

Bonding of Untreated Cellulose Fibers to Natural Rubber

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Synopsis

Sulfur- and peroxide-cured natural rubbers (NR) reinforced with short fibers of cellulose and carbon black have been studied with respect to water absorption, crosslink density, tensile strength, and the dependence of the dynamic storage modulus on strain amplitude. The results indicate that there is bonding between fiber and matrix even in the absence of a specific bonding system.

INTRODUCTION

Reinforcement of rubbers with short fibers is of practical and economic interest to the rubber industry, since it would in principle constitute a simple way of manufacturing reinforced rubber goods, e.g., hoses, tires, conveyor belts. One of the most important aspects of composite manufacture is to achieve adequate adhesion between fibers and matrix. Most attempts to solve this problem have involved grafting onto the fibers, the introduction of coupling agents to the rubber mix, or pretreatment of the fibers with such agents, one example of the latter approach being the Monsanto Santoweb series.¹ We have studied the effects of two different cure systems on the properties of the composite in order to see whether adhesion can be achieved by varying conventional cure systems. Details of the recipes are given in Table I.

EXPERIMENTAL

Materials

The mixing was done on an open two-roll mill. We started by putting the rubber on the mill and then adding half the carbon black and all the chemicals with the exception of the cure system. Mixing was performed for about 5 min before the fibers were added together with the rest of the carbon black and the cure system. Mixing then continued for a further 20 min. The samples were then press-cured to a thickness of 2 mm at 160°C for different times corresponding to t_{90} , the time at which 90% of maximum torque is achieved, determined from rheometer curves obtained using a Monsanto oscillating disc

TABLE I^a

	phr	phr
1. NR (SMR CV 50)	100	100
2. Dutrex 729	4	—
3. Stearic Acid	2	—
4. ZnO	5	—
5. Carbon black N330	20	20
6. TMQ	2	—
7. CBS	0.5	—
8. Sulfur	2.5	—
9. Flexon 876	—	4
10. Vulkanox MB	—	2
11. Santoflex 13	—	1.5
12. HVA 2	—	2
13. Varox	—	3

^a For each of the systems, samples were prepared with 0, 10, 20, 30, and 40 phr cellulose fibers and one sample with 30 phr Santoweb D. A total of 12 samples. phr = parts by weight per hundred part rubber. 1. Natural rubber. 2. High aromatic oil, a processing aid. 3. Dispersion agent and processing aid. 4. An activator together with 3. 5. High abrasion furnace black, a reinforcing filler. 6. Poly-2, 2, 4-trimethyl-1, 2-dihydroquinoline, an antioxidant. 7. *N*-Cyclohexyl-2-benzothiazyl sulfenamide. 8. Curing agent. 9. Paraffinic mineral oil, a processing aid. 10. Zinc methylmercaptobenzimidazole, an antioxidant. 11. *N*-(1,3-Dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine, an antioxidant. 12. *N,N'*-*m*-phenylene-dimaleimide, a coagent for peroxide cures. 13. 2, 5-Dimethyl-2, 5-(di-*tert*-butyl-peroxy) hexane, a curing agent.

rheometer. All samples were tested in the mill direction in the mechanical property evaluations.

The cellulose fibers were bleached kraft pulp fibers.

Water Swelling

Water uptake was measured because the hydrophilic nature of the cellulose fibers makes water uptake a potential cause of failure in rubber goods reinforced by such fibers. Water uptake at 23°C was measured by weighing the samples at different times over a total immersion period of 34 days.

Crosslink Density

The curing process introduces chemical links between rubber molecules, and these chemical links inhibit swelling of the rubber. By considering the amount of rubber, the molar volume of the swelling liquid and the interaction parameter between the rubber and the swelling liquid as done in the Flory-Rehner equation,² it is possible to estimate the crosslink density in moles per cm³. The crosslink density was determined on the samples, before and after mechanical measurement, in *n*-heptane at 30°C (interaction parameter = 0.433). The Flory-Rehner equation was derived for an unfilled rubber so that our crosslink densities are clearly not absolute values, but the relative differences within a series should be accurate.

Mechanical Measurements

Conventional measurements of tensile strength and elongation at break were made at room temperature on dumbbell-shaped samples (ASTM die C) in an Instron stress-strain tester with the crosshead speed set at 50 mm/min.

The modulus of elasticity was determined on an electromagnetic vibrator as described by Stenberg³ at different amplitudes at room temperature in order to study effects such as those reported by Payne⁴ concerning the dependence of the storage modulus on dynamic amplitude. The samples were sulfur-cured,

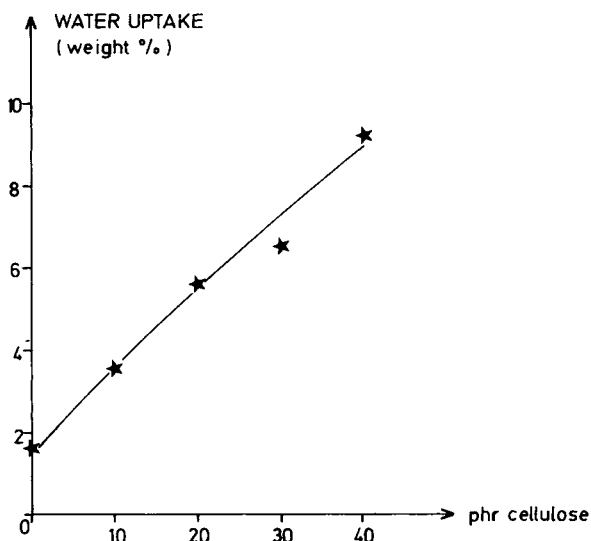


Fig. 1. Water uptake (wt %) vs. fiber content (phr) for sulfur cured samples. Immersion time 17 days.

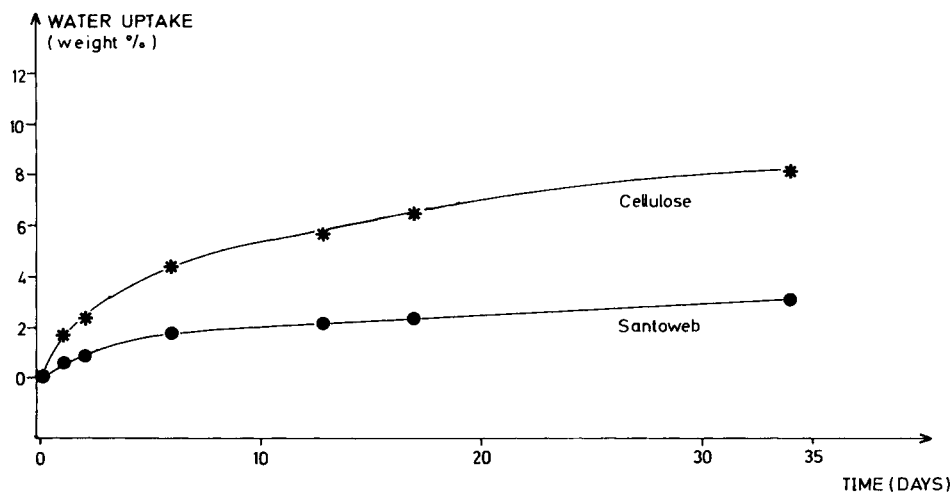


Fig. 2. Water uptake (wt %) vs. time for samples containing Santoweb D fibers (lower curve) and cellulose fibers (upper curve). Both samples were cured with sulfur.

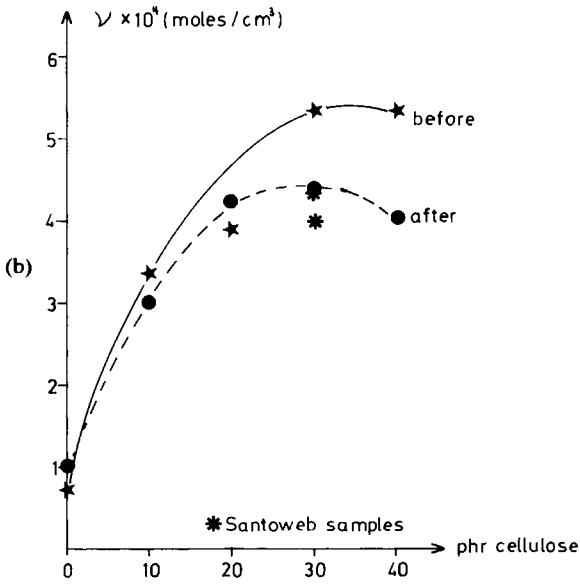
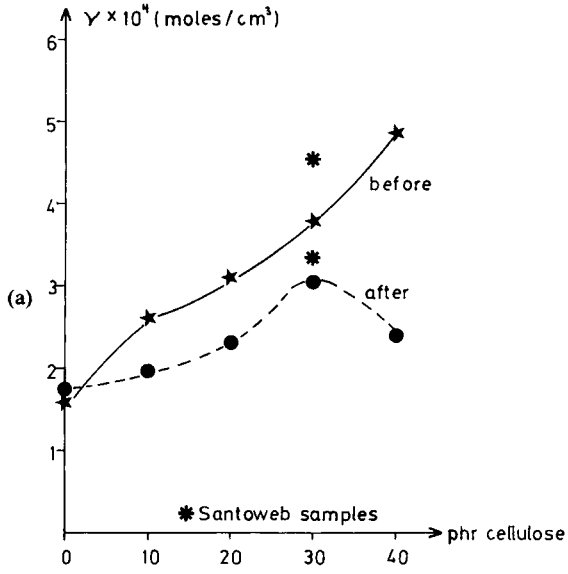


Fig. 3. Crosslink density (mol/cm³) for sulfur-cured (a) and peroxide-cured (b) samples vs. fiber content (phr), before and after amplitude dependence tests.

dumbbell-shaped, and prestrained to 120% of the original length, and the applied deformation was varied sinusoidally (2 Hz). The double strain amplitude is expressed as a percentage of the original length of the sample.

RESULTS

Water Swelling

The water uptake increased with immersion time and with increasing content of cellulose fibers. The water uptake for the sulfur-cured samples after immersion for 17 days is presented in Figure 1. The samples containing

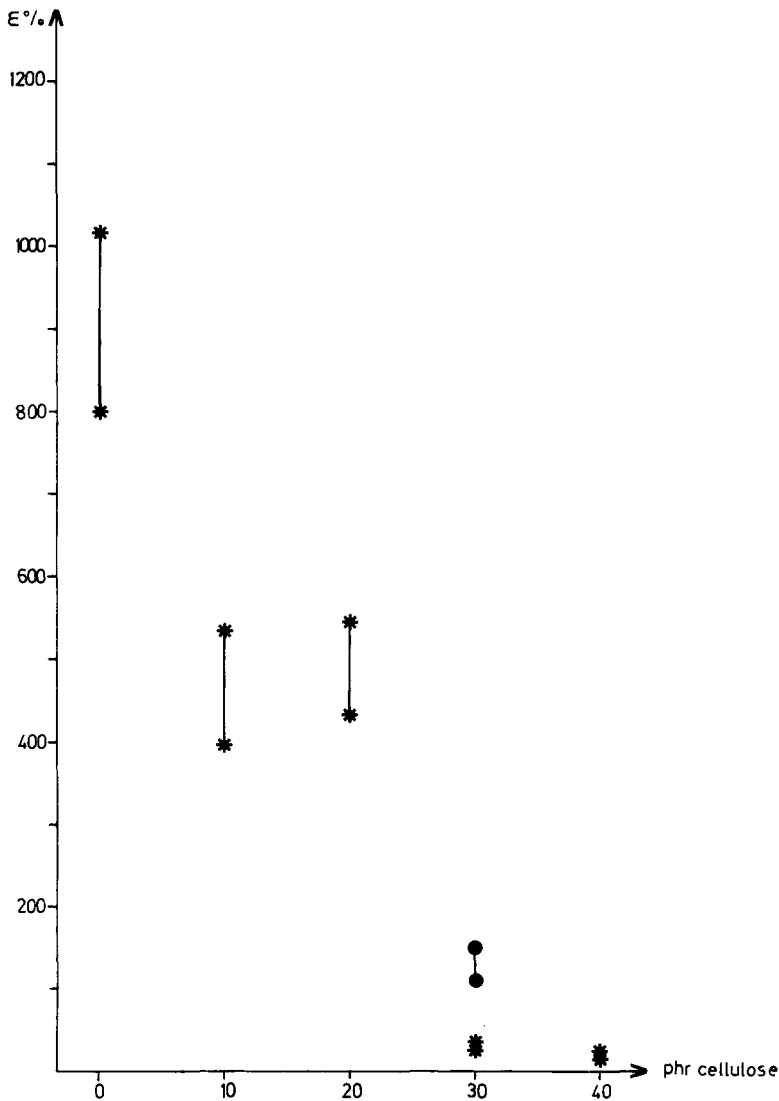


Fig. 4. Elongation at break (% of original length) for peroxide-cured samples: (●) samples filled with Santoweb D. Maximum and minimum values are indicated.

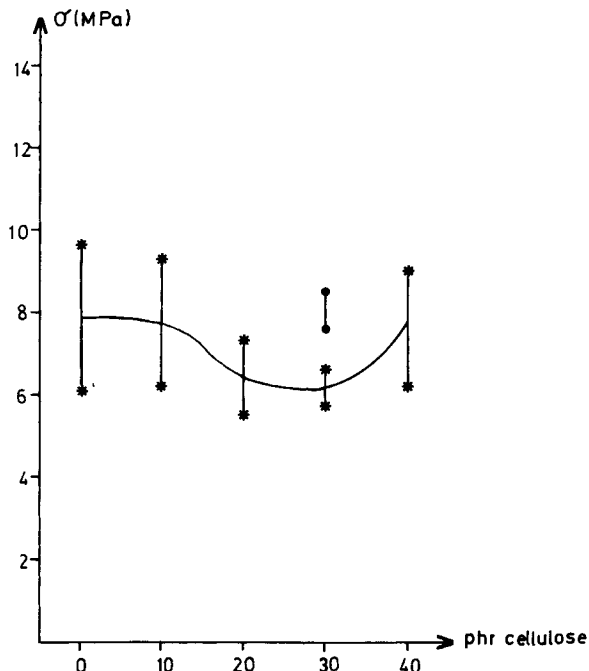


Fig. 5. Tensile strength of peroxide-cured samples: (●) samples filled with Santoweb D. Maximum and minimum values are indicated.

Santoweb D fibers absorbed less water than the samples containing cellulose fibers, as is illustrated in Figure 2.

Crosslink Density

There was an increase in crosslink density with increasing fiber content [Figs. 3(a) and (b)] for both the cure systems.

Mechanical Measurements

The elongation at break decreased with increasing amount of cellulose fibers (Fig. 4). The tensile strength decreased with increasing content of cellulose fibers for the sulfur-cured system, but in the case of the peroxide-cured system started to increase again at a loading of 40 phr fibers (Fig. 5).

Figure 6 shows the modulus of elasticity vs. the amplitude of deformation (double strain amplitude) for samples containing 10 and 20 phr cellulose fibers, both sulfur-cured. At a given amplitude of deformation, the modulus is higher for the samples having a higher cellulose fiber content.

DISCUSSION

For both cure systems, the crosslink density measurements showed an increasing amount of crosslinks as the fiber content increased. One of the limitations of the equilibrium swelling method is, however, that it does not differentiate between chemical and physical crosslinks,⁵ so that it is not clear

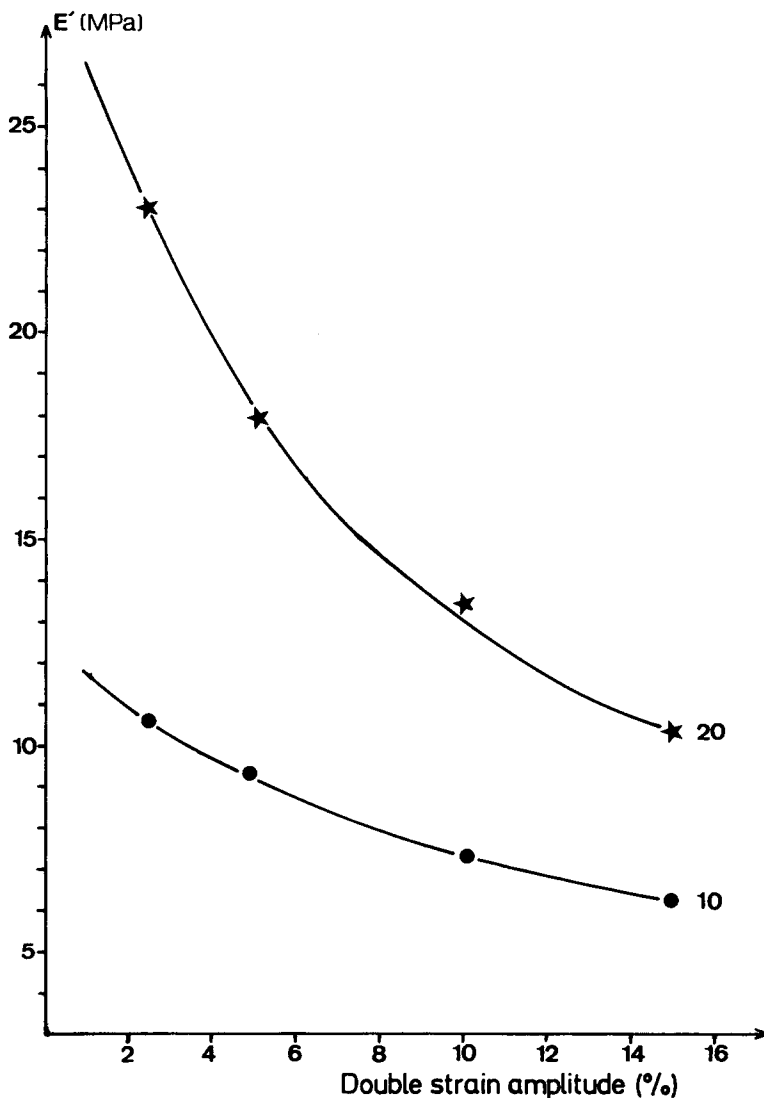


Fig. 6. Modulus vs. amplitude of deformation for sulfur-cured samples.

whether the increase in crosslink density is an effect of an increased amount of entanglements or is due to chemical bonds. Our assumption is that the cellulose fibers are too large and too immobile to take part in entanglement formation. They may, however, restrict rubber mobility and thus influence the equilibrium swelling, but probably the increase in crosslink density is caused primarily by chemical links between fibers and rubber. The reasons for this assumption are as follows: In the water swelling tests it was evident that the water uptake increased with increasing content of cellulose fibers. Chemical links introduced directly between fibers and rubber by the cure system would probably only block the hydroxyl groups where they are situated and not greatly stop water diffusion. We believe that Santoweb's lower water uptake is

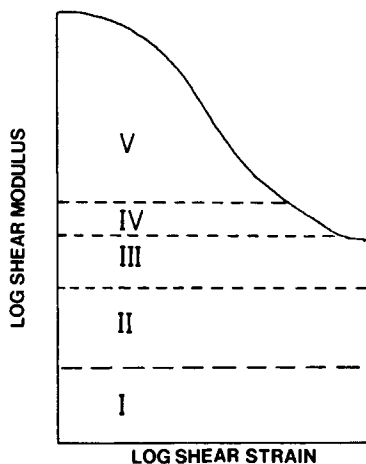


Fig. 7. Shear modulus vs. shear strain. Build-up of rubber modulus: region I—due to pure gum; region II—hydrodynamic effect of carbon black; region III—matrix crosslinks; region IV—matrix/fiber links; region V—interaggregate interaction.

due to the fact that the pretreatment blocks more hydroxyl groups on these fibers.

The tensile strength (Fig. 5) decreased with an increasing amount of fibers. Since the crosslink density increased at the same time and since the fibers lack the elasticity of the rubber molecules, the rubber-to-fiber links probably experience a greater strain earlier than the rest of the rubber phase and so rupture earlier, leaving a matrix weakened by holes⁶ around the fibers.

Figure 7 shows our interpretation of Payne's⁴ theories of how the modulus of elasticity of rubber can be divided into five different regions. Payne's model was proposed for a carbon-black-filled rubber. The sizes and number of the regions may vary with filler type, cure system, and rubber type. At the bottom are regions attributed to pure gum (I) and hydrodynamic effects due to carbon black (II).

Perhaps there should be a region above this attributed to rubber-rubber crosslinks (region III). If cellulose fibers are introduced into the rubber mix, new sites for the cure reaction become available. It can be assumed that region III diminishes in size while the additional crosslinking due to filler-rubber linkages means that region (IV) increases in size. The fact that crosslink density increases with increasing fiber content may mean that sulfur takes part in rubber-filler linkages instead of in intramolecular bridges, so that the size of regions III and IV together increases although the rubber-rubber crosslinks region is smaller than it is in the sample having no cellulose fibers.

If the region of filler-rubber crosslinks lies above the rubber-rubber crosslinks region, this should be reflected in the amplitude dependence measurements. Figure 8 shows the modulus of elasticity for each sample vs. the double strain amplitude. In this figure the curves have been normalized with respect to the extrapolated value of a strain of 1% which has been set equal to unity. The extent to which the modulus was retained with increasing amplitude of deformation decreased with increasing content of fiber material. This is

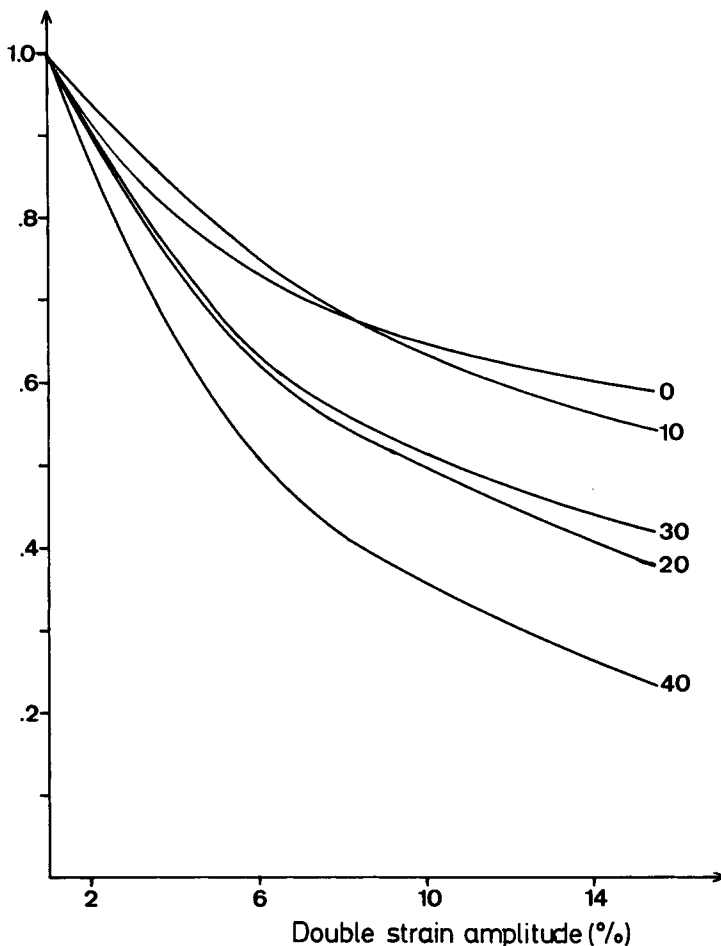


Fig. 8. Modulus normalized to 1% amplitude of deformation vs. amplitude of deformation for the sulfur-cured samples. Curves for samples with 0, 10, 20, 30, and 40 phr cellulose fibers.

consistent with our assumption that an increasing amount of fibers increases the size of the region associated with rubber-filler crosslinks.

New crosslink density measurements were made on the samples that had been used in the amplitude dependence test. If there were indeed crosslinks between the fibers and the rubber, these should be ruptured to a greater degree than the rubber-rubber crosslinks during the modulus determination. The crosslink density would therefore be expected to decrease more in samples with fibers than in the sample without fibers. Figures 3(a) and (b) shows that this was indeed so.

CONCLUSIONS

The main question when we started these preliminary investigations was: Is it possible to achieve direct bonding between cellulose fibers and rubber through a conventional cure system? We believe that the results of these studies indicate that the answer is "yes." The next step seems to be to find a

way to make the links between the fibers and the rubber more flexible and thus less sensitive to large deformations.

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