

# Structural Differences Exhibited by Networks Prepared by Chemical and Photochemical Reactions IV Chemical Relaxation

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## Synopsis

Chemical stress relaxation has been used for the characterization of elastomeric networks obtained either by peroxide curing or by photocrosslinking. It has been shown that the differences observed between photocrosslinked and peroxide-cured elastomers are not limited to their structure and physical properties but are also due to the very nature of the created bonds.

## INTRODUCTION

In previous papers<sup>1-5</sup> we reported experiments related to photocrosslinking processes occurring in elastomeric films (EPDM) containing photosensitive initiators (benzoin derivatives, and benzene, for example) and the characterization of the resulting networks. By comparing the photocrosslinked materials with peroxide-cured EPDM we were able to establish structure-property relationships and to show that the structure of the networks is strongly dependent on the crosslinking process used. We were particularly able to devise a new technique for the characterization of elastomeric materials: inverse GPC. This method, providing a direct access to the size of the network strands, entitled us to show that photocrosslinking yields more homogeneous materials than does peroxide curing. This effect is, moreover, strongly enhanced when the chromophore is grafted on the polymer backbone.

In order to provide an interpretation for the difference (properties and structure) exhibited by the networks depending on their crosslinking process, we attempted after each treatment the characterization of the created bonds. Due to the different reaction mechanisms involved in each photocrosslinking process, the nature of the created bonds should indeed be different. We anticipated that chemical relaxation at high temperature would provide the expected information.

## EXPERIMENTAL

### Materials and General Procedures

The polymer selected for study was a terpolymer EPDM Nordel 1440, obtained from E. I. du Pont de Nemours, poly(ethylene-co-propylene-co-1,4 hexadiene).

The equipment used to perform the ultraviolet (UV) irradiations (254 nm), as well as the processes selected to characterize the crosslinked materials (including infrared spectroscopy and swelling in cyclohexane) were described previously.<sup>1-4</sup>

All chemicals used were reagent grade and were purified by standard procedures. The curing of the elastomer with variable amounts of dicumyl peroxide resulted from heating it at 160°C under  $25 \times 10^6$  Pa for 2 h. The chemical bonding of the chromophore (benzene) on the EPDM backbone was performed by means of Friedel-Crafts reactions and was described previously.<sup>2-4</sup>

Prior to any measurement, all networks were submitted to a prolonged extraction with hexane in order to eliminate uncrosslinked rubber.

These studies were performed on two series of samples, those resulting from peroxide curing (1–10% by weight), and those resulting from photocrosslinking of the phenylated Nordel (irradiation time, 5–60 min).

Comparisons were performed on samples exhibiting the same average crosslinking degree determined by swelling in cyclohexane (Table I).

### Chemical Relaxation Measurements

The samples, placed in a thermostated enclosure, were strained to a 30% elongation. Two temperature ranges were selected, 100–120 and 160–180°C.

At constant temperature ( $\pm 2^\circ\text{C}$ ), stress evolution was studied and the curves  $\log [f(t)/f(0)]$  versus time were plotted. They were analyzed according to the X method devised by Tobolsky and Murakami.<sup>6</sup> Such analysis provided an estimation of the characteristic parameters of the different reactions taking place.

The deformation and the size of the samples were carefully selected in order to avoid a diffusion-controlled rate of the chemical relaxation.<sup>7</sup> For this purpose we used thin test pieces (thickness of  $200 \pm 10$   $\mu\text{m}$ ).

## RESULTS AND DISCUSSION

The relaxation of a strained elastomer is measured by following the evolution of stress versus time (usually in the time range 1 to  $10^6$  s).<sup>8</sup> It is, moreover, strongly dependent on the temperature. Thus, considering these

TABLE I  
Characterization of Samples from Series A and B

A			B		
Perox (%)	$M_{cv2m} \times 10^{-3}$ (g mol <sup>-1</sup> )	$N(0) \times 10^5$ (chains ml <sup>-1</sup> )	Irrad (mn)	$M_{cv2m} \times 10^{-3}$ (g mol <sup>-1</sup> )	$N(0) \times 10^6$ (chains mL <sup>-1</sup> )
1	37.0	2.1	5	35.0	2.3
3	12.6	6.4	15	13.0	6.1
5	7.0	10.1	20	7.0	11.4
7	6.3	12.7	25	5.9	13.6
8	5.0	16.0	30	4.8	16.7
10	4.0	20.0	60	4.2	19.1

two parameters, three domains of relaxation could be defined<sup>9,10</sup> as short times, low temperatures: the relaxation of van der Waals forces is predominant; long times, high temperatures: the relaxation is due to chemical cleavages occurring in the network structure; and intermediate times and temperatures (practical domains of use for rubber goods): stress relaxation phenomena are of small importance, and the network is in a state of equilibrium.

In elastomers strained at constant elongation, the evolution of stress relaxation versus time has been shown by Tobolsky to be a useful tool for investigating chemical degradation.<sup>8,11</sup> It has been shown that in the domain selected for the study of chemical stress relaxation, the kinetic theory of elasticity is valid as long as (whatever the time or the temperature) relaxation is proportional to the number of elastic chains.<sup>12-16</sup> Thus

$$f = NkT(\lambda - \lambda^{-2}) \quad (1)$$

where  $f$  = stress  
 $N$  = number of elastic chains  
 $T$  = temperature  
 $\lambda$  = elongation  
 $k$  = Boltzmann constant

As a consequence, one has

$$\frac{f(t)}{f(0)} = \frac{N(t)}{N(0)} \quad (2)$$

where  $f(0)$ ,  $N(0)$  and  $f(t)$ ,  $N(t)$  correspond to the stress and number of elastic chains at times 0 and  $t$ , respectively. It must be emphasized that chemical stress relaxation can be due either to a single degradation process (scission along main chains or at the crosslink points) or to a multidegradation process of the crosslinked polymer (cleavages at crosslinks and along the main chains).

The study of the kinetics of these different processes led to the following equations and interpretations.

#### *Cleavage at the Crosslinks*

For an ideal network, it was shown that

$$\frac{f(t)}{f(0)} = 1 - 2 \frac{q(t)}{N(0)} \quad (3)$$

where  $q(t)$ , the number of scissions after time  $t$ , is given by

$$q(t) = (1 - e^{-Kt}) \frac{N(0)}{2} \quad (4)$$

thus,  $f(t)/f(0) = e^{-Kt}$  with  $K = A e^{-E/RT}$ . With  $E$  the energy of degradation, the stress relaxation curve is expressed by a typical maxwellian decay. Moreover,  $f(t)/f(0)$  is independent of the crosslinking degree.

*Scission along Main Chains*

For a network of uniform chain length

$$\frac{f(t)}{f(0)} = \frac{N(t)}{N(0)} = e^{-[q(0)/N(0)]t} = e^{-K't} \quad (5)$$

$q(0)$  is the number of scissions per unit of time. The functional dependence of  $K'$  on temperature can be expressed by an Arrhenius equation

$$K' = A e^{-E_a/RT}$$

where  $E_a$  is the apparent energy of activation of the degradation process. It thus appears that  $f(t)/f(0)$  depends on the crosslinking degree of the network.

*Multidegradation Process (Simultaneous Cleavage at Crosslinks and along the Main Chains)*

This case was particularly studied by Horikx,<sup>17</sup> who showed that, when  $n$  reactions occur simultaneously, chemical stress relaxation can be expressed by

$$\frac{f(t)}{f(0)} = \sum_{i=1}^n A_i \exp(-K_i t) \quad (6)$$

Using the  $X$  method (successive iteration) devised by Tobolsky and Murakami,<sup>6</sup> it is then possible to evaluate the rate constant  $K_i$  and the contribution  $A_i$  of the chemical reactions to total degradation.

Several observations can be formulated about chemical stress relaxation. At high temperature, simultaneously with the degradation mechanism, the broken chains can recombine. Such a process is associated with the formation of new unstrained strands that do, however, contribute to the network. This recombination process can be estimated by study of "intermittent relaxation."<sup>8,18</sup> As long as  $\lambda \leq 4$ ,  $f(t)/f(0)$  is independent of elongation; for  $\lambda > 4$ ,  $f(t)/f(0)$  begins to increase with elongation.<sup>19</sup> Chain cleavage can result either from thermal aging or from an oxidation process (in presence of air). In the latter case, the degradation rate is dependent on the relative oxygen pressure when it is lower than  $10^{-4}$  atm.

The electron-repelling groups make the chains more sensitive to oxidation; the reverse is observed with electron-withdrawing groups.<sup>20,21</sup> Previous studies performed in the field of chemical stress relaxation of EPDM showed that these elastomers are thermally more stable than polyisoprene.<sup>22</sup> Indeed, at 109°C in the presence of air, they exhibit no oxidation,<sup>23</sup> their degradation beginning at temperatures higher than 160°C.<sup>24</sup>

As a consequence, we performed our study within two temperature ranges: 100–120°C (moderate temperature) and 160–180°C (high temperature).

## Chemical Stress Relaxation of Peroxide-Cured Nordel

100–120°C

Whatever the crosslinking degree, in this temperature range the relaxation of a test piece strained at 300% elongation is first associated with a fast decrease of  $f(t)/f(0)$ . It then tends toward a plateau whose value depends on the crosslinking degree of the network (Fig. 1). It should be stressed that none of the test pieces exhibit any permanent set and no difference could be detected in the behavior of a given sample depending on the temperature. Moreover, the same relaxation curves are obtained at 120°C and at room temperature.

According to Murakami and Tamura,<sup>23</sup> such behavior is associated with purely physical relaxation processes (such as chain rearrangement), which for a given crosslinking degree can be expressed by a constant  $C_p$ , which is independent of time:

$$\frac{f(t)}{f(0)} = C_p \quad (7)$$

160–180°C

In this temperature range the physical relaxation previously observed is followed by a linear decrease of the stress whose rate depends on the crosslinking degree of the sample (Fig. 2).

According to Murakami and Tobolsky,<sup>6</sup> the purely chemical stress relaxation process  $(f(t)/f(0))_c$  is accessible by correcting the experimentally measured values from the physical relaxation  $C_p$ . Figure 3 provides the corresponding curves. It appears that  $\log (f(t)/f(0))_c$  is directly proportional

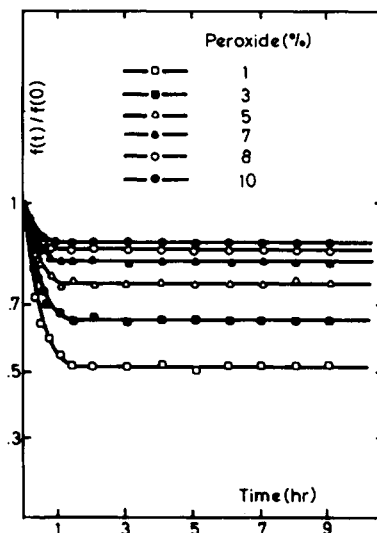


Fig. 1. Peroxide-cured samples, relaxation at 120°C.

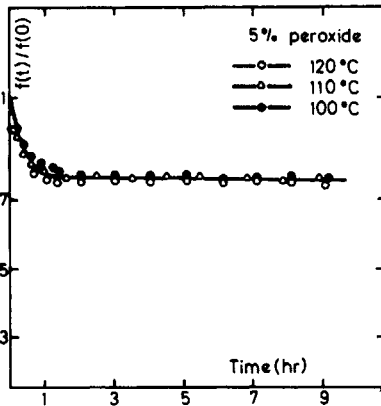


Fig. 2. Peroxide-cured samples, relaxation at 160°C.

to the relaxation time. Thus

$$\left(\frac{f(t)}{f(0)}\right)c = e^{-Kt} \quad (8)$$

or more generally

$$\left(\frac{f(t)}{f(0)}\right)c = e^{-Kt} + C_p \quad (9)$$

where  $K$  is the rate constant of the reactions associated with the chemical stress relaxation.

Table II provides the values of  $C_p$  and  $K$  depending on the quantity of peroxide used in the crosslinking process, that is, versus crosslinking degree. It appears on the one hand that  $C_p$  decreases when crosslinking degree increases; such behavior can be associated with a restriction of the degree

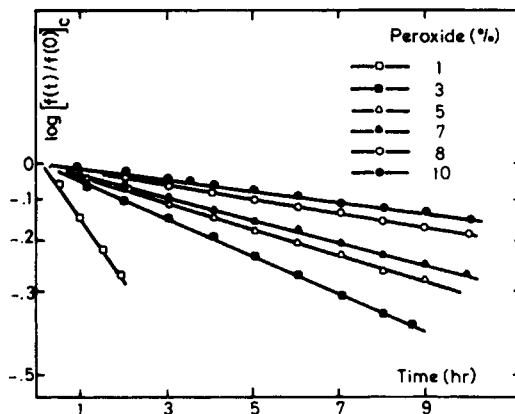


Fig. 3. Peroxide-cured samples, chemical relaxation at 120°C.

TABLE II  
Peroxide-Cured Samples, Relaxation Rate Constants at 160°C

Peroxide (%)	$C_P$	$K$ ( $h^{-1}$ )
1	0.47	0.32
3	0.34	0.10
5	0.23	0.065
7	0.17	0.06
8	0.13	0.038
10	0.11	0.03

of freedom and as a consequence of the rearrangement possibilities of the macromolecular chains upon formation of the network. On the other hand,  $K$  appears to be dependent on the crosslinking degree, which suggests, according to the theories of chemical stress relaxation, that scissions are occurring on the main chain and are associated with the cleavage of C—C bonds.

By study of the relaxation processes at different temperatures,  $K$  was shown to exhibit an Arrhenius-type behavior, that is

$$K = \alpha e^{-E_a/RT} \quad (10)$$

where  $E_a$  is the activation energy of the degradation reactions arising during the chemical relaxation process. This activation energy was shown to be independent of the crosslinking degree:

$$E_a = 32 \pm 3 \text{ kcal mol}^{-1} \quad (134 \text{ kJ mol}^{-1})$$

This value, in good agreement with similar studies performed on EPDM,<sup>25</sup> is small, however, compared with the activation energy of thermal degradation of a polymer (e.g., polyisoprene = 250 kJ mol<sup>-1</sup>).<sup>26</sup> One could account for such a difference by the energy provided when straining the sample to the desired elongation.<sup>27</sup> This fraction of so-called deformation energy is evidently not included in the calculation of  $E_a$ .

It appears from these experiments that peroxide-cured Nordel is thermally stable up to 120°C but degrades above 160°C. The corresponding cleavages mainly occur between the network points on the main polymer chains, that is, on C—C bonds. Only one degradation mechanism is observed. Such results suggest that all bonds, including those created during the crosslinking process, are of identical stability, that is, of the same nature.

### Chemical Stress Relaxation of Photocrosslinked Phenylated Nordel

#### 100–120°C

The curves obtained by plotting  $f(t)/f(0)$  vs relaxation time exhibit 3 distinctive features. At short relaxation times, a fast physical relaxation process, similar to that observed with peroxide-cured samples; at inter-

mediate relaxation times, a continuous stress decrement; and at long relaxation times a plateau is attained whose value depends on crosslinking degree.

We took care to check that at room temperature the relaxation of photocrosslinked samples is identical to that observed for peroxide-cured materials of same crosslinking degree at temperatures up to 120°C. Thus for a given crosslinking degree, physical relaxation processes are identical for both series of compounds. After subtracting the values associated with physical relaxation  $C_p$ , one can get the evolution of chemical relaxation as  $\log (f(t)/f(0))_c$  versus time (Fig. 4). The applications of the X method to the plots thus obtained yields 2 distinct curves. One at short relaxation times is associated with the cleavage of relatively weak chemical bonds. The other, in relation to the constant stress observed for a long enough time of relaxation, is associated with chemical bonds of higher stability. Over the whole temperature range they indeed are not submitted to any modification.

The global evolution of  $f(t)/f(0)$  versus time can thus be represented by

$$\frac{f(t)}{f(0)} = A e^{-Kt} + C_c + C_p \quad (11)$$

where  $C_p$ ,  $C_c$ , and  $K$  correspond to the physical relaxation constant, the chemical relaxation constant associated with high-energy bonds, and the chemical relaxation rate constant corresponding to weak energy bonds, respectively.  $A$  being a coefficient that takes care of the contribution of the latter to the total degradation process.

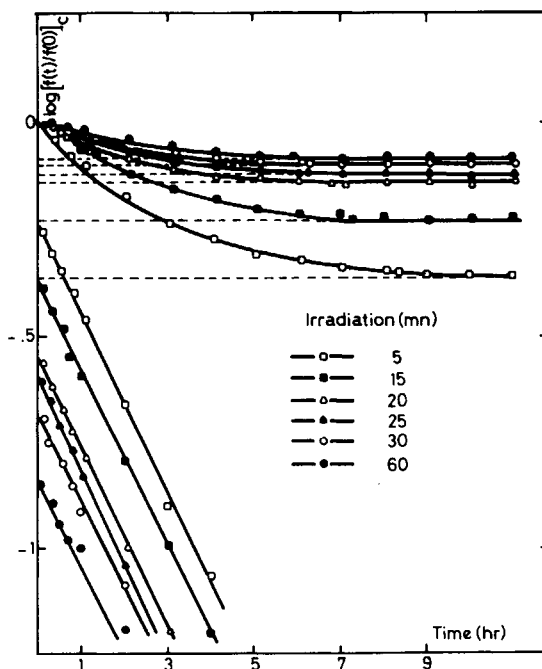


Fig. 4. Photocrosslinked samples, chemical relaxation at 120°C.



At  $t = 0$ , equation (11) yields

$$A + C_p + C_c = 1 \quad (12)$$

Since we are only interested in chemical relaxation, one can write

$$A' + C'_c = 1$$

with

$$A' = \frac{A}{A + C_c} \quad \text{and} \quad C'_c = \frac{C_c}{A + C_c}$$

The evolution of purely chemical relaxation versus time is thus given by

$$\left(\frac{f(t)}{f(0)}\right)_c = A' e^{-Kt} + C'_c$$

The values of  $A'$ ,  $K$ , and  $C'_c$  obtained at 120°C with samples of different crosslinking degree are reported in Table III. It is remarkable that  $K$  could be considered as independent of the crosslinking degree of the sample. Such a behavior is thus characteristic of a cleavage arising at the crosslink points. Simultaneously at this temperature, the contribution  $C'_c$  of the strongest bonds (i.e., their amount) increases with crosslinking degree, in the meantime that of the weakest bonds ( $A'$ ) is decreasing.

In the selected range of temperature, from the evolution of  $K$  versus  $T$ , the activation energy of chemical relaxation can be obtained. Thus

$$K = \alpha e^{-E/RT} \quad (14)$$

with a calculated value of  $E$  equal to 17 kcal mol<sup>-1</sup> (71 kJ mol<sup>-1</sup>).

#### 160–180°C

As previously, the evolution of  $f(t)/f(0)$  versus time was shown to include both physical and chemical relaxation processes.

Analyzing the curves according to the methods previously developed (subtraction of physical relaxation, the  $X$  method treatment), the purely chem-

TABLE III  
Photocrosslinked Samples, Relaxation Rate Constants at 120°C

Irradiation (mn)	$A'$	$K$ (h <sup>-1</sup> )	$C'_c$
5	0.56	0.48	0.44
15	0.41	0.47	0.59
20	0.27	0.49	0.73
25	0.25	0.50	0.75
30	0.20	0.48	0.80
60	0.18	0.47	0.82

ical relaxation can be obtained. The evolution of  $\log (f(t)/f(0))_c$  versus time is provided in Figure 5.

The occurrence of two mechanisms has to be considered. If the first one is observed for short relaxation times, the second is inversely associated with longer times. The evolution of  $f(t)/f(0)$  versus  $t$  can thus be expressed by the general equation

$$\frac{f(t)}{f(0)} = A_1 e^{-K_1 t} + A_2 e^{-K_2 t} + C_p \quad (15)$$

where  $A_1$  and  $A_2$  are coefficients providing the contribution of each mechanisms to the total degradation and  $K_1$  and  $K_2$  are the corresponding rate constants.

At  $t = 0$ , equation (15) yields

$$A_1 + A_2 + C_p = 1 \quad (16)$$

that is, when considering pure chemical relaxation

$$A'_1 + A'_2 = 1 \quad (17)$$

with

$$A'_1 = \frac{A_1}{A_1 + A_2} \quad \text{and} \quad A'_2 = \frac{A_2}{A_1 + A_2}$$

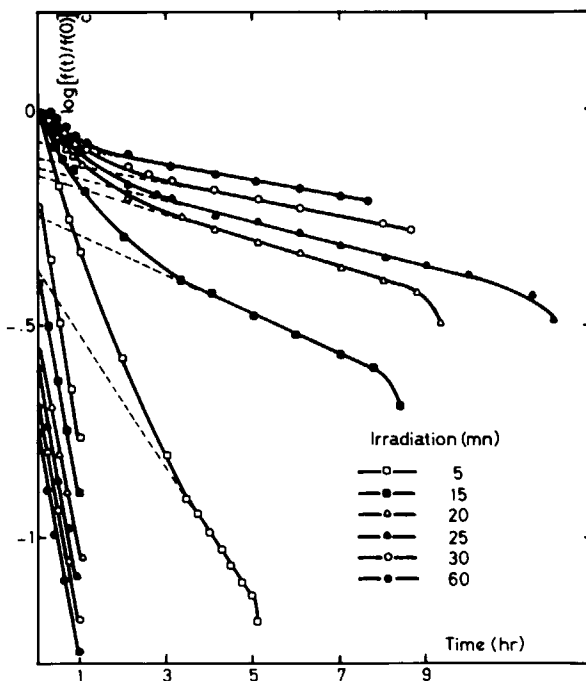


Fig. 5. Photocrosslinked samples, chemical relaxation at 160°C.

Thus

$$\left(\frac{f(t)}{f(0)}\right)_c = A'_1 e^{-K_1 t} + A'_2 e^{-K_2 t} \quad (18)$$

Depending on the crosslinking degree of the samples, the values of the different parameters are reported in Table IV. The  $K_2$  dependence on the crosslinking degree suggests that, for long times of relaxation, the cleavage reactions are performed on the main elastomeric chains. On the contrary,  $K_1$  being constant on the whole range of crosslinking degrees suggests that the first cleavages occur at the crosslink points. The evolution of  $K_1$  and  $K_2$  vs  $T$  in the selected range of temperatures provides the corresponding activation energies, which are

$$E_1 = 18 \pm 4 \text{ kcal mol}^{-1} \quad (75 \text{ kJ mol}^{-1})$$

and

$$E_2 = 34 \pm 5 \text{ kcal mol}^{-1} \quad (142 \text{ kJ mol}^{-1})$$

$E_1$  and  $E_2$  are close to the values found for the relaxations of the phenylated Nordel at 120°C and of the peroxide-cured Nordel at 160°C, respectively.

These results suggest that the first cleavages, happening at the level of crosslink points, are associated with the breaking of relatively weak bonds; the second, corresponding to the cleavage of polymer chain, are associated with strong bonds.

From  $A'_1$  and  $A'_2$  one can get the relative proportion of these different bonds (weak or strong). Indeed, if  $N(0)$  is the number of chains per unit volume

$$N(0) = \frac{\rho}{M_c}$$

where  $\rho$  = polymer specific gravity,  $M_c$  = average molecular weight of a

TABLE IV  
Photocrosslinked Samples, Chemical Relaxation Rate Constants for the Two Cleavage Mechanisms at 160°C

Irradiation (mn)	$A'_1$	$K_1$ (h <sup>-1</sup> )	$A'_2$	$K_2$ (h <sup>-1</sup> )
5	0.58	1.20	0.42	0.35
15	0.42	1.16	0.58	0.11
20	0.29	1.19	0.71	0.07
25	0.26	1.17	0.74	0.067
30	0.21	1.15	0.79	0.047
60	0.18	1.20	0.82	0.04

network strand, one has

$$N(0) = N(A_1') + N(A_2')$$

with  $N(A_1') = A_1' N(0)$  and  $N(A_2') = A_2' N(0)$ . The corresponding values are reported in Table V. It appears that the weak bonds play a more important role at the very beginning of the crosslinking process and quickly reach a nearly constant value. In the meantime the number of strong bonds continuously increases.

It must be emphasized that, for all samples, intermittent and continuous relaxation curves are superposed. Such behavior is characteristic of the absence of any recombination of the broken chains after cleavage.

### CONCLUSION

Chemical stress relaxation was used for the characterization of elastomeric networks obtained either by peroxide curing (A) or by photocrosslinking (B). The comparison of materials with the same average crosslinking degree led to the following conclusions:

A and B exhibit identical physical relaxation processes; and in the 100–120°C temperature range A exhibits only physical relaxation processes; B, on the contrary, shows the occurrence of a chemical relaxation. The latter is the result of bond cleavages arising at the level of crosslink points. A part of the bonds generated during the photocrosslinking process is thus of a different nature (weak bonds) than the C—C bonds constituting the EPDM backbone. The activation energy of this degradation reaction was shown to be equal to about 17 kcal mol<sup>-1</sup>.

In the 160–180°C temperature range, both A and B exhibit chemical relaxation processes due to the breaking of the polymer backbone between network points (i.e., C—C bonds). The activation energy associated with such a reaction is equal to about 32 kcal mol<sup>-1</sup>. Moreover, in the case of a photocrosslinked network, a second mechanism attributed to a bond cleavage at the level of crosslink points has to be considered (activation energy, 18 kcal mol<sup>-1</sup>). Thus some of the bonds formed during the photocrosslinking process are much weaker than C—C bonds.

These weak bonds are for the most part formed at the very beginning of the crosslinking reaction. Their relative proportion continuously decreases with irradiation time. They could be associated with the formation of hy-

TABLE V  
Number of Chains Bonded by "Weak" and "Strong" Bonds Versus Crosslinking Degree

Irrad (mm)	$M_{cv2m} \times 10^{-3}$ (g mol <sup>-1</sup> )	$N(0) \times 10^5$ (chains cm <sup>-3</sup> )	$N_{A_1} \times 10^5$ (chains cm <sup>-3</sup> )	$N_{A_2} \times 10^5$ (chains cm <sup>-3</sup> )
5	35.0	2.3	1.3	1.0
15	13.0	6.1	2.5	3.6
20	7.0	11.4	3.1	8.3
25	5.9	13.6	3.4	10.2
30	4.8	16.7	3.3	13.4
60	4.2	19.1	3.4	15.7

droperoxide groups previously observed during the photocrosslinking of phenylated Nordel.<sup>28</sup>

The differences observed between photocrosslinked and peroxide-cured elastomers are thus not limited, as shown previously,<sup>3-5</sup> to their structure and physical properties but also to the very nature of the bonds created.

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