THE INFLUENCE OF FIBER ASPECT RATIO ON THE TENSILE AND TEAR PROPERTIES OF SHORT-FIBER REINFORCED RUBBER

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SUMMARY: Both tensile and tear properties of short-fiber reinforced Chloroprene rubber have been studied as a function of fiber aspect ratio and volume content. Both properties increased with the fiber aspect ratio and fiber content. The fiber reinforced rubbers exhibited maximum properties at a fiber aspect ratio of about 300. For rubber with a fiber aspect ratio over 400, the properties of fiber reinforced rubbers decreased with fiber content because of a dispersion problem during the mixing. It was found that the ultimate tensile strength, torque, tearing energy and tensile modulus of the bonding agent treated rubbers were higher than that of omitted ones. Also, the interphase conditions have an important affect on the dilution ratio and critical fiber content.

KEYWORDS: rubber, fiber aspect ratio, fiber content, bonding agent, tensile modulus, tearing energy, dilution effect, interphase

INTRODUCTION

Recently, short-fiber reinforced rubbers have gained a wide importance due to the advantages in processing and improvements in their mechanical properties. The primary effect of short-fiber reinforcement on the mechanical properties of rubbers included increased modulus, increased strength with good bonding at a high fiber content, decreased elongation at rupture, increased hardness even with relatively low fiber content, and possible improvements in cut, tear, and puncture resistance. The properties of short-fiber reinforced rubbers depended on the fiber aspect ratio(AR), fiber content, fiber dispersion, fiber orientation and fiber-matrix adhesion. The reinforced rubbers, in which short fibers were oriented uniaxially in rubber, generally, have a good combination of high strength and stiffness from the fiber and of elasticity from the matrix.

These materials have been utilized in some practical commercial uses such as hoses, V-belts, diaphragms, tires and gaskets[1]. According to Coran *et al*.[2], the properties of cellulose fiber reinforced elastomer composites depend on the types of elastomer used, fiber content, fiber aspect ratio, and fiber orientation. O'Conner[3]` compared the rubbers reinforced with five types of fiber, and found that their mechanical properties depended on the fiber type, volume

loading percentage, aspect ratio, orientation, dispersion of fiber and fiber-matrix adhesion. However, there are no systematical studies to investigate the effects of fiber aspect ratio in rubber.

The objectives of this study were to analyze the optimization of the fiber aspect ratio (AR : length, *L*/diameter, *d*); to investigate the effects of fiber volume on the mechanical properties of short-fiber reinforced chloroprene rubber; and to examine the influence of interphase conditions on the mechanical properties of the rubber after the bonding agent and rubber solution were coated on the fiber surface to improve the interfacial strength between the fiber and the rubber.

EXPERIMENTAL PROCEDURES

The Chloroprene rubber used for this study was S-40V(ML_{1+4} at 100 ; 48 5) made by the DENKA Company of Japan. We also used carbon black(FEF, SRF), nylon 66 fiber(ø15) as reinforcing materials and other ingredients of commercial grade quality. The short-fiber reinforced rubbers were made with various fiber AR and fiber content as shown Table 1. Also we treated the fiber surface with bonding agent(Chemlok 402) and rubber solution by dipping method. A schematic representation of coated short-fiber surface is shown in Fig. 1.

Table 1: Formulation of the reinforced rubber(left side), and the mechanical properties of rubber matrix and short-fiber(right side)

Ingredients	phr*	
	I	II
Polymer, S40-V	100.0	←
Stearic Acid	1.0	←
Carbon Black, FEF	10.0	24.0
SRF	25.0	
DOP	10.0	←
MgO	4.0	←
3P	1.5	←
Sunnoc, MB	2.0, 1.0	←
ZnO	5.0	←
TS, NA22	1.0, 1.0	←
Sulfur	0.3	←
Nylon66 Fiber	+α	←
SUM.	161.8+α	150.8+α

	I	II	Short-Fiber
Tensile strength	21.56MPa	19.65MPa	690MPa
Tensile modulus	7.56MPa	3.66MPa	2.7GPa
Elongation	338%	454%	30%
Hardness(JIS A)	60.0	55.0	
Fiber AR	70, 155, 265, 400, 550	265 const.	
Fiber Content(phr)	5, 15, 30	10, 20, 30	
Fiber Surface Treatment	Type A of Fig. 1	Types A-D of Fig. 1	
Characteristic Factor	Fiber AR, Fiber Content, Adhesion	Interphase, Fiber Content	

phr* ; Parts per hundred grams of rubber

The fabrication of reinforced rubber was according to ASTM D3182 and D3190. The elastomer and carbon black were weighed to within a tolerance of 1g, and all other materials were weighed with 0.1g for the mixing. The mixes were prepared in a two-roll laboratory model of an open mixing mill(length 406 diameter 203) at a nip of 1.5 . The mixing

time and number of passes were maintained in all cases. To eliminate residual stress during the milling process, the sheeted compound was conditioned for 24 hours at 20 3 at a relative humidity of 55%. Orientation of the fiber in the grain direction of mill was achieved by a repeated passing of the uncured compound through a controlled nip. A square preform cut from the uncured sheet was marked in the direction of the mill grain and vulcanized at 170 in a hydraulic press heated platen at 1.5 times of its' respective optimum cure time(tc90), based on data obtained from a rheometer. The test pieces were punched from the molded sheet (thickness=2) in the direction of the fiber orientation.

The tensile properties were measured using an Autograph(Model AG-5000E) of Shimadzu tensile machine with a testing speed of 50 /min. The geometry of the specimen was a Dumbbell-3 type of Korean Standard Material 6518. Tear tests were performed with the same tensile machine with a testing speed of 10 /min. The hardness was measured by the JIS-A(Japan Industrial Standard) hardness test. Typically, five specimens were used for a single evaluation at room temperature.

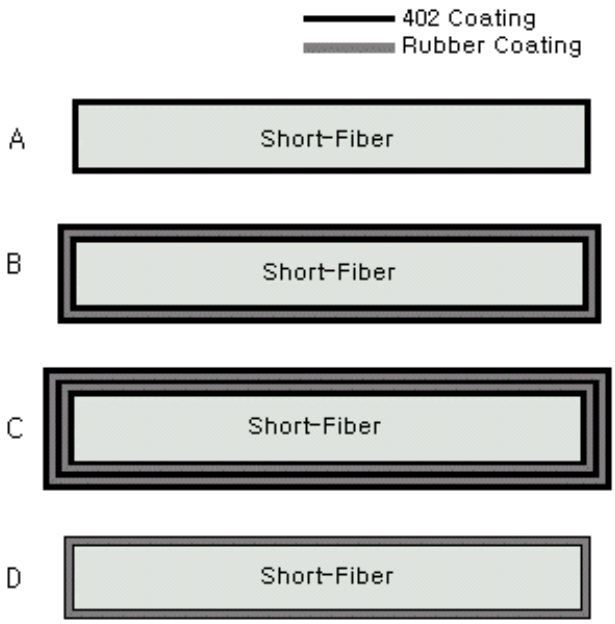


Fig. 1: Schematics of coated short-fiber surface

RESULTS AND DISCUSSION

Among many testing methods for the uncured compound, we used the Oscillating Disc Rheometer(Monsanto Company, Model D-100) according to ASTM D2084 for measurement of the curing properties. The scorch times, torque(max. & min.), optimum curing time, cure velocity etc., can be determined from the rheograph. The increase of torque(max.), which is a scale of interior shear stress due to physical and chemical reactions, indicates the reinforcing effects. This has an effect on the increase in stiffness and hardness of the reinforced rubber[4-5]. The torque and hardness of the reinforced rubbers are shown in Figs. 2 and 3. From Figs. 2 and 3, we can confirm the laxation of the increasing rate at a fiber aspect ratio of 100 200 for torque and a fiber aspect ratio of 200 300 for hardness. This difference comes from the following ; the former was the test of the uncured state and the latter was the test for the cured state. The testing temperature(170) was the same in both cases. However, the testing time was different. The former was 12 min. and the latter was 1.5 times longer than the optimum curing times(original rubber=6'45" and reinforced rubbers=7'10" 7'30") which were obtained from the rheometer. The difference of torque by the different curing times influenced in the fiber aspect ratio of the reinforced rubber. Therefore, the increase of torque had an effect in decreasing the critical fiber aspect ratio. The Chloroprene and Silicone rubbers, etc. need special attention in determining the curing time because the rubbers had a curing curve to the non-equilibrium in maximum torque.

Our results for the ultimate tensile strength(rubber=21.56) are summarized in Fig. 4. With a low fiber content, the tensile strength($_c$) was dominated by the rubber and reinforcing fibers that acted as the network defects. As a result, $_c$ decreased with the fiber content until a

critical fiber level was reached. At higher fiber contents, $_c$ became the fiber-dominating property and it increased with the fiber content[1,6-7]. An initial drop of $_c$ reaching a characteristic minimum around 15 30phr was derived from the dilution effect of the fibers, which weakened the rubber if its fiber content was not yet high enough to sustain the corresponding fraction of the tensile load. The critical fiber content level, at which the rubber strength recovered, varied directly with the fiber aspect ratio. In the absence of interfacial bonding, it was never attained, based on this work. A dilution effect was found to be different in non-strain crystallizing rubbers(SBR, NBR, etc.,) and in other cases(NR, CR, etc.,). The former rubbers did not show a dilution effect. The latter rubbers(NR, CR, etc.,) displayed the classical drop due to a dilution effect until the critical fiber content was reached. The presence of carbon black and the fiber aids increased stress dissipation. In this study, we used the strain-induced crystallizing Chloroprene rubber with short fiber as the reinforcing material. Therefore, the dilution effect can be seen in the reinforced rubbers, and the dilution ratio was increased with the fiber aspect ratio as shown in Fig. 4. With the fiber aspect ratio less than 155, $_c$ was recovered at around a fiber content of 30phr. Over 400 of the aspect ratio, $_c$ was recovered around 15phr(dilution ratio 0.5). When we consider that the maximum mixing content of fiber is 40phr, the case of L/d=265 was more advantageous than others because of the low dilution and recovery of $_c$ at 15phr.

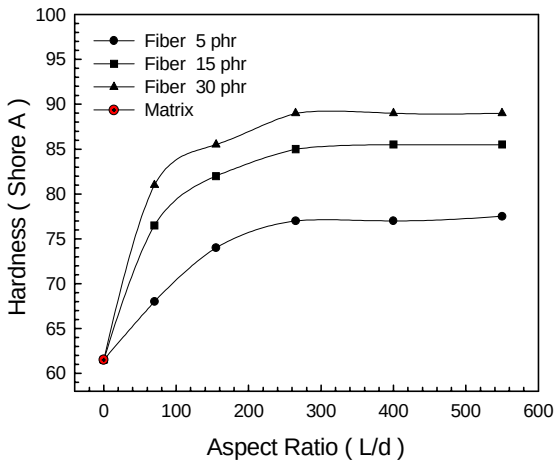


Fig. 2: Effects of fiber AR and content on the torque(M_H)

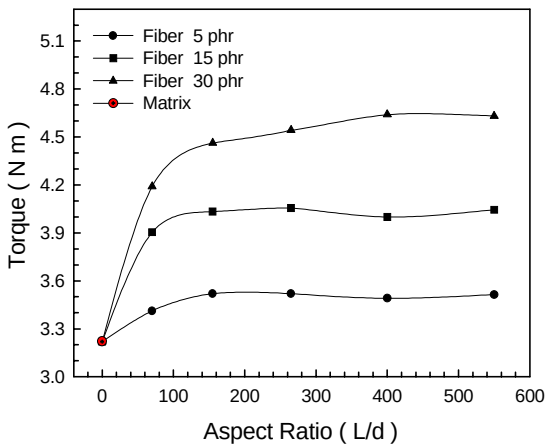


Fig. 3: Effects of fiber AR and content on the hardness

Tensile modulus(Young's modulus) was calculated from the initial slope of the stress-strain curve. The modulus ratio(E_f/E_m) was 356, the tensile moduli(E_C) of the reinforced rubbers were significantly improved when compared to the virgin rubber(7.57). Tsai and Pagano[8] showed that the modulus for randomly oriented short-fiber composites can be predicted approximately as,

$$E_C = (3/8)E_L + (5/8)E_T \qquad (1)$$

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

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

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

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

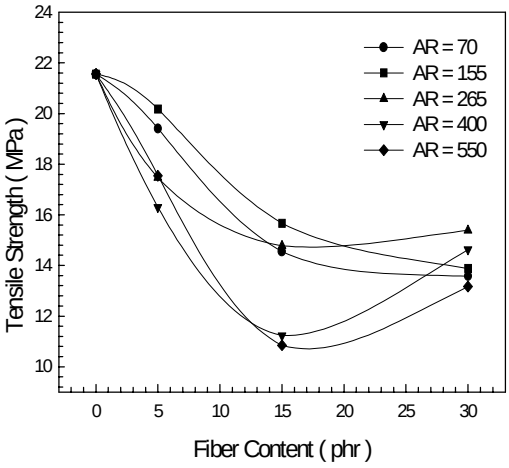


Fig. 4: Effects of fiber AR and content on the tensile strength

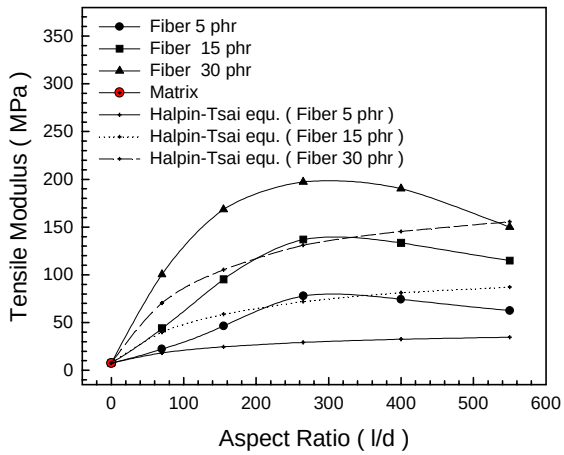


Fig. 5: Effects of fiber AR and content on the tensile modulus

Fig. 5 shows the differences between theoretical data and experimental data except for the fiber aspect ratio when less than 50. The Tsai and Pagano equations, which were in good agreement with the low modulus ratio(E_c/E_m<100) of randomly oriented short-fiber polymer composites, were in poor agreement with the reinforced rubbers of this study. It seems that there was a significant difference of mechanical properties between the matrix and reinforcing fiber. The hysteresis effects of rubbers increased as the fiber aspect ratio and the property ratio increased and had a significant effect on that phenomenon. The experimental data shows the maximum tensile modulus when the fiber aspect ratio was around 300. A decrease of tensile modulus in the respective fiber content at a fiber aspect ratio over 400 was probably caused by the poor conditions of fiber distribution. The critical fiber length was that fiber length which was required for the fiber to develop its' fully stressed condition in the matrix. If the fiber length was much longer than the critical fiber length, it was difficult to maintain the shape of the original fiber due to the entanglement and overlapping of short-fiber during the mixing process. Also, these problems led to an uneven distribution of short-fiber in the rubber sheet(2 thick) that molded as specimen. Therefore, it was found that if the tensile load acts on the specimen, the tensile moduli were decreased due to defects, which were produced in the mixing procedure. The decreasing slope of the high fiber content was sharper(higher) than in the low fiber content and this indicates the difficulty of proper dispersion in short-fiber reinforced rubber.

In this study, we used Chloroprene rubber which usually contains the most crystalline region by regular polymerization of Chloroprene monomer. When crystallizing behavior occurred in the rubber by tensile deformation, strain induced crystallization(SIC), the tensile strength and modulus, hardness, oil resistance improved. But, the fracture elongation and elasticity decreased[9]. Since the relative distance of molecular with short-fibers and the crosslinked rubber was shorter than one without those, it can be assumed that rubber with fiber and crosslinked point will be crystallized more quickly under tensile loading. Therefore, the

tensile moduli of the crystallizing rubbers were rapidly increased when compared to the non-crystalline rubbers due to the resistance of the crystallized region for external loads. In cases of short-fiber reinforced rubbers, the tensile moduli were significantly increased by the resistance of regular aligned fibers for external loads because the space between fibers decreased with fiber aspect ratio and content. However, the elongation at fracture was decreased by the relatively reduced distance of rubber molecules. It is found that short-fiber reinforcement has an important effect on tensile modulus because of the acceleration in the crystallizing behavior of reinforced rubber.

During the deformation of rubber, a part of the mechanical energy was converted into heat and other forms of energy. The loss of mechanical energy is called the "hysteresis loss". The mechanism of hysteresis loss in a rubber compound is still obscure, although many properties like wear, modulus, tear, heat generation, etc., are often correlated with hysteresis loss in research literature. However, it has been amply demonstrated that the energy loss in the compound plays a key role in enhancing better performance, particularly in applications where an elastomer is subjected to repeated deformation of sufficient magnitude and frequency[10-11]. The hysteresis loss is measured up to half of the rupture elongation for 3 cycles with a testing speed of 10 /min. It is noted that there was a significant change after the first cycle. It shows the maximum hysteresis ratio at a fiber aspect ratio between 100 and 200 which decreased over 30phr of fiber content due to the crystallizing behavior of the reinforced rubber.

Three types of tear pattern were observed in the tearing tests(Fig. 6), namely, 1) straight, 2) stable and 3) unstable tearing. In the case of straight tearing(Fig. 6-b), the tear force fluctuates only slightly and the rate of tear propagation is basically constant and cracks growing continuously[11]. The second type of tearing pattern of reinforced rubbers with fiber aspect ratio around 155 is shown in Fig. 6-c. Crack propagation is advanced with a certain angle from the pre-crack direction. The angle between pre-crack direction and propagating direction appeared somewhat larger as the fiber aspect ratio and content increased. The third type of tearing pattern of reinforced rubbers with the fiber aspect ratio around 400 is shown in Fig. 6-d. The unstable tearing referred to as "stick-slip" tearing was often observed. Instead of the steady tear propagation type, the tear growth was irregular. It shows the crack arrested and re-initiated at fairly regular intervals. Correspondingly, the force necessary to propagate the tear varied widely from a minimum at tear arrest to a maximum at tear initiation. This type of tearing led to surface irregularities with periodic "knots". These irregularities increased with fiber content. In the second pattern, the aligned short fibers interrupted the crack propagation of reinforced rubber, and the straight crack propagation can be considered as the proper dispersion of short-fiber. In the case of Fig. 6-d, the crack was growing through some weak places which were defects due to the entanglement and others during the mixing and compressive molding.

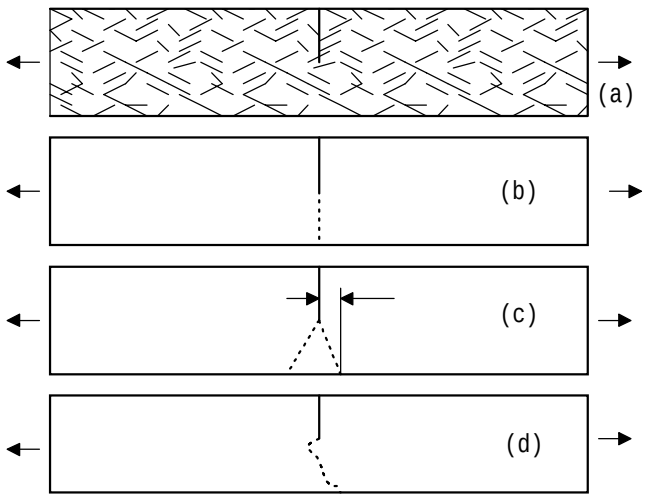
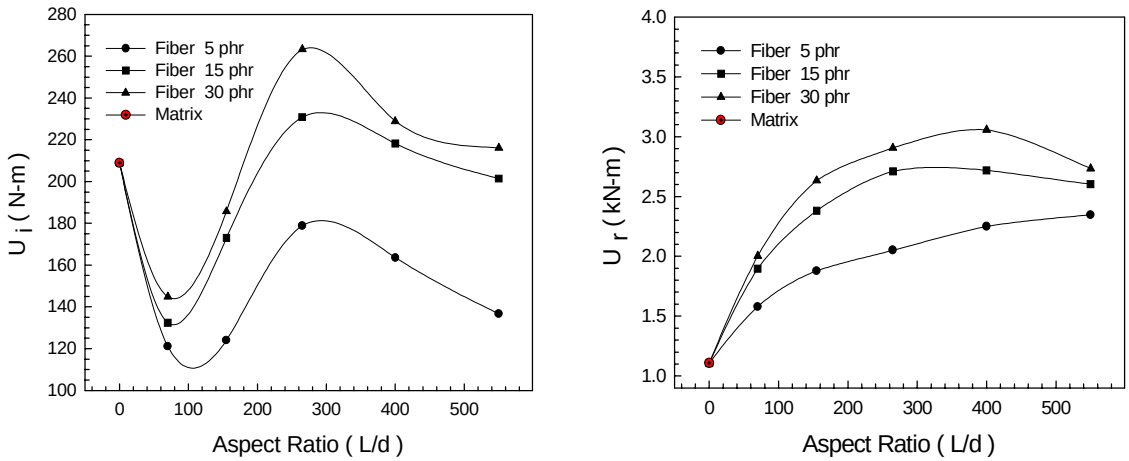


Fig. 6: The tearing patterns of the tested specimen

Fig. 7(a) shows the tearing energy until crack initiation and Fig. 7(b) shows the tearing energy until final rupture as a function of fiber aspect ratio and content. At the crack initiation point, the short-fiber reinforced rubber(fiber aspect ratio<155 and fiber content 5phr) showed high tensile load but low tearing energy. This phenomenon was caused by fast crack initiation compared to the virgin rubber due to high stress concentration at the crack tip. As mentioned before, adding the fiber will accelerate the crystallizing behavior even with small tensile deformations and will increase the modulus which leads to high stress concentration at the crack. However, the Figs. show the maximum tearing energy at the fiber aspect ratio of about 300 and it decreased somewhat with the fiber aspect ratio over 400 because of defects during processing. In the final rupture state, the tearing energy was significantly improved by the fiber bridging effect with fiber aspect ratio and content. To pass the maximum load point, the specimen didn't fracture immediately and maintained for the time being. The reinforced rubbers' defects somewhat increased during processing when the fiber aspect ratio>400 and fiber content>15phr.



(a) (b)

Fig. 7: Effects of fiber AR and content on stored energy: (a) at the crack initiation and (b) at the rupture

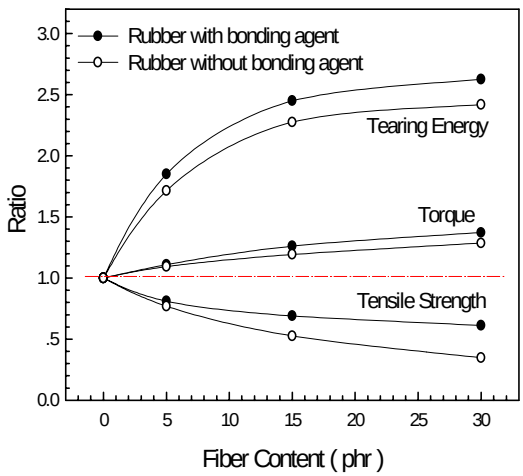


Fig. 8: Effects of fiber content and the bonding agent on various properties with AR=265

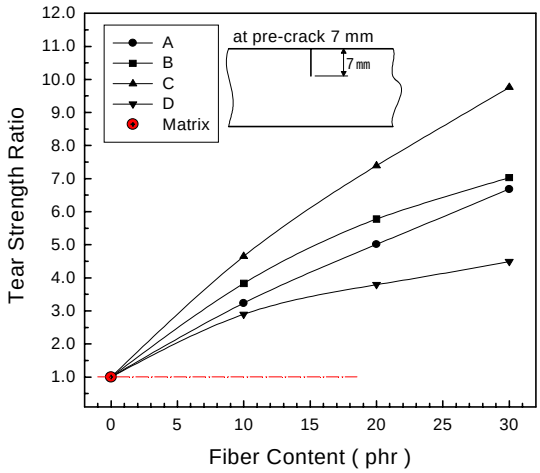
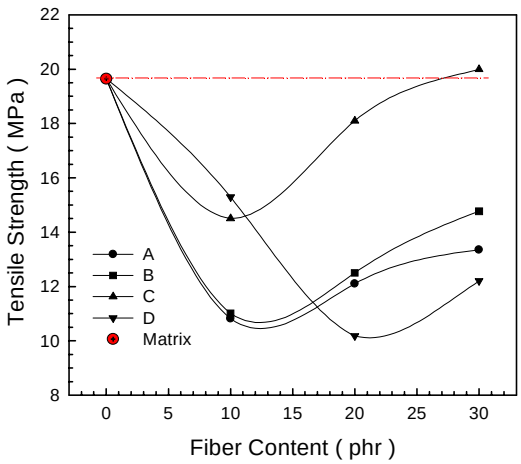


Fig. 9: Effects of interphase and fiber content on the tear strength ratio

Good interfacial strength between fiber and rubber was an essential factor in order to achieve good fiber reinforcement. The adhesion treating method of fiber was different according to fiber types and there were a lot of variables in the complex treating process. Fig. 8 shows the ratio of tensile strength, torque and tearing energy with and without the bonding agent treatment. The differences in those properties were increased with greater fiber content.

Fig. 9 shows the tear strength with initial crack length of 7 mm. The tear strength of double coated specimen(C in Fig. 1) is 9.8 times stronger than the virgin rubber. Even the single coating of rubber is 4.5 times stronger than the virgin one. Likewise, the interphase conditions show the significant affects on the dilution ratio and critical fiber content(Fig. 10). Fig. 11 shows the tensile modulus ratio as functions of interphase conditions and fiber content. Even the tensile modulus increases as the coating number is increased. As shown, the theoretical prediction of the tensile modulus ratio agree well with experimental in general.



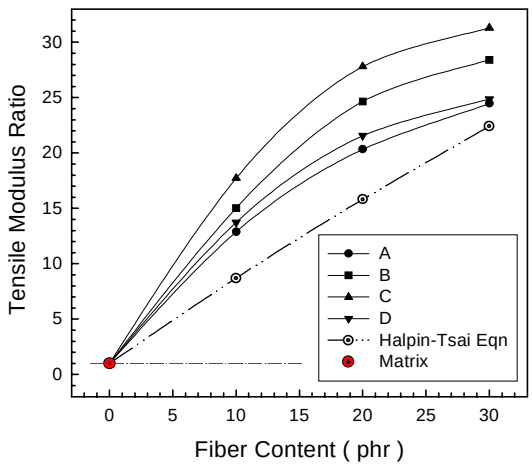


Fig. 10: Effects of interphase and fiber content content on the ultimate tensile strength

Fig. 11: Comparison of the tensile modulus ratio between experimental results and theoretical prediction

CONCLUSIONS

Both tensile and tear properties of short nylon66 fiber reinforced Chloroprene rubber have been investigated as functions of fiber aspect ratio, fiber content, interphase, and the bonding agent. From this study, we found the following conclusions;

1. Fiber aspect ratio and volume

The increasing rate of torque and hardness of short-fiber reinforced CR is slowed with a fiber aspect ratio of 200 300. The ultimate tensile strength, tensile modulus and tearing energy until crack initiation showed a maximum value with the fiber aspect ratio at about 300. Tearing energy until final rupture showed a maximum value with the fiber aspect ratio at 300 400. The results of tensile modulus was compared with the Halpin-Tsai Equation which considered the fiber aspect ratio for randomly oriented polymer composites and found to be in poor agreement. The ultimate tensile strength showed a dilution effect similar to other works. The dilution ratio was increased with the fiber aspect ratio. The recovery of tensile strength was found to be at a low fiber content with fiber aspect ratio increase. It is important to search

for an optimum bonding condition because the optimum fiber aspect ratio and dilution ratio can be different than the suggested interfacial condition.

2. The bonding agent and interphase

The various properties of reinforced rubbers have been compared with and without the bonding agent at fiber aspect ratio of 265. The treated rubbers showed a dilution effect at fiber content of 15phr, and the untreated rubbers never experienced a dilution effect. Also, torque, tearing energy until final rupture showed large differences in all ranges of the fiber content. The interphase conditions had an important affect on all mechanical properties. Double coatings of bonding agent and rubber solution became the best interphase model. To achieve superior strength, it was necessary to find the optimum bonding agent and their content and refine the steps in the treating sequence.

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