

Tensile Stress Relaxation of Short-Coir-Fiber-Reinforced Natural Rubber Composites

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ABSTRACT: The stress relaxation behavior of natural rubber (NR) and its composites reinforced with short coir fibers under tension was analyzed. The rate of stress relaxation was a measure of the increase in the entropy of the compounds: the higher the rate was, the greater the entropy was. At lower strain levels, the relaxation mechanism of NR was independent of strain level. However, the rate of relaxation increased with the strain level. Also, the strain level influenced the rate of stress relaxation considerably in the coir-reinforced NR composites. However, the relaxation mechanisms of both the unfilled compound and the composite were influenced by the strain rate. The rate of relaxation was influenced by fiber loading and fiber orientation. From the

rate of stress relaxation, we found that fiber–rubber adhesion was best in the composite containing fibers subjected to a chemical treatment with alkali, toluene diisocyanate, and NR solutions along with a hexaresorcinol system as a bonding agent. In this study, the stress relaxation curves could not be viewed as segments with varying slopes; however, a multitude of inflection points were observed on the curves. Hence, we propose neither a two-step nor three-step mechanism for the coir-fiber-reinforced NR composites as reported for some other systems. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 96–104, 2004

Key words: composites; fibers; relaxation; rubber; stress

INTRODUCTION

Although elastomers are popular for their rubber-like elasticity, high flexibility, and abrasion resistance, these are ignored in many applications because of their low strength and stiffness. To compensate for these drawbacks, elastomers are very often reinforced with short fibers; this leads to the formation of a new class of materials known as *short-fiber-reinforced elastomeric composites*. These composites possess the strength and stiffness of the fibers and the elasticity of the matrix. Elastomeric composites are advantageous because of their easy processability, high green strength, and enormous possibilities in product design. Extensive research has been done on composites containing short synthetic fibers, including polyester, nylon, carbon, and kevlar. Hamed and Coran¹ reviewed the reinforcement of elastomers with short fibers.

Unfortunately, polymers are often criticized materials today because of their nonbiodegradability. Hence, research has been carried out to develop a completely biodegradable and inexpensive polymer with suffi-

cient strength and other required properties. However, these attempts have not been successful so far. As an alternative method, polymer composites have been prepared with natural fibers, such as wood pulp, jute, sisal, flax, pineapple fiber, and oil palm fiber, to thereby decrease the nonbiodegradable polymer content in the product. Natural fibers have advantages over synthetic fibers, including their renewable nature, their amenability to chemical modification, and their nontoxicity.

In this study, we examined natural rubber (NR) composites containing short coir fibers as reinforcements. Coir is a lignocellulosic fiber obtained from the fibrous mesocarp of coconuts, the fruit of coconut trees (*Cocos nucifera*), which is cultivated extensively in tropical countries. Coir is used to make certain traditional products, such as furnishing materials and rope, which consume only a small percentage of the total production.² Hence, research has been in progress to innovate new fields of application for coir as a reinforcement material in polymers.^{3–8} However, coir has been found to be a poor reinforcement material in polymers because of its large and variable diameter, its high microfibrillar angle, and its high lignin/hemicellulose content.

Some authors have already reported that the efficiency of its reinforcement can be increased by the surface modification of coir through treatment with an

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TABLE I
Comparison of the Cost and Properties of Coir Fibers and Other Natural Fibers

	Coir	Banana	Sisal	Pineapple	Jute
Diameter (μm)	100–460	80–250	50–200	20–80	30–150
Density (g cm^3)	1.15	1.35	1.45	1.44	1.45
Microfibrillar angle ($^\circ$)	30–49	11	10–22	14–18	8.1
Cellulose/lignin content (%)	43/45	65/5	67/12	81/12	63/12
Elastic modulus (GPa)	4–6	8–20	9–12	43–81	20–22
Tensile strength (MPa)	131–175	529–759	568–640	413–1627	533
Elongation (%)	15–40	1.0–3.5	3–7	0.8–1.6	1–1.2
Cost (relative to coir)	1	3	1.5	1.5	2

alkali solution and that it can be further enhanced by treatment with a toluene diisocyanate (TDI) and NR solution on the alkali-treated fibers.^{9,10} Studies on their mechanical properties and directional swelling have proven this. The rheological properties of these composites have also been analyzed.¹¹

The determination of mechanical properties such as tensile strength and elongation at break is widely accepted as the simplest and easiest quality control experiment. Also, these data provide us with a fundamental notion about the behavior of a material. However, it is known that these experiments are futile as far as the service performance of articles are concerned because only a very few rubber articles, such as rubber bands, are subjected to an elongation at break of more than about 10%. Similarly, most rubber articles, except things like toy balloons and rubber bands, are not loaded up to their breaking strength.

Moreover, these experiments are time-dependent and so cannot provide a complete idea about the time-dependent viscoelastic nature of polymers. Hence, short-term analysis of mechanical properties does not give insight into the real properties of polymers. Therefore, long-term properties, such as stress relaxation, creep, and dynamic mechanical properties, need to be analyzed to get a complete idea about a polymer compound.

Hence, in this study, stress relaxation, a time-dependent, long-term property, was chosen as the tool to study the long-term behavior of short-coir-fiber-reinforced NR composites. This study included analysis of the stress relaxation behavior of these composites under the influence of strain level, strain rate, fiber loading, fiber modification, aging, and fiber orientation. Attempts were made to probe into the mechanism of stress relaxation behavior.

EXPERIMENTAL

Materials

The coir fiber was supplied by the local processing unit in Kollam, Kerala, India. The composition of coir is compared to that of other fibers in Table I. The NR

used for the study was ISNR 5 grade (light in color) obtained from the Rubber Research Institute of India (Kottayam), and its properties are given in Table II. All of the other ingredients were commercial grade.

Fiber preparation

Coir pith and other undesirable materials were separated from the coir fiber. It was then chopped to a length of about 10 mm and subjected to the following chemical treatments:

1. Coir fibers were soaked in a 5% sodium hydroxide solution at 28°C for 48 h. Fibers were taken out, washed repeatedly with water, and dried in air.
2. TDI and NR treatment: at first, TDI was dissolved in dimethyl sulfoxide (1 wt %) and treated with coir fibers in the presence of triethyl amine as a catalyst. Fibers were filtered and washed with dioxane to remove unreacted diisocyanate and solvent. The TDI-treated fibers were heated with 1% NR in toluene at 50°C and oven-dried.
3. Potassium permanganate treatment: alkali-treated fibers were soaked in a 0.1% solution of potassium permanganate in acetone for 1 min. The solution was decanted, and the fibers were oven-dried.

Preparation of the composites

The formulations of the mixes are given in Table III. The composite materials were prepared on a two-roll

TABLE II
Properties of NR

Property	Value
Dirt content (mass %)	0.03
Volatile mass (mass %)	0.50
Nitrogen (mass %)	0.30
Ash (mass %)	0.40
Initial plasticity	38
Plasticity retention index	78

TABLE III
Base Formulation of the Mixes

NR (ISNR 5)	100 parts
Zinc oxide	5 phr
Stearic acid	1.5 phr
Polymerized 2,2,4-trimethyl-1,2-dihydroxyquinoline	1 phr
Resorcinol	7.5 phr
Hexamethylenetetramine	4.8 phr
N-Cyclohexyl-2-benzothiazyl sulfenamide	0.6 phr
Sulfur	2.5 phr
Coir fiber (untreated/treated)	As specified

Description of mixes: mix J contained NaOH treated fiber, NR solution, and TDI solution (J_{60} contained 60-phr-treated coir fiber).

Mix W contained untreated fiber, with no hexamethylenetetramine or resorcinol.

Mix X- NaOH-treated fiber with no hexamethylenetetramine or resorcinol.

Mix Y contained $KMnO_4$ -treated fiber. All of the compounds except the unfilled rubber compound are described in the longitudinal direction and contained 30 phr fiber loading unless otherwise specified by subscripts, (e.g., J_{60}).

laboratory mill (150 × 300 mm). The nip gap, roll speed ratio, and number of passes were kept the same for all of the mixes. The samples were milled for a sufficient time to disperse the fibers in the matrix at a mill opening of 1.25 mm. The dicomponent dry bonding system, consisting of resorcinol (7.5 phr) and hexamethylenetetramine (4.8 phr), was incorporated along with other compounding ingredients. The coir fibers were incorporated at the end of the mixing process, with care taken to maintain the direction of compound flow so that the majority of fibers were aligned in the same direction. The curing properties were measured with an oscillating disc rheometer (Monsanto R-100, Monsanto Industrial & Chemical Company, Akron, Ohio) at a temperature of 150°C. The composites were cured at their respective cure times. Aged samples were prepared by the immersion of samples in boiling water for 1 h.

Stress relaxation experiments

These were carried out on a Zwick universal testing machine (model 1465) (Zwick EmbH & Company, Ulm-Ein, Germany) in uniaxial tension mode at 28°C. The dumbbell specimens were extended to different strain levels, namely, 6 and 60% at different strain rates, namely, 0.00175, 0.017, and 0.05 s⁻¹. When the appropriate strain was reached, it was maintained, and the stress was recorded for a time span of 10,800 s.

Because stress relaxation is exponential, the decrease in stress is very prominent during the initial period of relaxation, and therefore, stress monitoring was started immediately after the required strain was attained. The results are shown as stress relaxation

plots with the stress at a specific time (σ_t) divided by the maximum stress when the required strain was attained (σ_0) versus time or the stress relaxation modulus at a particular time (E_t) versus time. We obtained E_t by dividing σ_t by the strain. The slope was obtained by regression analysis of the data for the best fit to a straight line.

RESULTS AND DISCUSSION

Phenomenology of stress relaxation in unfilled rubber

The term *relaxation* denotes the process of the establishment of statistic equilibrium in a physical or physicochemical system, and its rate depends on the probability of the transition of the system from one stage of equilibrium to another.¹²

The ideal crosslinked rubber behaves like a perfect Hookean spring. When it is under constant strain, the resulting stress remains constant as long as it is strained, and so it is time-independent. When the strain is removed, the stress returns to zero instantaneously, and the material recovers its original dimensions. Hence, no decrease in stress is observed during the stress relaxation experiment of an ideal crosslinked rubber.

However, when a real viscoelastic rubber sample is strained at a constant rate as rapidly as possible to attain a fixed deformation and then the stress required to maintain that fixed strain is measured as a function of time at a constant temperature, the stress decays with time. This is known as *stress relaxation*.

There are mainly two instances where stress relaxation is of direct practical interest.¹³ First, when a mechanical connection is attained by a friction fit, the stress responsible for the connection is not supposed to relax significantly. Hence, stress relaxation is important in rubbers to measure their efficiency as seals or gaskets, which often involves both heat aging and exposure to liquids and causes the loosening of container caps, nuts, and other threaded parts. However, in other cases where an unfavorable stress distribution results from the fabrication of a part, it is desirable to relax such stress. The stress relaxation test can also be used to study aging properties, low-temperature resistance, resistance to chemicals, and so on.

There are two distinct causes for stress relaxation: physical causes and chemical ones. The physical effect is due to the entropic removal of order; that is, the molecules return to the most stable conformation. This results in higher entropy.

This happens because of weak secondary van der Waal's forces, which constitute the intermolecular interaction. The amorphous nature and greater mobility of flexible chains in rubbers is also a reason for the increase in entropy. Thus, a reorientation of the mo-

lecular network occurs with the disengagement and re-engagement of chain entanglements, which breaks the secondary bonds between chains, filler particles, and chain and filler particles.¹⁴ As a result, internal relaxation occurs, and so the force (and stress) needed to sustain the constant strain decreases with time. Because the molecular reorganization is temperature-dependent, the relaxation is more rapid at higher temperatures.

The chemical effect is due to the aging of rubber by oxidative chain scission, crosslink breakage, or crosslink formation. However, elastomers exhibit a higher extent of physical relaxation and apparently less chemical relaxation at short times and low temperatures. However, chemical relaxation dominates at longer durations and higher temperatures.¹⁵

Unvulcanized rubbers contain a large number of molecular chains of different lengths. Being viscoelastic material, rubbers exhibit characteristics of both viscous and elastic materials. As a result of crosslinking, the viscous behavior of the rubber decreases, and the elasticity increases. In practice, crosslinked rubbers (unfilled) are imperfect network structures that contain chain ends, loops in rubber chains, branched molecules that are partly incorporated into the network, molecules entrapped in the network but not attached to it by chemical bonds, and so on. Hence, when the strain is removed, the stress does not return to zero, and so the material does not recover its original dimensions. Therefore, the stress relaxation curve levels off to a finite stress instead of zero stress at long times.¹⁶

Thus, the freedom of movement of rubber chains depends on the degree of crosslinking, crystallinity, molecular dimensions, perfection, and morphology of the network structure. Hence, the rate of stress relaxation of a rubber molecule depends on its surrounding structure and will be different from other molecules even in a homogeneous, unfilled rubber compound.

Oriented short-fiber-reinforced rubber composites

The situation is more complicated in fiber-reinforced composites, even if the fibers are oriented. The behavior of random composites is highly complex and not discussed here because, in this study, we focused on oriented fiber composites only. When one compares a matrix and a fiber section in a composite, with the former being a matrix alone and the latter constituting a single short fiber surrounded by matrix, it is clear that a higher load has to be applied to the fiber section to obtain the same strain as in the matrix section. This is due to the higher modulus of the fiber compared to that of the rubber.

Thus, the contribution of strain in the matrix section is greater than that of the fiber section toward the overall strain. Similar to the behavior during the de-

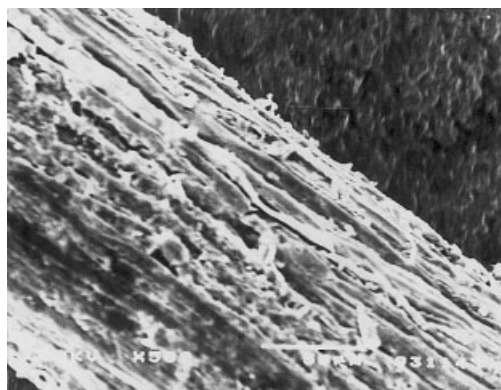


Figure 1 SEM micrograph of the surface of the untreated coir fiber (500 \times).

formation stage, the behavior of these two sections will be different during the relaxation stage also. When the behavior of a single fiber section is considered with the composite loaded axially, the longitudinal strain in the matrix will be higher than that in the adjacent fibers. This difference in longitudinal strain creates a shear stress distribution across the fiber-matrix interface if a perfect bond is assumed between the two constituents. The resulting shear strains are produced in the direction parallel to the fiber axis.

Thus, it is clear that the deformation of the matrix is not symmetrical, even in a single-fiber section. Hence, it can be assumed that the deformation pattern will be highly complex in a short-fiber-reinforced composite system, which contains an enormous number of such fiber sections.

Short-coir-fiber-reinforced NR composites

The complexity is further enhanced by the presence of short coir fibers. We already stated that coir fibers have many disadvantages as reinforcement materials in polymeric matrices. They possess variable diameters ranging from 0.3 to 2 mm, and this results in a complex deformation process; namely, during the deformation of a fiber-rubber composite, the resistance offered by a thin fiber is less than that offered by a thick fiber. Also, coir has a variable length, and so it is difficult to obtain a bulk quantity of chopped fibers with a specific length.

In addition to these drawbacks, coir fibers undergo breakage during mill mixing, even though this breakage is lower compared to that of synthetic fibers. Hence, the final vulcanizate contains chopped fibers of variable diameter and length. Also, the surface of the coir fiber is not smooth but carries certain protrusions, as shown in the scanning electron microscopy (SEM) photograph in Figure 1.

Thus, during analysis of the microstructure of the coir-fiber-reinforced NR composites, it was obvious

that there were innumerable modes of deformation under loading, which varied from point to point in the material. Naturally, this variation in deformation was expected to result in innumerable modes of stress relaxation behavior.

Studies on the stress decay of pineapple-fiber-reinforced polyethylene and oil palm fiber phenol formaldehyde resin composites have been conducted.^{17,18} The mathematics of stress relaxation measurements have been extensively developed and were reviewed by Dunn and Scanlan.¹⁹ Bhagawan et al.²⁰ studied the stress relaxation behavior of short-jute-fiber-reinforced acrylonitrile butadiene rubber composites and reported that a two-stage relaxation pattern existed in these composites. Flink and Stenberg²¹ reported that stress relaxation studies could provide an idea about the interfacial adhesion in NR composites reinforced with short cellulose fibers. Kumar et al.²² analyzed the stress relaxation behavior of polyacetal/thermoplastic polyurethane blends. Varghese et al.²³ studied the stress relaxation behavior of acetylated short-sisal-fiber-reinforced NR composites.

A two-step relaxation mechanism has been reported in different articles, which is explained as follows. The first part of the relaxation is due to the orientation at the fiber–matrix interface, and the second part is due to the progressive failure of polymer–fiber bonding, the breakage of fiber or polymer molecules. However, Kutty and Nando²⁴ reported the existence of two-step and three-step relaxation patterns in unfilled thermoplastic polyurethane and its short-kevlar-fiber-reinforced composites, respectively.

This was explained on the basis of soft and hard segments present in thermoplastic polyurethanes, in which the hard segments act as physical crosslinks. The initial relaxation is due to the orientation at the interface of hard and soft segments. The second relaxation is due to the flow of the soft matrix under tension at longer times. For fiber-filled thermoplastic polyurethanes, relaxation at the fiber–matrix interface was also involved in addition to the mechanisms mentioned for the unfilled system.

However, neither two-step nor three-step relaxation patterns were reported by Harget and Hepburn for polyether-based polyurethane elastomers.²⁵ Thus, it is understood that the relaxation mechanism in composites is dependent on many factors, such as the nature of the matrix, fibers, and interface; strain level; strain rate; bonding agent; fiber surface modification; and temperature.

In this study, the system followed neither two-step nor three-step mechanisms. There were two reasons for this. The first reason was the multitude of inflection points caused by the innumerable physical processes observed during the continuous monitoring of stress decay, which lasted for 10,800 s of the experiment. Second, this study was conducted at tensile

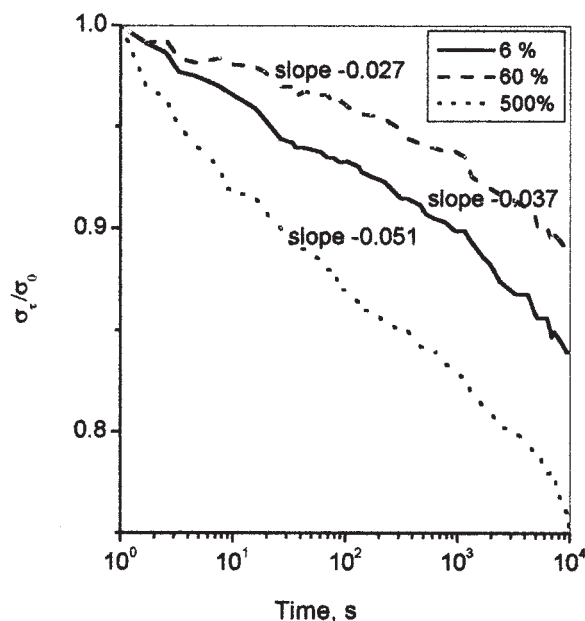


Figure 2 Effect of strain level on the stress decay of the NR compound.

strains of 6 and 60% to avoid breakage of the samples. (However, the experiment was also conducted at 500% strain to identify the effects at a high strain level.) Then, if breakage of the fiber or polymer molecules occurred, it would not have been predominant at short intervals of time. Also, as discussed earlier, chemical stress relaxation occurs only at high temperatures or at long times. This eliminated the possibility of fiber breakage in this study.

Effect of strain level

Figure 2 presents the stress relaxation plot with the stress ratio (σ_t/σ_0) against time of the unfilled rubber compound sample at different strain levels, namely, 6 and 60% at a constant strain rate of 0.0017 s^{-1} and 500% at a constant strain rate of 0.05 s^{-1} . The stress decay was influenced by numerous microlevel physical processes occurring during the stress relaxation process, which manifested as a multitude of inflection points on the curves. However, because the experiment lasted for 10,800 s, these inflection points were ignored during analysis of the curve.

The slopes of the curves for 6 and 60% strain were almost the same. This was in agreement with the observation that the slope of the stress relaxation plot of unfilled NR was independent of strain levels below the threshold strain, which caused strain-induced crystallization.²⁶

However, it was obvious from the slope values that the rate of relaxation increased considerably at a higher strain level of 500%. In strain-induced crystallizable rubbers, crystallites are formed at higher exten-

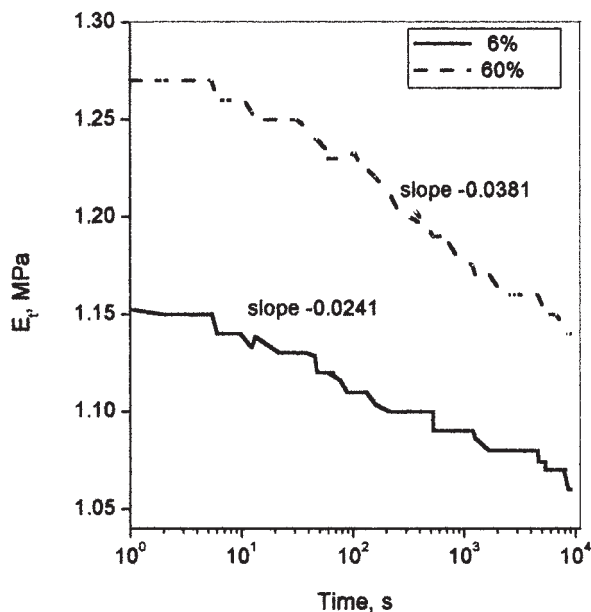


Figure 3 Effect of strain level on the stress decay of mix J.

sions due to the increased molecular order. The chains in the crystallites are oriented parallel to the applied force. Then, the nature of crystallization quantitatively changes, and it becomes energetic like ordinary crystals. This means that similar to ordinary crystals, vibrations of atoms occur in rubber about their equilibrium position under the influence of an external field. This causes the stress to relax rapidly.

Figure 3 represents the stress relaxation plot with E_t versus time of composite J at two different strain levels, namely, 6 and 60%, but at a constant strain of 0.0017 s^{-1} . The (negative) slopes of the composites were 0.0241 and 0.0381, respectively. The higher slope at the higher strain level could be explained as due to the higher relaxation rate because of the higher extent of permanent changes occurring in the material.

Effect of strain rate

The plot of σ_t/σ_0 against time of the unfilled rubber sample is given in Figure 4, which presents the stress relaxation behavior at two different strain rates, namely, 0.0017 and 0.017 s^{-1} , but at a constant strain level of 60%.

It is expected that conditions favoring an increase in entropy will enhance the rate of stress relaxation. Hence, when the material is deformed at a higher strain rate, much of the deformation will be reversible and elastic, whereas if it is stressed at a lower strain rate, the individual molecules get time to slip past one another, and this results in irreversible, plastic deformation. Hence, one expects to obtain a lower relaxation rate at a higher strain rate and vice versa. From the slope value of our curves, it was obvious that the

rate of relaxation was very much dependent on the strain rate.

When the sample was subjected to a tensile deformation with a strain rate of 0.017 s^{-1} , initially the time constant for the conformational change was too large to respond with irreversible flow. Hence, the material responded elastically. For the same reason, during the relaxation stage, elastic recovery also occurred, and the relaxation rate was lower than that caused at a strain rate of 0.0017 s^{-1} . The (negative) slopes of the curves, 0.069 and 0.040, at the two different strain rates, namely, 0.0017 and 0.017 s^{-1} , were clear evidence for this.

Effect of fiber orientation

The effect of fiber orientation on the stress relaxation behavior was investigated for composite X, which contained 30 phr alkali-treated fibers. Figure 5 presents the stress relaxation plot with E_t versus time of mix X in the longitudinal and transverse directions at a strain level of 6% and a strain rate of 0.0017 s^{-1} .

In the longitudinal direction, the fibers were oriented in the direction of the applied force, and in the transverse direction, the fibers were aligned in the perpendicular direction. In the latter case, the fiber-rubber interface had only a small role in the stress transfer, and the majority of relaxation was due to the rubber molecules alone. However, in the longitudinal composite, the relaxation was a combined effect of the rubber molecules and the fiber-rubber interface. As a result, the increase in entropy decreased, and so the stress relaxation rate was lower for the longitudinal

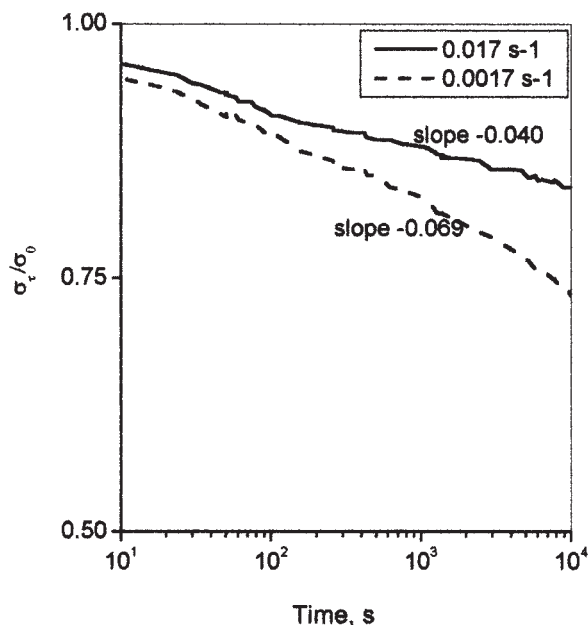


Figure 4 Effect of strain rate on the stress decay of the NR compound.

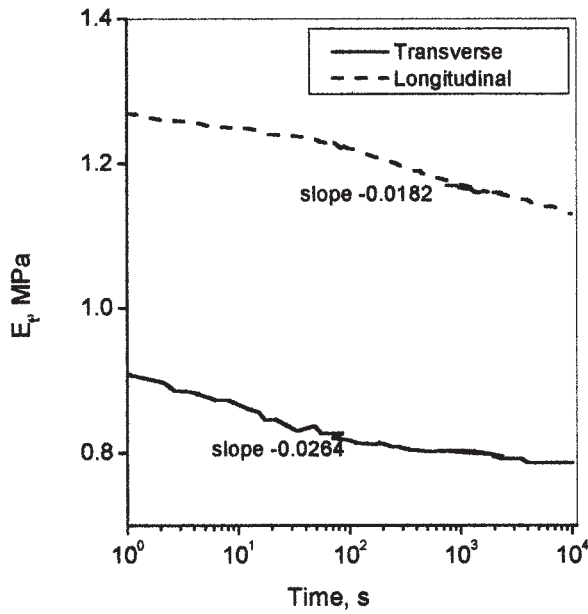


Figure 5 Effect of fiber orientation on the stress decay of mix X.

composite. This was clear from the (negative) slopes of the longitudinal and transverse composites, which were 0.0182 and 0.0264, respectively.

Effect of fiber loading

Figure 6 presents the stress relaxation plot with E_t versus time of the unfilled rubber compound sample and mixes J_{30} and J_{60} at a strain level of 6% and a strain rate of 0.0017 s^{-1} . Mixes J_{30} and J_{60} contained alkali-treated coir fibers subsequently treated with TDI and

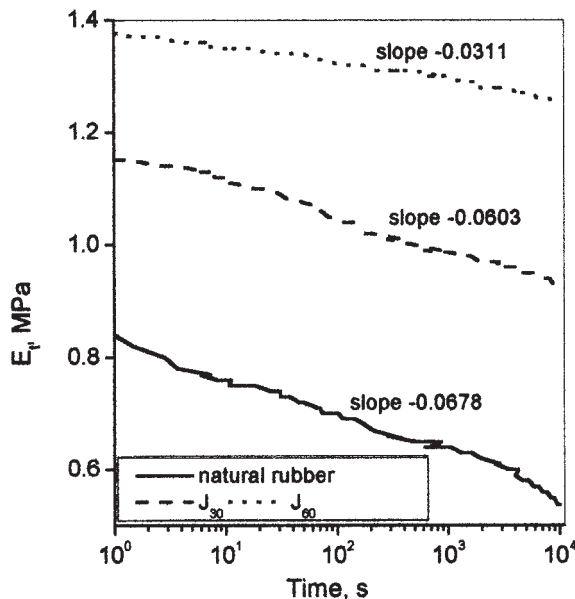


Figure 6 Effect of fiber loading on stress decay.

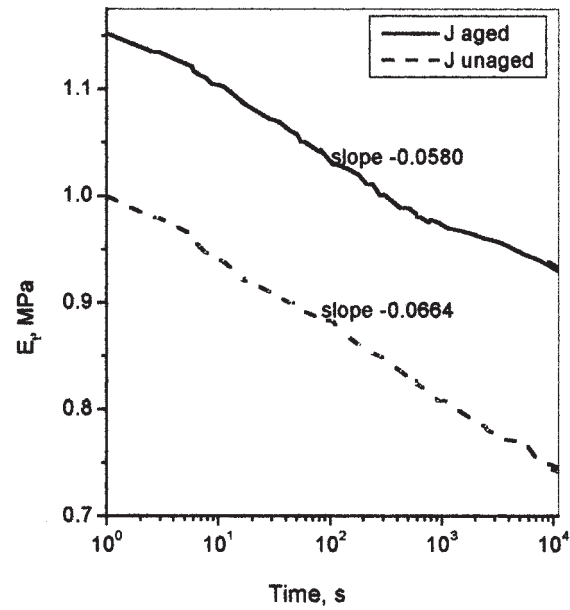


Figure 7 Effect of aging on stress decay.

NR solutions. In the unfilled rubber compound, the entire relaxation was due to the rubber molecules alone, but when the fibers were added, the relaxation was hindered because of the fiber–rubber interface, and the relaxation decreased with increasing fiber loading. This was evident from the (negative) slopes of the unfilled rubber compound and mixes J_{30} and J_{60} , which were 0.0678, 0.0603, and 0.0311, respectively. The rate of relaxation was the highest for the unfilled rubber compound, and it decreased with fiber content.

Effect of aging

A comparison of the stress relaxation behavior of the aged and unaged samples of mix J is shown in Figure 7. The experiment was carried out at a strain level of 6% and a strain rate of 0.0017 s^{-1} . The stress relaxation in tension can be used as a general guide for aging studies.²² During aging at high temperatures, the following phenomena can occur: first, an increase in bonding between the fibers and rubber matrix due to increased activity at the fiber surface; second, additional crosslink formation; and third, chain or crosslink scission.

Thus, a considerable amount of irreversible, permanent changes can occur in the material during aging. Hence, such a sample is not expected to relax more when the stressed sample is allowed to relax with time. This was evident from the (negative) slopes of the curves corresponding to the unaged and aged compounds, which were 0.0664 and 0.0580, respectively. The decrease in the slope for the aged sample indicated a decrease in the entropy and relaxation rate of the compound.

Role of interfacial adhesion

As mentioned earlier, coir-rubber adhesion is not good. Hence, various techniques were adopted to improve the interfacial adhesion of the composites. Mix W contained untreated fibers without a bonding agent, mix X contained alkali-treated fibers without a bonding agent, and mix Y contained fibers treated with a potassium permanganate solution along with a hexaresorcinol (RH) system as a bonding agent. Mix J contained fibers subjected to a chemical treatment with alkali and subsequently with TDI and NR solutions along with the RH system as a bonding agent.

Figure 8 presents the stress relaxation plot with E_t versus time for mixes J, W, X, and Y. Among the four composites, the rate of stress relaxation was at a minimum for composite J and at a maximum for composite W, and this could be attributed to the best fiber-rubber adhesion in the former. Composite X showed intermediate values for the rate of stress relaxation. This indicated that even though some modifications were achieved by the alkali treatment, such as the removal of surface protrusions and the waxy cuticle layer, it was not very effective in increasing the overall performance of the composite. Also, the stress relaxation of composite Y was somewhat high. Thus, it was clear that the potassium permanganate treatment was not suitable for increasing the coir fiber-NR bonding. The slope, regression coefficient, and standard deviation values of the stress relaxation curves for these mixes are given in Table IV.

CONCLUSIONS

The stress relaxation behavior of NR and its composites reinforced with short coir fibers under tension was

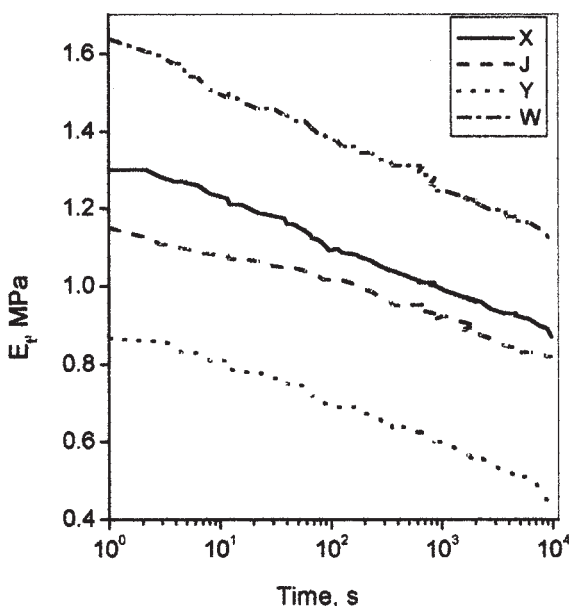


Figure 8 Effect of fiber modification on the stress decay of mixes W, X, J, and Y.

TABLE IV
Analysis of the Curves

Mix	Slope (negative)	Regression coefficient	Standard deviation
J	0.0878	-0.99	1.383
X	0.1135	-0.99	0.978
Y	0.1088	-0.99	1.400
W	0.1287	-0.99	1.230

analyzed. The rate of stress relaxation was a measure of the increase in the entropy of the compounds; the higher the rate was, the greater the entropy was. At lower strain levels, the relaxation mechanism of the unfilled NR was independent of strain level. However, the rate of relaxation increased with the strain level because of strain-induced crystallization. The strain level influenced the rate of stress relaxation considerably in the coir-reinforced NR composites.

Also, the relaxation mechanism of both the unfilled compound and the composites was influenced by the strain rate. At a high strain rate, the rate of stress relaxation was low because of the major contribution of elastic components in the system, and so the increase in entropy was small. Just the reverse happened at lower strain rates. The rate of relaxation was highest for the NR compound, and it decreased with coir fiber loading from 30 to 60 phr. This indicated a decreased entropy of the elastomeric matrix because of the incorporation of fibers.

The rate of relaxation of the longitudinally oriented fiber composites was lower than that of the transverse composites because of the decreased plastic flow of the former. Interestingly, a decrease in the rate of relaxation was observed for the aged sample, and this was due to the formation of extra crosslinks at high temperatures.

From the rate of stress relaxation, we found that fiber-rubber adhesion was best in the composite containing fibers subjected to a chemical treatment with alkali, TDI, and NR solutions along with the HR system as a bonding agent. Also, the alkali treatment and potassium permanganate treatment were not suitable methods for increasing coir fiber-NR bonding.

In this study, the stress relaxation curves could not be viewed as segments with varying slopes; however, a multitude of inflection points were observed on the curves. Hence, neither a two-step nor a three-step mechanism is proposed for the coir-fiber-reinforced NR composites as reported for some other systems.

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