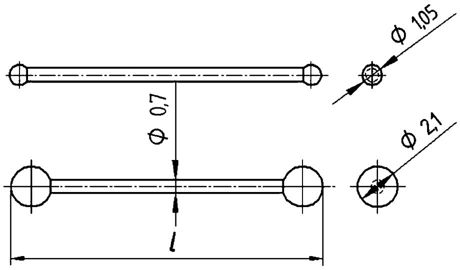

Fig. 1 Schematics of dumbbell short-fiber

Table 2 Composition of dumbbell shaped short-fiber

Type	Fiber length, *l* (mm)	Fiber end sphere, *S* (mm)
A	14 (aspect ratio = 20)	1.05 (diameter ratio = 1.5)
B	7 (aspect ratio = 10)	2.1 (diameter ratio = 3)
C	14 (aspect ratio = 20)	2.1 (diameter ratio = 3)
D	28 (aspect ratio = 40)	2.1 (diameter ratio = 3)
E	42 (aspect ratio = 60)	2.1 (diameter ratio = 3)

*Fiber diameter: ∅ 0.7 mm

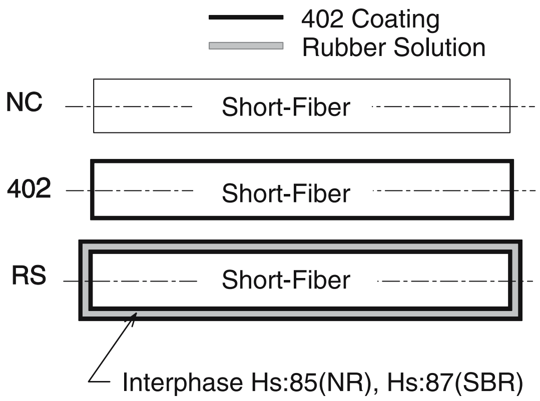

Fig. 2 Schematics of coated cylindrical short-fiber

tensile machine with a testing speed of 50 mm/min. The geometry of the specimen was Dumbbell type #1 of the Korean Standard Material 6518 as shown in Fig. 3. The pull-out test was carried out using the same tensile machine to investigate the effects of diameter ratio. The end shape of fiber was classified a standard cylindrical fiber, cylindrical fiber with a small end sphere (diameter ratio = 1.5) and cylindrical fiber with a big end sphere (diameter ratio = 3) as shown in Fig. 4. The testing speed was 1.5 mm/min and specimen geometry shown in Fig. 5. Typically, five specimens were used for a single evaluation at room temperature.

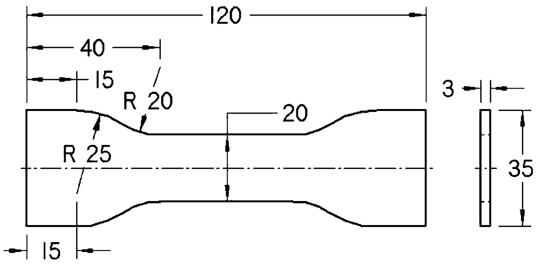

Fig. 3 Specimen geometry for the tensile test

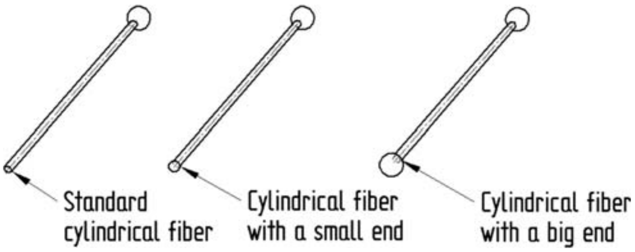

Fig. 4 Schematics of single fiber for the pull-out test

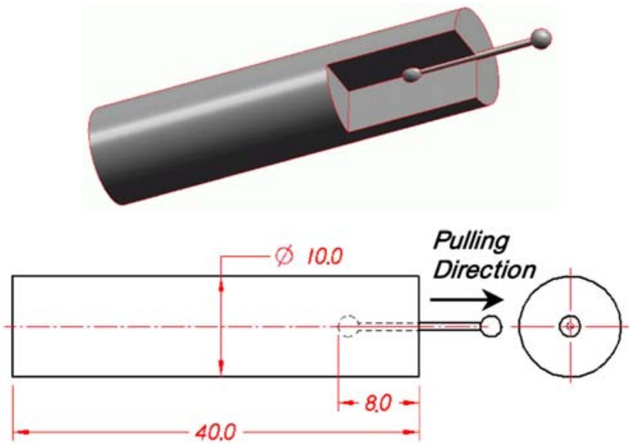

Fig. 5 Specimen geometry of the pull-out test

Results and discussion

Pull-out force

To investigate the fiber end factor, the pull-out force is measured [8, 9]. Figure 5 shows the specimen geometry and pulling direction. Figure 6 shows the typical force–displacement curve of the cylindrical fiber with a big end inserted in SBR. The maximum pull-out force means the peak in this figure. The maximum pull-out force is compared as functions of fiber diameter ratio and interphase condition as shown in Fig. 7. The maximum pull-out force of reinforced NR and SBR shows the similar trend and increases with diameter ratio for good interphase condition. Especially, the pull-out force with diameter ratio = 3 and **RS** coating is significantly increased when it is compared with the case of standard cylindrical fiber and **NC**. Also, the

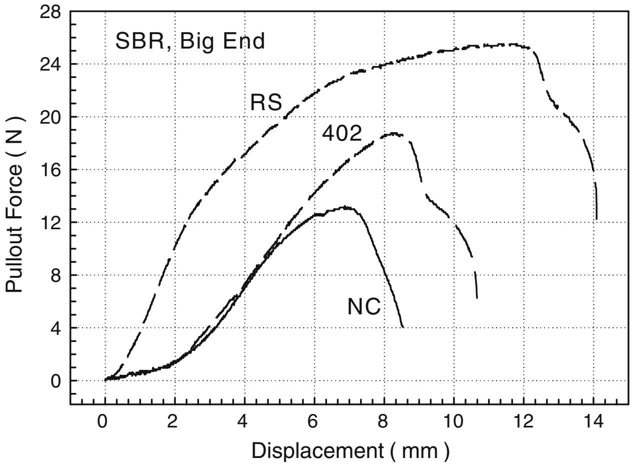

Fig. 6 Force–displacement curve of the cylindrical fiber with a big end

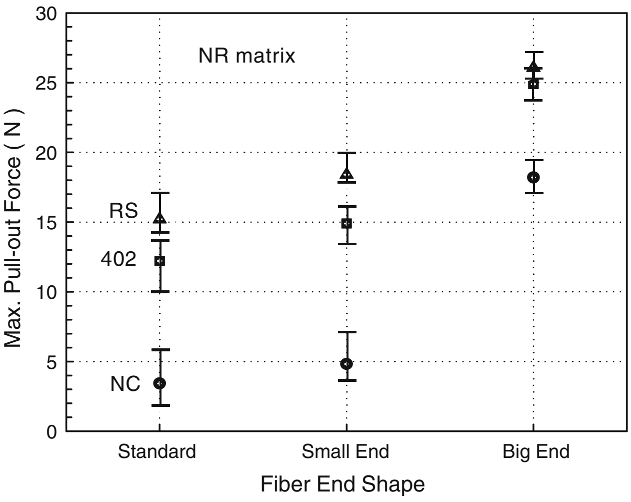

Fig. 7 Effects of interphase and diameter ratio on pull-out force

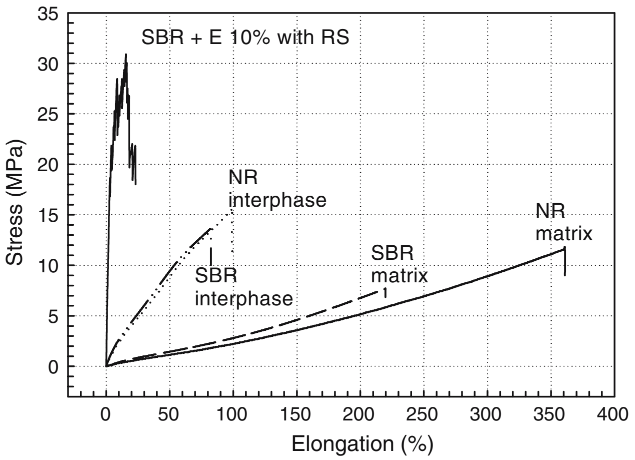

Fig. 8 Stress–elongation curves of the matrix, interphase rubber and **E** type reinforced SBR

maximum pull-out force of standard cylindrical fiber showed a big difference depending on the interphase condition. It was found that the pull-out force of the specimen with increasing the diameter ratio, it is less sensitive to different condition as shown in Fig. 7. Therefore, it is believed that there is a chance to prevent the dilution effect of short-fiber reinforced rubber under the high diameter ratio and good interphase. In general, there are big differences depending on the interphase condition and fiber end shape in the sequence of failure. In case of the standard cylindrical fiber, it is very sensitive to the pull-out force under various interphase conditions. If there was no surface treatment, the fiber showed easy pull-out in short time. In case of the cylindrical fiber with a big end, it seems to be less sensitive to the pull-out force under various interphase conditions. Even if there was no surface treatment, the fiber did not pull-out easily because of mechanical bonding. To study the bridging capability of bone shaped short-fiber, Beyerlein et al. [6] examined the effects of increasing the size of the enlarged fiber end on the pull-out characteristics with short-fiber reinforced composites and identified the sequence of failure mechanisms involved in the pull-out process.

Tensile properties

Figure 8 shows the stress–elongation curve of the matrix, interphase rubber and **E** type reinforced SBR. Our results for the ultimate tensile strength are summarized in Figs. 9–14. A dilution effect was found to be different in non-strain induced crystallizing rubbers (SBR, Nitrile Butadiene Rubber, etc.,) and in

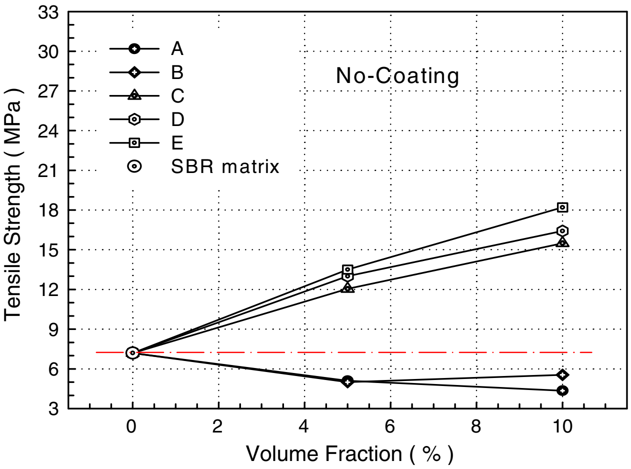

Fig. 9 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength without coating in SBR matrix

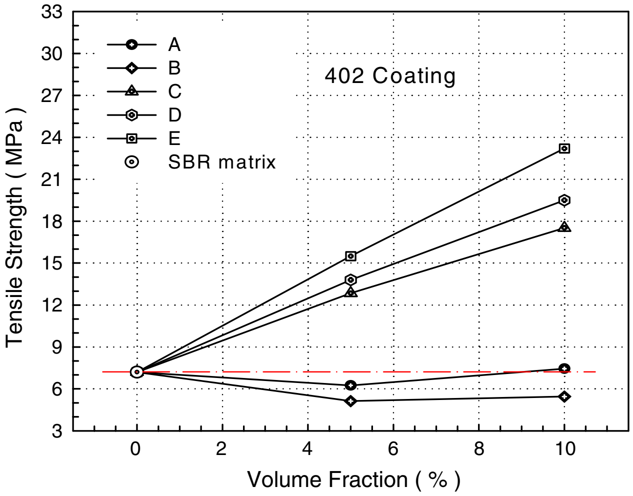

Fig. 10 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength with **402** coating in SBR matrix

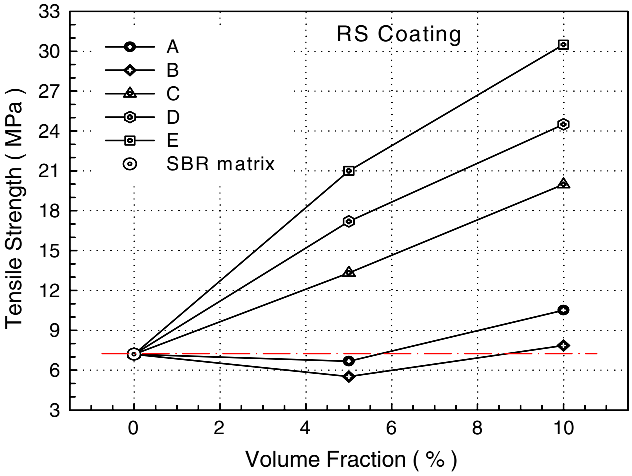

Fig. 11 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength with **RS** coating in SBR matrix

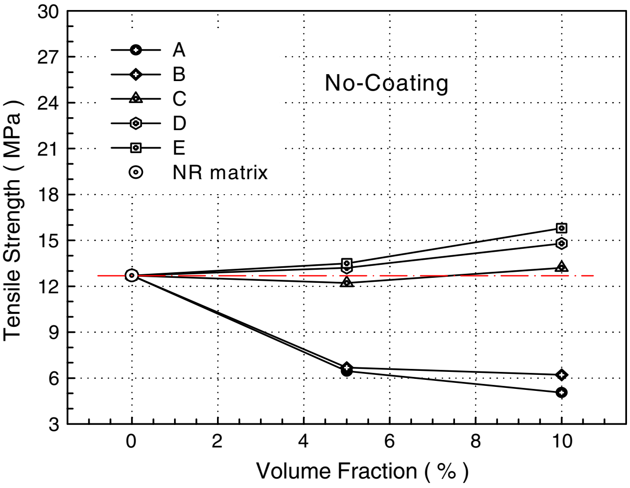

Fig. 12 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength without coating in NR matrix

other cases (Chloroprene Rubber, NR, etc.,). The former rubbers did not show a dilution effect. The latter rubbers exhibited the classical drop due to a dilution effect until the critical fiber content was reached. The presence of carbon black and fibers aids the stress dissipation [1]. As a result, the short-fiber reinforced rubber has experienced the dilution effect. In this study, we used the strain-induced crystallizing NR and non-strain induced crystallizing SBR with short fibers and carbon black as the reinforcing materials. However, the dilution effect can't be seen in the **C**–**E** types reinforced SBR and NR except for the **NC** of **C** type. It seems that the cases with diameter ratio = 3 and aspect ratio = 20 minimum are difficult to pull-out when compared with diameter ratio = 1.5,

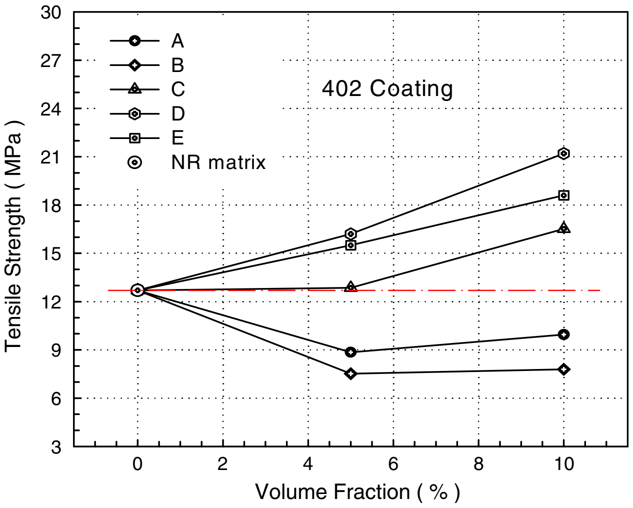

Fig. 13 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength with **402** coating in NR matrix

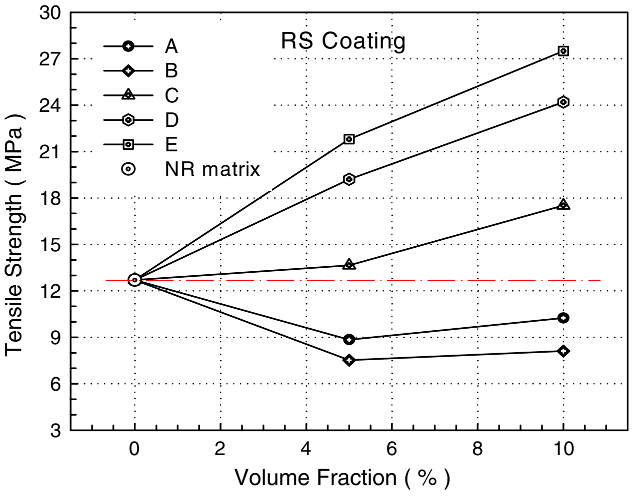

Fig. 14 Effects of fiber aspect ratio, diameter ratio and V_f on tensile strength with **RS** coating in NR matrix

aspect ratio = 10. The better interphase condition showed the higher the tensile strength (σ_c) at the same diameter ratio. The σ_c of **RS** coated SBR and NR increased 4.2 times and 2.1 times, respectively, when compared to the rubber matrix. In comparison between **A** and **B** types, the σ_c of reinforced rubber with **402** or **RS** was more sensitive to differences in the fiber aspect ratio for **A** type. However, the σ_c of reinforced rubber without coating was mainly affected by the diameter ratio for **B** type. Since the σ_c of NR is higher than that of SBR, the dilution effects of the **A** or **B** type reinforced NR were higher compared to the **A** or **B** type reinforced SBR.

The tensile modulus was calculated from the initial slope of the stress–elongation (0–5%) curve. The tensile modulus was 4.9 Mpa for NR, and 5.1 Mpa for SBR, respectively. The tensile moduli (E_c) of the **B**–**E** types reinforced rubbers were significantly improved when compared to the rubber matrix (E_{matrix}) as shown in Figs. 15–17. These Figures are expressed tensile modulus ratio (E_c/E_{matrix}) vs. fiber aspect ratio for each interphase condition. It was found that the specimen with higher V_f, higher aspect ratio and good interphase showed higher tensile modulus. The tensile modulus (E_c) of the NR was somewhat higher when compared to the SBR with same interphase condition because of strain induced crystallization behavior. The **RS** coated NR and SBR is increased 33 times and 31 times, respectively, for tensile modulus at $V_f = 10\%$, when compared to the rubber matrix.

Figure 18 shows the difference between standard cylindrical fiber (a) and dumbbell shaped short-fiber (b). As the effects of fiber end geometry in tensile properties, it is believed that the fiber end geometry plays an important role in fiber/matrix stress transfer mechanisms. The standard cylindrical fiber can pull free of the matrix if the fibers bond weakly with the surrounding matrix. On the other hand, if the fibers are bonded strongly with the matrix, they can snap under high stresses and generate a crack in the matrix. The dumbbell shaped short-fiber connects mechanically with the matrix predominantly at their ends. When they have a weak interface, and so do not experience the extreme stress but remain anchored at their ends, they still help carry the load felt by the composite [6, 10]. Based on the previous works [11], we found that the fiber axial stress of the cylindrical fiber with a big end sphere increased 1.15 times compared with standard cylindrical fiber and the interphase shear stress of the cylindrical fiber with a big end sphere showed 83% compared with standard cylindrical fiber. Therefore, it can be assumed that the fiber pull-out is more difficult and possibly it prevents the interface fracture by stress concentration when acted on the external load.

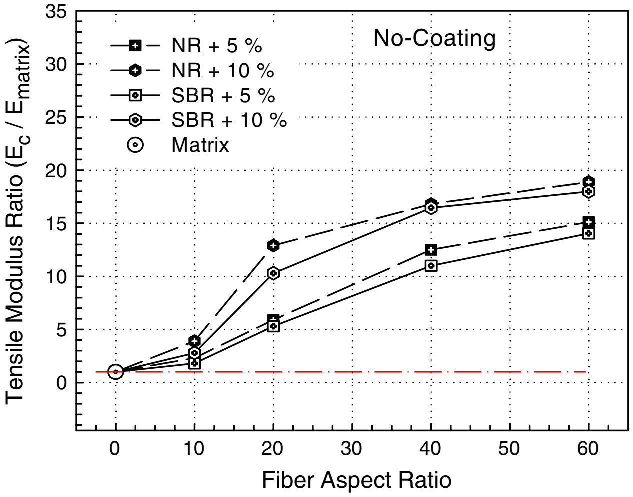

Fig. 15 Effects of fiber aspect ratio and V_f on tensile modulus ratio without coating

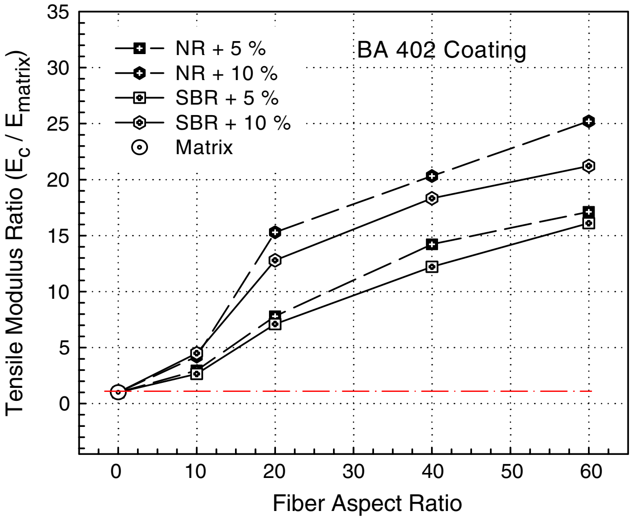

Fig. 16 Effects of fiber aspect ratio and V_f on tensile modulus ratio with **402** coating

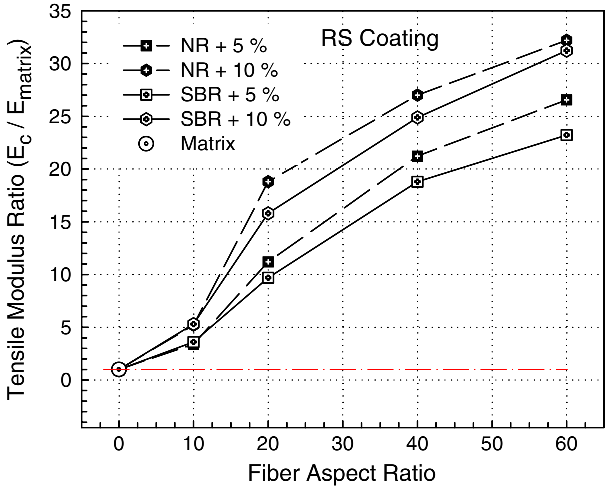

Fig. 17 Effects of fiber aspect ratio and V_f on tensile modulus ratio with **RS** coating

From these results, the dumbbell shaped short-fiber reinforced rubber with DR = 3 and AR ≥ 20 has outperformed tensile properties when compared to the rubber matrix. Especially, it is possible to prevent the dilution effect that was a shortcoming of short-fiber reinforced rubber.

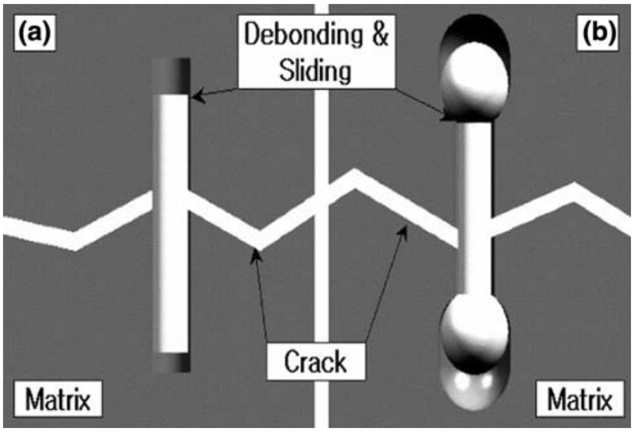

Fig. 18 Comparison between standard cylindrical fiber (**a**) and dumbbell shaped short-fiber (**b**)

Conclusions

In this study, the tensile properties of short-fiber reinforced rubber have been investigated as functions of fiber aspect ratio, diameter ratio, interphase condition and volume fraction. From this study, we found the following conclusions.

1. The tensile moduli were significantly improved up to 32 times by optimizing the fiber aspect ratio, diameter ratio and volume fraction at the same interphase condition.
2. The pull-out force increased up to two times with the diameter ratio. The better interphase condition showed the higher the pull-out force at the same diameter ratio.
3. The short-fiber reinforced SBR with fiber shape of DR = 3 and AR ≥ 20 did not show the dilution effect for all interphase conditions. And the short-fiber reinforced NR with fiber shape of DR = 3 and AR ≥ 20 did not show the dilution effect except for the no-coating of **C** type.
4. In comparing the tensile strength between **A** and **B** types, the reinforced rubber with **402** or **RS** was more sensitive depending on the aspect ratio. The specimen without coating came into effect due to the diameter ratio. With good interphase condition and same diameter ratio, the higher the aspect ratio is, the higher the tensile strength of composite is obtained.
5. From these results, it is possible to prevent the dilution effect of short fiber reinforced rubber when the short-fibers with DR = 3 and AR ≥ 20 and the surface treatment are used. To achieve the superior strength, it is necessary to find the optimum fiber end shape and its size depending on the fiber content.

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