

Effects of Fiber Aspect Ratio, Fiber Content, and Bonding Agent on Tensile and Tear Properties of Short-Fiber Reinforced Rubber

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Both tensile and tear properties of short-fiber reinforced Chloroprene rubber have been studied as functions of the fiber aspect ratio and fiber content. Both properties increased when both the fiber aspect ratio and fiber content were increased. The fiber reinforced rubbers exhibited maximum values of these properties at a fiber aspect ratio of about 300. When the fiber aspect ratio exceeds 400, the mechanical properties decreased with the fiber content because of the non-uniform dispersion of fibers. The tensile modulus was compared with the prediction by the Halpin-Tsai equations for randomly oriented cases. A bonding agent was used in the fiber treating process. It was found that the ultimate tensile strength, torque, tearing energy and tensile modulus of the rubbers with treated fibers were much higher than those with untreated ones.

Key Words : Reinforced Rubber, Fiber Aspect Ratio, Fiber Content, Bonding Agent, Dilution Effect, Tearing Energy

1. Introduction

Recently, short-fiber reinforced rubbers have gained great importance due to their advantages in processing and their improved mechanical properties. The primary effects of short-fiber reinforcement on the mechanical properties of rubbers include increased modulus, increased strength with good bonding at a high fiber content, decreased elongation at rupture, increased hardness even with a relatively low fiber content, and possible improvement in the cut, tear, and puncture resistance. The properties of short-fiber reinforced rubbers depend on the fiber aspect ratio (AR), fiber content, fiber dispersion, fiber orientation, and fiber-matrix adhesion. Reinforced rubbers, in which short fibers are oriented uniaxially in rubber, generally have a good com-

ination of high strength and stiffness from the fiber and of high elasticity from the matrix.

These materials have been utilized in some commercial uses such as hoses, V-belts, diaphragms, tires, and gaskets (Goettler, 1988). Derringer (1971) used short fibers of rayon, nylon, and glass in natural rubber to increase the Young's modulus of vulcanizates. Moghe (1976) reported the milling parameters that affect the fiber orientation and its influence on composite properties. According to Coran et al. (1974), 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 (1977) 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 have been no systematic studies that investigated the effects of fiber aspect ratio in rubber.

The objectives of this study are to find the optimum fiber aspect ratio (length, L /diameter, d); to investigate the effects of the fiber content on the mechanical properties of short-fiber rein-

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forced Chloroprene rubber ; and to examine the influence of the bonding agent on the mechanical properties of the rubber after a bonding agent is mixed in the compound to improve the interfacial strength between the fiber and rubber.

2. Experimental Procedure

The Chloroprene rubber used for this study was S-40V (ML₁₊₄ at 100°C ; 48±5) made by DENKA, Japan. We also used carbon black (FEF, SRF), nylon 66 fiber (ϕ 15 μ m) as reinforcing materials and other ingredients of commercial grade quality. The tensile modulus, tensile strength and elongation was 7.57 MPa, 21.56 MPa and 338 % for the rubber and 2.7 MPa, 690 MPa and 30 % for the fiber, respectively. The short-fiber reinforced rubbers were made with fiber aspect ratios of L/d=70, 155, 265, 400, 550 and fiber contents of 5, 15, 30 phr (parts per hundred grams of rubber) supplied by KABOOL LTD, Korea.

The formulation of the test compound is given in Table 1. The reinforced rubber was fabricated according to the ASTM D3182 and D3190. The elastomer and carbon black were weighed to within a tolerance of ± 1 g, and all other materials ± 0.1 g for the mixing. The mix was prepared in a two-roll laboratory model of an open mixing mill (length 406 mm \times diameter 203 mm) at a nip of 1.5 mm. The mixing time and number of passes were maintained constant in all cases. To eliminate residual stress during the milling process, the sheeted compound was conditioned for 24 hours at 20 \pm 3°C, and at a relative humidity of 55%. Approximately uniform orientation of fibers in the grain direction of mill was achieved by repeatedly passing 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°C in a hydraulic press at 1.5 times its respective optimum cure time (t_{c90}), based on the data obtained from a rheometer. The test pieces were punched from the molded sheet (thickness: 2 mm) along the fiber orientation. A schematic representation of specimens showing the fiber orientations is

Table 1 Formulation of the rubber matrix

| Ingredients | phr* | Remarks |
|--|-----------------|----------|
| Polymer (S-40V) | 100.0 | 1st step |
| Stearic acid | 1.0 | |
| Carbon black FEF | 10.0 | |
| SRF | 25.0 | |
| Dioctyl Phthalate (DOP) | 10.0 | |
| Magnesium Oxide | 4.0 | |
| N-isopropyl-p-phenylenediamine (3P) | 1.5 | |
| Diphenylamine-acetone reaction products (Sunnoc) | 2.0 | |
| 2-mercaptobenzimidazole (MB) | 1.0 | |
| Bonding agent (R-6) | 3.0 | |
| Zinc oxide | 5.0 | 2nd step |
| Tetramethylthiurammonosulfide (TS) | 1.0 | |
| Ethylene thiourea (NA22) | 1.0 | |
| Sulfur | 0.3 | |
| Bonding agent (M-3) | 1.5 | |
| Nylon66 fiber | + α | |
| SUM | 157.3+ α | |

Phr* : Parts per hundred grams of rubber

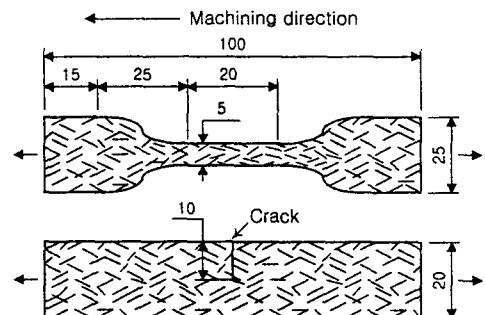


Fig. 1 Specimen geometry and fiber orientation for the tensile and tear tests

shown in Fig. 1.

The tensile properties were measured using an Autograph (Model AG-5000E) of a Shimadzu tensile test machine at a testing speed of 50 mm/min. The geometry of the specimen (Dumbbell-3 of Korean Standard Material 6518) is shown in Fig. 1. Tear tests were performed using the same

tensile test machine at a testing speed of 10 mm/min. The hardness was measured by performing the JIS-A (Japan Industrial Standard) hardness test. Typically, five specimens were used for a single evaluation at room temperature.

3. Results and Discussion

3.1 Curing properties

Among many testing methods for uncured compound, we used an Oscillating Disc Rheometer (Monsanto Company, Model D-100) according to the ASTM D2084 for the measurement of curing properties. The scorching time, torque (max. & min.), optimum curing time, cure velocity, etc. can be determined from the rheograph. The increase of torque (max.), which is a measure of the interior shear stress due to the physical and chemical reactions, indicates an increase in the reinforcing effects. This has an effect on the increase of stiffness and hardness of the reinforced rubber (Ismail, 1997). The torque and hardness of the reinforced rubbers are shown in Figs. 2 and 3. The former is for the uncured state and the latter is for the cured state. From Figs. 2 and 3, we can confirm a slow-down 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 reason. The testing temperature was 170 °C in both cases. However, the testing time was different: that in the former case was 12 minute and that in the latter case was 1.5 times longer than the optimum

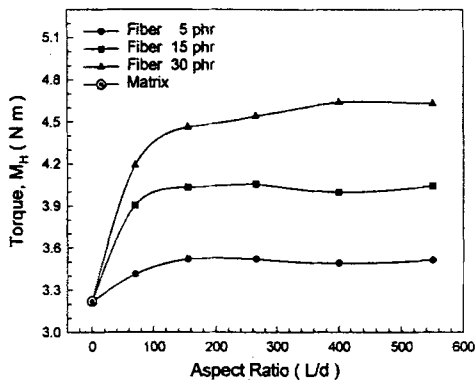


Fig. 2 Effects of fiber AR and content on torque (M_H)

curing times (original rubber: 6 min 45 sec and reinforced rubbers: 7 min 10 sec~7 min 30 sec) which were obtained from the rheometer. Therefore, the increase of torque showed a tendency to decrease the critical fiber aspect ratio. The Chloroprene and Silicone rubbers, etc., need special attention in determining the curing time because the rubbers have a non-equilibrium curing curve for the maximum torque (Fig. 4).

3.2 Ultimate tensile strength

Our results for the ultimate tensile strength (rubber: 21.56 MPa) are summarized in Fig. 5. At low fiber contents, the tensile strength (σ_c) was dominated by the rubber and reinforcing fibers that acted as network defects due to high difference in their moduli. As a result, σ_c decreased with the fiber content until a critical level of fiber content was reached. At higher fiber contents, σ_c became a fiber-dominated property and increased with the fiber content (Terminia, 1994). An initial drop of σ_c reaching a characteristic mini-

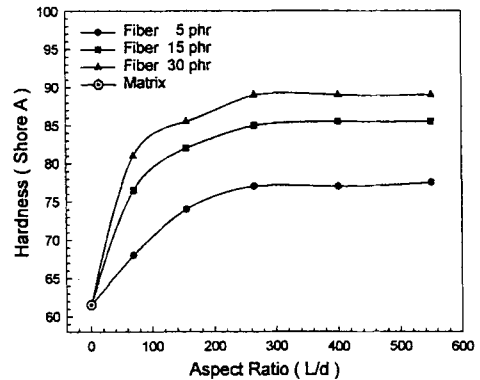


Fig. 3 Effects of fiber AR and content on hardness

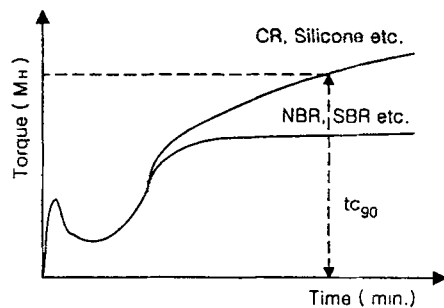


Fig. 4 Torque during curing process

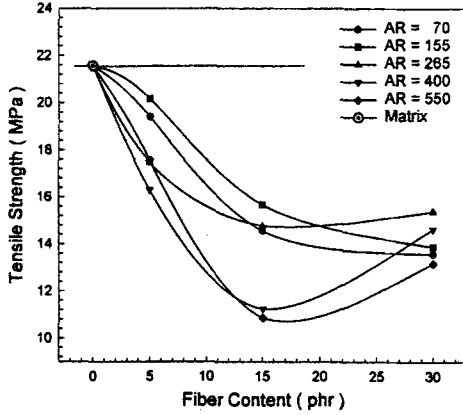


Fig. 5 Effects of fiber AR and content on ultimate tensile strength

mum around 15~30 phr was due to the dilution effect of fibers, which weakened the rubber because its fiber content was not high 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 fiber aspect ratio. In the absence of interfacial bonding, it was never attained, based on a reference (Lee, 1999). 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 whereas the latter rubbers (NR, CR, etc.) exhibited the classical drop due to a dilution effect until the critical fiber content was reached. The presence of carbon black and fibers aids stress dissipation. In this study, we used the strain-induced crystallizing Chloroprene rubber with short fibers as the reinforcing material. Therefore, the dilution effect can be seen in the reinforced rubbers, and the dilution ratio (the tensile strength of reinforced rubber, σ_c / that of rubber, σ_{matrix}) increased with the fiber aspect ratio as shown in Fig. 5. With the fiber aspect ratio less than 155, σ_c was recovered at around a fiber content of 30 phr. Over 400 of the aspect ratio, σ_c was recovered around 15 phr (dilution ratio ≈ 0.5). When we consider that the maximum mixing content of fiber is 40 phr, the case of $AR=265$ was more effective than others because of the low dilution ratio and the recovery of σ_c with 15 phr.

3.3 Tensile modulus

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 MPa). Tsai and Pagano (1994) showed that the modulus for randomly oriented short-fiber composites can be predicted approximately as

$$E_c = (3/8)E_L + (5/8)E_T$$

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

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

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

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

Figure 6 exhibits differences between the theoretical and experimental data, except for the cases where the fiber aspect ratio is less than 50. The Tsai and Pagano equations, which were in good agreement with the experimental data for randomly oriented short-fiber polymer composites having low modulus ratio ($E_c/E_m < 100$), were in poor agreement with those for the reinforced rubbers in this study. It seems that a significant difference in mechanical properties between the matrix and reinforcing fiber, and the hysteresis effects of rubbers that increase with the fiber aspect ratio and the property ratio, etc. are the main causes of this disagreement between experiments and theories. The experimental data exhibit the maximum value of tensile modulus when the fiber aspect ratio is around 300. A decrease of tensile modulus at fiber aspect ratios exceeding 400 is probably due to the non-uniform dispersion of fibers. The critical fiber length is the fiber length which is required for the fiber to develop its fully stressed condition in the matrix. When the fiber length is much longer than the critical

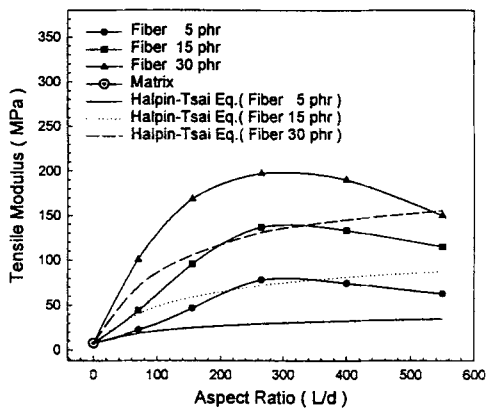


Fig. 6 Effects of fiber AR and content on tensile modulus

fiber length, it is difficult to maintain the shape of the original fiber due to the entanglement and overlapping of the fibers during the mixing process. Also, these problems led to an uneven distribution of short fibers in the rubber sheet (2 cm thick) that was molded into specimens. Therefore, it was found that when a tensile load acted on the specimen, the tensile moduli were decreased due to the defects which were produced in the mixing process. The decreasing slope for high fiber contents was greater than for low fiber contents and this demonstrates the difficulty in achieving proper dispersion of fibers 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 crystallization, more precisely strain induced crystallization (SIC), occurred in the rubber by tensile deformation, the tensile strength, tensile modulus, hardness, and oil resistance improved. But, the fracture elongation and elasticity decreased (Bras, 1957). Figure 7 shows a schematic representation of SIC with short fibers and cross-linked network (Gedde, 1995). Since the relative distance of molecules with short fibers and the cross-linked rubber was shorter than the one without them, it can be assumed that rubber with fibers and cross-linked points will be crystallized more quickly under tensile loading. Therefore, the tensile moduli of the crystallizing rubbers were rapidly increased when compared

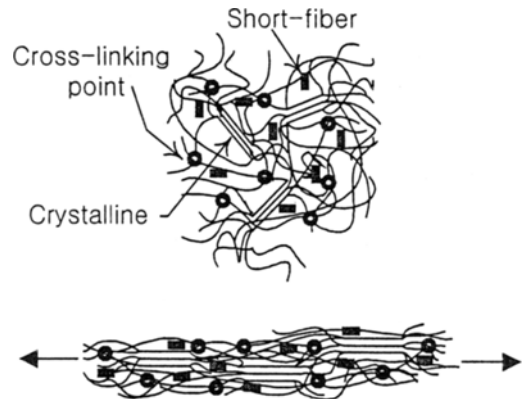


Fig. 7 Schematic representation of the network for cross-linked rubber with crystalline and fiber reinforced molecules

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

3.4 Hysteresis

During the deformation of rubber, a part of the mechanical energy is 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, and heat generation, etc. are often related to the hysteresis loss in the literature. However, it has been amply demonstrated that the energy loss in the compound plays a key role in enhancing the performance of rubber, particularly in the applications where it is subjected to repeated deformation of sufficient magnitude and frequency (Kar, 1996; Wolff, 1993). Figure 8 shows the hysteresis loss of the reinforced rubbers in this study. The hysteresis loss is measured up to

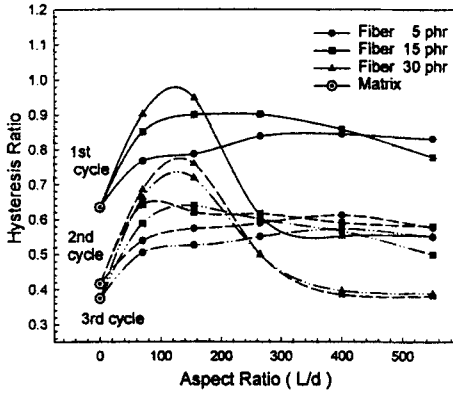


Fig. 8 Effects of fiber AR and content on hysteresis ratio

half of the rupture elongation for 3 cycles at a testing speed of 10 mm/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. When the fiber aspect ratio exceeds 200 and the fiber content exceeds 30 phr, the hysteresis ratio decreased probably due to the crystallizing behavior of the reinforced rubber.

3.5 Tearing properties

Three types of tear pattern were observed in the tearing tests (Fig. 9): namely, (1) straight, (2) stable, and (3) unstable tearing. In the case of straight tearing (Fig. 9(b)), the tear force fluctuates only slightly and the rate of tear propagation is basically constant and cracks grow continuously (Wolff, 1993). The second type of tearing pattern of reinforced rubbers with a fiber aspect ratio around 155 is shown in Fig. 9(c). Crack propagation advances in a direction at a certain angle measured from the pre-crack direction. This angle appeared somewhat larger as the fiber aspect ratio and fiber content increased. The third type of tearing pattern of reinforced rubbers with a fiber aspect ratio around 400 is shown in Fig. 9(d). The unstable tearing referred to as “stick-slip” tearing was often observed. Instead of the steady tear propagation, the tear growth was irregular. That is, the crack was arrested and re-initiated at fairly regular intervals. Accordingly, the force necessary to propagate the tear varied

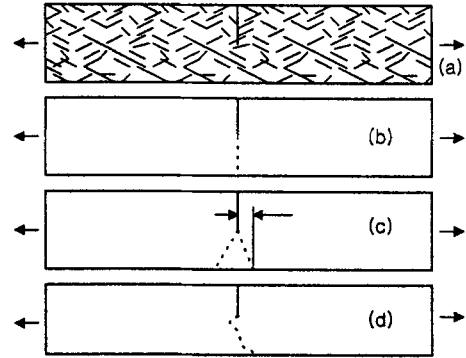


Fig. 9 Three tearing patterns of the tested specimen, (a) : (b) straight, (c) stable, and (d) unstable

widely from a minimum at a tear arrest to a maximum at a tear initiation. This type of tearing led to surface irregularities with periodic “knots”. These irregularities increased with the fiber content. In the second pattern, aligned short fibers interrupted the crack propagation in the reinforced rubber, and the straight crack propagation may imply the proper dispersion of short fibers. In the case of Fig. 9(d), the crack propagated through weak locations where defects existed due to the entanglement and overlapping of the fibers during the mixing and compressive molding.

Figure 10 shows the tearing energy (U_i) until crack initiation takes place, and Fig. 11 shows the tearing energy (U_r) until the final rupture occurs as functions of the fiber aspect ratio and content. At the crack initiation point, the short-fiber reinforced rubber (fiber aspect ratio < 155 and fiber content 5 phr) shows low tearing energy compared to the virgin rubber. This phenomenon was caused by the fast crack initiation, compared to the virgin rubber, due to high stress concentration at the crack tip. As mentioned before, adding fibers 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, Figure 10 shows that the tearing energy becomes maximum at the fiber aspect ratio of about 300 and it decreases somewhat with the fiber aspect ratio over 400 because of defects during the processing of rubber. In the final rupture state, as shown in Fig. 11, the tearing energy (U_r) increases with the

fiber aspect ratio and fiber content because of the fiber bridging effect. Before the crack initiation, the specimen acted upon the same stress state as the tensile mode. However, after the crack initiation, the stress state at the crack tip became different because the crack grew at large angles deviated from the crack tip. Therefore, the specimen did not fracture immediately and maintained for the time being after passing the maximum load point. Based on these results, it can be assumed that the defects in reinforced rubber generated during the processing increase when the fiber aspect ratio is greater than 400 and the fiber content is greater than 15 phr.

3.6 Bonding effects

Good interfacial strength between fibers and rubber is an essential factor for good fiber rein-

forcement. The adhesion treating method for fibers is different for different fiber types and there are a lot of variables in the complex treating process. In this study, we used ingredients which do not treat the fiber surface directly, and mixed them with the rubber compound to eliminate the variables which may be produced in the fiber treating process. The bonding agent used in this study was R-6 and M-3 supplied by the Uniroyal Company. The procedural steps in mixing were carefully taken, e. g. the mixing temperature was kept over 100 °C when R-6 was mixed with carbon black master batch (see Table 1 for the first-step ingredients). And then, M-3 was mixed together with the cure accelerators at low temperatures. Figure 12 shows the ratio (the property of

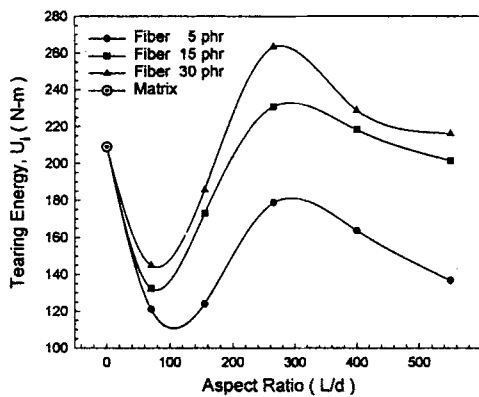


Fig. 10 Effects of fiber AR and content on stored energy at the crack initiation

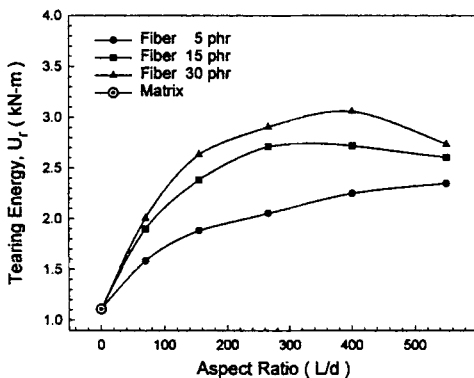


Fig. 11 Effects of fiber AR and content on stored energy at the rupture

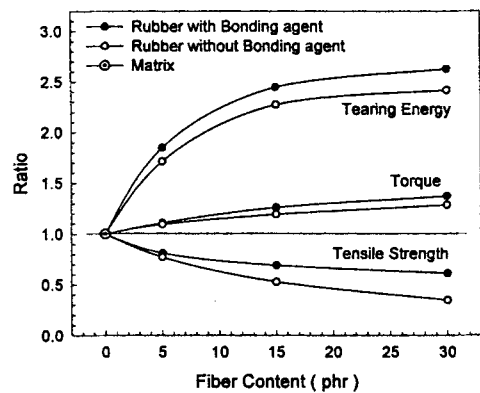


Fig. 12 Effects of fiber content and the bonding agent on various properties with AR=265

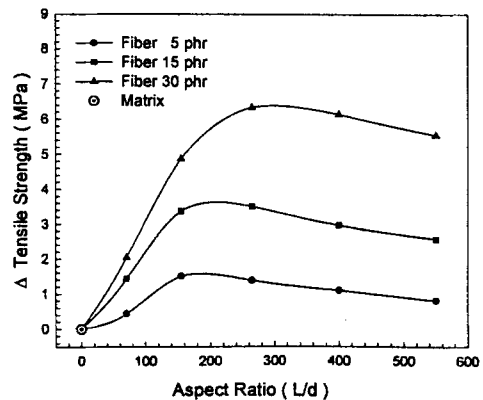


Fig. 13 Effects of fiber AR and content on tensile strength difference with and without bonding agent

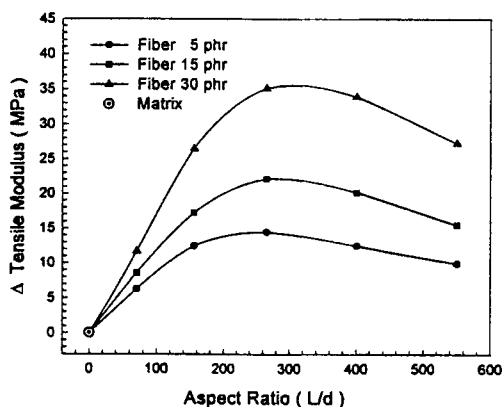


Fig. 14 Effects of fiber AR and content on tensile modulus difference with and without bonding agent

reinforced rubber divided by that of matrix) of tensile strength, torque and tearing energy with AR=265. The differences in those properties increased with greater fiber content. Figures 13 and 14 show the difference in the tensile strength and the tensile modulus with and without the bonding agent treatment as functions of the fiber aspect ratio and content. The maximum difference caused by the bonding agent treatment was found when the fiber AR was around 300. The decrease of the data with the fiber AR over 400 was probably due to the poor conditions of fiber distribution. In this study, we added R-6 (3 phr) and M-3 (1.5 phr), but we need a further study to obtain the optimum content of the respective applications. Products such as tires, hoses, etc. must have excellent interfacial strength for the maximum reinforcement effect on the various properties. To achieve superior interfacial strength, the method of dipping the fiber into the resorcinol-formaldehyde latex in the first stage and then mixing the ingredients with the rubber compound must be considered.

4. Conclusions

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

sions.

4.1 Fiber aspect ratio and content

The torque and hardness of short-fiber reinforced CR increased with the fiber aspect ratio, but this increase slowed down at fiber aspect ratios of 200~300. The ultimate tensile strength, tensile modulus and tearing energy until the crack initiation showed maximum values with the fiber aspect ratio of about 300. The tearing energy until the final rupture showed a maximum value at the fiber aspect ratio of 300~400. The results of tensile modulus were in poor agreement with the Halpin-Tsai equation for randomly oriented polymer composites. The ultimate tensile strength showed a dilution effect, as in other previous work. The dilution ratio increased with the fiber aspect ratio. The recovery of tensile strength was found at low fiber contents with high fiber aspect ratios. It is important to search for an optimum bonding condition because the optimum fiber aspect ratio and dilution ratio may become different by the interfacial condition.

4.2 Treatment with bonding agent

The properties of reinforced rubbers have been compared, with and without a bonding agent at the fiber aspect ratio of 265. Treated rubbers showed a dilution effect at the fiber content of 15 phr, whereas untreated rubbers did not. Also, the torque and tearing energy until the final rupture showed large differences in all ranges of fiber content. The differences in the ultimate tensile strength and tensile modulus between the cases with and without the bonding agent treatment showed maximum values at the fiber aspect ratio of about 300. The method involved in the mixing of the bonding ingredients with the rubber compound could eliminate the variables that occur in the fiber treatment process. To achieve superior interfacial strength, it is necessary to find the optimum bonding agent and their content, and refine the steps in the treating process.

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