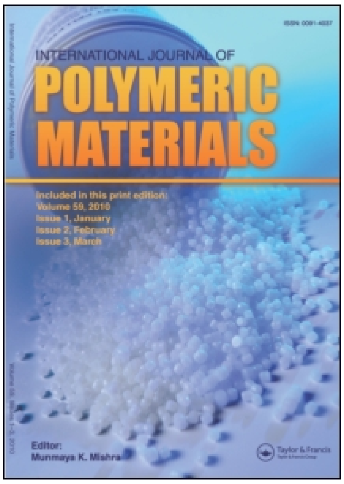

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Properties of Isoprene Rubber Reinforced with Treated Bleached Kraft Cellulosic Fibers or Rayon Fibers

B. Westerlind[ab]; S. Hirose[a]; S. Yano[a]; H. Hatekayama[a]; M. Rigdahl[ab]
[a] Industrial Products Research Institute, Ibaraki, Japan [b] Swedish Forest Products Research Laboratory, Paper Technology Department, STOCKHOLM, Sweden

To cite this Article Westerlind, B. , Hirose, S. , Yano, S. , Hatekayama, H. and Rigdahl, M.(1987) 'Properties of Isoprene Rubber Reinforced with Treated Bleached Kraft Cellulosic Fibers or Rayon Fibers', International Journal of Polymeric Materials, 11: 4, 333 — 353

To link to this Article: DOI: 10.1080/00914038708078670

URL: http://dx.doi.org/10.1080/00914038708078670

Intern. J. Polymeric Mater., 1987, Vol. 11, pp. 333–353
Photocopying permitted by license only

Printed in the United Kingdom

Properties of Isoprene Rubber Reinforced with Treated Bleached Kraft Cellulosic Fibers or Rayon Fibers

B. WESTERLIND*, S. HIROSE, S. YANO, H. HATEKAYAMA and M. RIGDAHL*

Industrial Products Research Institute, 1-1-4 Yatabe-Machi, Higashi, Tsukuba-Gun, Ibaraki 305, Japan

(Received February 7, 1986)

Both native and regenerated (rayon) cellulosic fibers are potential reinforcing elements in rubbers due to their relatively good mechanical properties, suitable aspect ratio, low cost and low density. The properties of the cellulosic fibers can also be changed fairly easily by chemical treatment. The effects of two treatments, mercerization (NaOH-immersion) and benzylation, on the mechanical properties of a rubber-cellulose composite are here reported. The rubber matrix was isoprene and the fiber content 20% by volume (27% by weight). Mercerization of bleached kraft fibers gave a composite with a higher modulus and strength than was attained when untreated kraft fibers were used, whereas benzylation of both kraft fibers and rayon fibers caused a reduction in the strength and stiffness of the rubber composites. This is interpreted as being due to a decrease in the degree of interaction between the cellulosic fiber and the matrix due to the benzylation. The effect of these treatments on the mechanical properties of single rayon fibers is also reported.

INTRODUCTION

Interest in cellulosic fibers as reinforcing elements or as fillers in rubbers and plastics appears to be steadily increasing. Native

---

* Swedish Forest Products Research Laboratory, Paper Technology Department, Box 4506, S-114 86 STOCKHOLM, Sweden

cellulosic fibers certainly have the potential of being effective reinforcing elements since their tensile modulus is in the range of 20–70 GPa, depending on the fibril angle, the tensile strength is *ca* 1 GPa[1] and the aspect ratio is of the order of 50–200. Other advantages of using cellulosic fibers which are rather obvious are their low cost and low density.[2] Furthermore, they are not as brittle as glass fibers which is beneficial from the processing point of view, i.e. the aspect ratio of the cellulosic fibers will not be so drastically reduced.[3,4] It is well known that the elastic properties of rubber-cellulose composites are significantly influenced by the degree of fiber orientation and, as already mentioned, the aspect ratio of the fibers.[5–9] The mechanical properties of the composites are to a large degree determined not only by the properties of the matrix and the fibers, but also by the amount of fibers, the dispersion of the fibers in the matrix and the adhesion between the fiber and the matrix. In this context is may also be mentioned that Murty and De have extensively studied the behaviour of jute fibers as reinforcing elements in different rubber matrices.[10–12]

In general the elastic modulus increases when cellulosic fibers are incorporated in the rubber matrix and the elongation at rupture decreases.[3,5–9,12]. The tensile strength often decreases at low fiber contents and then increases at higher loadings. The decrease in strength at low fiber contents results if the matrix is not sufficiently restrained by the fibers, i.e. high matrix deformations may occur at low stresses and the matrix is weakened by broken or debonded fibers.[5,12] An increase in the aspect ratio of the fibers can shift the minimum in tensile strength to lower fiber concentrations.[5] In some situations no minimum in the tensile strength is observed but the strength increases monotonically with the amount of fibers.[12] In order to obtain a high tensile strength, bonding agents are often required to improve the stress transfer between the fiber and the matrix.[5,7,12] For cellulosic fibers, hexamethylenetetramine-resorcinol systems can be used[3,4] but other bonding agents may also be appropriate.[3,5,13] The addition of cellulosic fibers to rubber may also improve the time dependent mechanical properties and the resistance to solvent swelling.[5,7]

The primary aim of the present work has been to study the effect of chemical treatments of either native (bleached kraft) or regenerated (rayon) cellulosic fibers on the mechanical properties of isoprene rubber filled with such fibers. Two fairly straightforward chemical routes for modifying the fibers were investigated, mercerization, i.e. a simple immersion in a NaOH-solution, and benzylation. In the first place, an effect on the tensile modulus of the composite was looked for, but it was also hoped that the treatments would affect the adhesion between the fibers and the isoprene and consequently the tensile strength of the composite. It should however be stressed that the fiber content was relatively low (20% by volume) and in view of the critical fiber concentration concept discussed above, a pronounced and easily interpreted effect on the strength can perhaps not be expected. A few preliminary tests on the interlayer shear strength between the rayon fibers and the isoprene matrix were also performed using the single fiber pull-out test.

EXPERIMENTAL

Materials

The isoprene rubber used in this work was Nipol IR 2200 (Nippon Zeon Co Ltd). Bleached kraft fibers from Stora Kopparberg, Sweden or discontinuous (chopped) rayon fibers with an average fiber length of 2 mm were used as reinforcing elements in the elastomeric composites. Continuous rayon fibers were used for the pull-out tests. The rayon fibers (Daiwabo Corona SB) were prepared by Daiwa Boseki Co Ltd. Some of the fibers were chemically treated as described in the next section. The recipe for the isoprene-matrix of the composites is given in Table I. The fiber

TABLE I

Recipe of the compounded rubber composite

Isoprene	100.00 g
ZnO	5.00
Stearic acid	2.00
Sulfur	2.00
Accelerator:	
Dibenzothiazyl disulfide	1.25
Tetramethylthiuram disulfide	0.15
Reinforcing pulp (rayon or bleached kraft)	40.00

content was kept constant in the elastomeric composites, 27% by weight and 20% by volume.

Methods

Benzylation of the cellulosic fibers. It is known that benzylation does not alter the shape of the fibers.[14] Here the benzylated cellulosic fibers have been prepared by a two-stage reaction. In the first stage, the fibers are immersed in a sodium hydroxide solution and alkali cellulose is formed. In the second stage benzylchloride is added, which after reaction yields benzylcellulose.[15] The degree of substitution can easily be varied by changing the reaction time at constant temperature.

On a small scale the detailed benzylation procedure was as follows:

a) Immerse 0.5 g cellulosic fibers in 5 ml of a 13% sodium hydroxide solution for 2 h.

b) Press out the excess NaOH solution (2.75 ml)

c) React the fibers with 10 ml benzylchloride at 105°C for a predetermined time (0.5–2 h).

d) Wash the fibers several times with methanol and water.

The benzylation of the fibers was also carried out on a larger scale using a 4.5 dm^3 volume autoclave and 150 g of fibers. The procedure was similar to that outlined above.

Infrared (IR) spectroscopy of the benzylated samples. For the small-scale reaction, the weight increase after reaction was determined and from that the degree of benzylation was calculated. For these fibers and the fibers benzylated in the larger scale reaction, infrared spectroscopy (IR) was also used to evaluate the degree of substitution. The IR-spectrum was evaluated using a Jasco infrared spectrophotometer model A-3 (Japan Spectroscopic Co Ltd) and the KBr-disc technique was used to prepare samples for the IR-analysis (2 mg sample and 200 mg KBr).[16,17]

Interlayer shear strength between fiber and matrix evaluated by the support pull-out experiment. The shear strength of the interlayer between the benzylated or untreated rayon fibers and the pure isoprene rubber was measured using the single fiber pull-out method.[18,19] This method has been developed and frequently used for materials such as glass fiber reinforced plastics in order to quantify the degree of adhesion between the matrix and the reinforcing element. The principle of this method is to partly embed one fiber in the matrix and measure both the force required to pull the fiber out of the matrix and the embedded fiber length. From these data and the diameter of the fiber the interlayer shear strength (τ_B) can be calculated. The preparation of fiber pull-out specimens has been described in detail earlier.[19]

Figure 1 shows schematically the experimental set-up for the pull-out test in the present work. The rayon fiber was first threaded through a hole with a diameter of 0.5 mm in a thin metal plate. The fiber was centered in the hole and fixed at both ends. A small drop of pure unvulcanized isoprene dissolved in benzene (5% concentration) was placed on the hole. After the assembly had been dried, one side of the fiber was cut close to the rubber film or rubber button with a razor blade. A spot of epoxy resin was attached around the hole on the same side as that where the fiber had been cut close to the isoprene matrix. The epoxy was applied only to the reverse side of the rubber button to prevent excessive deformation

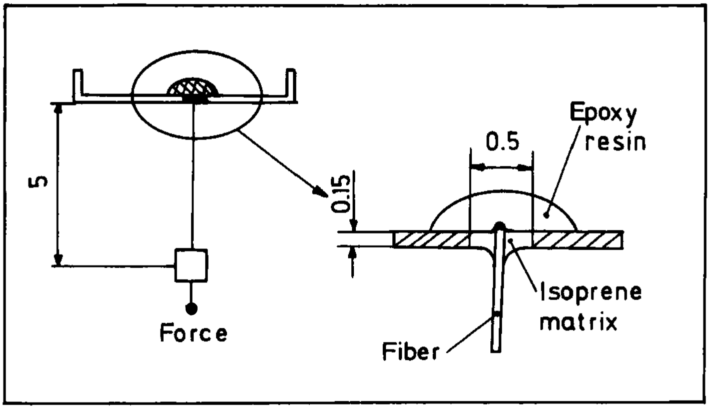

FIGURE 1 Schematic picture of the pull-out experiment. Notice the epoxy glue applied on one side of the steel plate to prevent the deflection of the flexible isoprene matrix.

of the rubber during testing. The other end of the fiber was glued to a brass plate at a distance of 5 mm from the isoprene matrix (rubber button). The whole assembly was then placed in the tensile tester which was equipped with specially designed clamps. The velocity of the moving grip was 10 mm/min, the temperature was approximately 19°C and the relative humidity around 50%. The force required to pull the rayon fiber out of the matrix and the displacement of the moving clamp were recorded. From the force-displacement curve, Figure 2, the pull-out force and the embedded fiber length were obtained. The embedded length of the fiber is in this case taken to be equal to the total displacement of the moving clamp of the machine since, after debonding of the fiber from the matrix, friction forces hold the fiber to the matrix to some extent until it has been completely pulled out.[18] The influence of the epoxy resin on the reverse side of the isoprene button has not been studied separately, but there are two justifications for neglecting the influence of the epoxy resin. The first is that the fiber area in contact with the epoxy resin is very small compared with the area of the fiber in contact with the isoprene matrix. The corresponding ratio is between 0.5 and 3.5%. The second reason is that a fairly

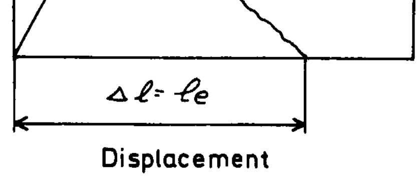

FIGURE 2 Force-displacement curve from the pull-out experiment with rayon fibers embedded in an isoprene matrix. Both the pull-out force and the embedded length were determined from such curves. Δl is the displacement of the crosshead and equals l_e.

linear correlation is obtained between pull-out force and embedded length. Such a relation would not be expected if the epoxy resin had a major influence.

Preparation of the cellulose-containing rubber. The Irumagawa Rubber Co Ltd (Japan) prepared the cellulose-rubber composites used in this work using a laboratory compounding machine with heated open mixing rolls with a diameter of 152 mm. The mixing of the fibers and the rubber was carried out as follows:

1) Compounding pure isoprene rubber for 5 min.

2) Adding zinc oxide, stearic acid and sulfur and then compounding for 5 min.

3) Adding the accelerator and compounding for 5 min.

4) Adding the cellulosic fibers and compounding for 10 min.

5) Passing the compound through the thin nip between the rolls. The compound was passed between the rolls 10 times (multi-pass mixing). After each pass, the sheet produced was rolled into a rod and replaced vertically into the mixing rolls. This compounding method resulted in well-dispersed elastomeric composites in all cases except for the one containing untreated bleached kraft fibers, which exhibited some degree of fiber agglomeration.

Vulcanization of the cellulose fiber reinforced rubber. The vulcanization rate was measured at 150°C using an oscillating rheometer, Toyoseiki Co Ltd. The induction time was defined as the time to the onset of the increase in the torque (T_2) and the vulcanization time was taken as the time required to reach 90% of the maximum torque (T_{90}). The minimum torque, the maximum torque, the induction time and the vulcanization time are listed in Table II. It may be noted that the vulcanization time was reduced by a factor of at least two by incorporation of the cellulosic fibers.

The specimens used for evaluating the mechanical properties of the composites were vulcanized in a heated press (150°C). The vulcanization times for these specimens were chosen, depending on their composition, to be exactly the same as given in Table II.

Tensile tests. The tensile properties of the composites were measured at 19°C and 45% relative humidity using an Instron

TABLE II

Vulcanization conditions

Fiber	Min torque (Nm)	Max torque (Nm)	Induction time (min) T_2	Vulcanization time (min) T_{90}
Kraft	0.1	5.8	7	11
Mercerized kraft	0.15	6.5	6	8
2 hour-benzylated kraft	0.1	4.8	4	7
Rayon	0.1	5.4	7	8.5
30 min-benzylated rayon	0.05	4.4	9	13
2 hour-benzylated rayon	0.05	4.4	8.5	12
Vulcanized rubber without fibers	0.08	3.2	10	25

tensile tester (model TMM). The velocity of the moving clamp was 50 mm/min. Two types of test specimens were prepared: rectangular specimens with a width of 5 mm and a thickness of 2 mm for evaluation of Young's (elastic) modulus and standard dumbbell shaped test specimens number C (ASTM D412-68) for determining the stress and strain at failure. The gauge length was in both cases 50 mm. Eight rectangular and four dumbbell specimens of each type of composite were prepared.

Abrasion tests. The abrasion resistance of the composites was evaluated using a Toyo Seiki Taber type of abrasion tester. A cellulose-containing rubber sheet ($10 \times 10\,\mathrm{cm}^2$) was placed on a rotating disc. The rotational velocity was set to 70 rpm and the total number of revolutions was 1000. Two cylindrical files were placed on the rotating rubber sheet. The files used (Calibrade H18) were specially designed for rubber testing. The total load on each file was 10 N. The abrasion resistance was evaluated from the weight loss of the sample during the test.

Scanning electron microscopy (SEM). The fracture surfaces of the composites were studied with a scanning electron microscope (Cambridge 600).

RESULTS AND COMMENTS

The degree of substitution of benzylated bleached kraft and rayon fibers

For the fibers benzylated on a small scale, the degree of substitution was calculated from:

$$n = 1.8(W_a/W_b - 1) \tag{1}$$

where n is the degree of substitution, W_a the weight of the fibers after the reaction and W_b the weight before the reaction.

A completely benzylated cellulose sample should exhibit a weight increase of 167% and the corresponding degree of substitition would be 3. Figure 3 shows the degree of substititition as a function of the benzylation (reaction) time for both bleached kraft and rayon fibers. There appears to be a difference between the bleached kraft and the rayon fibers in this respect. For the bleached kraft fibers the degree of substitution increased linearly with the reaction time up to

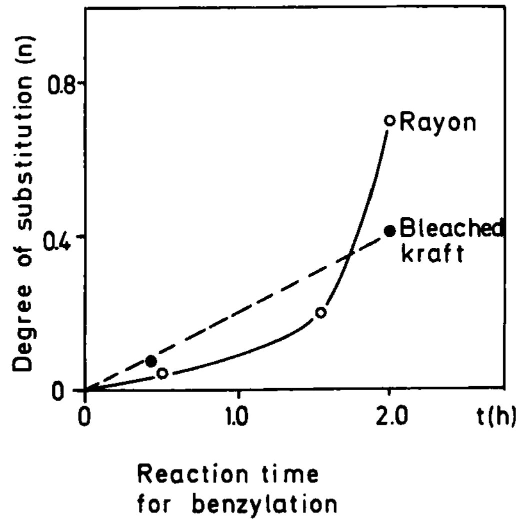

FIGURE 3 The degree of benzylation vs. reaction time for bleached kraft fibers and rayon fibers.

2 hours, whereas for rayon the initial rate was lower but increased strongly after *ca* 1.5 h. A certain interaction time is apparently required for the benzyl chloride to diffuse into the structure of the rayon fibers and react with the cellulose molecule.[16] Mercerization of the bleached kraft fibers for 2 hours resulted in a weight decrease of approximately 8%, since hemicelluloses dissolve in the NaOH-solution. This weight reduction was compensated for when calculating the degree of substitution of the kraft fibers shown in Figure 3.

In order to analyse the effect of benzylation on the fibers using the large scale reaction described earlier (with 150 g cellulosic fibers) IR was used. IR-spectra were recorded for all samples produced, using both the small scale reaction and the large scale reaction. Figure 4 shows typical spectra for benzylated rayon fibers (2 hours, produced in the small scale reaction) and untreated rayon. The benzylated sample has four clearly discernible absorption bands, which originate from the aromatic group, at wavelengths of

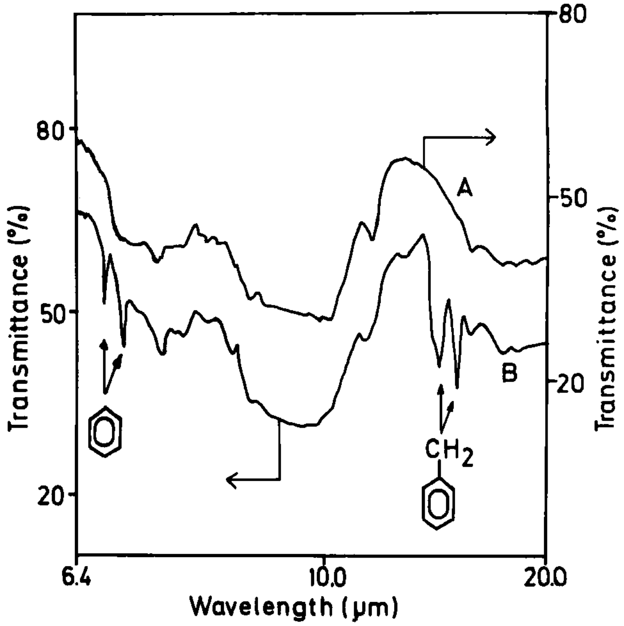

FIGURE 4 Infrared spectra of rayon fibers benzylated in the small-scale reaction. *A* = untreated rayon fibers and *B* = 2 hour-benzylated rayon fibers.

6.65, 6.85, 13.5 and 14.3 μm[16] as indicated in Figure 4. From the IR-spectra it is thus obvious that the fibers have been benzylated as required. The area under the 13.5 μm-peak for unit weight of cellulose in the sample, i.e. the optical density/unit weight, is proportional to the degree of substitution.

A comparison of the IR-spectra for the fibers reacted on a small scale with those for the fibers produced on the larger scale at the same reaction time shows a somewhat lower degree of substitution (lower value for the optical density/unit weight) for fibers treated on the larger scale. This is expected since, on the large-scale, 30 min was required to reach the reaction temperature of 105°C compared with only a few minutes for the small-scale reaction.

Effect of benzylation and NaOH-immersion on the mechanical properties of single rayon fibers

Even a low degree of substitution with a few benzyl groups in the surface structure has a profound effect on the mechanical properties of the single rayon fibers. It should be pointed out that the fiber diameter increased with increasing degree of substitution and that the density decreased, the increase in diameter being evident from scanning electron microscope studies on single rayon fibers. The tensile strength data have been corrected for the increase in fiber cross-section area. The tensile strength decreased with increasing degree of substitution as shown in Figure 5. The untreated (virgin) rayon fiber strength was *ca* 180 MPa and immersion of the fibers for 2 hours in the NaOH-solution reduced the tensile strength to 115 MPa. This is perhaps to be expected since the fibers were subsequently dried without any tension. The introduction of benzyl groups into the structure further decreased the strength to *ca* 80 MPa at very low degrees of substitution (0.1) whereas higher degrees of substitution did not affect the fiber strength appreciably, Figure 5.

The elongation at failure showed a somewhat different dependence on the degree of substitution, Figure 6. The untreated rayon fibers had an elongation at failure of *ca* 30% and this was doubled to *ca* 60% after immersion of the fibers for 2 hours in the NaOH-solution. Again this may be an effect of the free drying of the fibers after the NaOH-treatment. The benzylation, on the other

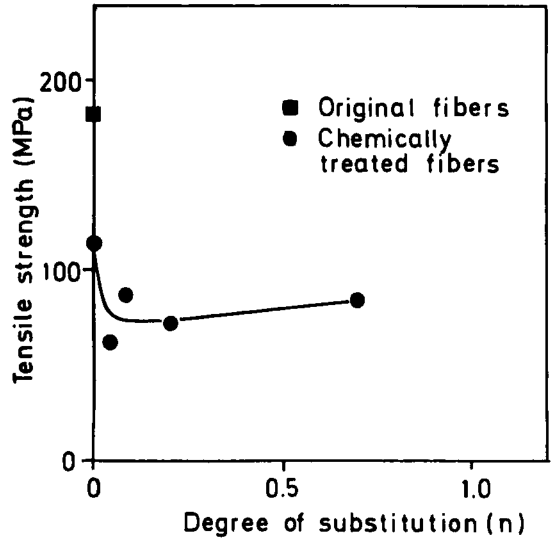

FIGURE 5 The tensile strength of the single benzylated rayon fiber vs. the degree of substitution.

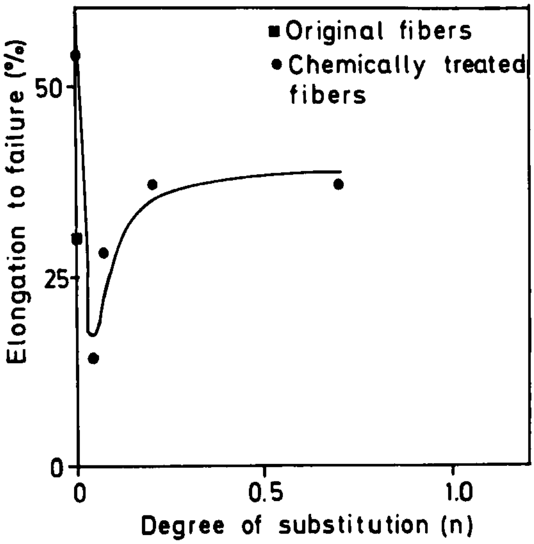

FIGURE 6 Elongation to failure as a function of the degree of substitution for rayon fibers. A low degree of substitution gives a fiber with very low elongation.

hand, reduced the ductility drastically down to only 14% at a low degree of substitution. For higher contents of benzyl groups the ultimate elongation increased rapidly to a plateau value of *ca* 35%, Figure 6. One explanation of this behaviour may be that a short reaction time yields a heterogeneous fiber structure with a benzylated fiber surface and an unchanged fiber core. A longer reaction time results in a more homogenous fiber with a greater elongation to failure.

Single fiber pull-out tests with rayon fibers

In Figure 7 the force required to pull a single rayon fiber out of the matrix is plotted against the embedded fiber length. In these experiments the matrix (isoprene) was unvulcanized and it was supported by the epoxy resin as shown in Figure 1. The nominal tensile strength of the unvulcanized isoprene matrix was only 0.2 MPa and it had an elongation to failure of 480%. The true tensile strength (corrected for the area reduction) was *ca* 1.2 MPa. Figure 7 includes results for untreated fibers as well as for rayon fibers benzylated for 1 hour. The least-squares fitted straight lines have an intercept with the embedded-length axis at approximately 200 μm for both types of fibers. The reason why the lines do not pass through the origin is not clear at present but some causes are discussed in Ref. 18. The measured embedded length was corrected for this intercept on the l_e-axis i.e. l_0, and the interlayer shear strength (τ_B) was calculated from:

$$\tau_B = F_d / \pi \, d \, (l_e - l_0) \qquad (2)$$

where F_d is the pull-out force, d the fiber diameter, l_e the embedded fiber length and l_0 the intercept with the l_e-axis.

The average value of τ_B was somewhat higher for the 1 hour-benzylated rayon fibers, 0.9 ± 0.1 MPa, than for the untreated rayon fibers, 0.7 ± 0.3 MPa. This difference in τ_B cannot however be considered to be significant. The interlayer shear strength was also rather low compared with earlier results obtained with thermoplastic matrices.[19,20] The τ_B-values here obtained can be considered to be rather reasonable since it is difficult, using the pull-out test, to obtain τ_B-values which are higher than the cohesive strength of the matrix.[19] The results of the single-fiber pull-out test and of the

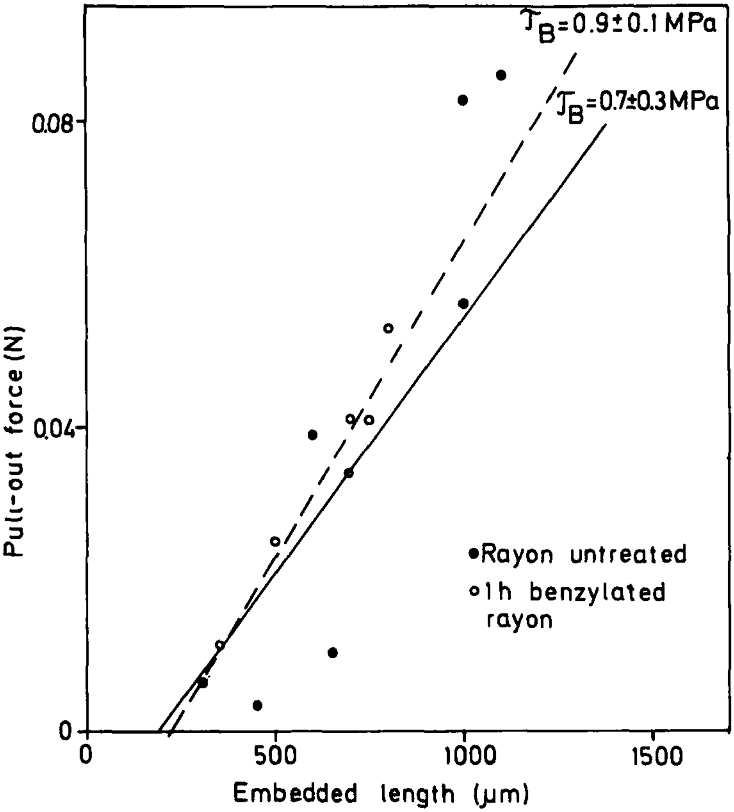

FIGURE 7 Pull-out force as a function of the embedded fiber length for untreated rayon fibers and 1 hour-benzylated rayon fibers (degree of substitution = 0.08) embedded in an unvulcanized isoprene matrix. No significant change in the interlayer shear strength could be observed.

microscopic studies of the pulled-out fibers thus indicate that the failure mode in this case is significantly influenced by the cohesive failure of the rubber matrix. This makes the fiber pull-out test less valuable in quantifying the degree of adhesion between the fiber and the rubber. It is quite possible that the vulcanization can have a significant influence on the interlayer shear strength in addition to the improvement in matrix strength, and that for such systems a more defined adhesive failure would be obtained. Due to experimental difficulties no pull-out tests were however performed using vulcanized isoprene rubber.

Continuous rayon fibers only were used in the study of the effect of benzylation on the single fibers and when making the pull-out tests. Obviously, it is possible to use short kraft fibers, but this would be very tedious.

Properties of the rubber composites reinforced with short cellulosic fibers

The original strength of the non-reinforced vulcanized isoprene rubber, used as matrix material was *ca* 7.5 MPa, the small-strain elastic modulus *ca* 1 MPa and the elongation at failure 850%. When 27% by weight of the short rayon fibers were incorporated into the rubber matrix the elastic modulus increased substantially up to 44 MPa in the roll direction while the tensile strength was slightly reduced to 6.8 MPa, see Table III. Benzylation of the rayon fibers reduced the Young's modulus down to *ca* 14 MPa and the strength decreased to less than half of the original rubber strength (unfilled material). Whether the reaction time was 30 min or 2 h appeared to have no major effect on the mechanical properties of the composites. Benzylation of the bleached kraft fibers resulted in a composite with a comparatively poor property profile. A rubber containing

TABLE III

Mechanical properties of isoprene rubber composites containing 27% by weight rayon or kraft fibers

Reinforcing fiber	Elastic modulus (MPa)	Tensile strength (MPa)	Anisotropy E_0/E_{90}
Kraft	30	4.8	4.4
Mercerized kraft	74	9.2	3.0
2 hour-benzylated kraft	22	3.7	4.7
Rayon	44	6.8	4.3
30 min-benzylated rayon	13	2.6	2.7
2 hour-benzylated rayon	14	3.0	2.1
Vulcanized rubber without fibers	1	7.5	

Note: E_0/E_{90} denotes the ratio between the modulus in the roll direction and the modulus in the transverse direction. The modulus and the strength data in the first two columns refer to the roll direction of the composites.

untreated kraft fibers had higher modulus and strength (30 and 4.8 MPa, respectively) than one containing benzylated kraft fibers. Untreated rayon fibers appeared to be slightly superior to untreated kraft fibers as reinforcing elements, but the situation was the reverse when the fibers had been benzylated. By far the best performance was obtained with mercerized kraft fibers. The corresponding rubber composite had a tensile modulus of 74 MPa and a tensile strength of 9.2 MPa in the roll direction. This composite was the only one that had a strength value exceeding that of the unfilled rubber.

The rubber composites were rather anisotropic due to orientation of the cellulosic fibers during the compounding between the mixing rolls. The ratio of the elastic modulus in the roll direction to the modulus in the transverse direction varied from 2.1 to 4.4 depending on the type of cellulosic fiber which was used, see Table III.

Figure 8 shows stress–strain curves in the roll direction for composites containing mercerised and benzylated (2 hours) bleached kraft fibers. The stress-strain curves have completely different characters. It is quite obvious that benzylation does not produce a sufficient degree of bonding between the kraft fibers and isoprene.[5] Mercerization on the other hand appears to be promising as a way to improve the performance of native cellulosic fibers in this context. Figure 8 also includes stress-strain curves for composites containing untreated and benzylated (2 hours) rayon fibers. It is clear that the benzylated fibers debond from the matrix during straining and produce a material with a rather low strength and a high elongation to break.

Effect of cellulosic fibers on abrasion resistance

No great differences were observed between the different composites with regard to their abrasion resistance. The abrasion, measured as the weight decrease of the square samples, was about 5% for all materials; somewhat lower for composites based on mercerized kraft fibers and untreated rayon and somewhat higher for composites containing untreated kraft fibers and benzylated kraft and rayon fibers. The abrasion resistance correlates to some extent with the strength of the composites, i.e. higher tensile strength corresponds to a lower weight loss in the abrasion test.

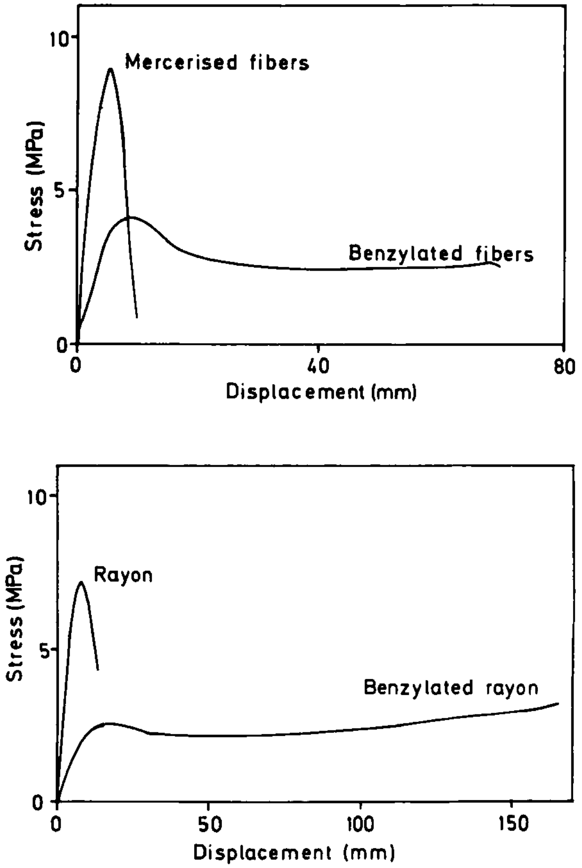

FIGURE 8 Stress-displacement curve for isoprene rubber composites containing bleached kraft fibers (mercerised or 2 hour-benzylated) or rayon fibers (untreated or 2 hour-benzylated).

Scanning electron microscope (SEM) studies of fracture surfaces

The fracture surface (after tensile testing) of isoprene rubber reinforced with 2 hour-benzylated rayon fibers is shown in Figure 9. In general the fracture surfaces have a more or less similar appearance regardless of the fiber treatment. Only in a few cases was fiber fracture observed. The fibers are apparently pulled out of

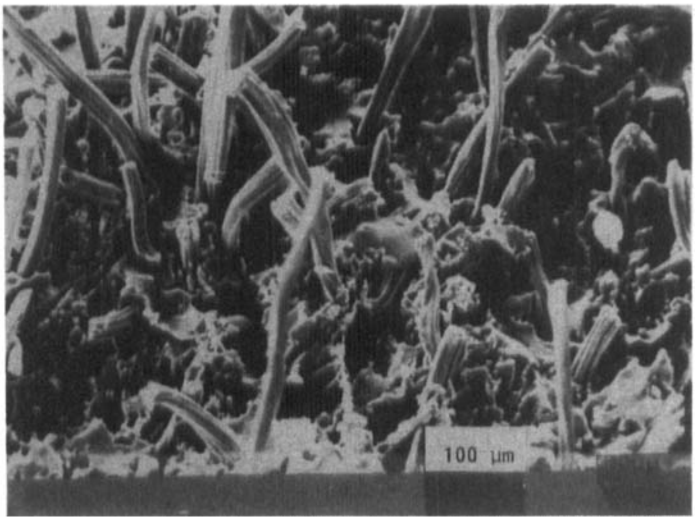

FIGURE 9 Scanning electron micrograph of fracture surfaces of a rubber composite containing 2 hour-benzylated rayon fibers. Only in a few cases could fiber fracture be observed.

the isoprene matrix or the matrix itself has failed. The micrographs indicate that the adhesion between the fibers and the isoprene rubber is not very significant. This is in agreement with the mechanical properties of rubber containing benzylated fibers but for the mercerised kraft fibers this is not necessarily true.

DISCUSSION

Short cellulosic fibers are, as previously stated, of interest as potential reinforcing elements in both plastics and elastomers for a number of reasons.[2–13] Some treated cellulosic fibers are commercially available. As with other kinds of fiber-reinforced polymers, a sufficient degree of interaction or adhesion between the cellulose fiber and the matrix is usually desired to take advantage of the mechanical performance of the fibers. In many cases bonding agents are considered to be essential to achieve this goal. The purpose of the present work was to investigate the effect of rather simple chemical treatments of cellulosic fibers on the performance in rubber composites. These treatments, NaOH-immersion and benzylation, are obviously not the bonding agent type of modification but may be considered to be interesting, especially since these procedures are fairly simple. With both procedures it was hoped to improve the compatibility between the cellulosic fiber and the rubber. The treatments cannot be expected to improve the fiber properties themselves, cf. Figure 5, especially since the fibers after the treatment were dried without any restraint.

As expected,[2-13] the addition of cellulosic fibers increased the modulus of the composite significantly compared with that of the unfilled rubber. The greatest increase in modulus was observed when mercerized bleached kraft fibers were used, and in this case a similar increase in the tensile strength was also observed. Benzylation of both kraft and rayon fibers however produced composites with lower tensile modulus and strength than composites containing the corresponding untreated fibers. In part, this reduction is due to the decrease in the modulus and strength of the fibers following the benzylation, but it also appears that the benzylation produces a lower degree of adhesion and the expected effect of entanglement between the benzyl groups and the isoprene molecules was not observed. The IR-spectra clearly indicated that the fibers had indeed been benzylated. It may also be that isoprene rubber is not suitable as matrix material for benzylated fibers. Styrene-butadiene rubber is perhaps more suitable, since it has been reported that benzylation of cellulosic material can improve the interaction of this material with a polystyrene matrix.[21]

It is certainly interesting that a simple mercerization of native cellulosic fibers can have a strong positive effect on the properties of the rubber composite. It is not at present clear why this treatment is beneficial. However, a few possible reasons may be mentioned. During mercerization, the hemicellulose is dissolved and the remaining fiber has, as revealed by SEM, a rather rough surface. The adhesion between the rubber and the cellulosic fiber may then increase due to the effect of mechanical interlocking (increased surface roughness). Moreover, any remaining alkali in the fiber may act as an accelerator for the vulcanization of the rubber close to the mercerized fiber and thus lead to an improvement in adhesion.

It would certainly be worthwhile to extend the present investigation to include the effect of different contents of fibers, partly with the aim of studying any possible lower critical content of fibers especially since the fiber content in this work was rather low (20% by volume). At higher volume contents the effect of the mercerized kraft fibers may be even more pronounced.

Both mercerization and benzylation can be regarded as relatively simple methods of modifying the structure. Another way, besides the use of bonding or coupling agents, may be graft polymerization. However, the development of such techniques and procedures is expected to be rather time-consuming and the products can be rather expensive. Perhaps, research into or developments of suitable cure systems[7] can offer an alternative route to optimize the performance of both untreated and chemically treated cellulosic fibers.

Acknowledgements

One of the authors (B.W.) thank JITA (Japan Industrial Technology Association) and AIST (Agency of Industrial Science and Technology) for awarding him a scholarship during his stay at the Industrial Products Research Institute, Tsukuba, Japan. The authors gratefully acknowledge discussions with Dr B. Stenberg, Royal Institute of Technology, Stockholm, Sweden, and thank Mr T. Nakamura and Mr S. Shiotani (Irumagawa Rubber Co Ltd) for preparing the rubber composites. The authors also thank Dr J. A. Bristow for the linguistic revision of the manuscript.

References

1. D. H. Page and F. El-Hosseiny, *Sv. Papperstid.*, **79**, 471 (1976).
2. H. -E. Strömvall, Ph.D. Thesis, Chalmers University of Technology, Gothenburg, Sweden, 1984.
3. K. Boustany and P. Hamed, Rubber India., Oct. 1975, p. 14.
4. L. A. Goettler, J. A. Sezna and P. J. Di Mauro, Rubber World, Oct. 1982, p. 33.
5. A. Y. Coran, K. Boustany and P. Hamed, *Rubber Chem. Techn.*, **47**, 396 (1974).
6. A. Y. Coran, P. Hamed and L. A. Goeteller, *Rubber Chem. Techn.*, **49**, 1167 (1976).
7. Hamed and P. C. Li, *J. Elastomers and Plastics*, **9**, 395 (1977).

8. S. R. Moghe, *Rubber Chem. Techn.*, **49,** 1160 (1976).
9. S. R. Moghe, *Rubber World,* Febr. 1983, p. 16.
10. V. M. Murty and S. K. De, *Rubber Chem. Techn.*, **55,** 287 (1982).
11. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.,* **27,** 4611 (1982).
12. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.,* **29,** 1355 (1984).
13. US Patents 3, 697, 364 (October 19, 1972) and 3, 709, 845 (January 9, 1973).
14. H. Okada, *Cellulose Chemie,* **12,** 11 (1931).
15. E. J. Lorand, *Ind. Eng. Chem.,* **31,** 891 (1939).
16. R. T. O'Conner, E. F. Du Pre' and E. R. McCall, *Textile Res. J.,* **28,** 542 (1958).
17. R. T. O'Conner, E. F. Du Pre' and E. R. McCall, *Anal. Chem.,* **29,** 998 (1957).
18. J. P. Favre and M. -C. Merienne, *Int. J. Adhesion Adhesives,* **1,** 311 (1981).
19. B. Westerlind, M. Rigdahl, H. Hollmark and A. de Ruvo, *J. Appl. Polym. Sci.,* **29,** 175 (1984).
20. D. B. Eagles, B. F. Blumentritt and S. L. Cooper, *J. Appl. Polym. Sci.,* **20,** 435 (1976).
21. T. Fujimaura and T. Seino, *Chem. High. Polym. (Japan),* **28,** 910 (1971).