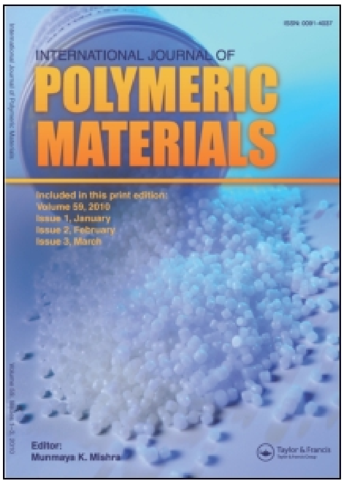

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EFFECTS OF INTERPHASE CONDITIONS ON THE TENSILE AND FATIGUE PROPERTIES OF SHORT-FIBER REINFORCED RUBBER

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The effects of the amount of nylon-66 short-fiber and its bonding to a chloroprene rubber were studied. The following results were obtained: (a) The tensile strength of short-fiber reinforced rubber (SFRR) exhibits a dilution effect in each interphase. It was found that the interphase conditions have an important effect on the dilution ratio and the critical fiber content. The specimen with double coatings of the bonding agent and a rubber solution, becomes the best of 5 interphase models. Both the yield strength and tensile moduli significantly improve with fiber content. (b) The spring constant (SC) of unreinforced rubber decreases after the fatigue test, however, the SC of all reinforced rubbers increases. The change in SC of reinforced rubber decreases with fiber content. The better the interphase condition, the smaller the change of the SC. (c) The temperature of rubber increases about 2.6 fold after the fatigue test. The reinforced rubbers show a 1.4 to 2.2 fold increase in temperature. The temperature changes during the fatigue test of the reinforced rubbers decrease with increasing fiber content, as well as with improved interphase bonding.

Keywords: SFRR, interphase, dilution effect, fiber aspect ratio, fiber content, spring constant, internal temperature

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1. INTRODUCTION

The reinforcement of rubber with fibers creates a type of rubber with high strength and stiffness. Composites of this type can be a useful engineering material. Rubbers reinforced with continuous fibers are well known, but this composite is limited mainly to applications in tires, belts, and hoses. The manufacture of complex shaped products cannot be easily accomplished with continuous fiber reinforced rubber. On the other hand, the preparation of a complex engineering component can be accomplished by using short fibers as the reinforcing medium for the rubber. Such an easy process is used in extrusion and transfer molding techniques that are well-known in the rubber industry [1]. Composites, consisting of high-strength reinforcing fibers embedded in a variety of matrix materials, have found widespread use and acceptance in recent years. The properties and usage of thermoplastic composites reinforced with discontinuous fibers have been expanded in the past several years. This same extension of properties and uses can be developed in the rubber industry by using short-fiber reinforced rubber (SFRR). The primary effects of short-fiber reinforcement on the mechanical properties of rubbers include increased modulus, increased strength with good bonding with 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. The properties of short-fiber reinforced rubbers depend on the fiber aspect ratio (AR: length/diadiameter), fiber content, fiber dispersion, fiber orientation, and fiber-matrix adhesion [1–3]. We studied the effects of the 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 [4].

In this study, the interphase condition was modified to obtain the best mechanical properties with a fiber aspect ratio of 265. Therefore, the effects of multiple coatings with various combinations of rubber and bonding agent were investigated by measuring the tensile and fatigue properties of nylon short-fiber reinforced chloroprene rubber.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The Chloroprene rubber used in this study was S-40V (ML_{1+4} at 100°C; 485) made by DENKA, Japan. We also used carbon black (FEF), nylon 66 fiber as reinforcing material and other ingredients of commercial grade quality. The formulation and mechanical properties of the test compound, which were used to check the effect of an interphase condition, are given in Table 1. The short-fiber reinforced rubbers were made with fiber aspect ratio of AR = 265 and fiber contents of 10, 20, and 30 phr supplied by KABOOL LTD, Korea. We treated the fiber surface with a bonding agent (BA, Chemlok 402 of the UNIROYAL Co.) and a rubber solution (RS) by the dipping method. A schematic representation of the coated short-fiber surface ("A" ~ "E") is shown in Figure 1. Interphase model "A" is the case of BA coated short-fiber; interphase model "B" is the case of BA coated twice and RS coated; interphase model "C" is the case of BA coated three times and RS coated twice; and interphase model "D" is the case of only RS coated. Interphase model "E" is the same as Interphase model "C", however we controlled the interphase hardness by the carbon black (FEF) content, as shown in Table 1. In general, the mechanical properties of the rubber, *i.e.*, hardness, tensile strength, tensile modulus and wear increased with the carbon black content. Samples of the reinforced rubber were fabricated according to ASTM D3182 and D3190. The mixes were prepared in a two-roll laboratory model of a 14″ open mixing mill at a nip of 1.5 mm. The mixing time and number of passes were maintained the same in all cases. The orientation of the fiber in the rolling direction was achieved by a repeated passing of the uncured compound through a controlled nip. 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 of its respective optimum cure time (tc_{90}), based on data obtained from a rheometer.

2.2. Testing Method

The tensile properties were measured using an Autograph (Model AG-5000E) of the Shimadzu tensile machine with a testing speed of 50 mm/min. The geometry of the specimen (thickness = 2 mm) was Dumbbell type #3 of the Korean Standard Material 6518. The fatigue properties of the SFRR were also investigated as function of the interphase condition and the fiber content. Figure 2 shows a schematic of the fatigue testing device. The specimen geometry was 50 mm in diameter and 60 mm in height. The fatigue tests were conducted using an Instron 8516 testing machine. The load control was used with a sinusoidal waveform at a frequency of 5 Hz. The mean load was $-180\ kg_f$ and the load amplitude was $120\ kg_f$. The number of cycles was one million. The measurement of the spring constant (SC) and the specimen size were carried out within 30 minutes before and after the

TABLE 1 Formulation of the Reinforced Rubber and the Mechanical Properties of the Rubber Matrix and Short-Fiber

Ingredients	Matrix (phr*)	2nd Interphase (phr*)	1st Interphase (phr*)		Matrix	2nd Interphase	1st Interphase	Short-fiber
Polymer, S40-V	100			Tensil strength (MPa)	19.65	22.23	18.06	600
Stearic acid	1			Tensile modulus (MPa)	3.66	11.58	22.20	2.0(Gpa)
FEF	24	45	60					
DOP	10			Elong. (%)	454	240	121	30
MgO	4			Hs (JIS A)	55	72	82	
3P	1.5				Fiber AR →			265 const 10, 20, 30 Type A–E of Figure 1
Sunnoc	2				Fiber Content (phr) →			
MB	1				Fiber Surface Treatment →			
ZnO	5							
TS	1							
NA22	1				Characteristic factors			Interphase, Fiber Content
Sulfur	0.3							
Short-fiber	$+\alpha$							
SUM.	$150.8+\alpha$							ϕ15 µm

phr*; Parts per hundred grams of rubber.

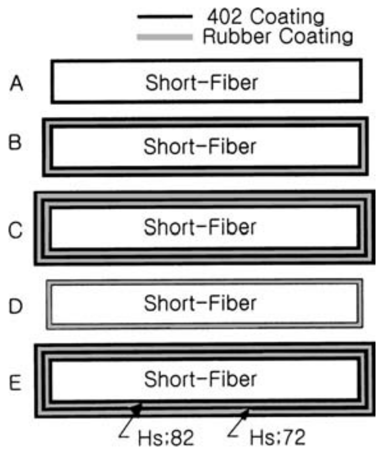


FIGURE 1 The schematics of the coated short-fiber surface.

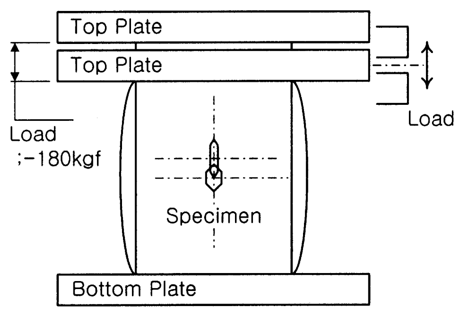


FIGURE 2 The schematics of the fatigue testing device.

fatigue test, according to Korean Standard Material 6675. Also, we checked the surface crack of the specimen after the tests. To measure the internal temperature of the specimen, a thermocouple (Φ5 mm) was used as shown in Figure 3. The AUTONICS Co. T3SI Model (range: $0.0 \sim 99.9^{\circ}C$) was used as an indicator of the internal temperature. Typically, five specimens were used for a single evaluation at room temperature.

3. RESULTS AND DISCUSSION

3.1. Tensile Properties

Figure 4 shows the stress-elongation curves of the rubber and the SFRR with the interphase model “B”. The elongation of the SFRR

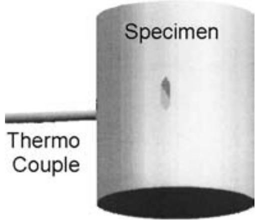


FIGURE 3 The schematics of the temperature measuring device.

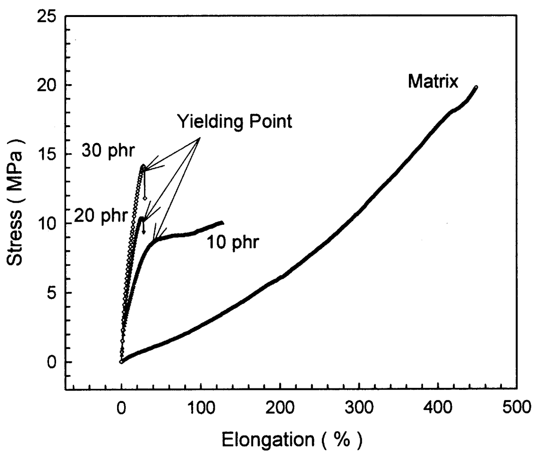


FIGURE 4 Stress-elongation curves of reinforced rubber (B) as a function of fiber content.

rapidly decreased, and the stress in the low strain region increased significantly when compared to that of the matrix. In the case of very high fiber content, the stress-elongation curve exhibited nearly linear behavior. We defined the yield point as the ending point of the elastic region. In Figure 5, the yield strength increased with increasing fiber content, and the better interphase conditions showed a higher yield strength with the same fiber content. At a low fiber content (less than 10 phr), the SFRR kept supporting the external load by the rubber matrix though it passed the yield point as an indication that the rubber dominated the SFRR. At a higher fiber content (more than 20 phr), the SFRR displayed fiber-dominated behavior that failed soon after it passed the yield point. These behaviors show the different trends according to various interphase conditions. The good

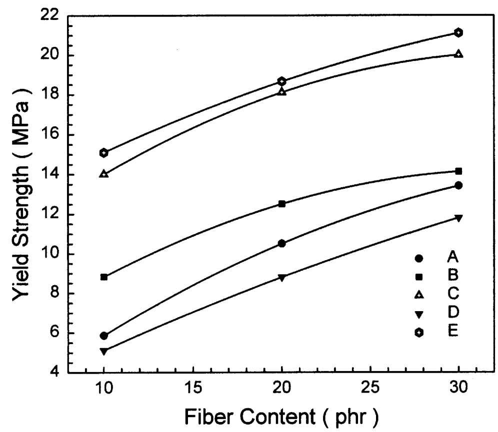


FIGURE 5 Effects of interphase and fiber content on yield strength.

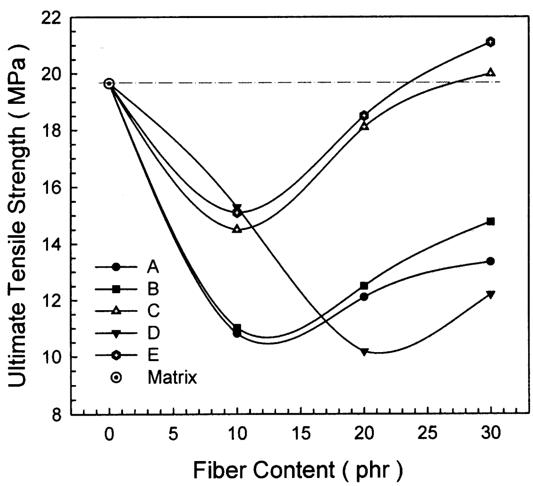


FIGURE 6 The effects of interphase and fiber content on ultimate tensile strength.

interphase condition (models "E" and "C") showed fiber-dominated behavior when fiber content was more than 10 phr and the bad interphase condition (model "D") showed fiber-dominated behavior when the fiber content was more than 30 phr.

Our results for the ultimate tensile strength (σ_c) are summarized in Figure 6. With low fiber content, σ_c was dominated by the rubber and reinforcing fibers that acted as material defects due to significant differences in their moduli. As a result, σ_c decreased with the fiber content until a critical fiber level was reached. At higher fiber contents, σ_c became the fiber-dominating property and increased with the fiber content [1, 5]. An initial drop of σ_c reaching a characteristic minimum around $10 \sim 20$ phr was due to the dilution effect of the fibers, which weakened the rubber because its fiber content was not sufficient enough to sustain a significant fraction of the tensile load. The critical fiber content level, at which the rubber strength recovered, varied directly with the interphase conditions. In the absence of interfacial bonding, it never recovered its strength [3]. The better interphase condition showed a lower critical fiber content and dilution ratio (σ_c/σ_{matrix}). The dilution ratio of interphase models "E", "C", "B", "A", and "D" was 0.77, 0.74, 0.54, 0.53 and 0.51, respectively. We believe that the case of the good interphase condition lowered the stress concentration, when compared to the case of the poor fiber/matrix interface condition. The tensile modulus (Young's modulus) was calculated from the initial slope of the stress-elongation curve. The modulus ratio (E_{fiber}/E_{matrix}) was 546, the tensile moduli (E_c) of the reinforced rubbers were significantly improved, when compared to the virgin rubber (3.66 MPa). Tsai and Pagano [6, 7] showed that the modulus for randomly oriented short-fiber polymer composites could be predicted approximately as

$$E_C = (3/8)E_L + (5/8)E_T \tag{1}$$

The Halpin-Tsai equations for the longitudinal (E_L) and transverse (E_T) moduli of the aligned short-fiber composites can be written as

$$\frac{E_L}{E_m} = \frac{1 + 2(L/d)\eta_L V_f}{1 - \eta_L V_f}, \quad \frac{E_T}{E_m} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \tag{2}$$

Where

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(L/d)}, \quad \eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2}$$

Where E denotes the modulus, V is the volume fraction, and the subscripts c, m and f denote composite, matrix and fiber, respectively.

Figure 7 shows a similar trend between the predictive model and experimental data. The tensile modulus increases with the fiber

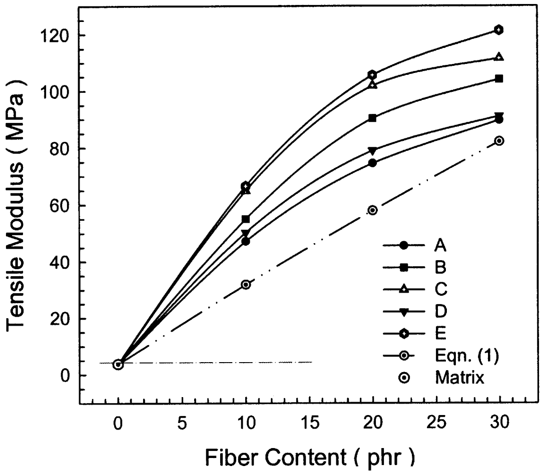


FIGURE 7 The effects of interphase and fiber content on tensile modulus.

content in each interphase and shows the highest level in the case of hardness controlled double coatings as model "E".

3.2. Fatigue Properties

The SC (spring constant) was measured in a static load between 150 kg_f and 200 kg_f. Figure 8 shows the SC before the fatigue test,

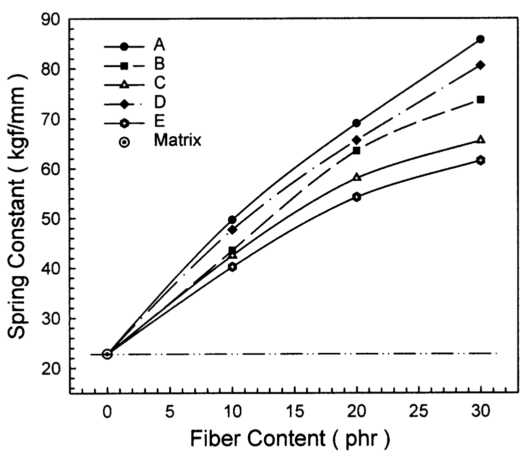


FIGURE 8 The effects of interphase and fiber content on the spring constant (SC).

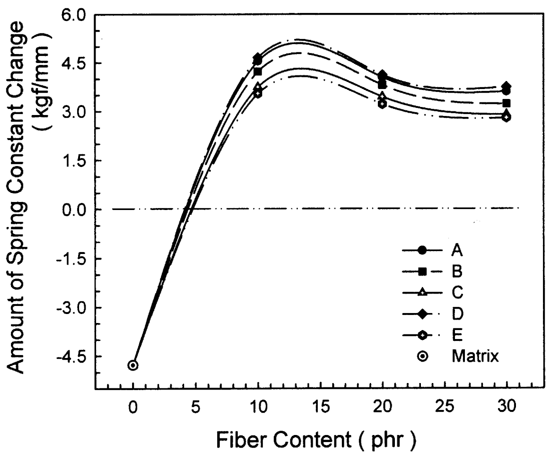


FIGURE 9 The effects of interphase and fiber content on the spring constant change after the fatigue test.

and Figure 9 shows the amount of SC changes after the fatigue test. The SC of the SFRR before the test was significantly improved, when compared to the virgin rubber (22.5 MPa). The better interphase conditions showed a lower SC with the same fiber content. We surmised that the case of model "A" included the greatest fiber volume fraction because of the specific gravity difference (rubber: 1.3494, 1st interphase: 1.3703, 2nd intherphase: 1.3984 and fiber: 1.15) when put into the same short-fiber content. After million cyclic loadings, the SC of the rubber decreased about 21% (4.78 kg_f/mm), and those of the reinforced rubber increased in the range of $4.5 \sim 10\%$. With the same fiber content, the better interphase conditions exhibited lower SC changes, though at a higher testing amplitude. Because of the strong interphase between the rubber and the fiber, the sample was difficult to deform during the test and recovered quickly after the test. Also, we measured the diameter change and the height change before and after the fatigue loading by the digital caliper. The diameter changes and height changes were similar in both the virgin rubber and the reinforced rubber. The changing rate of the rubber was about 7.5%, and those of the reinforced rubber were $3.5 \sim 1.5\%$.

The internal temperature of the specimen was measured up to a certain number of repeating cycles where temperature remained constant. The heat generation of the rubber reflects the amount of internal friction causes by the external load. It has an important effect on fatigue life [8, 9]. Figure 10 shows the temperature change as compared to the room temperature before the test. The case of the rubber increased about 2.6 times in temperature. However, the rate of temperature increment for the reinforced rubber decreased with the fiber content. It is noted that with the same fiber content there were some differences according to the interphase condition. The better interphase condition showed a lower change of temperature. It was thought that with the repeat of cycles model "A" increased the internal friction because of a bad interphase although the amplitude of the test was small for the high SC. With increasing fiber content, the temperature changes were 1.9 ~ 2.2 times at 10 phr, 1.5 ~ 1.9 times at 20 phr and 1.4 ~ 1.6 times at 30 phr, respectively. Figures 11–13 show the relationship between the repeating cycles and the varying temperatures based on the respective fiber content.

Figure 14 shows a half model of the specimen. Compressive stress was concentrated in regions (a) and (b) after repeated loading. After the fatigue test, we found that the rubber initiated a crack about 1.35 mm in region (a) and the surface crack at region (b) is shown in Figure 15. On the contrary, the reinforced rubbers did not show cracks anywhere else. Figure 16 shows a photograph of model "C (10 phr)" after the test.

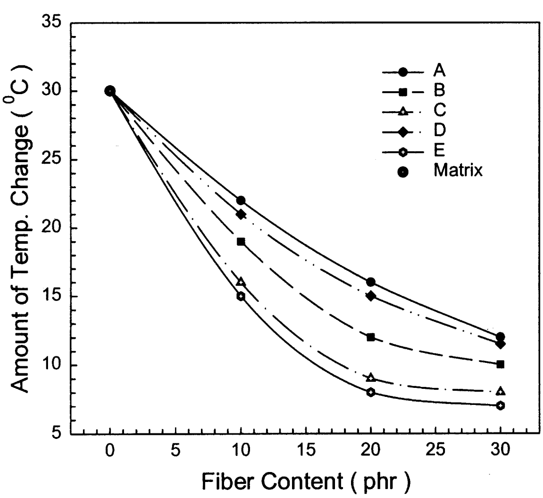


FIGURE 10 The effects of interphase and fiber content on temperature change after the test.

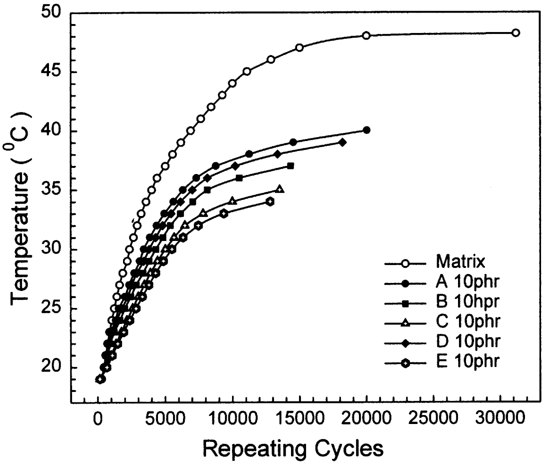


FIGURE 11 The effects of interphase on temperature with a fiber content of 10 phr.

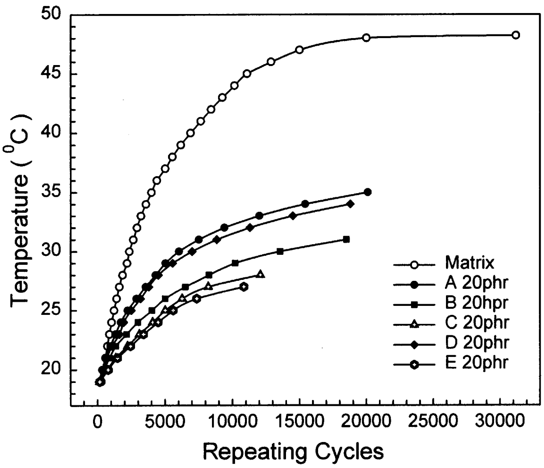


FIGURE 12 The effects of interphase on temperature with a fiber content of 20 phr.

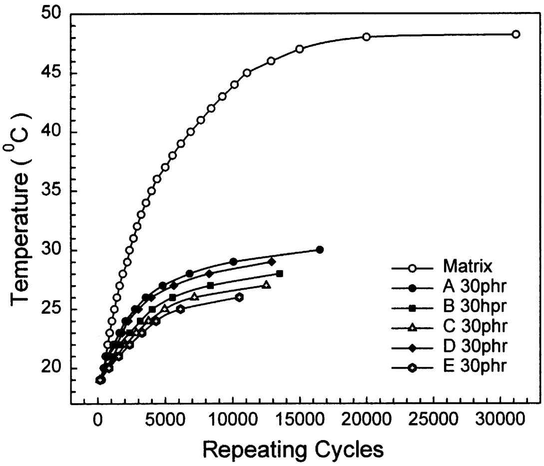


FIGURE 13 The effects of interphase on temperature with a fiber content of 30 phr.

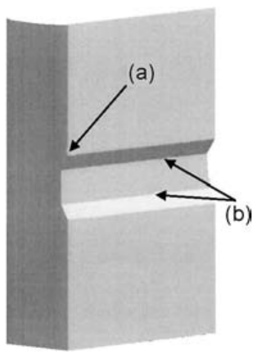
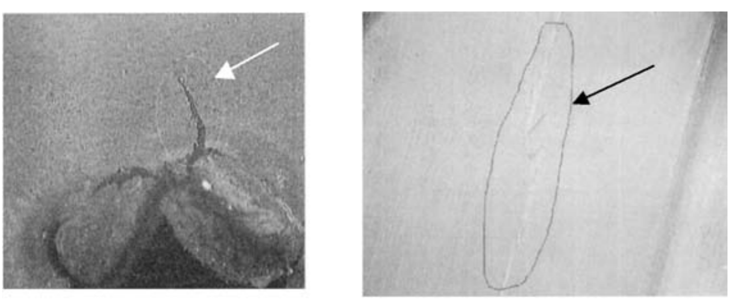


FIGURE 14 A half solid model of the specimen.



Region (a) Region (b)

FIGURE 15 Photograph of the matrix after the fatigue test showing the cracked region.

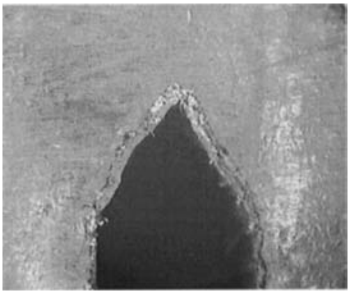


FIGURE 16 Region (a) photograph of reinforced rubber "C" after the fatigue test without a crack.

4. CONCLUSION

From this study, the following conclusions can be drawn:

1. The tensile strength of short-fiber reinforced rubber exhibits a dilution effect in each interphase. It is found that the interphase conditions have an important effect on the dilution ratio and the critical fiber content. Model "E", the specimen with double coatings of the bonding agent 402 and a rubber solution becomes the best interphase model in comparison to the five different models. The dilution ratio and critical fiber content of model "E" is 0.77 and 10 phr as compared with model "D" that showed 0.51 and 22 phr, respectively. Both the yield strength and tensile moduli are significantly improved with the fiber content.
2. The spring constant (SC) of rubber decreases by about 21% after the fatigue test. On the contrary, that of reinforced rubber increases in all cases. The changes of the SC for reinforced rubber decrease with the fiber content. The better the interphase condition, the smaller the changes of the SC.
3. The temperature of the matrix increases about 2.6 times and those of the reinforced rubber show a $1.4 \sim 2.2$ times increase after the fatigue test. The changes of the temperature for the reinforced rubber during the fatigue test decrease with the fiber content. It is found that the better the interphase condition, the smaller the changes of specimen temperature with the same fiber content. The interphase model "E" becomes the best interphase model in this study. Additionally, we have investigated the possibilities of applying short-fiber reinforced rubber to automotive rubber mounts, bushings, and stoppers.

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