EFFECT OF ADHESION ON THE EQUILIBRIUM SWELLING OF SHORT SISAL FIBER REINFORCED NATURAL RUBBER COMPOSITES

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ABSTRACT

Solvent swelling of natural rubber composites, containing both untreated and acetylated short sisal fiber, has been investigated in a series of normal alkanes such as pentane, hexane, heptane and octane. The restriction on elastomer swelling exerted by sisal fiber as well as the anisotropy of swelling of the composite have been confirmed by this study. The results showed that increased fiber content and the addition of bonding agent reduced the swelling considerably. It has been demonstrated that with improved adhesion between short fiber and rubber, the factor, $(V_l - V_F)/V_l$, decreases, where V_l and V_F, are the volume fraction of rubber in dry and swollen samples, respectively.

INTRODUCTION

Short fiber reinforced rubber composites have gained wide importance due to the advantages they impart in processing and low cost coupled with high strength. These composites combine the elastic behavior of rubber with strength and stiffness of fiber. Moreover, reinforcement with short fibers offers some attractive features such as high modulus, tear strength, etc. Major factors which affect the performance of rubber–fiber composites are: fiber loading, dispersion, orientation, fiber-to-rubber adhesion and the aspect ratio of the fiber. The properties of natural rubber (NR) composites reinforced with short rayon, nylon and glass fibers have been extensively studied.[1] The influence of milling parameters which bring about the fiber orientation and hence affect the composite's properties have been reported.[2] Coran *et al.*[3] studied the properties of cellulosic fiber–elastomer composites and found that aspect ratio of the fiber has a major role on composite properties. O'Connor[4] concluded that a two component dry bonding system consisting of hexamethylene tetramine (Hexa) and resorcinol is sufficient for getting good fiber–rubber adhesion with cellulosic fibers instead of the normal three component dry bonding system.

Though both synthetic and natural fibers have been used for reinforcing polymers, the natural fibers gained importance because of their low cost, easy availability and good adhesion with the polymer matrix. De and coworkers[5–8] have reported the results of their studies on short jute fiber and silk fiber reinforced natural rubber, styrene–butadiene rubber (SBR), carboxylated nitrile rubber (XNBR) and blends of NR and polyethylene. Now-a-days sisal fiber has become important as a reinforcing filler both for plastics and rubbers. Recently, sisal fiber has been successfully used for the reinforcement of thermoplastics, thermosets and rubbers.[9–15] Varghese, Kuriakose and Thomas[11] have studied the mechanical properties of raw and acetylated short sisal fiber reinforced NR composites and found that acetylation improves adhesion between NR and the fiber.

Swelling of rubber vulcanizates in a wide range of solvents has been studied by Whitby, Evans and Pasternack.[16] An essential difference between vulcanized and raw rubber is that

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TABLE

FORMULATIONS

	A	B	C	J	K	L	L_0
Natural rubber	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5
Resorcinol	0	0	8.8	0	2.5	5	0
Hexamethylene tetramine	0	0	5.6	0	1.6	3.2	0
Sisal fiber (untreated)	35	0	0	0	10	20	20
Sisal fiber (acetylated)	0	35	35	0	0	0	0
TDQ[a]	1	1	1	1	1	1	1
CBS[b]	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5

[a] 2,2,4-trimethyl-1,2-dihydroquinoline (polymerized form, molecular weight 173.26).

[b] N-cyclohexylbenzothiazyl sulphenamide.

the former possesses a structure which cannot be broken down completely by any solvent; the material, therefore, swells but cannot be dispersed. The sorption and transport of organic solvents by polymer membranes have been studied extensively by Aminabhavi and co-workers.[17,18] They also investigated the diffusion characteristics of polyurethane membranes in normal alkanes and observed that the diffusion mechanism followed the Fickian trend and the kinetics of sorption was of first order.

Swelling of vulcanized rubber in various liquids has been investigated by Gee.[19] He found that the entropy of swelling of vulcanized rubber is independent of the nature of the swelling liquid. Kraus[20] determined the degree of cure in particulate filler reinforced vulcanizates by swelling methods. In order to understand the correlation between molecular structure and intermolecular attraction, Salomon and Van Amerongen[21] have made a comparison of swelling equilibria of different polymers under the influence of polar and polarizable groups which were introduced in solvents and polymers having different molecular structures. They concluded that the strength of interaction depends on the mutual attraction of both the components. Coran, Boustany and Hamed[22] have studied the solvent swelling of unidirectional rubber–fiber composites. From their studies it was concluded that fibers restrict the amount of swelling in unidirectional fiber composites.

Numerous techniques such as H-block and strip adhesion, both static and dynamic in nature, have been used to measure adhesion between fiber and rubber. While most of these give a good relative indication of adhesion, the time dependent nature of the viscoelastic materials some times overshadows the real effect. Equilibrium swelling is another technique which has been used to asses rubber–fiber adhesion, since fibers — if bonded — are supposed to restrict the swelling of elastomers. The adhesion between rubber and short glass and asbestos fibers has been studied by Das using restricted swelling measurements.[23] This study established that with improved adhesion between short fibers and rubber, the factor

$$\frac{V_I - V_F}{V_I} \tag{1}$$

decreases, where V_I and V_F are the volume fraction of rubber in dry and swollen samples, respectively. Kraus[24] has shown that the degree of restriction exerted by a reinforcing filler follows an equation of the form,

$$\frac{v_{ro}}{v_{rf}} = 1 - [3C(1 - v_{ro}^{1/3}) + v_{ro} - 1]\frac{\phi}{1 - \phi}; \tag{2}$$

where, v_{ro} represents the volume fraction of rubber in the unfilled vulcanizate; v_{rf} is the volume fraction of rubber in the filled vulcanizate; ϕ is the volume fraction of filler; and C

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OF COMPOSITES

M	N	P	P_0	Q	Q_0	R	R_0	S	S_0
100	100	100	100	100	100	100	100	100	100
1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
5	5	5	5	5	5	5	5	5	5
7.5	10	2.5	0	5	0	7.5	0	10	0
4.8	6.4	1.6	0	3.2	0	4.8	0	6.4	0
30	40	0	0	0	0	0	0	0	0
0	0	10	10	20	20	30	30	40	40
1	1	1	1	1	1	1	1	1	1
0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

is a constant characteristic of the filler and indicative of the degree of adhesion. Lorenz and Parks[25] also investigated the restriction from swelling exerted by a filler, using carbon black in a natural rubber vulcanizate. Their results followed an empirical relation that is exponential in nature.

$$\frac{Q_{\text{black}}}{Q_{\text{gum}}} = ae^{-z} + b; \tag{3}$$

where Q_{black} and Q_{gum} are the weight of swelling agent imbibed per unit weight of rubber; z is the weight of filler per unit weight of rubber; and a and b are constants. This dependence was explained as due to a restricted swelling of the rubber matrix in the neighborhood of filler particles. Parks[26] reported that natural rubber vulcanizate loaded with brass powder showed an increase in crosslink density by swelling measurements, indicating an intraction or bonding between the rubber and the brass.

In this paper the restricted equilibrium swelling is evaluated as a means to measure the degree of adhesion between short sisal fiber and NR.

EXPERIMENTAL

Sisal fiber used in this study is *lignocellulosic* in nature. It is reported to contain 78 % cellulose, 10 % hemicellulose, 8 % lignin, 2 % waxes and 1 % ash.[27] It has an average diameter of 0.103 mm and a specific gravity of 1.45. NR used for the study was Indian Standard Natural Rubber–light color grade (ISNR-3L). Hexamethylene tetramine (Hexa) and resorcinol were laboratory reagent grade. All other ingredients were commercial grade.

Sisal fiber was chopped to a length of 10 mm and when used as such was designated as untreated fiber. Acetylated fiber was prepared from the chopped raw sisal fiber as per the methods reported by Chand, Varma and Khazanchi,[28] and described in one of our earlier communications.[11]

PREPARATION OF COMPOSITES AND MOLDING

Formulations of composites are given in Table I. The quantity of resorcinol and Hexa was varied based on the fiber content, maintaining a ratio of 35 : 8.5 : 5.6 for fiber : resorcinol : Hexa. The composites were prepared in a laboratory model two roll mixing mill (150 x 300 mm) at a nip gap of 1.3 mm. The fiber orientation was achieved by passing the uncured composite repeatedly (three times) through the mixing mill at a tight nip. However, achieving

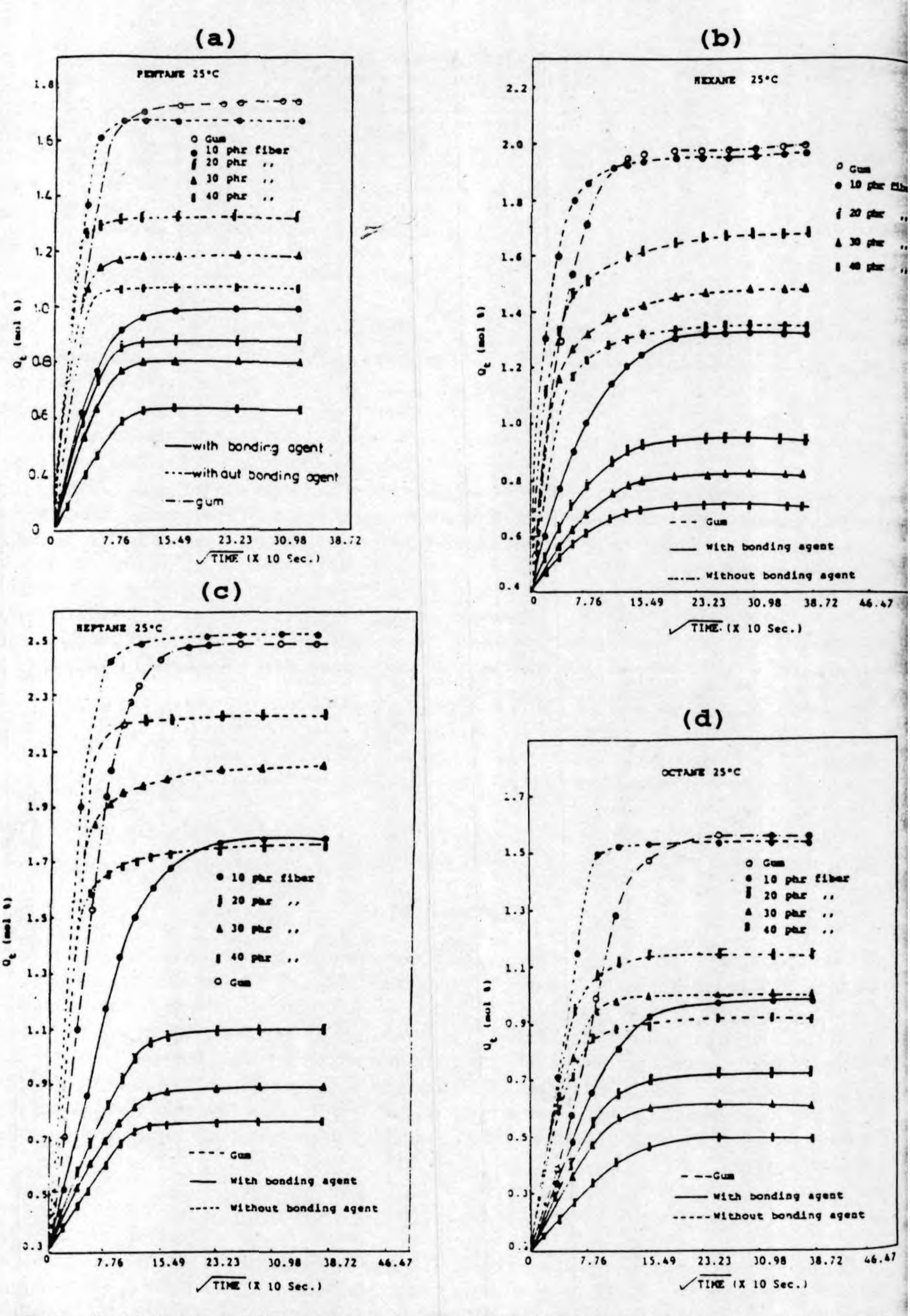

FIG 1. — Sorption curves at 25°C for mixes: J (gum), P, Q, R, S (with bonding agent); and mixes: P_0, Q_0, R_0 and S_0 (without bonding agent); swelling solvents at 25°C: **(a)** pentane, **(b)** hexane, **(c)** heptane, **(d)** octane. Note: units for *y*-axes are mole %.

TABLE II

AMOUNT OF SOLVENT ABSORBED BY COMPOSITES
Q and Q_0 AT EQUILIBRIUM SWELLING

Solvent	Bonded composite, Q (mol %/100 g composite)	Unbounded composite, Q_0 (mol %/100 g composite)
Pentane	0.88	1.32
Hexane	0.95	1.68
Heptane	1.10	2.23
Octane	0.72	1.14

more than 90 % orientation of the fiber in one direction is practically impossible. Blanks cut from the uncured sheet were marked in the mill-grain direction. The sheets were vulcanized at 150°C in a steam heated hydraulic press to the respective cure times obtained from running samples on a Monsanto rheometer. Tests such as tensile and tear strengths were carried out along (longitudinally oriented fiber) and across (transversely oriented fiber) the mill grain direction according to ASTM standards.

For swelling studies vulcanized composites were cut circularly (diameter 1.94 cm) by means of a sharp edged steel die. The thickness of the composite was measured using a micrometer screw gauge. The dry weight of the cut sample was obtained before immersion in the liquid contained in an air-tight weighing bottle. The samples were removed from the bottles at periodic intervals. The wet surfaces were quickly dried using a piece of blotting paper and the sample was weighed immediately in an air-tight weighing bottle. During swelling, changes in the diameter and thickness of the sample were measured by means of a vernier caliper and micrometer, respectively.

The uptake of the solvent by the rubber during swelling was expressed as moles of solvent sorbed by 100 g of the rubber. This method was found to be more convenient for comparison of sorption data and was adopted by many researchers.

To determine the volume fraction of rubber in the unswollen vulcanizate, the test specimens were weighed both in air and in water. The difference between the two weights gave the volume of sample. Using the base formulation, the amount of rubber present in the weighed samples of each specimen and its volume were calculated. From these data the

TABLE III

CHANGE IN VOLUME FRACTION OF RUBBER DUE TO SWELLING
OF SISAL FIBER COMPOSITES

Mix No.	Vol. fraction rubber in dry specimen (V_I)	Vol. fraction rubber in swollen specimen (V_F)	$V_T = \frac{V_I - V_F}{V_I}$
J	0.98	0.20	0.79
P	0.84	0.31	0.63
P_0	0.86	0.25	0.70
Q	0.77	0.33	0.57
Q_0	0.80	0.31	0.61
R	0.72	0.34	0.52
R_0	0.76	0.28	0.63
S	0.65	0.33	0.48
S_0	0.71	0.26	0.63
L	0.79	0.32	0.59
L_0	0.84	0.24	0.71

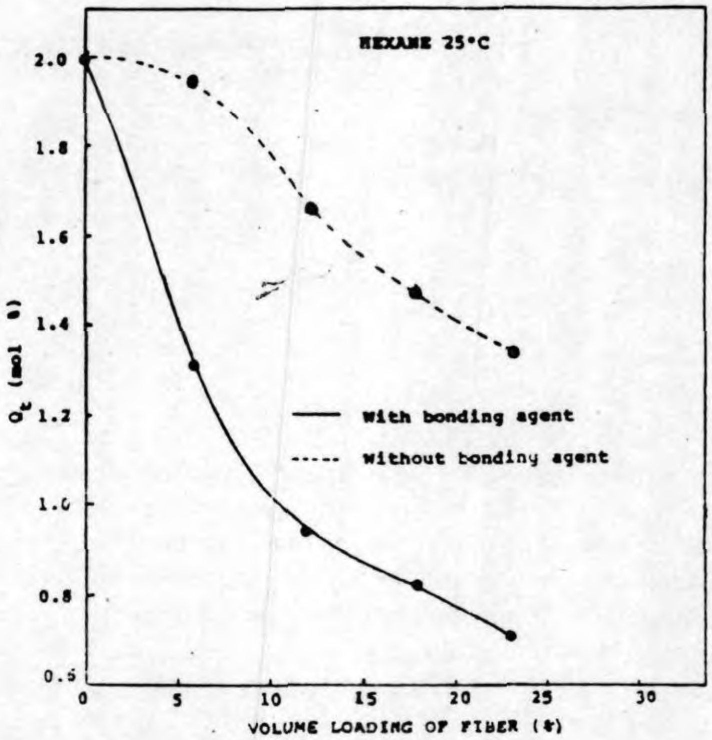

FIG. 2. — Effect of fiber loading on equilibrium sorption for NR-sisal composites with and without bonding agents; swelling solvent, hexane at 25°C.

volume fraction of rubber present in the dry specimen was calculated. It is denoted as These dry specimens were then swollen to equilibrium in hexane. The volume of swoll samples was determined by weighing the swollen sample immersed in hexane. The displac volume of hexane was corrected for actual volume of swollen sample by multiplication usi

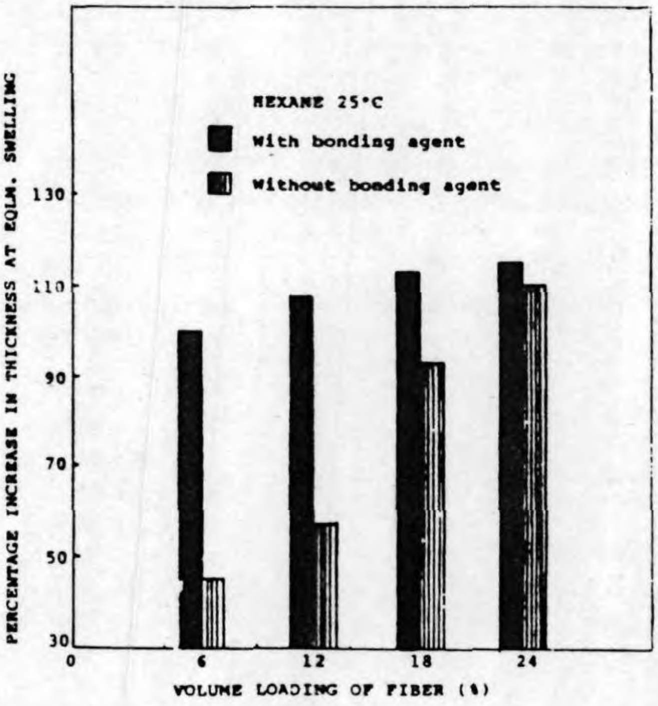

FIG. 3. — Percentage increase in thickness following swelling vs. fiber loading with and without bonding agents; swelling solvent, hexane at 25°C.

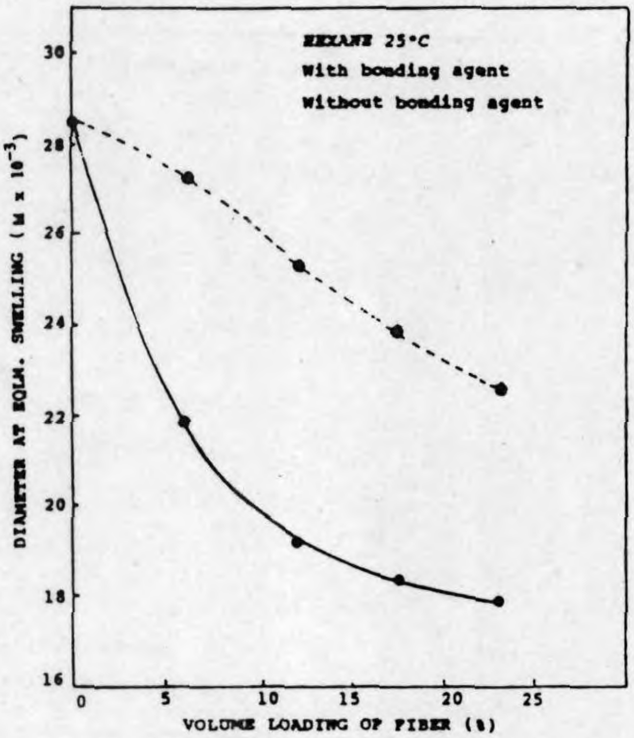

FIG. 4. — The change in diameter of the composites following swelling to equilibrium in hexane vs. fiber loading with and without bonding agents; swelling solvent, hexane at 25°C.

the density of hexane.[23] The volume of rubber in both dry and swollen samples were assumed unchanged. The volume of rubber in the sample divided by the volume of swollen sample gave the volume fraction of rubber (V_F) in the swollen state.

We have conducted the swelling studies in a series of alkanes. *i.e.* pentane, hexane, heptane and octane. Optical photographs of swollen samples were taken for studying the dimensional changes. The scanning electron miscroscopy (SEM) studies were conducted using a JEOL 35 C model scanning electron microscope.

RESULTS AND DISCUSSION

EFFECT OF BONDING AGENT

Ambient temperature (25°C) sorption curves for the gum vulcanizates and fiber composites, obtained by plotting Q_t — mole % solvent uptake per 100 g of polymer — versus $\sqrt{t}$ for

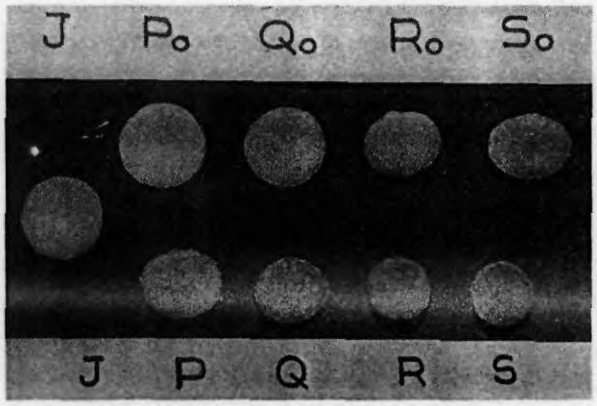

FIG. 5. — Optical photograph of the swollen samples in hexane; mixes defined in Table I.

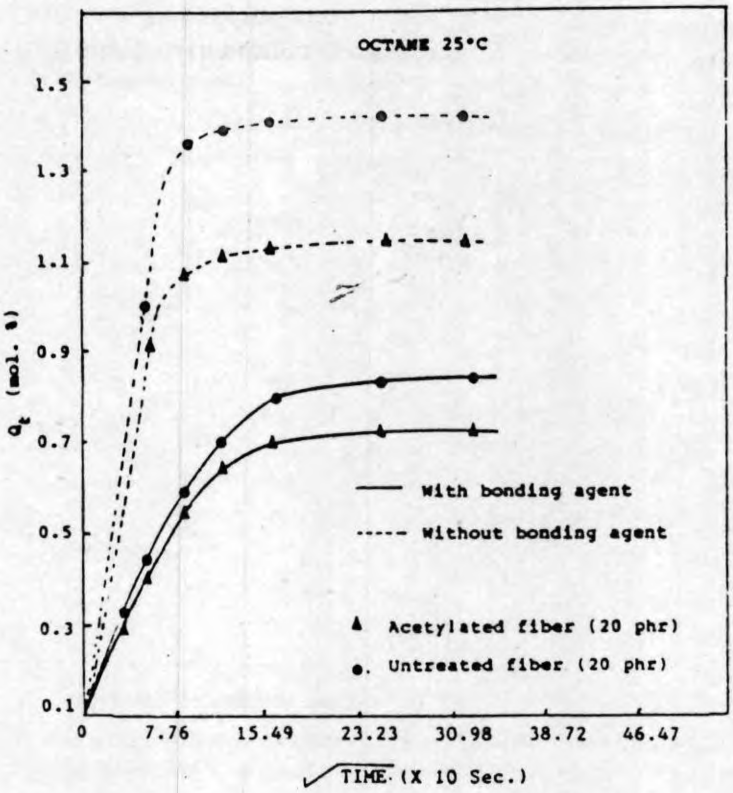

FIG. 6. — The equilibrium sorption curves of mixes L, L_0, Q and Q_0 in octane at 25°C.

pentane, hexane, heptane and octane, are given in Figures 1(a), 1(b), 1(c) and 1(d), res tively. (The sorption curves of composites containing bonding agent are represented by s lines and the dashed lines represent the composites without bonding agent.) Since all solvents followed the same diffusion pattern, as evident from the shapes of the diffu curves, the discussion is limited to the hexane case. It is seen from Figure 1(b) that the compound takes up the maximum amount of solvent at equilibrium. This is expected s there is less restriction for the penetrant to enter into the vulcanizate.

At equal volume loading of fiber, the amount of solvent sorbed by a composite at e librium swelling is less for the composites containing bonding agent compared to that wit bonding agent [Figure 1(b)]. Another interesting observation from the sorption curves o composites in hexane is the difference in initial rates of diffusion for different compos The initial rates of diffusion is fast for composites without bonding agent. This is bec of the fact that in unbonded fiber–rubber composites the solvent can penetrate into polymer along the thickness direction and also through the weak interfaces parallel perpendicular to the fiber orientation. The weak interface allows easy entrance of the

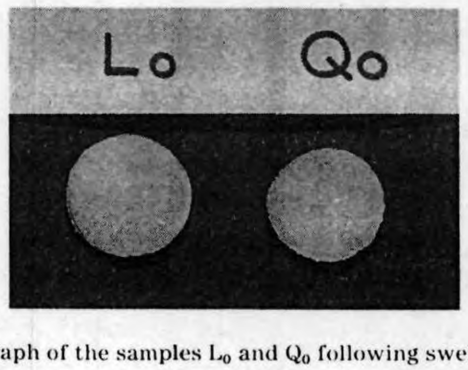

FIG. 7. — The optical photograph of the samples L_0 and Q_0 following swelling to equilibrium in hexane.

etrant and these interfaces act as solvent pockets at equilibrium. It is interesting to note that the rate of swelling of unbonded composites (containing 10 phr fiber loading) is faster than the gum compound [Figure 1(c)]. This is because the initial driving force for swelling is higher in unbonded composites as a result of the large number of voids at the interfaces. But in the case of composites which contained the bonding agent, the inerface is strong and the liquid can penetrate into the polymer only through the space between two fiber ends, *i.e.*, in the thickness direction. As a result, the diffusion rate is slow in well bonded composites. At the same fiber loading, a composite which contained no bonding agent absorbed more solvent at equilibrium compared to a composite which contained the bonding agent.

Though the pattern of diffusion curves obtained for pentane, hexane, heptane and octane is the same, the quantity of solvent sorbed by the polymer was found to depend on the size of the solvent molecule. Table II shows the amount of different solvents absorbed by mixes Q and Q_0. As the molecular size (chain length) increases, the liquid uptake increases and reaches a maximum for heptane and then decreases. This type of absorption is also reported earlier by Salomon and Van Amerongen.[21]

Table III gives the V_I, V_F and V_T values of the composites. It is evident that the composites containing bonding agent (mixes L, P, Q, R, and S) have substantially lower V_T values than those without bonding agent (L_0, P_0, Q_0, R_0, and S_0). Das[23] has demonstrated that with improved adhesion between short fiber and rubber, the factor $V_T = (V_I - V_F)/V_I$ decreased by more than 0.04 units. A highly bonded system would exhibit high resistance to swelling — compared to the unbonded one — consequently V_F would have a relatively higher value and V_T a relatively lower value. On the other hand, if bonding is poor V_F will be relatively lower, resulting in higher V_T values.

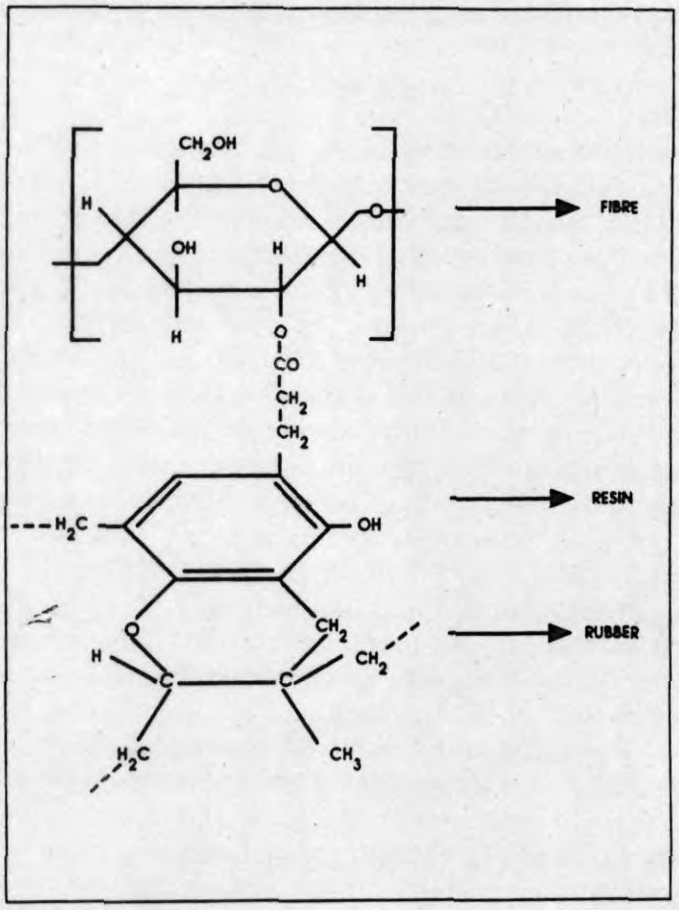

FIG. 8. — Schematic representation of rubber attached to the acetylated fiber through the bonding resin.

TABL

TENSILE PROPERTI

	Orientation[a]	A	B	C	J
Modulus at 10% elongation	L	2.56	5.03	13.20	0.3
(MPa)	T	1.02	0.93	1.84	0.3
Modulus at 20% elongation	L	—	—	—	0.4
(MPa)	T	—	—	—	0.4
Modulus at 30% elongation	L	—	—	—	0.5
(MPa)	T	—	—	—	0.5
Tensile strength	L	4.53	5.79	14.90	17.3
(MPa)	T	3.73	4.49	6.61	17.1
Elongation-at-break	L	388	213	17	1072
(%)	T	576	586	126	1060
Tear strength	L	47.6	47.3	87.5	37
(kNm^{-1})	T	38.8	40.8	66.2	37

[a] L = Longitudinal fiber orientation; T = Transverse fiber orientation.

EFFECT OF FIBER LOADING

As the fiber loading increases the amount of penetrant sorbed by the specimen at equ librium decreases, as shown in Figure 2. This is due to increased hindrance exerted by th fiber at higher loading. As the fiber loading increases, in bonded and unbonded cases, th liquid uptake decreases gradually but the reduction is sharp in the case of bonded composite In the case of composites containing bonding agent the magnitude of $(V_I-V_F)/V_I$ graduall decreases with increasing fiber loading due to restricted swelling. The V_T value is alway greater in the unbonded composite compared to the bonded one having the same fiber loadin

DIMENSIONAL CHANGES

The percentage increase in thickness of the specimen at equilibrium swelling is show in Figure 3. It is observed that the change in thickness is maximum for composites containin the bonding agent and it increases marginally with fiber loading. Though increase in thicknes during swelling is shown by both types of composites, the effect is more pronounced in th case of composites containing the bonding agent, especially at low fiber loading. In a wel bonded, oriented-fiber rubber composite, swelling will be anisotropic. It will swell to a greate extent in a direction perpendicular to the fiber orientation. This is because the oriented fiber will prevent the penetration of the liquid in the direction perpendicular to the flat surfac of the specimen. Hence the penetrant can diffuse into the polymer only through a directio parallel to the fiber orientation. Thus swelling was considered to be constrained in one direction and as a result: the thickness of the specimen increased considerably and the diamete change is negligible (since a circular specimen was used).

Although the control sample (mix J) with no fiber also showed greater swelling in th thickness direction — probably due to the alignment of the polymer molecules in a particula direction during the sheeting operation in the mixing mill — the anisotropic swelling become pronounced when fibers are added. At high fiber loading (23 volume %), the increase i thickness in both composites (bonded/unbonded) are comparable. As the fiber loading increases the number of fibers in a unit volume increases and the penetrant molecule finds i more difficult to diffuse into the polymer; therefore the entire swelling will take place in th thickness direction. In the bonded composite, even at low fiber concentration (12 volum %), the entire swelling will take place in thickness direction. In the bonded composite at lo fiber loading, the penetrant can enter into the matrix both in the direction parallel an perpendicular to the fiber orientation. When the bonding is poor, the matrix swells both i

IV
of Composites

K	L	M	N	P	Q	R	S
1.13	3.38	3.74	6.82	3.43	7.02	10.17	13.5
0.73	1.19	1.49	2.04	0.98	1.25	2.76	3.47
1.62	3.32	3.98	7.90	3.93	—	—	—
1.08	1.68	2.16	2.95	1.42	1.86	3.22	3.47
1.92	3.28	3.86	—	5.85	—	—	—
1.32	1.98	2.80	3.39	1.67	2.22	3.24	4.11
12.2	8.70	7.15	8.07	13.6	9.6	11.15	13.55
11.6	6.50	5.01	3.96	11.4	8.7	5.29	4.7
792	565	445	20	748	16	15	14
796	586	466	101	872	453	319	110
37	42	47.1	59	44	59	67	83
37.1	41.8	44.1	44.8	42.9	52.1	48.2	52

diameter and thickness. As a result at low loading, in the absence of bonding agent, the net swelling in the thickness direction will be less. However, as the fiber loading increases, the swelling takes place predominantly in the thickness direction which makes a higher contribution for the thickness increase.

A plot of the diameter of the specimen at equilibrium swelling against fiber loading is given in Figure 4. In the case of bonded composites at higher loadings, the swelling is restricted and takes place mostly in the thickness direction. The hydrostatic pressure of the solvent inside the specimen will expand the polymer in the thickness direction and as a result the diameter of the sample decreases compared to the initial diameter (*i.e.*, before swelling). This decrease in diameter is less abrupt in the case of the unbonded composites.

An optical photograph of the swollen samples in hexane is given in Figure 5. From this photograph it is clear that as the fiber loading increases, the diameter of the swollen samples decreases. At the same fiber loading, the diameter of the bonded composite is lower than that of the unbonded composite. From this it is established beyond doubt that in highly bonded composites swelling occurs predominently in the thickness direction. Therefore, this restricted swelling can be used to measure the bonding between fiber and rubber.

EFFECT OF ACETYLATION

The effect of chemical treatment can be understood from the equilibrium sorption curves of mixes L_0 and Q_0 given in Figure 6. Mix Q_0 which contains acetylated fiber, absorbed less

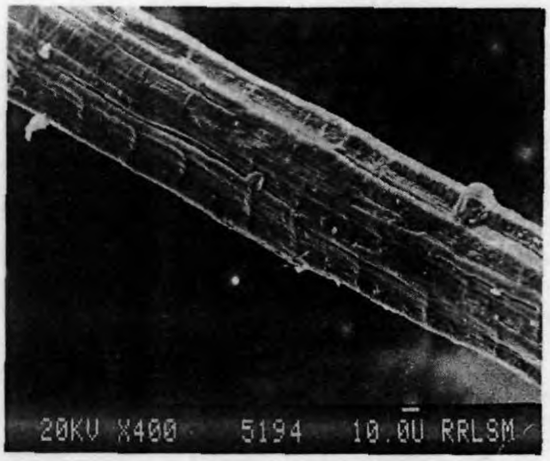

Fig. 9. — SEM photomicrograph of the surface of raw sisal fiber.

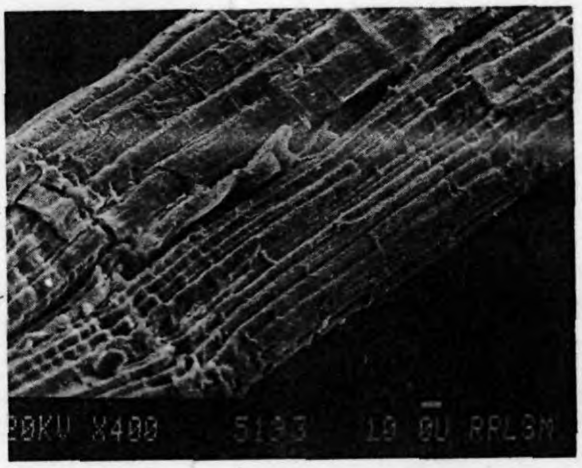

FIG. 10. — SEM photomicrograph of the surface of acetylated sisal fiber.

octane compared to mix L_0 which contains untreated fiber. In both these systems the bonding agent is absent. In the case of composites containing bonding agent, the same trend was observed. The composite Q absorbed less liquid at equilibrium than mix L. This establishes that acetylation improves bonding between fiber and rubber. The initial rate of diffusion is slow when the composite contained the bonding agent. This is because bonding created a *strong interface. The optical photograph of the samples L_0 and Q_0, swollen to equilibrium* in hexane, is given in Figure 7. Since the bonding in mix L_0 is poor, it swells like a gum compound. This observation further confirmed that acetylation of sisal fiber improved its adhesion with NR. Physical property measurements also lead to the same conclusion.

TENSILE PROPERTIES

Tables IV gives the tensile properties of all the composites. Acetylation of fiber and the addition of bonding agent increased the tensile strength but lowered the elongation-at-break of these composites. Composite B, incorporating acetylated fiber, showed better physical properties than the untreated composite (mix A). The bonding agent further enhanced the mechanical properties as evident from the properties of mix C. Better tensile properties of composites P, Q, R and S, compared with those of L, M, N and P, respectively, further confirm the effect of acetylation in enhancing the interfacial bonding. The bonding between the rubber and acetylated fiber, through the bonding resin, may be depicted as shown in Figure 8.

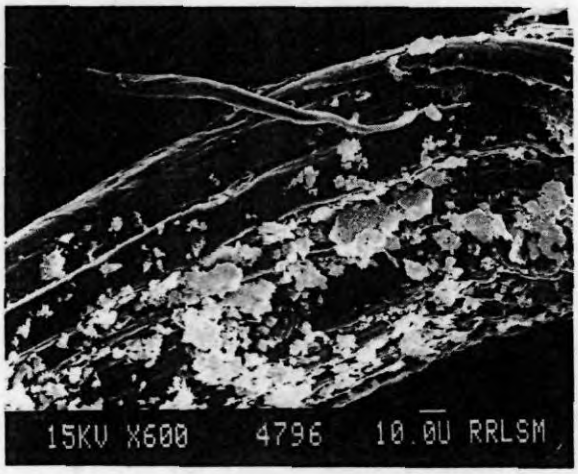

FIG. 11. — SEM photomicrograph or the surface of acetylated sisal fiber stripped out of mix C during tensile testing.

SCANNING ELECTRON MICROSCOPY STUDIES

The surfaces of the untreated and acetylated sisal fiber were examined by means of a scanning electron microscope (SEM). These are shown in Figures 9 and 10, respectively. The acetylated fiber surface is very rough and this facilitates better mechanical anchoring between fiber and rubber. Figure 11 is the SEM photomicrograph of acetylated fiber stripped out from mix C during tensile testing. It is interesting to note that rubber phase remains adhered to the fiber due to good bonding between fiber and the rubber. The effect of acetylation in improving the properties of the composite is evident from the better physical properties of compounds P, Q, R and S versus the respective untreated compounds K, L, M and N.

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CONCLUSIONS

Restriction to swelling of natural rubber exerted by sisal fiber as well as the anisotropy of swelling of the composites are evident from the results of this study. It is confirmed that for fiber composites containing bonding agent the value of $V_I - V_F)/V_I$ is substantially lower than the corresponding value for composites without bonding agent. Increased fiber content brings about a greater restriction to swelling and the use of a bonding agent reduced swelling considerably. In well bonded composites, swelling takes place mainly in the thickness direction. Composites incorporating acetylated fiber, absorbed less solvent compared to composites containing untreated fiber. This indicated that acetylation improves bonding between natural rubber and short sisal fiber.

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