

Stress-Strain and Stress Relaxation in Oxidated Short Carbon Fiber-Thermoplastic Elastomer Composites

L. IBARRA*, A. MACÍAS, and E. PALMA

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

SYNOPSIS

Stress-strain and stress relaxation properties are studied in composites consisting of a thermoplastic elastomer butadiene styrene copolymer (SBS) matrix and oxidated carbon fiber. The results obtained from samples at different degrees of oxidation are contrasted with those obtained from SBS filled with commercial carbon fiber. Carbon fiber oxidation with nitric acid gives rise to an increase in functional surface groups, which in turn enhance the capacity in the fiber to interact with the matrix. In the experimental composites, the increase in fiber-matrix interactions translates into proportionally greater strain necessary to reach the yield point, as well as into an increase in stress at the yield point. In addition, at initial strain below the strain at yield point, a slower stress relaxation rate is observed in oxidated fiber composites, as compared with those recorded for the matrix filled with commercial fiber. In the oxidated fiber composites, stress relaxation occurs in three stages, the first two of which may be associated to the fiber-matrix interface. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers (TPE) offer a great variety of practical benefits over conventional thermostable elastomers, such as easier processing, as well as the possibility to recycle waste and residues. They possess a major inconvenience of softening at high temperature. This latter property, inherent in TPEs, precludes their application, whenever exposure to temperatures close to the melting point of the hard segment is at stake.

Styrene block copolymers are typical thermoplastic elastomers, consisting of hard styrene and soft diene segments.

In reinforcements with fiber, it is relevant to mention the fiber-matrix interface together with other characteristics of the fiber, for instance its aspect ratio, length/diameter (L/d) ratio. Carbon fiber is one of the fibers these materials can be reinforced with, but, at least for the conventional elastomers,

they present the serious inconvenience of severe deterioration during processing. On the other hand, they are susceptible of surface modification, when considerably increasing the number of functional groups capable of interaction with the matrix, by means of simple methods, such as liquid phase oxidation with oxidating agents.

For the present work, composites were prepared based on a thermoplastic styrene-butadiene elastomeric matrix (SBS) filled with commercial carbon fiber or oxidated fiber, at different oxidation levels, to study the effect of fiber oxidation on the stress-strain response. In addition and due to the fact that short fiber is increasingly used in static and dynamic applications, where stress relaxation is essential, this latter behavior was also determined for the materials under study.

Carbon fiber oxidation, according to long-standing experience in our laboratory, gives rise to surface modifications based on functional groups, fundamentally, although there exist others, carboxylic groups (—COOH) capable of increasing the fiber-matrix interactions and hence enhancing the mechanical properties of the composite.¹

In this work the authors endeavor to study the tensile stress relaxation behavior of materials rein-

* To whom correspondence should be addressed.

forced with fiber oxidated at variable degrees, comparing it to that of the thermoplastic elastomer filled with unmodified commercial fiber and with regard to the effect exerted on the SBS matrix.

EXPERIMENTAL

Carbon Fiber

A cylindrical polyacrylonitrile carbon fiber was used, supplied by Hercules Aerospace España S.A. under the trade name 1815/AS. This fiber is subjected to an oxidation process, as described in previous work,² varying the exposure time to obtain different levels of oxidation. The characteristics of the experimental oxidated fibers are compiled in Table I, together with those of the commercial fiber. The mean fiber lengths and L/d ratios indicated refer to postprocessing measurements.

Composite Materials

The polymeric matrix was a 70/30 SBS copolymer block with a radial structure, supplied by Repsol Química S.A. under the trade name Calprene 416. For each of the fiber types obtained at different treatment times, composites were prepared containing a fiber portion of 10 vol %. All the blends were prepared under the same conditions, the components were blended in a cylinder mixer, length 300 mm, friction ratio 1 : 1.25, heated by thermofluid to a temperature of $140 \pm 5^\circ\text{C}$, and maintaining the same rotor direction to favor uniform fiber orientation within the matrix. Finally, the samples were rolled to 2-mm-thick slabs.

Moulding was conducted in a thermofluid-heated compression press, at 190°C , holding the samples for 15 min. The die was then placed on a cold plate applying pressure for 5 min.

Property Measurement

The stress-strain and stress relaxation tests were conducted on dumb-bell samples, 6 mm width at the straight edge using an Instron dynamometer, model 4301 with a separation rate of 500 mm/min and a gauge length of 25 mm. The values are expressed as the mean value from five samples in the case of stress-strain test and from three samples in stress relaxation measurements. The stress was recorded as a function of time.

RESULTS AND DISCUSSION

Stress-Strain Behavior

Figure 1 shows the effect of oxidated fiber addition, at different treatment times and hence with a variable number of functional groups, on the stress-strain properties of two of the experimental oxidated fibers composites together with those of a control composite, prepared with untreated fibers, and those of SBS matrix. In the case of oxidated fibers composites, the measurements were conducted taking into account the direction of the strain applied, either longitudinal (L) or transverse (T) to preferential fiber orientation and only in longitudinal direction in the other cases.

The shape of the graphs varies as a function of fiber orientation. Thus, in longitudinal measurements, all composite materials present a peak, a point of inflection, which is absent in the graphs obtained from transverse strain measurements, whose shape is similar to that of the graph obtained for the SBS matrix. The point of inflection corresponds to that of maximum stress in the composites (i.e., their yield point) that may be attributed to failure in fiber-matrix adhesion, as in the pure matrix there does not exist any such yield point.³

Table II shows the stress and strain values at the yield point determination of different samples. If

Table I Fiber Characteristics

Oxidation Time (h)	Specific Surface Area, S_{BET} (m^2/g)	Mean Lengths (μm)	Aspect Ratio (L/d)	COOH ($\mu\text{Eq}/\text{g}$ fiber)	Sample
5	0.71	276	56.5	91	OXI-5
10	0.63	248	49.4	155	OXI-10
15	0.59	222	48.2	260	OXI-15
24	0.57	197	38.8	350	OXI-24
48	0.68	103	21.6	840	OXI-48
Commercial	0.44	286	56.2	—	Control

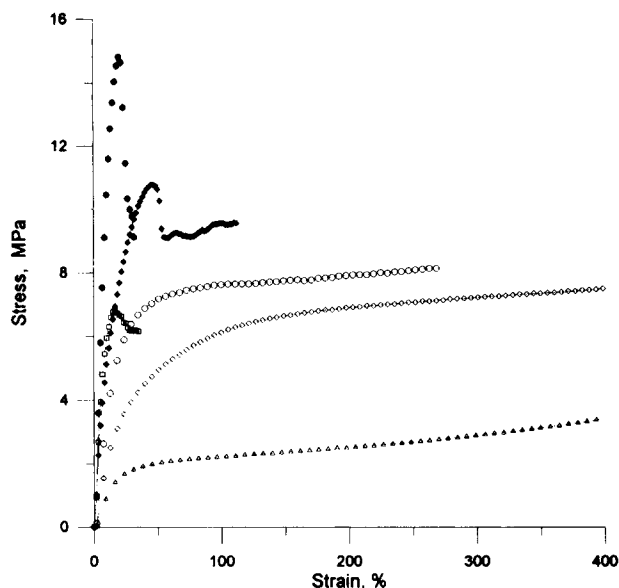


Figure 1 Stress-strain curves: (Δ) SBS matrix; (\square) control composite, filled with commercial fiber. Initial strain applied in longitudinal direction, (\bullet) Composite material with 5 h oxidated fiber. Initial strain applied in longitudinal direction; (\circ) idem, initial strain applied in transversal direction; (\blacklozenge) composite material with 48 h oxidated fiber. Longitudinal direction; (\diamond) idem, transversal direction.

the yield point, as stated above, is assumed to correspond to a failure in fiber-matrix adhesion (i.e., interfacial breakdown), there seems to exist a relationship between the degree of oxidation and the strain value at which the yield point appears, in such a way that the greater the number of functional surface groups incorporated by means of oxidative treatment, the greater the strain the interface is able to support until interfacial failure occurs, as shown in Figure 2.

In addition, the stresses at the yield point in all composites filled with oxidated fiber are greater than those in the material reinforced with commercial fiber. Stresses are observed to grow as a function of oxidation time, yet this trend is reversed for very long oxidation times. This decrease correlates to a loss in fiber strength, consequential to long oxidation exposure⁴ and apparent in a significant drop in the L/d ratio,⁵ as shown in Table I.

Obviously, the yield point strain sets the limit for maximum initial strain in the stress relaxation tests.

Stress Relaxation

Due to the growing demand of composite materials in static and dynamic applications, where stress re-

laxation plays an important role, studies in this area have become more frequent. Thus, the stress relaxation behavior of nitrile rubber and short jute fiber composites has been studied in depth by Bhagawan et al.⁶ on the existence of a relaxation in two stages in these materials. Flink and Stenberg⁷ examined the stress relaxation behavior in natural rubber and short cellulose fiber composites by means of plots of $F(t)/F(0)$ against $\log t$, where $F(t)$ is the stress at a given time and $F(0)$ represents initial stress. The same authors state that stress relaxation measurements would provide a clear idea regarding the level of rubber-fiber adhesion in the composites. Stress relaxation of a material consisting of a thermoplastic polyurethane matrix and short Kevlar fiber was studied by Kutty and Nando⁸ to suggest a two-stage relaxation mechanism for the unfilled material and a relaxation process in three stages for the reinforced composite. Later, Varghese et al.⁹ studied stress relaxation in natural rubber composites reinforced with short sisal fiber. The relaxation process of these latter materials adjusts to a single episode for pure rubber and a two-stage process for the reinforced material.

Thus, stress relaxation process is defined by the slope and the ordinate of each of the straight lines to which the experimental points can adjust, representing the different relaxation episodes. Obviously, each phase has its own relaxation mechanism. The intersection of the lines is the point in time which marks the end of the first mechanism and, hence, the transition toward the ensuing one.

Figure 3 gives the stress relaxation plots— $F(t)/F(0)$ versus $\log t$ —of the thermoplastic elastomeric matrix compound at different initial strain level. The rate at which the initial strain is attained is kept constant in all the runs. It is interesting to note that in all cases the points fall on two intersecting straight lines, unlike the behavior reported for conventional elastomer gum compounds. The stress relaxation plot consisting of two straight lines of unequal slopes indicates a different mechanism of re-

Table II Strain and Stress at Yield Point in Fiber Filled Composites

Type of Fiber	Strain (%)	Stress (MPa)
Commercial	15.98	6.88
OXI-5	20.07	14.45
OXI-10	26.81	14.96
OXI-15	29.21	16.95
OXI-24	31.02	13.29
OXI-48	47.16	10.92

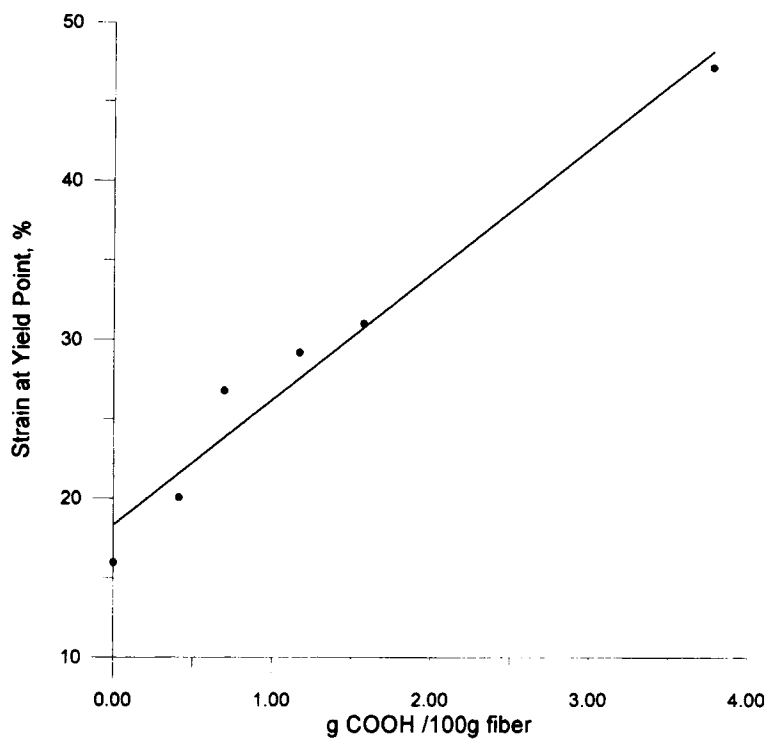


Figure 2 Strain at yield point as a function of the oxidation degree.

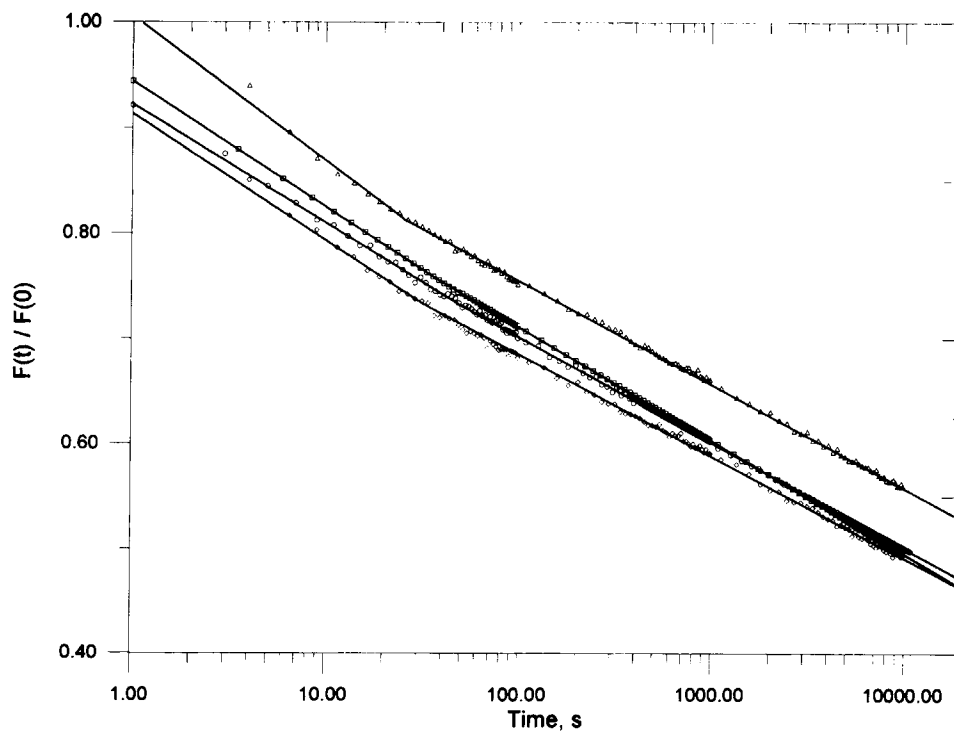


Figure 3 Stress relaxation of the SBS matrix as a function of the initial strain: (○) 15%; (□) 25%; (◇) 50%; (△) 100%.

Table III Stress Relaxation Parameters of SBS Matrix at Different Initial Strains

% Strain	Slope 1 ($\times 10^2$)	Slope 2 ($\times 10^2$)	Intercept 1	Intercept 2	Time (s)
15	4.88	4.35	0.9227	0.9019	49.94
25	5.17	4.67	0.9445	0.9265	37.67
50	5.21	4.20	0.9137	0.8788	31.67
100	5.93	4.27	1.00	0.9516	18.65

laxation operating—one that operates at shorter times (<200 s, slope 1) and another that is prominent at the later stages of relaxation¹⁰ (slope 2).

Table III shows the features that characterize the two lines, slopes, and intercepts, together with the point of intersection of these two straight lines, expressed as time (s) in table, that is the time at which a changeover takes place from one mechanism of relaxation to the other. The slopes were calculated using a linear regression method.

The slope at short times is steeper than the slope at long times indicating a faster stress relaxation and thus a faster process. A probable explanation, assuming that the change in slope is significant, is that the short-term relaxation is associated with small segments or domains of the molecular chains,

whereas the long-term relaxation is caused by a long-range rearrangement of molecular chains.⁷

At lower than 100% initial strain level, the relaxation processes are found to be independent of strain level, as indicated by respective slopes. At higher initial strain (100%), a slight increase of the first relaxation process rate is observed.

The crossover point is shifted to shorter times at higher strain levels, indicating that the initial mechanism of relaxation is exhausted at the short period under higher deformations.

Effect of Fiber Loading

Figure 4 shows the stress relaxation behavior in a semilogarithmic representation for the material

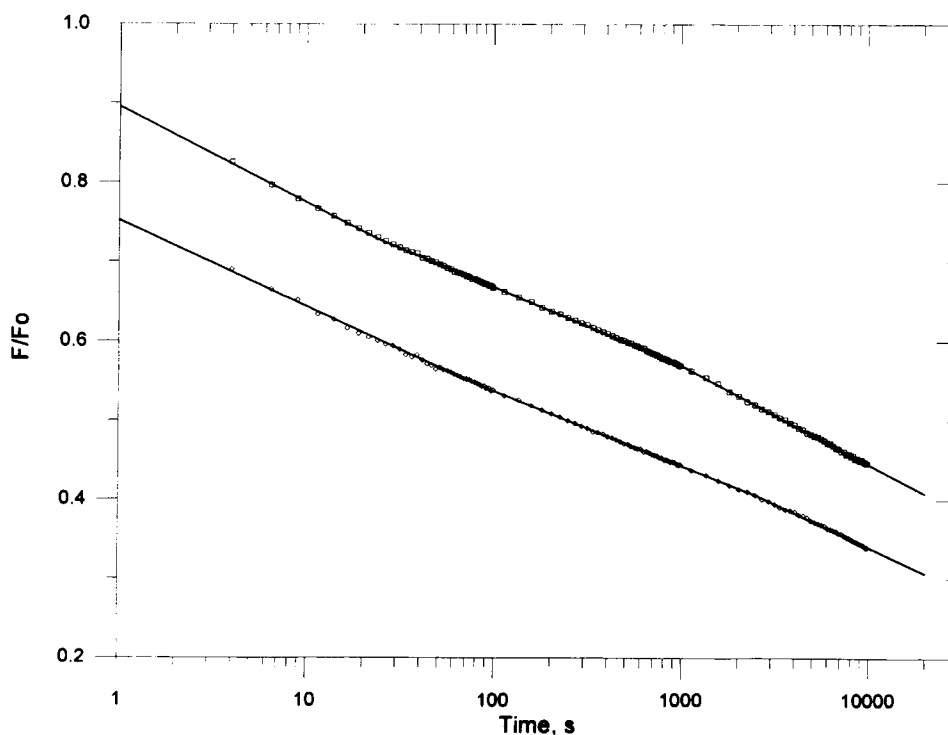


Figure 4 Stress relaxation of composite materials: (◇) with commercial fiber; (□) with 5 h oxidized fiber. Initial strain 15%. Strain applied in longitudinal direction.

reinforced with commercial fiber, as compared with a composite filled with oxidated fiber (5 h oxidation), at an initial strain of 15%. In the present case, incorporation of fiber results in three relaxation processes, as indicated by three different slopes, that persist even in presence of the oxidized fiber.

Table IV summarizes the parameters defining relaxation process in the composite filled with untreated commercial fiber and oxidized fibers with variable degrees of oxidation, at different initial strains. For untreated fiber composite, control sample, unlike the case of SBS matrix, the rate of stress relaxation due to the first process (as indicated by slope 1) decreases with strain level. This is because, taking into account the strain at which the yield point appears in this composite (see composite with commercial fiber in Table II), the three experimental strains are positioned before, during, and after the appearance of the yield point. It goes without saying that, once the yield point strain has been surpassed, relaxation rates are bound to slow down.

With the aim of determining if the fact of surpassing the yield point strain actually changes the rate of the relaxation process, the values of the relaxation parameters of the different oxidated fiber composites for an initial strain of 25% are also shown in Table IV. The values are very similar, except those of sample OXI-5, whose yield point is below the initial strain applied.

In comparison with the values corresponding to an initial strain of 15%, no significant variations are recorded. This means that the interface formed by the oxidated fiber and the matrix remains unaffected by initial strain increases as long as the strain at

which the yield point appears has not been surpassed.

This is the reason why, for any comparison of stress relaxation between materials, initial strain should be established below the yield point strain value. As a consequence, the yield point strain values compiled in Table II advise the choice of an initial strain of 15% in the oxidated fiber composites for the comparative study of tensile stress relaxation behavior.

The parameters calculated for the composites filled with fiber oxidated at different oxidation degrees, at an initial strain of 15%, are also shown in Table IV.

When comparing the values of the samples Oxi-5 and control corresponding to an initial strain of 10%, it is legitimate to state that in the material reinforced with oxidated fiber, relaxation, which likewise presents in three phases, occurs at a slower rate.

The gum compound (SBS matrix) has the lowest rate of relaxation and composite with commercial fiber has the highest rate. The oxidation of fibers lowers the relaxation rate to some extent, as compared with untreated fiber composite. The increase in relaxation rate due to fiber addition could be attributed to stress softening and strain amplification.¹¹

Regarding the relaxation process rate, no significant differences are observed as a function of the degree of oxidation, although the most notable rate difference with respect to composite filled with commercial fiber appears in the second phase, showing approximately a decrease of 30%.

Table IV Stress Relaxation of Fiber Filled Composites at Different Initial Strains: Longitudinal Direction

Sample	Initial Strain (%)	Slope 1 ($\times 10^2$)	Slope 2 ($\times 10^2$)	Slope 3 ($\times 10^2$)	% Contribution	Time 1 to 2 (s)
Control	10	6.23	5.61	5.55	2.57	26.2
	15	5.19	4.11	5.57	4.79	31.2
	25	4.53	3.82	4.65	3.74	37.6
Oxi-5	10	5.43	4.71	5.55	2.6	25.5
	15	5.31	4.03	4.87	4.5	21
	25	3.33	2.97	4.44	1.14	7.16
Oxi-10	15	5.59	4.2	5.32	5.57	36
	25	5.06	3.86	4.45	5.35	36
Oxi-15	15	5.44	4.01	5.62	5.92	37.2
	25	5.8	4.1	5.07	7.1	29.1
Oxi-24	15	5.63	3.96	4.41	7.35	47.6
	25	5.30	3.98	4.21	5.77	35.3
Oxi-48	15	5.84	4.01	4.49	7.01	34
	25	5.9	4.22	4.9	6.74	30.2

A method¹⁰ of estimating the contribution of the early mechanism to the relaxation in the system is to divide the difference of intercepts of the two first lines by the intercept of the first line at $t = 1$ s. This fraction, expressed as a percentage, is also shown in Table IV. As can be seen, differences exist in the contribution of the first mechanism, which increases with increasing oxidation and, consequently, the crossover time (1 to 2) from one mechanism to the other also increases. Evidently, the higher the degree of oxidation, the greater the number of functional groups on the fiber surface. Hence, the lower relaxation rate in the oxidated fiber materials can be associated to the nature of the fiber-matrix interface.

In like manner, stress relaxation was measured in these materials initial strain being applied transversely or perpendicular to the preferential fiber orientation within the matrix. In the case of the unfilled matrix, the T strain was applied perpendicular to the flow direction of the material in the mixing cylinder.

The fact that in the stress-strain diagrams there does not appear any yield point, when strain is applied perpendicular to preferential fiber orientation, makes it possible to measure stress relaxation at higher initial strains. The results obtained for initial strains of 25 and 35% are shown in Table V.

For the reinforced composites, relaxation continues to occur in three phases. The values recorded demonstrate that, when initial strain is applied transversely, material relaxation is independent of the presence of fiber, and hence of fiber treatment. In other words, relaxation fundamentally follows a course similar to that of the unfilled polymeric matrix.

In addition, it is interesting to point out that the intersection time of the first two straight lines is approximately constant and independent of strain level and degree of fiber oxidation, together with the fact that the contribution in percent of the first mechanism of the matrix shows a striking similarity to the respective values calculated for the composites filled with oxidated fiber, whereas for the material filled with commercial fiber it is significantly higher.

CONCLUSIONS

In the light of the findings described above, it is legitimate to conclude the following. First, the materials reinforced with oxidated fiber show a higher stress-strain response for any oxidation level, as compared with the composite containing commercial fiber. Greater stresses and strains are required to reach the yield point, which is considered indicative of interfacial failure. The strain necessary to reach the yield point is directly proportional to the number of functional groups on the fiber surface. Yet the stress at this point also depends on the final L/d ratio of the fiber (i.e. on fiber strength).

Second, the tensile stress relaxation process in the fiber-filled materials, indistinctive of oxidation, occurs in three phases, whereas in the unfilled SBS matrix relaxation possesses only two. The relaxation rate is slower in the oxidated fiber composites than in the material filled with commercial fiber, as demonstrated by the lower slope values of the former, the degree of oxidation, however, having no effect at all.

Table V Stress Relaxation in Transversal Direction at Different Initial Strains

Sample	Initial Strain (%)	Slope 1 ($\times 10^2$)	Slope 2 ($\times 10^2$)	Slope 3 ($\times 10^2$)	% Contribution	Time 1 to 2 (s)
SBS	25	5.5	4.2	—	4.86	35.3
	35	5.2	4.1	—	5.07	61.7
Control	25	5.8	3.7	4.3	8.65	27.9
	35	6.2	4.1	4.8	8.55	27.1
Oxi-5	25	5.6	4.2	4.8	5.4	28.2
	35	5.0	3.8	4.9	4.64	33.3
Oxi-10	25	5.1	4.2	5.6	3.8	27.9
	35	5.3	3.6	4.6	5.98	23.4
Oxi-15	25	5.3	4.3	5.0	4.3	40.8
	35	5.4	3.8	4.7	6.41	29.3
Oxi-24	25	5.2	3.6	3.9	7	35.2
	35	5.5	3.4	4.5	8.3	31.7
Oxi-48	25	5.9	4.4	4.7	6.2	31.5
	35	5.5	3.8	4.2	6.92	35.7

Third, when increasing initial strain, the relaxation rate remains practically constant in all cases, but in composite filled with fibers, modified or not, the relaxation rate is constant as long as the strain at which the yield point appears has not been surpassed; if this takes place, the relaxation rate diminishes. And finally, when initial strain is applied perpendicular to preferential fiber orientation, relaxation follows a course comparable with that of the unfilled matrix for all the composites.

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