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Evaluation of silane treated regenerated cellulose in rubber composites

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ABSTRACT

Activity of filler should be related to any definite property of material. It was to introduce the concept of structural, kinetic, and thermodynamic activity of fillers. Structural activity of filler is its ability to change the polymer structure on molecular and sub molecular level (crystallinity degree, size and shape of sub molecular domains, and their distribution, crosslink density for network polymers, etc.). Kinetic activity of filler means the ability to change molecular mobility of macromolecules in contact with a solid surface and affect in such a way the relaxation and viscoelastic properties. Finally, thermodynamic activity is filler's ability to influence the state of thermodynamic equilibrium, phase state, and thermodynamic parameters of filled polymers -especially important for filled polymer blends. Cellulose is the biopolymer which is found in abundant and forms the centre of carbon cycle. Fibers manufactured from cellulose are either derivative or regenerated. In present work silane treated regenerated cellulose is formulated with natural rubber (NR) as well as with styrene butadiene rubber (SBR) separately and characterized for specific gravity, rheological measurements, mooney viscosity, mechanical properties and surface morphology.

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KEYWORDS

Natural rubber;
Styrene butadiene rubber;
Regenerated cellulose;
Morphology;
Mechanical properties.

INTRODUCTION

The structural components of plants are formed primarily from cellulose. The first successful attempt to make textile fibers from plants cellulose can be

traced to George Audemars. Wood is largely cellulose and lignin, while paper and cotton are nearly pure cellulose. Cellulose is a polymer made with repeated glucose units bonded together by β linkages. Humans and many animals lack enzyme to break the β linkages, so

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they do not digest cellulose. Certain animals such as termites can digest cellulose, because bacteria possessing the enzyme are present in their gut. Cellulose is insoluble in water. It does not change color when mixed with iodine, on hydrolysis cellulose yields glucose. Cellulose consists of linear chain of several hundred to many thousands of β (1 \rightarrow 4) linked D glucose units^[1]. Cellulose is the important structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form bio films. Cellulose is the most abundant organic polymer on earth. The cellulose content of cotton fiber is 90%, that of wood is 40% to 50% and that of dried hemp is approximately 45%. Cellulose is mainly used to produce paper board and paper. Smaller quantities are converted into a wide variety of derivative products such as cellophane and rayon. Conversion of cellulose from energy ropes into bio fuels such as cellulosic ethanol is under investigation as alternative fuel resources^[2]. Cellulose for industrial use is mainly obtained from wood pulp and cotton. Cellulose has no taste, is odorless, is hydrophilic with contact angle of 20° to 30°, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into glucose units by treating it with concentrated acids at high temperature. Cellulose is derived from D glucose units, which condenses through β (1 \rightarrow 4) glycosidic bonds. Cellulose is a straight chain polymer unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod like conformation, aided by the equatorial conformations of the glucose residues. The multiple hydroxyl groups on glucose from one chain form hydrogen bonds with oxygen atoms on the same or on the neighboring chain, holding the chains firmly together side by side forming micro fibrils with high tensile strength. This confers tensile strength in cell walls, where cellulose micro fibrils are messed into a polysaccharide matrix. Compared to starch, cellulose is much more crystalline, whereas starch undergoes a crystalline to amorphous transition when heated beyond 60°C to 70°C in water^[3]. Cellulose requires a temperature of 320°C and pressure of 25Mpa to become amorphous in water. Several different crystalline structures of cellulose are known corresponding to the location of hydrogen bonds between and within strands. Natural cellulose is cellu-

lose I, with structures Ia and Ib. Cellulose produced by bacteria and algae is enriched in Ia while cellulose of higher plants consists of Ib. Cellulose in regenerated cellulose is cellulose II. The conversion of cellulose I to cellulose II is irreversible, suggesting cellulose I is meta stable and cellulose II is stable. Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 to 1700units; cotton and other plants fibers, as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units. Molecules with very small chain length resulting from break down of cellulose are known as cellodextrins; in contrast to long chain cellulose, cellodextrins are typically soluble in water and organic solvents. Plants derived cellulose is usually found in a mixture with hemicelluloses, lignin, pectin and other substances, while bacterial cellulose is quite pure, has a much higher water content and tensile strength due to higher chain lengths. Cellulose consists of crystalline and amorphous regions, by treating cellulose with strong acid, the amorphous regions can be broken up, thereby producing crystalline cellulose, a material with many desirable properties. Fibers manufactured from cellulose are either derivative or regenerated, a derivative fiber is one formed when a chemical derivative of natural polymer is prepared dissolved and extruded as a continuous filament and the chemical nature of derivative is retained after fiber formation. In regenerated type a natural polymer or its chemical derivative is dissolved and extruded and the chemical nature of the natural polymer is either retained or regenerated after fiber formation process. The term silane coupling agent generally applies to silicon-containing species capable of forming chemical linkages between dissimilar materials, especially in reinforced polymer composites, but here we have used silane functionalized regenerated cellulose. The materials to be linked are often organic polymers and cellulose fibers, though silane functionality present on cellulose can also be useful with other kinds of fillers and polymers. Small amounts of silane functionalized, used at an interface, can greatly improve the mechanical properties of composite materials. They may also be used on formed parts as coatings to alter the surface properties of materials, or copolymerized into organic polymers.

Normally, additions of fillers increase the viscosity and contribute to non-Newtonian flow characteristics. Polymer crystallization and structure are affected by fillers. They may increase or decrease the nucleation rate (and thus the crystallization rate)^[4]. Fillers, especially fibers, may also decrease the mechanical properties of filled materials because of their effect on transcrystallinity. The polymer structure at the interface with fillers is different than in the bulk. Filler choice and the orientation of the filler particles are the other important determinants of mechanical performance. The average molecular weight of butyl rubber lies in the region of 300,000 to 500,000 which corresponds to Mooney viscosities M_L^{1+4} at 100°C of about 40 to 70. The Mooney viscosity influences primarily the processability and the amount of filler and oil which the rubber can accept. With increasing levels of unsaturation vulcanization rates increase, but the other beneficial properties becomes poor, hence moderate level of unsaturation is sought as a compromise. The average molecular weight of natural rubber ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution; this corresponds to about 3000 to 5000 isoprene units per polymer chain^[5]. As a result of its broad molecular weight distribution natural rubber has an excellent processing behavior. The present article is focused primarily on use of cellulose in rubber composites, where silane is used as interfacial modifiers between the rubber matrixes NR with cellulose, comparison study with untreated cellulose is also carried out.

MATERIALS

Natural Rubber was obtained from B.P. Chemicals Mumbai. Untreated Cellulose and Silane functionalized

cellulose (0.4wt percent and 0.8wt percent) was procured from SRL Pvt Ltd. Rubber additives like Zinc oxide [ZnO], Stearic acid, were procured from SRI Impex Pvt Ltd. N'-phenyl paraphenylene diamine [6PPD], N-cyclohexyl-2-benzothiazole sulphenamide [CBS], and Sulphur was obtained from National Organic Chemical India Limited, Mumbai.

PREPARATION OF NATURAL RUBBER CELLULOSE COMPOSITES

TABLE no 1, gives the recipe for the preparation of natural rubber cellulose composites. The mixing was carried out in a particular sequence so that proper incorporation and dispersion of the cellulose into the natural rubber takes place. The mixing was carried out in a Brabender Plasticorder PL 2500, at a temperature of 115°C with a mixing cycle time of 15 minutes – Initially natural rubber was added into the Brabender and allowed to shear mix in between the screws of Brabender for a period of 4 minutes simultaneously antioxidant 6PPD was added so that oxidation of natural rubber does not take place. Consequently Stearic acid, Zinc oxide and cellulose were added and mixed for 4 minutes for effective and proper incorporation and dispersion of cellulose into natural rubber matrix, left over material in mixing pan must be added and mixed for 2 minutes in Brabender. Curing Packet must be added at the end of the mixing cycle and sheared for 2 minutes in Brabender. (Note: The amount mentioned in TABLE 1 is in “phr”- parts per hundred rubbers)

Lump from Brabender is passed through mixing mill & 5mm sheet is obtained and compression

TABLE 1 : Recipe for cellulose natural rubber composites

Batch Code	NRC0	NRC4	NRC8
Natural Rubber	100	100	100
ZnO	5	5	5
Stearic Acid	2	2	2
CBS	0.8	0.8	0.8
6PPD	1	1	1
Sulphur	2.5	2.5	2.5
Cellulose	10	0	0
Cellulose,0.4	0	10	0
Cellulose,0.8	0	0	10

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molded for getting standard sheet and further specimen preparation by punching is done, for analyzing physio-mechanical properties/air permeability test/ surface morphology of composites.

RHEOMETRIC / MOONEY ANALYSIS (ASTM D2084)/ (ASTM D1646)

For preparation of Standard sheets which are to be further used for specimen preparation, natural rubber nanocomposites compounds have to go under a test, which indicate their processing parameters. Hence the nanocomposites have to undergo Rheometric Analysis to determine Maximum Torque, Minimum Torque, Scorch time and Optimum Cure time. (@ 150°C)

From the given data, maximum torque and minimum torque increases as the functionalization on cellulose increases. This shows that functionalized cellulose is improving curing characteristics. The compound having 10phr loading of 0.8 wt percent cellulose shows maximum torque. Scorch time increases with increase in weight percent loading of functionalized cellulose. Scorch time for 10phr loading of 0.4 wt percent cellulose is less as compared to 0.8 weight percent hence scorch safety is better for compound with 10phr loading of 0.4 wt percent cellulose. Optimum cure time increases with increase in cellulose loading. The optimum cure time value of 10phr loading of 0.8 wt percent cellulose loading is more than 0.4 and 0 weight percent of cellulose loading, to obtain 90% of the cure, hence loading of functionalized cellulose can also contribute in improvement in productivity.

The standard sheet was prepared with the optimum cure time mentioned in TABLE 2 at 150°C.

Mooney Analysis was tested as per ASTM D 1646-07. Mooney Viscosity and Mooney scorch was determined. Observed properties are listed below.

RESULTS AND DISCUSSIONS

Physio-mechanical properties

Tensile strength values from TABLE 4 show the effect of functionalized cellulose on tensile strength of natural rubber composites. As functionalized cellulose loading increases tensile strength increases. From the results obtained we can conclude that functionalized cellulose does improve the strength. Concentration (the relationship of tensile strength is not a linear function of concentration; there is a certain critical concentration above which a further increase in filler's concentration decreases tensile strength). Tensile strength improvement, associated with an increase in the elongation at break values, is a rather expected phenomenon for natural rubber/cellulose composites. This is due to the synergistic effect of particle orientation and polymer chain slippage.

Elongation values from TABLE 4 shows the gradual variations of elongation at break. As functionalized cellulose loading increases the elongation at break increases. Since functionalized cellulose does show a moderate reinforcing effect in natural rubber related with some agglomeration phenomena. Agglomeration causes premature failure, well manifesting in reduced ultimate stress and elongation at break val-

TABLE 2 : Rheometric data of the natural rubber cellulose composites

Properties	Unit	NRC0	NRC4	NRC8
M _H	Lbs.in	69.28	69.53	72.58
M _L	Lbs.in	4.75	2.68	5.32
TS ₁	min	4.33	4.79	5.89
TS ₂	min	4.63	5.10	6.24
TC ₉₀	min	8.59	9.00	10.45

TABLE 3 : Mooney viscometric data of the natural rubber cellulose composites

Batch Code	NRC0	NRC4	NRC8
Mooney Viscosity, ML (1+4 @ 100°C)	16	23	13
Mooney Scorch, ML @ 125°C	19	21	20

ues. The elongation at break value decreases after ageing operation. Since the change in tensile strength value is higher for many proportions (after ageing), its elongation at break value is low.

From the data in TABLE 4, as functionalized cellulose loading increases modulus at 300% elongation also increases gradually. Modulus increase is expected even at low concentration of functionalized cellulose content when functionalized cellulose particles are well dispersed (well intercalated and exfoliated).

Fillers which have relatively large particle size do not interact and therefore their effect on hardness is due to their higher hardness. But the gain in hardness is very small because these particles are surrounded by an elastic matrix which moderates the effect of their hardness. Much larger gains are observed with semi-reinforcing grades due to the formation of an interlayer with mechanical properties more similar to the filler than to the matrix. In this case, the actual size of the particle

is increased by the thickness of its adsorbed layer; therefore even small particles occupy a substantial space in composites. Reinforcing fillers introduce another variable related to formation of physical crosslink's which can be very numerous because of the small size of the particles. These physical crosslink's further reinforce the rubber resulting in its increased hardness. From the TABLE 4, NRC0 is the blank with lower hardness and the hardness increases gradually from NRC4. It shows that there is a gradual increase in hardness with increase in nanosilica loading.

Scanning electron microscopy

The SEM images of fractured natural rubber functionalized cellulose composites samples are shown in *Figure 1,2 and 3*. It is visible that the functionalized cellulose particles are dispersed throughout the natural rubber matrix in the form of aggregates and the functionalized cellulose aggregates begin to split as they

TABLE 4 : List's the physio-mechanical properties of the natural rubber composites with different weight percent of functionalized cellulose

Batch code	Units	NRC0	NRC4	NRC8
Tensile Strength	kg/cm ²	237	244	272
300% modulus	kg/cm ²	32	36	37
Elongation at break	%	710	670	680
Hardness	Shore A	50	52	53

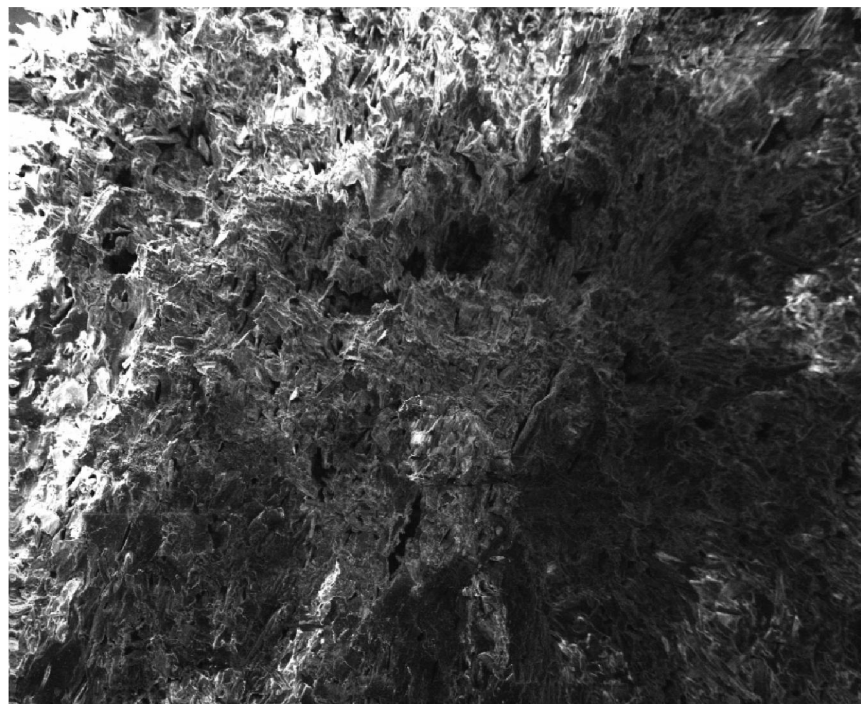


Figure 1 : SEM image for NRC4

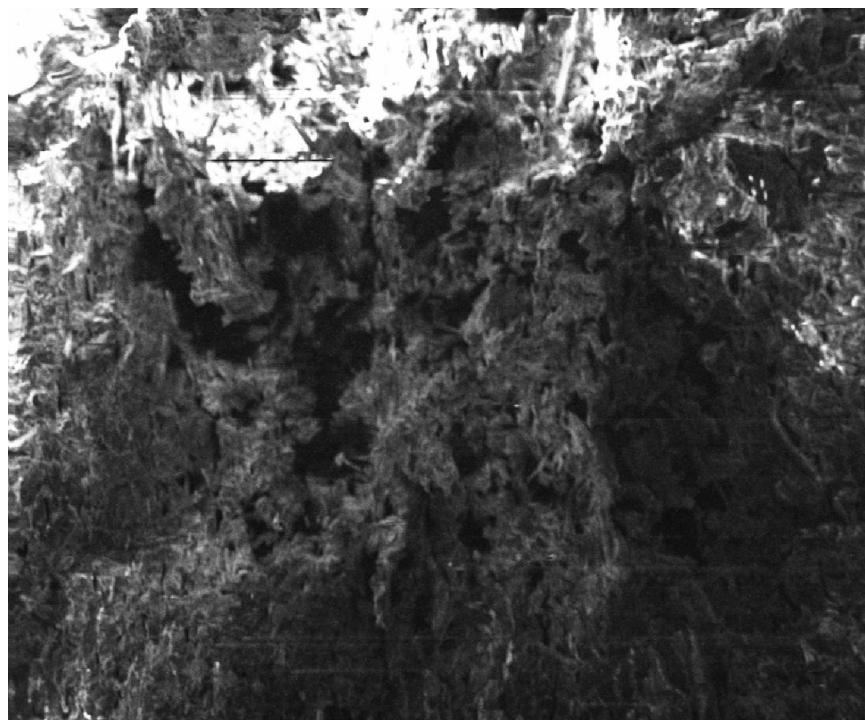


Figure 2 : SEM image for NRC8

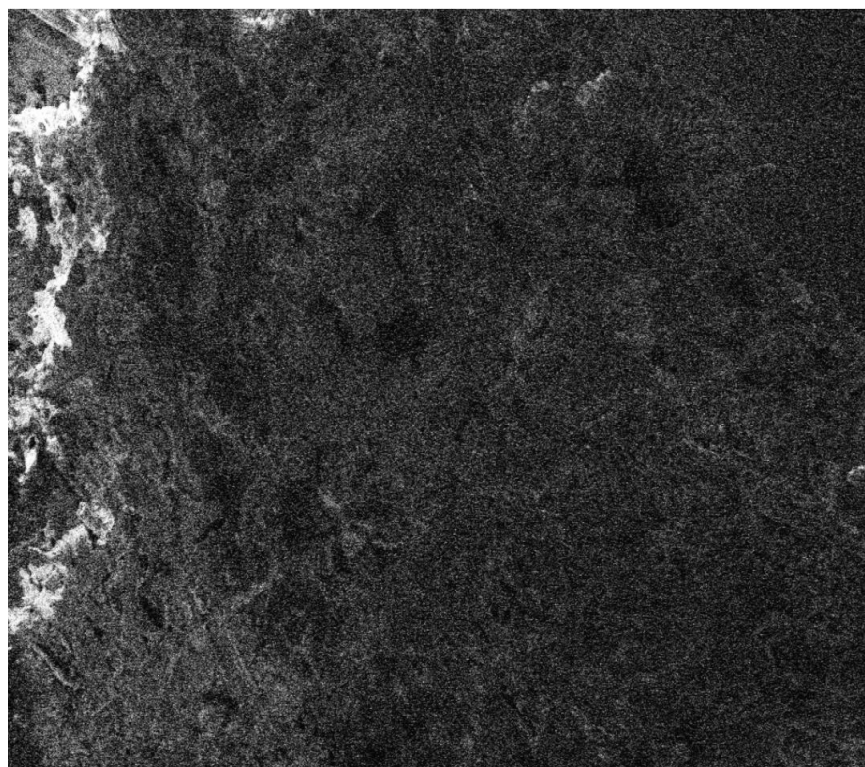


Figure 3 : SEM image for NRC0

are subjected to shearing and therefore functionalized cellulose particles become separated on coming with contact with natural rubber matrix. This gives rise to a significant proportion of exfoliated (*Figure 1 and 2*)

functionalized cellulose at early stages of compounding. Presence of exfoliated functionalized cellulose in the natural rubber matrix in the early stages of mixing can contribute to matrix properties ultimately contrib-

uting to development of composite. Proper dispersion of functionalized cellulose decreases the area available for diffusion as a result of impermeable functionalized cellulose replacing permeable rubber matrix and hence enhances air permeability property. The size of the dispersed functionalized cellulose phase in natural rubber matrix depends on the interfacial interactions between two phases. It should also be noted that the natural rubber matrix are covered by a layer of functionalized cellulose (*Figure 2 and 3*). Initially, the functionalized cellulose cannot penetrate into the rubber phase, but after adding curing agent, the rubber phase become more polar. Therefore, it is possible that some functionalized cellulose goes to natural rubber matrix phase before the curing cycle ends. Hence there is change in the viscosity ratio between the two phases, and consequently, the size of the rubber phase increases.

CONCLUSIONS

Functionalized cellulose show a slight improvement on physical properties with loading comparable to that of untreated cellulose. By the addition of functionalized cellulose, hardness of compound in-

creases. Natural Rubber composites containing functionalized cellulose filler show good tensile strength. Photographs from scanning electron microscopy indicate good dispersion level for the functionalized cellulose as compared with untreated cellulose. The optimum cure time increases as the functionalization level increases along with scorch time and induction time. Hence cellulose may be considered as a filler alternative or filler substitute in different natural rubber based compounds.

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