Stress-Induced Chemiluminescence from Nylon 66 Fibers

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Synopsis

The emission of visible light during the tensile deformation of medium- and high-tenacity nylon 66 yarns in air has been studied at strain rates of 0.63–200%/min and at temperatures of 20–110°C. Emission is observed only in an oxidative atmosphere and increases with temperature according to an Arrhenius relation. The activition energy decreases with applied stress. The intensity at any temperature can be described by the sum of a component linear with stress and another exponential in stress above ~60% of the ultimate strength. These results and the measured spectral distribution suggest that light emission arises from bimolecular termination of alkyl peroxy macroradicals. The chemiluminescence growth curves indicate that the applied stress increases the oxidation rate of the fiber due to internal and external frictional heating while, at high strains, stress-induced main-chain scission occurs up to fiber failure. The growth curve is sensitive to the load history of the fiber. The chemiluminescence decay curves are a sensitive probe of radical reactions such as cage termination and stabilizer scavenging in the amorphous region of the polymer.

INTRODUCTION

The oxidation of many solid polymers is accompanied by the emission of weak chemiluminescence.[1] The readily available methods for accurately and reproducibly measuring low light levels have led to the use of this chemiluminescence to provide mechanistic and kinetic information about the oxidation of polyolefins, polyamides, and unsaturated polymers.[2] In these kinetic studies it has been assumed that the mechanism of light generation is the exothermic bimolecular termination reaction of primary or secondary alkyl peroxy radicals.[3] Other exothermic reactions, including decomposition of polymer hydroperoxides, have been proposed.[4,5] However, the reaction scheme based on peroxy radical termination has successfully accounted for most oxidative chemiluminescent reactions and has provided rates of polymer degradation and stabilizer efficiencies over a wide temperature range.[1,2]

Weak light emission has also been reported during the mechanical deformation and fracture of polyolefins, polyamides, polyesters, fluoropolymers, and rubbers.[6,7] The luminescence has been attributed to several processes, including: (i) chemiluminescence from radical termination reactions; (ii) charge recombination luminescence; (iii) gas discharge and other piezoelectric effects due to the formation of new surfaces at fracture. The dominant process depends on the conditions of the deformation. For example, in the grinding of polymers in gases such as oxygen, hydrogen, or helium at pressures from 0.1 to 100 torr, the emission is dominated by gas discharge effects.[7] Low temperature grinding followed by heating produces luminescence from recombination of trapped charge and free radicals, while the room temperature uniaxial or biaxial tensile

deformation of a polymer produces light from gas discharge and chemiluminescence.[6]

Recently, a highly sensitive photon counting stress chemiluminescence apparatus has been described[8] and used to study the deformation of epoxy resin and nylon 66 moldings from 25°C to 110°C in oxygen.[9] Although the spectral distribution of the stress chemiluminescence differed from the thermooxidative chemiluminescence, the light generation process was considered to be the recombination of stress-generated alkyl peroxy macroradicals.[10]

Evidence for free radical formation during the tensile deformation of highly oriented fibers such as polyethylene, nylon 6, and nylon 66 has been obtained by ESR at low temperatures[11] and by IR analysis of the oxidation products from subsequent reactions.[12,13] That these radicals arise from macromolecular chain scission has been confirmed by molecular weight measurements.[14] The role that these polymer chain scission reactions play in determining the mechanical properties of the fiber is uncertain. It was initially attempted to develop a quantitative relationship between the free radical concentration and the ultimate strength of the fiber,[15,16] but it is now apparent that the process of microcrack nucleation and growth leading to failure is not a result of macromolecular scission reactions alone.[11,17]

The formation of free radicals during the tensile deformation of nylon 66 fibers in air should result in observable stress-induced chemiluminescence. It was the object of this investigation to determine the nature of the light emitted when nylon 66 yarns are stressed and assess if the technique could provide information about the stress-induced polymer radical reactions and their role in determining the performance of the material.

EXPERIMENTAL

Materials

Nylon 66 warp yarns for study were obtained from two plain woven fabrics of widely different weight and yarn properties, as shown in Table I. Yarns were tested either as complete fabric strips 12 mm wide (sample 1) and 25 mm wide (sample 2) or as groups of 16 yarns (sample 1) obtained by removing the fill. The

TABLE I
Properties of Nylon 66 Yarns

Property	Sample 1	Sample 2
Fabric weight (g/m^2)	280	45
Yarns per cm of fabric	13.5	40
Yarn linear density (tex)	97	5.3
Filaments per yarn	130	12
Filament diameter (μm)	27	21
Yarn breaking force (N)	61	2.3
Yarn tenacity (g/den)	7.1	4.9
Yarn tensile strength (MPa)	780	540
% Elongation at fail (yarn)	25%	29%
Polymer $\overline{M}_v$[a]	24,800	22,500
% Delustrant (TiO$_2$)	0.04%	0.28%

[a] Measured in m-cresol at 25°C.[18]

presence of the fill did not alter the stress-induced luminescence behavior and the intensity was only slightly decreased.

Apparatus

The apparatus used for measuring the light emitted during tensile deformation of the yarns in air consisted of an Instron Model 1026 bench top tensile testing machine and environmental chamber which was modified by attaching a lens system and cooled photomultiplier to the door and in line with the sample position. The light gathering efficiency was increased by placing a concave mirror behind the sample. The sample was held in flat grips lined with lead to eliminate grip failure. The only other modifications were the addition of a thermocouple adjacent to the sample and the removal of all light paths into the chamber. The EMI 6256S photomultiplier was cooled by a nitrogen stream at $-35°C$ and the signal detected by either a Brookdeal 5C1 Photon Counter or a Keithley 610C Electrometer and recorded on a Bascom Turner Model 8120 Data Acquisition System. The light intensity was represented as either an anode pulse count rate (Hz) or a dc anode current (nA). Under the conditions used here, 1 nA = 90 Hz. The amplified load cell voltage from the Instron 1026 was fed to another channel of the data system. The load cell voltage and the count rate from the photon counter as a function of time of straining were recorded on floppy disk for subsequent analysis. The maximum time constant in the light detection circuit was 1 s.

The spectral distribution of the emitted light over the wavelength range 360–610 nm was determined by placing calibrated cut-off filters between the sample and gathering lens and measuring the change in transmitted intensity. This was converted to intensity per unit wavelength interval over the band defined by any two filters.

The large volume of the environmental chamber precluded its use for experiments in gases other than air. Experiments on stress-induced luminescence in pure oxygen and nitrogen were performed in the oxyluminescence apparatus previously described.[19] This was modified by the addition of a small manual straining rig to the sample chamber. For these experiments sample stress was not measured.

RESULTS

Stress Luminescence Curves

Figures 1 and 2 show the change in luminescence intensity from the yarns of high and medium tenacity nylon 66 at 40°C during elongation in air at a strain rate of 10% per minute. This luminescence curve is replotted against the measured stress in Figures 1(b) and 2(b) and the following points are noted:

(i) There is a small increase in emission intensity with sample stress until about 60% of the ultimate tensile strength. This is more obvious in Figure 1 for high tenacity nylon.

(ii) Further elongation results in a rapid increase in emission intensity until the yarns fracture.

(iii) Fiber failure is accompanied by intense bursts of light. It can be seen
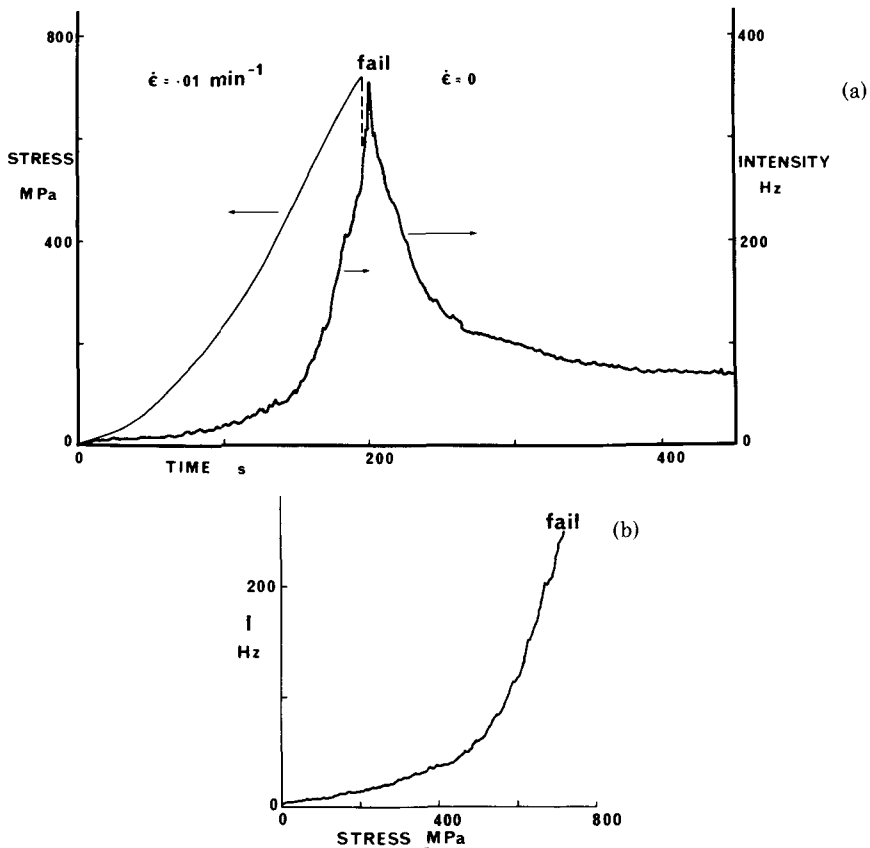
Fig. 1. A typical stress luminescence curve from high tenacity nylon 66 yarns in air at 40°C. (a) Simultaneous stress and intensity data collected as a function of time of elongation at a rate of 10%/min up to failure; and the decay of intensity with time after failure when elongation is stopped. (b) Data from 1(a) up to yarn failure replotted as intensity of luminescence as a function of applied stress.

from both Figures 1 and 2 that the maximum in the emitted light occurs after the sample has failed.

(iv) After most yarns have failed, or if the sample is rapidly unloaded, the luminescence slowly decays.

The luminescence growth curves of Figures 1(b) and 2(b) can be analyzed as the sum of a component linear in stress and one exponential in stress. Figure 3 shows the analysis of the rapid growth region of these curves after an underlying linear component (obtained by extrapolating the low stress luminescence curve to higher stress levels) is subtracted. This fits an exponential curve and the following relation has been found to hold for both nylon 66 samples over a wide range of temperatures:

$$I(\sigma) = I_0 + A\sigma + Be^{C\sigma}$$

where I_0 is the chemiluminescence intensity from the sample in the absence of stress. I_0 is a function of sample geometry and instrument sensitivity, and for a fixed set of operating conditions is a characteristic of the material. I_0, A, B, and C are temperature-dependent.
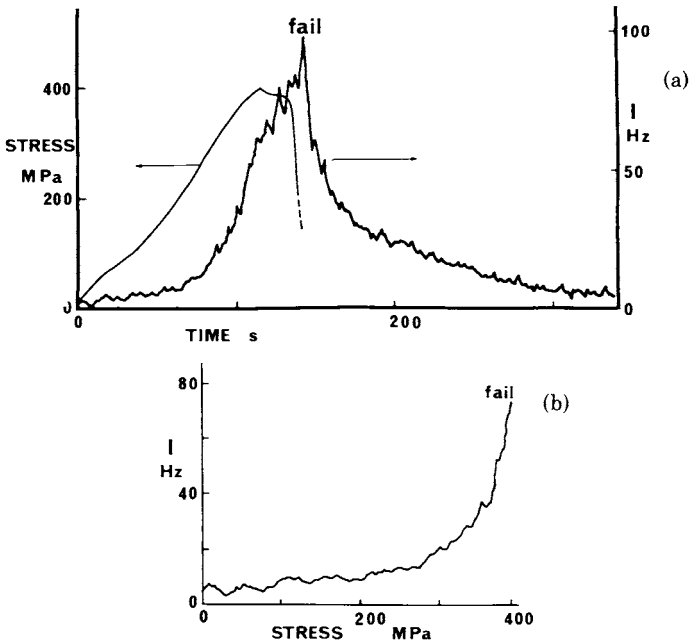
Fig. 2. (a) A typical stress luminescence curve from medium tenacity nylon 66 yarns in air at 40°C generated as in Figure 1(a). The decrease in fiber stress from the peak stress to failure is accompanied by bursts of light due to individual fiber failure. (b) Data from 2(a) up to peak yarn stress plotted as intensity of luminescence, I, as a function of applied stress.

The following experiments were performed to determine the origin of the luminescence and to explain the stress luminescence curve.

Stress-Induced Luminescence under Nitrogen and Oxygen

In order to determine if the observed luminescence resulted from gas discharge, triboluminescent phenomena, or an oxidative chemiluminescent reaction, rapid straining experiments were performed on small samples in the oxyluminescence apparatus under atmospheres of oxygen and high purity nitrogen.
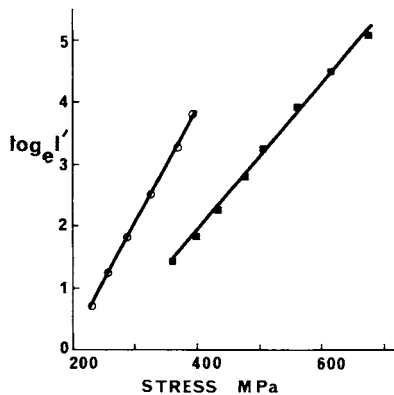
Fig. 3. Exponential analysis of stress luminescence from (O) medium tenacity yarns [Fig. 2(b)] and (■) high tenacity yarns [Fig. 1(b)] in the region of rapid intensity increase above 60% of ultimate strength. I' is the emission intensity after the linear portion of the curve is subtracted.

Figure 4 shows the stress induced luminescence from sample 1 manually strained to failure in oxygen and nitrogen at 80°C. The strain rate was 200%/min. When the sample was purged with nitrogen, no stress-induced luminescence was observed at the limits of sensitivity of the present apparatus.

Spectral Distribution of Stress-Induced Luminescence

The spectral distribution of the emission was determined by measuring the light intensity behind cut-off filters for a series of runs under identical conditions of temperature and strain rate. Because the emission intensity at failure depends on the number of yarns failing simultaneously, which may vary from run to run, the spectral distribution was measured at the onset of exponential intensity increase where reproducibility is excellent. This is shown in Figure 5 for stressing at 60°C and compared with the spectral distribution of the chemiluminescence during thermal oxidation of unstressed nylon 66 fibers at 90°C using the same cut-off filters and a photomultiplier with an identical spectral response.[19]

While the spectral distribution from the thermal chemiluminescence at 90°C appears broader than the stress-induced luminescence at 60°C, the close similarity suggests a common emitting species. The calculated equivalent thermal component of the stress luminescence at 60°C [eq. (4); see later] is shown as the cross-hatched region in Figure 5. The stress appears to enhance the intensity of the thermal chemiluminescence.

Temperature and Strain Rate Dependence of Stress-Induced Luminescence

The stress-induced luminescence from both medium and high tenacity nylon 66 increases with temperature over the range 20–110°C. This is shown in Figure 6 up to 70°C. The effect of this increase in temperature on the stress–strain curve of nylon 66 is to increase the elongation to fail and lower the ultimate tensile strength. An increase in temperature both increases the chemiluminescence
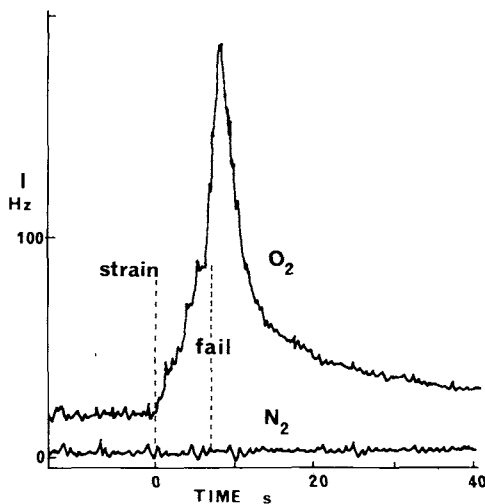

Fig. 4. Intensity of luminescence from high tenacity yarns strained to failure at 200%/min at 80°C in oxygen and nitrogen atmospheres.
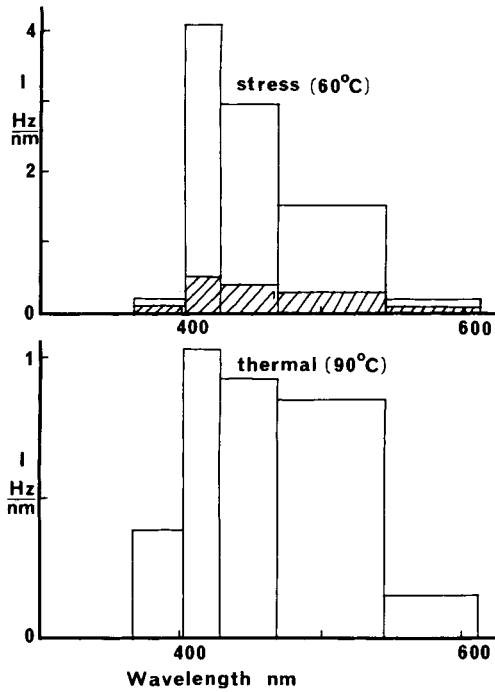
Fig. 5. Spectral distribution of stress luminescence in air at 60°C and thermooxidative chemiluminescence in oxygen at 90°C.

intensity at zero stress and the stress chemiluminescence according to an Arrhenius relation, as shown in Figure 7. The Arrhenius parameters A, the preexponential factor, and E_a, the activation energy, decrease with an increase in fiber stress. This is plotted in Figure 8, and there is an almost linear decrease in A and E_a with fiber stress.
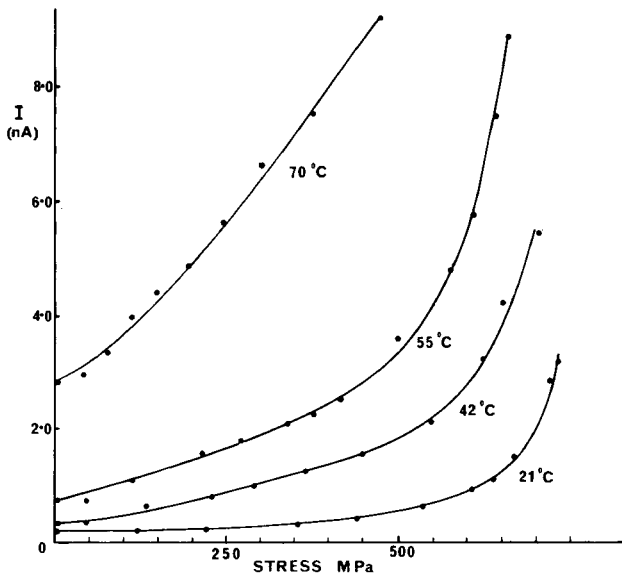

Fig. 6. The effect of temperature on the stress luminescence curves of high tenacity yarns.
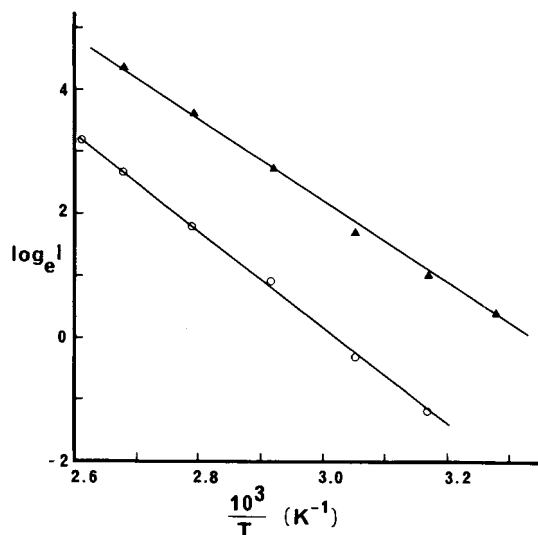
Fig. 7. Arrhenius plots of the dependence of luminescence intensity on stress for applied stresses of zero (O) and 625 MPa (▲).

The effect of strain rate on the luminescence intensity from sample 1 at 80°C is shown in Figure 9 for strain rates 0.63–25%/min. The instantaneous emission intensity increases with strain rate over all regions of the curve. In all cases the exponential increase in intensity occurs at 60% of the ultimate stress. The ultimate stress also increases with strain rate.
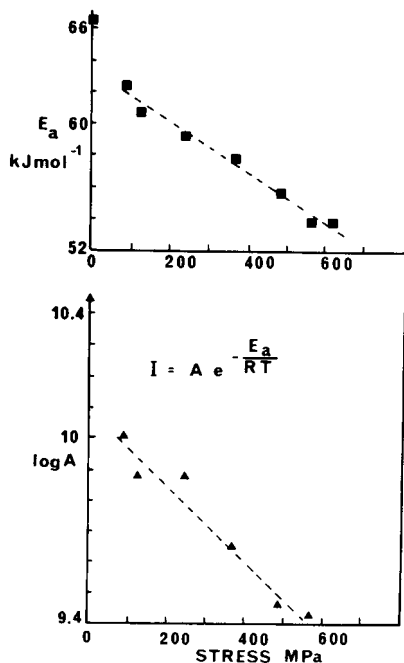

Fig. 8. The effect of applied stress on the Arrhenius parameters A and E_a obtained from the temperature dependence of the stress luminescence of high tenacity yarns.
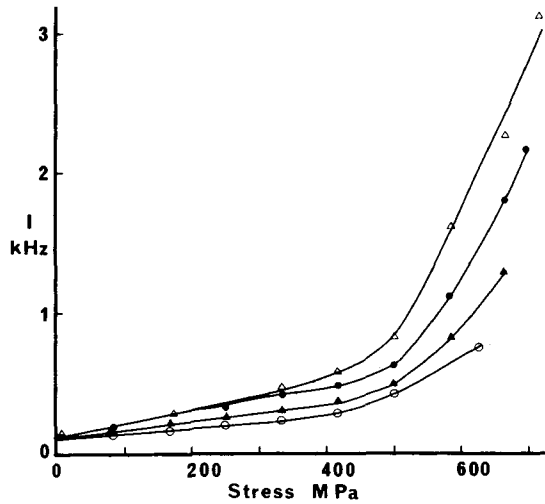
Fig. 9. The dependence of the stress luminescence from high tenacity yarns at 80°C on the strain rate. $\dot{\epsilon}$ (min^{-1}): ($\triangle$) 0.25; ($\bullet$) 0.1; ($\blacktriangle$) 0.025; ($\circ$) 0.0063.

Cyclic Incremental Loading

The effect of repeated straining of high tenacity nylon 66 on the luminescence intensity is shown in Figure 10. In this experiment the sample, at 40°C, was strained at 10%/min to a load of 10 kgf (82 MPa), unloaded at the same rate, and then reloaded to 20 kgf. This process was repeated, giving eight incremental load cycles before failure of the yarns. Sufficient time was allowed between each load cycle for the chemiluminescence to decay. This is not shown in Figure 10.

The following points are noted:

(i) Stress-induced luminescence is weak up to load cycle 5 (60% of the ultimate stress) but independent of load history.
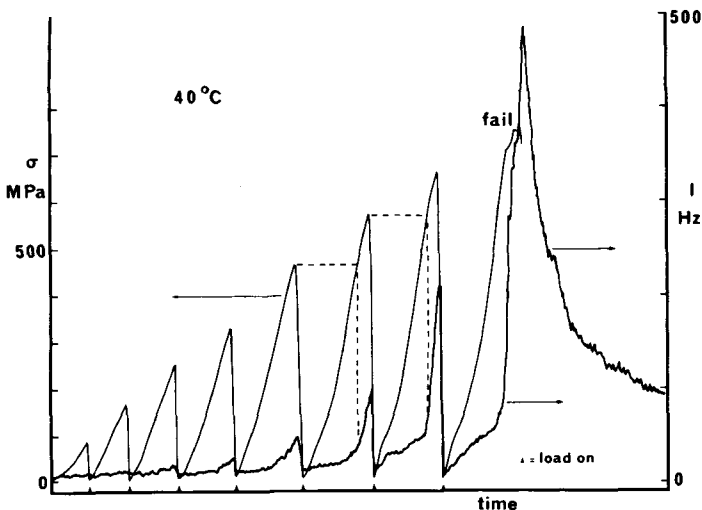

Fig. 10. The change in luminescence intensity from high tenacity yarns during cyclic incremental loading at 60°C. There is a time delay between each load/unload cycle to allow the luminescence to decay. σ is the fiber stress (MPa).

(ii) The stress luminescence at higher loadings (cycles 5–8) is sensitive to the load history of the fiber. The exponential intensity increase at higher loads does not occur until just before the load previously experienced by the sample is exceeded. This is shown by the dotted lines in Figure 10. The ultimate intensity is not affected by the number of load cycles.

(iii) The previous exponential region is replaced by a weak underlying emission that increases linearly with applied stress and is independent of load history.

The medium tenacity nylon 66 (sample 2) showed a similar load history effect, but the underlying linear region of the stress luminescence curve was only a minor component of the total emission intensity.

Decay of Stress Luminescence

When the fibers failed or if elongation was stopped, the emission intensity slowly decayed with a rate depending on several factors, the most important being temperature and the remaining load on the fibers. If the chemiluminescence arises from a bimolecular free radical reaction, the decay would be expected to follow second order kinetics.

Figure 11 shows the analysis of the decay of chemiluminescence after failure of sample 2 at temperatures of 34, 45, 60, 74, 84, and 102°C. At temperatures up to 60°C, simple second-order kinetics are obeyed, and a radical lifetime of 65 s is obtained. At higher temperatures the decay consists of a short-lived
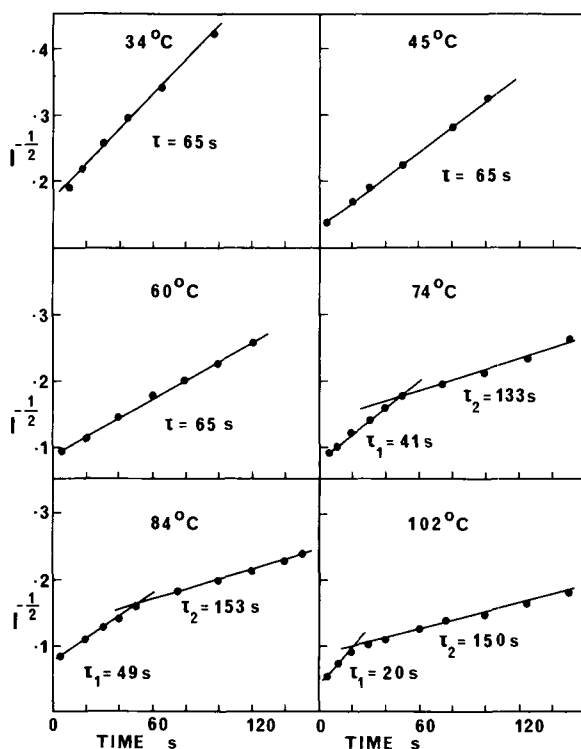

Fig. 11. Second order kinetic analysis of the chemiluminescence decay from medium tenacity yarns after failure. The measured radical lifetimes (τ) at each temperature are marked.

component, with a lifetime that decreases with temperature, and a long-lived component.

The effect of the load on the fiber on the stress luminescence decay was illustrated by:

(i) Holding the material at a constant elongation below failure: In this case the stress will relax. This is shown in Figure 12.

(ii) Holding the material at constant load: This was achieved by a slight increase in the sample elongation with time to hold the load cell output from the Instron constant. This is also shown in Figure 12.

Plots of these decays, assuming second order kinetics, are given in Figure 13 for high tenacity nylon 66 at 60°C and strain rates of 10 and 100%/min. Also shown in this diagram is the analysis of the luminescence decay curve for a ramp load/unload cycle to 330 MPa at 100%/min.

DISCUSSION

Origin of Stress Luminescence

The close similarity of the spectral distribution of the stress-induced luminescence to that of the chemiluminescence from nylon 66 during thermal oxidation at a higher temperature (Fig. 5) suggests that stress luminescence may arise from a similar sequence of free radical reactions in the polymer. The stress luminescence is observed only under oxidative conditions (Fig. 4), and the intensity increases with temperature according to an Arrhenius relation (Fig. 7). From the results of Figure 4 it is considered that, under the experimental conditions employed here (i.e., gases at atmospheric pressure and temperature from 20°C to 110°C) triboluminescence and gas discharge effects due to polymer fracture are not contributing significantly to the stress-induced luminescence.

In the following discussion the stress-induced luminescence is interpreted within the accepted mechanistic and kinetic framework[3] for thermooxidative
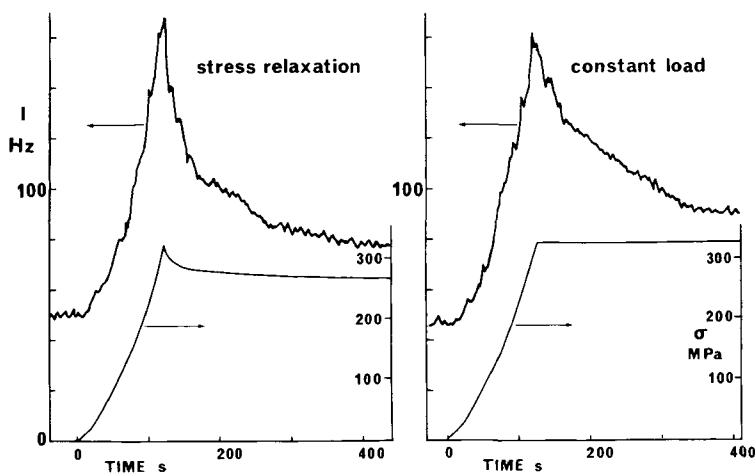

Fig. 12. Decay of luminescence from high tenacity nylon at 60°C after straining at 10%/min to: (a) 20% elongation that is held constant. The stress relaxation during the decay of luminescence is shown. (b) A stress of 330 MPa that is held constant during the decay of luminescence.
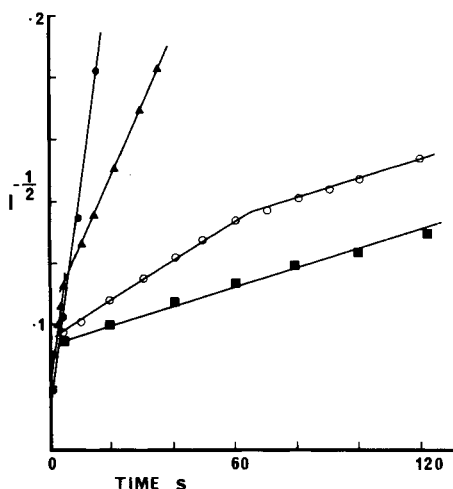
Fig. 13. Second order analysis of chemiluminescence decay from high tenacity yarns at 60°C. (●) Unloaded at 100%/min after being loaded to 330 MPa at 100%/min. (▲) Held at 20% elongation after being loaded to 330 MPa (20% elongation) at 100%/min. (○) Held at 20% elongation after being loaded to 330 MPa (20% elongation) at 10%/min. (■) Held at 330 MPa after being loaded to 330 MPa at 10%/min.

chemiluminescence arising from the exothermic bimolecular termination reaction of secondary alkyl peroxy radicals of nylon 66. The oxidative sequence is summarized in Table II and reaction 5 is the chemiluminescent reaction. Emission occurs from the first excited triplet state of the carbonyl oxidation product. The intensity I of chemiluminescence is given by

$$I = \phi k_5 [RO_2\cdot]^2 \qquad (1)$$

where ϕ is the probability that the termination reaction leads to the emission of a quantum from the excited carbonyl oxidation product. ϕ is typically 10^{-10}.

In the steady state, rates of initiation and termination are equal so that

$$I = \phi r_i \qquad (2)$$

TABLE II
Simplified Scheme for Free Radical Oxidation of Nylon 66

	Reaction	Rate
Initiation	RH $\xrightarrow{\text{heat}}$ R·	(1) r_i
Propagation	R· + O$_2$ $\xrightarrow{\text{light}}$ RO$_2$·	(2) $k_2[R\cdot][O_2]$
	RO$_2$· + RH → R· + ROOH	(3) $k_3[RO_2\cdot][RH]$
Termination	R· + R· → RR	(4) $k_4[R\cdot]^2$

$$RO_2\cdot \ + \ RO_2\cdot \ \longrightarrow \ \left(\begin{matrix} R \\ \diagdown \\ R' \diagup \end{matrix} C{=}O \right)^* \ + \ O_2 \ + \ ROH \qquad (5)\, k_5[RO_2\cdot]^2$$

$$R\cdot \ = \ \text{------}\!\!\!\overset{}{\underset{\parallel}{C}}\!\!\!\text{------NH------CH------CH}_2\text{------}$$
$$O$$

When the nylon 66 fibers are stressed, the emission intensity increases, suggesting from (2) that the rate of initiation of free radical oxidation is increasing with applied stress.

Stress-Induced Free Radical Formation in Nylon 66 Fibers

Evidence for the formation of polymer free radicals during the tensile deformation of nylon 6 and nylon 66 has been obtained by ESR studies in vacuum at temperatures from -67 to $100°C$.[11] The stable free radical formed under these conditions is the alkyl radical, (I) α to the amide group

$$\text{\textasciitilde\textasciitilde}CONH—\dot{C}H—CH_2\text{\textasciitilde\textasciitilde}$$
$$(I)$$
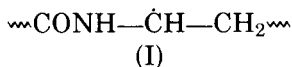
which is the radical observed during thermal or photochemical degradation in vacuum. The primary radical formed during tensile straining of the fibers is believed to be an alkyl radical resulting from main chain scission which then abstracts a hydrogen atom to give the stable radical (I).

The rate of free radical formation, r_b, on application of a stress σ to the polymer chain at a temperature T (°K) is given[12,15] by the Zhurkov equation:

$$r_b = n_c \omega_0 e^{[-(U_0 - \beta\sigma)/RT]} \qquad (3)$$

where n_c is the number of polymer chains available for scission, ω_0 is the fundamental bond vibration frequency, U_0 is the main-chain bond strength, and β is the activation volume for bond scission.

This equation describes radical formation as a thermally activated process in which the applied stress lowers the activation energy for chain scission. It predicts an exponential dependence of the formation rate on the microstress on the polymer chain.

Experimental studies of radical formation in nylon 6 and nylon 66 by ESR have shown[20]:

(i) Free radical formation is not observed by ESR until the fiber strain is ~60% of the ultimate, where it then increases exponentially to failure.

(ii) Cyclic step straining experiments in this region show that further radical formation occurs only after the previous maximum strain on the fiber is exceeded.

These data have been interpreted within a model of preferential scission of taut tie molecules in the amorphous region.[20] Referring to the lamellar model for oriented nylon 66 fibers, the crystalline blocks are connected by a number of tie molecules with a distribution of lengths. When the fiber is strained, those tie molecules which are fully extended will be unable to relieve the applied stress by conformational changes and slippage and will thus rupture, producing two free radicals. This process becomes significant only at strains ~60% of the ultimate elongation. If the load on the fiber is removed and then the sample is strained again, no further tie molecules can be ruptured until the previous strain is exceeded. The concentration of free radicals measured by ESR during these step strain experiments has been used to determine the length distribution of the tie molecules, their fraction of the amorphous region, and their load-bearing properties.

At high strains and during load cycling the behavior of the stress luminescence

curves (Figs. 1, 2, and 10) is very similar to the reported step-strain ESR data discussed above. It is thus likely that at high strain the alkyl peroxy radicals required to observe stress luminescence result from the scission of taut tie molecules of nylon 66. While noting the close similarities in the results from the two experimental techniques, it is important to recognize the fundamental differences between ESR and stress luminescence. Most ESR studies have measured the concentration of stable free radicals formed at low temperatures in vacuum. In contrast, chemiluminescence can be observed only from the termination reaction of alkyl peroxy radicals. Thus oxygen is required to form the peroxy radicals from the original stress-produced main-chain alkyl radicals, and these radicals must then terminate in sufficient number to produce measurable luminescence. The experimental conditions for a high-stress luminescence intensity are thus an oxidizing atmosphere at elevated temperatures which contrasts with the usual conditions for radical detection by ESR.

Chemiluminescence at Low Elongation

The analyses of the stress luminescence in Figures 1(b), 2(b), and 3 showed the curves comprised a weakly emissive component linear in stress and a strongly emissive component that increased exponentially with stress after a critical strain was exceeded. By analogy with ESR studies this latter component has been attributed to macro free radical formation by scission of tie molecules. This exponential component is removed on stress cycling and the underlying weak emission is then apparent (Fig. 10). ESR studies[20] show no evidence for stable free radical formation at either low strains or after stress cycling—the regions in which the weak luminescence is observed. It is therefore concluded that the portion of the stress luminescence curve linear in stress does not arise from free radicals formed by scission of tie molecules. The application of strain to an oriented polymer results in conformational changes in the polymer and internal frictional losses as a result of slip of chain segments. This may produce a local temperature rise in the polymer,[21] which would then lead to an increase in the rate of the thermal oxidation of the fiber. From eqs. (1) and (2), this will produce an increase in the chemiluminescence intensity. The consequences of this process being responsible for the chemiluminescence at low strain can now be considered.

The temperature dependence of the chemiluminescence in air from nylon 66 in the absence of stress is given by the Arrhenius plot (Fig. 7) as

$$I \text{ (nA)} = 2.75 \times 10^{10} e^{-7960/T} \tag{4}$$

The equivalent temperature rise in the polymer that would produce the stress-induced chemiluminescence intensity for a particular stress in the linear region of the curves of Figure 6 can be calculated from eq. (4). These are plotted in Figure 14 as local temperature rise for applied stress. This shows that the local temperature rise does not depend on the temperature at which the sample is tested. If this equivalent local temperature rise results from viscoelastic dissipation, it should be possible to calculate this component from the loss spectrum of the polymer, the measured stress–strain curve and the heat capacity for each test temperature.

The calculated values for test temperatures of 40 and 85°C are given in Table
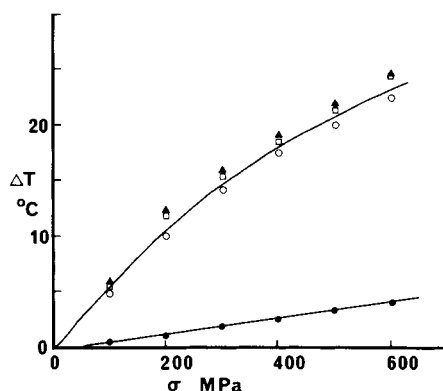
Fig. 14. Temperature rise equivalent to stress induced luminescence. Experiment temperature: (▲) 42°C; (□) 70°C; (O) 85°C. (●) Calculated temperature rise for viscoelastic loss.

III. It is noted that ΔE, the calculated energy dissipated during tensile deformation at 40°C is quite close to the reported value for nylon 6 by microcalorimetric measurements during elongation at room temperature at a strain rate of 14%/min.[21] The latter are shown as the bracketed values in Table III. The expected temperature rises in Table III are based on heating of the entire polymer and not the amorphous fraction of the polymer which will be around 50%. The chemiluminescence requires oxygen to be dissolved in the polymer, so the equivalent temperature rises in Figure 14 are for the amorphous region. The calculated temperature rise for the amorphous region will be approximately $2\Delta T'$. The temperature rise cannot be explained by viscoelastic loss alone, so other processes must be contributing to the underlying chemiluminescence. Interfilament friction—which can be significant in a twisted bundle of 130 filaments, as studied here—could be responsible for the increase in temperature over that calculated from the reported value of tan δ and the measured stress–strain curve. The significance of interfilament friction in the measured loss spectrum of yarns has been considered by Murayama.[22] For example, tan δ for a nylon 66 twisted yarn (helix angle 45°) is twice that of an untwisted yarn. This frictional heating

TABLE III
Equivalent Temperature Rise (ΔT) for High Tenacity Nylon 66 Fibers to Produce Stress Luminescence and Estimated Temperature Rise ($\Delta T'$) Due to Viscoelastic Loss on Straining[a]

Stress (MPa)	$T = 40°C$, tan $\delta = 0.05$, $C_p = 1.484$ J/g/°C			$T = 85°C$, tan $\delta = 0.07$, $C_p = 1.675$ J/g/°C		
	ΔT (°C)	ΔE (J/g)	$\Delta T'$ (°C)	ΔT (°C)	ΔE (J/g)	$\Delta T'$ (°C)
100	5.5	0.3	0.2	5.5	0.51	0.3
200	12.8	1.2(0.8)[b]	0.8	10.0	1.8	1.1
300	16.0	2.4	1.6	14.0	3.1	1.8
400	19.0	3.4(3.0)[b]	2.3	17.4	4.5	2.7
500	22.0	4.8	3.2	20.0	6.0	3.6
600	24.5	6.1(5.8)[b]	4.1	22.4	8.2	4.9

[a] ΔT is calculated from the stress luminescence intensity using eq. (4). $\Delta E \sim 2\pi$ tan δ A, where A is the work to deform the polymer up to the measured stress. $\Delta T' = \Delta E/C_p$; C_p is the heat capacity in J/g/°C. Values for tan δ and C_p are taken from Refs. 22 and 23.

[b] Reported values of energy dissipated during straining of nylon 6 from microcalorimetry (Ref. 21).

process has to account for a temperature rise, depending on strain, of 5°C to 16°C more than is attributable to the viscoelastic loss as calculated in Table III. A change in tan δ by a factor of 2 cannot account for this. Microcalorimetric measurements on twisted yarn bundles would be required to determine if this mechanism for the increased chemiluminescence intensity is operative. It is possible that triboluminescent phenomena such as microcrack opening could be occurring. However stress cycling should eliminate any light-emitting process from crack formation, and it has been shown in Figure 10 that the linear stress luminescence is unaffected by stress cycling.

The linear portion of the stress luminescence curve shows an increase in chemiluminescence intensity with an increase in strain rate (Fig. 9). This is again consistent with both a viscoelastic and frictional process for heat generation, resulting in a temperature rise as a result of a decrease in the fraction of heat dissipated at the higher strain rate. Further experiments are proceeding to study the effect of interfilament friction on the stress luminescence curve and the dynamic mechanical properties of yarns with different extents of twist.

The implications for the load-bearing properties of the nylon 66 fiber of the observation of chemiluminescence at quite low strains can now be considered. The increase in luminescence intensity implies an increased rate of initiation of oxidation of the polymer with strain. This process is repeated with each successive load cycle, and it is clear that there is a mechanism for cumulative damage in the fiber with each cycle. The termination reaction of nylon 66 that leads to chemiluminescence (reaction 5 of Table II) is significant in that the alcohol product formed is thermodynamically unstable.[24] Each termination reaction by the Russell mechanism will thus lead to a main-chain scission as the α-hydroxy amide dissociates to the primary amide and aldehyde:

$$—\wwww—CONH—CH—CH_2—\wwww—\rightarrow—\wwww—CONH_2 + HCO—\wwww—$$
$$\diagdown OH$$
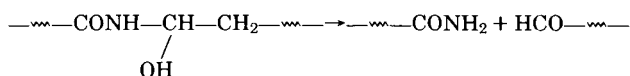
The rate of chain scission is equal to the rate of termination as given by the luminescence intensity. The important result here is that, at stresses lower than those at which main-chain scission of taut tie molecules by the processes described by eq. (3) dominate, it is possible to have scission of polymer chains in the amorphous region because of the increased rate of oxidation of the fiber.

Temperature Dependence of Stress Luminescence

The data presented in Figure 7 show that at a particular stress level the temperature dependence of the chemiluminescence intensity follows an Arrhenius relation. The Arrhenius parameters depend on the polymer stress as shown in Figure 8.

Studies of the dependence of the concentration of oxidation products of polyethylene and polypropylene on applied mechanical stress and temperature showed that the activation energy for the rate of product formation in the temperature range 233–320°K decreased linearly with applied stress above ~200 MPa.[12] The extrapolated activation energy at zero stress was identical to that for thermal degradation of the polymer.

The activation energy for the chemiluminescence during thermal oxidation of nylon 66 in the absence of stress has been related[19] to that for thermolysis of impurities such as polymer hydroperoxides responsible for initiation of the ox-

idation ($E_a \sim 65$ kJ/mol). At high stress levels, the rate of initiation will increase due to main-chain scission as described by eq. (3). At both low and high stress levels the increased emission intensity also results in part from internal and external friction effects in the yarn, producing local heating and thus an increased rate of initiation. The apparently linear dependence of A and E_a on applied stress thus represents the sum of several processes, and the physical interpretation of the stress dependence in terms of the simple reaction rate model [eq. (3)] is not possible.

Decay of Chemiluminescence

The decay of the chemiluminescence intensity observed when loading of the fiber is stopped or the fiber fails will follow the consumption of peroxy radicals in the polymer. The kinetic equation describing this decay will be given by the solution to the equation for peroxy radical concentration at any time for the boundary condition that the rate of formation of radicals is zero at zero time. For an unstabilized polymer, using the scheme of Table II,

$$d[RO_2\cdot]/dt = r_i - k_5[RO_2\cdot]^2$$

When free radical formation ceases, the chemiluminescence decays according to the relation

$$(I_0/I)^{1/2} = (k_5 r_i)^{1/2} t \tag{5}$$

A plot of $I^{-1/2}$ as a function of time should be linear and the radical lifetime τ is given by the ratio of the intercept to the slope

$$\tau = 1/k_5[RO_2\cdot]_0 = 1/(k_5 r_i)^{1/2}$$

Decay after Fiber Failure

Figure 11 shows the decay of chemiluminescence after failure of the medium tenacity nylon 66 (sample 2) analyzed in this way. Second-order kinetics are obeyed at temperatures from 34°C to 60°C, giving a radical lifetime of 65 s.

The lifetime of the alkyl radical in strained polyamides has been reported[20] as 714 s at 75°C. The termination rate constant of the alkyl peroxy radical (k_5) at 100°C has been reported[19] to be eight times that of the alkyl radical (k_4) in nylon 66. The corresponding lifetime of the peroxy radical would thus be 89 s, which is on the order of the value obtained here. The lifetime may be used to determine the peroxy radical concentration in the polymer at failure provided the termination rate constant is known. From reported[25] values for k_4 in irradiated nylon 66 of 10^2 L·mol^{-1}·min^{-1} at this temperature, the relationship $k_5 \sim 8k_4$, and the lifetime of 65 s, the peroxy radical concentration in these samples of medium tenacity nylon 66 at failure is estimated as 7×10^{17} radicals/cm^3. This value must be regarded as an estimate to about 1 order of magnitude, but it is comparable to the reported value[14] of stable alkyl radicals (8×10^{16} cm^{-3}) and polymer chain scissions (9×10^{17} cm^{-3}) for tensile deformation of nylon 66 under ambient conditions.

The material studied here is known to contain a stabilizer, and it would be expected that if the antioxidant could compete with the bimolecular self-termination reaction for consumption of the peroxy radicals, simple second-order

kinetics would not be observed. Deviations from second-order decay are observed at higher temperatures, and the curves can be analyzed, as shown, as the sum of a fast component at short times and a slow component at longer times. The lifetime of the fast component decreases with increasing temperature above 60°C while that for the long component increases. This can be rationalized by considering the fate of peroxy radicals formed in a single initiation event. These radicals will be trapped in the initiation cage and terminate by recombination unless they can diffuse out of the cage within the lifetime of the radical. Even if escape from the primary cage occurs, the radicals from the same initiation event may undergo diffusion or propagation steps and still terminate—the so-called secondary cage effect.[26] The lack of a temperature effect on the stress-induced nylon 66 peroxy radical termination rate at temperatures up to 60°C suggests cage termination is predominant. Deviations from a simple second-order decay at higher temperatures suggests a number of termination processes are occurring, including scavenging of peroxy radicals by the antioxidant.

It is interesting to note that the radical lifetime apparently increases with temperature. It would be expected that, as both $[RO_2 \cdot]_0$ and k_5 would increase with temperature, the radical lifetime would shorten. It is possible that as the peroxy radicals escape the cage, the time between the statistical termination events will increase, resulting in a longer radical lifetime. It has been shown that the increase in the free volume of the polymer with temperature will result in an increased cage escape efficiency.[27] It should also be recognized that the measured decay parameters could be the sum of several different processes from morphologically different regions of the polymer.

Decay while the Fibers Are Loaded

If high tenacity yarns are held at either a constant stress or a constant strain in the linear region of the stress–luminescence curve, the emission decays as shown in Figure 12. The chemiluminescence in this low stress region has been attributed to local heating of the fibers during loading. Thus, when sample elongation ceases, free radical formation should also cease and the intensity should decay according to eq. (5). It is possible that the decay of the emission results in part from the cooling of the fiber; i.e., the lifetime of the alkyl peroxy radicals is short compared to the time taken for the stressed fiber to return to ambient temperature. In this case the decay would be expected to follow first-order kinetics (Newton's law of cooling) and the estimated lifetime of the decay for a 20-μm nylon 66 fiber heated 16°C above ambient is 1 s. Considering the time scale of the decay shown in Figure 12, this is not expected to have a significant effect on the kinetics.

The decay rate depends on the rate at which the sample is strained and on the residual load. In Figure 13, the sample rapidly loaded and unloaded at 100%/min shows simple second-order kinetics, giving a radical lifetime of 10 s. The sample loaded at the same rate to 20% elongation and held at this strain shows the same initial luminescence intensity and decay rate for the first 5 s, followed by a much slower decay with a lifetime of 46 s. The effect of the retained fiber strain is thus to decrease the termination rate of the alkyl peroxy radicals. A similar effect has been reported for the alkyl radical termination rate in polyamides held at a load just below failure. This rate is decreased by a factor of 4 compared to an

unloaded fiber.[20] If the fast component corresponds to cage termination, then the residual fiber strain must be increasing the probability of cage escape, resulting in the appearance of the longer-lived components. This would be consistent with an increase in the free volume of the strained polymer.

The samples loaded at 10%/min show a lower initial chemiluminescence intensity and a longer radical lifetime, consistent with a lower alkyl peroxy radical concentration. The sample held at constant load shows the slowest decay (τ = 370 s), while the sample held at a constant elongation shows a shorter lived component (τ = 144 s) over the first 60 s. This corresponds to the region of rapid stress relaxation.

CONCLUSIONS

The luminescence observed when oriented fibers of nylon 66 are strained in air at temperatures from 20°C to 100°C arises from the chemiluminescent termination reaction of stress-generated alkyl peroxy macroradicals. The luminescence increases linearly with stress at low strains and exponentially with stress at higher strains. The linear component has been interpreted as due to a local temperature rise from internal and external frictional effects in the fiber bundle. The exponential component results from progressive scission of taut tie molecules in the amorphous region of the polymer, although individual fiber fracture contributes to the luminescence intensity at high strains. The increased rate of oxidation during straining, as evidenced by the increased chemiluminescence intensity, suggests that damage to the fiber can occur at low strains. The sensitivity of the stress luminescence growth curve to the load history of the fiber is of potential use in studying load bearing woven structures. The decay of stress luminescence is sensitive to the strain rate, temperature, and residual fiber stress. This could provide a sensitive probe of the radical reactions in the loaded fiber and the reactions of antioxidants and other stabilizers.

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