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BEHAVIOUR OF CHLOROSULFONATED POLYETHYLENE UNDER GAMMA IRRADIATION

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Abstract: The behaviour of chlorosulfonated polyethylene on gamma irradiation was investigated over the range of total absorbed dose of 5 to 550 kGy. The structural modifications were followed by infrared spectroscopy and some main kinetic characteristics of the process were assessed. Determinations of gel content and evaluation of changes in sulphur and chlorine content were correlated with the evolved amounts of hydrochloric acid and with changes in unsaturation of polymers.

INTRODUCTION

The initial properties of polyethylene are changed by chlorosulfonation and subsequently result in an elastomer with intrinsic stability against atmospheric factors, chemical agents on a rather large scale of temperature. Due to its performances, chlorosulfonated polyethylene (CSM) is the elastomer of choice for a range of applications including seals, gaskets, and cable sheetings in nuclear power plants.

The literature data concerning the behaviour of CSM on irradiation are limited (Refs. 1 - 4) in spite of the fact it is specifically recommended for sheeting of cables in nuclear energetics (Refs. 1, 4). The present work was conducted with the aim to investigate the behaviour of CSM in a field of gamma rays supplied by a ^{137}Cs source that causes structural modifications.

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EXPERIMENTAL

In the experimental programme two types of CSM were used: *Hypalon 40 (DuPont de Nemours and Co.*, USA), and *Carom CSM (Chimcomplex S.A.*, Romania) and their main characteristics are listed in *Tab. 1*.

Tab. 1 The main characteristics of the investigated CSMs

Elastomer type	Chlorine content, %	Sulphur content, %	Unsaturation degree, %	Gel content, %
Hypalon 40	36.0	1.2	0.75	nil
Carom CSM	33.8	1.3	0.40	nil

The behaviour of CSM by gamma irradiation (^{137}Cs) was investigated in the range of total absorbed dose of 5 to 550 kGy (dose rate: 0.57 kGy/h). The exposure to high energy radiation carried out in air at room temperature brings about:

- structural modifications of the polymer as revealed by infrared spectra (using a Perkin Elmer 577, USA);
- change in gel content determined by known method (Ref. 5);
- change in chlorine and sulphur content (Ref. 6);
- evolution of hydrochloric acid from polymer;
- modification of degree of unsaturation (Ref. 7).

The infrared spectra were recorded using films casted from polymer solution in benzene and/or *o*-dichlorobenzene, at room temperature.

RESULTS AND DISCUSSION

The infrared spectra of CSM supply useful details on the main groups belonging to its structure, based on the bands assigned to methylene groups, chlorinated and chlorosulfonated units (Refs. 8, 9).

As a result of irradiation, some changes take place. The most important alterations were observed in the regions of 3600 - 3200 cm^{-1} and 1800 - 1650 cm^{-1}, where the accumulation of

OOH/OH and C=O groups occurs. Thus, in the domain 3600 - 3200 cm^{-1}, a new band of low intensity centered at 3400 cm^{-1} is formed providing the appearance of intermolecular associated OH groups. Over another infrared range (1800 - 1650 cm^{-1}) a new band assigned to carbonyl group (νC=O) is developed. Significant increase in absorbance at 1725 cm^{-1} can be observed. The growth of the absorbance at 3400 and 1725 cm^{-1} depends on absorbed dose (*Figs. 1, 2*). Two kinds of CSM investigated in present study show similar behaviour in respect to the formation/accumulation of OOH/OH groups (*Fig. 1*). The process occurs fast up to a dose of 100 kGy, but later on it becames slower.

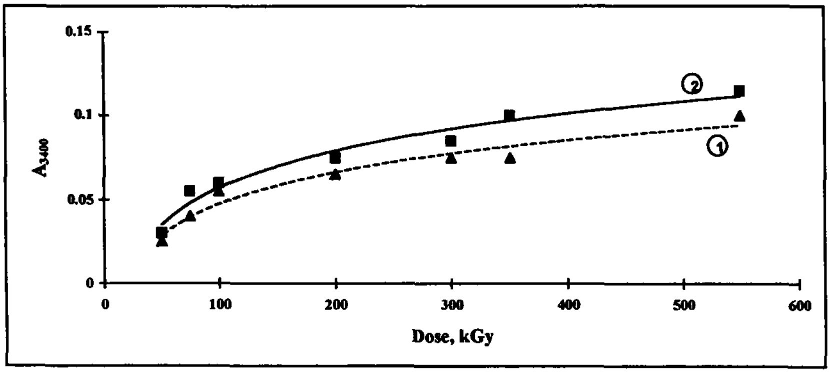


Fig. 1. Development of the content of OOH/OH groups as a function of absorbed dose:
1 - Hypalon 40; 2 - Carom CSM

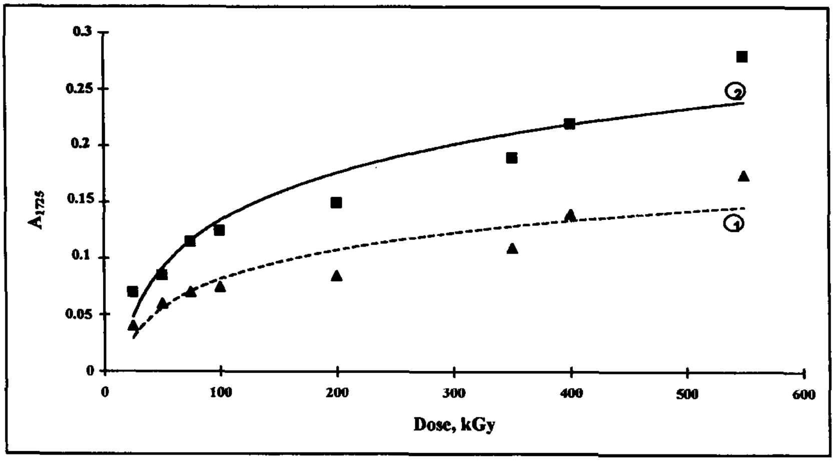


Fig. 2. Development of the content of C=O groups as a function of absorbed dose:
1-Hypalon 40; 2-Carom CSM

The evolution of carbonyl groups proceeds monotonously for both CSM samples (*Fig. 2*) but the C=O content of *Carom CSM* increases more rapidly than that of *Hypalon 40* above the absorbed dose of 200 kGy.

When total dose exceeds 200 kGy, the content of OH groups increases slower. It can be assumed that hydroxyl units belong to OOH groups formed during the first step of the oxidative process and they are subsequently decomposed so that the overall concentration remains at a low level. On the other hand, the content of C=O groups continuously increases along of all duration of exposure to radiation.

Even after exposure with a small dose, the modification of the bands at 1370 and 1155 cm^{-1} assigned to δ vibrations of the groups SO_2Cl and SO_2 were observed emphasizing that the chlorosulfonated group is quite sensitive to gamma radiation exposure.

For quantitative evaluation of this behaviour, the changes in the band at 1370 cm^{-1} were followed selecting the band at 1460 cm^{-1} as internal standard. *Fig. 3* shows that the decrease in SO_2Cl content is more enhanced in initial stage of exposure. It can be supposed that the splitting of SO_2Cl units takes place in a large extent during the first 100 kGy after that its content remains at a rather constant level.

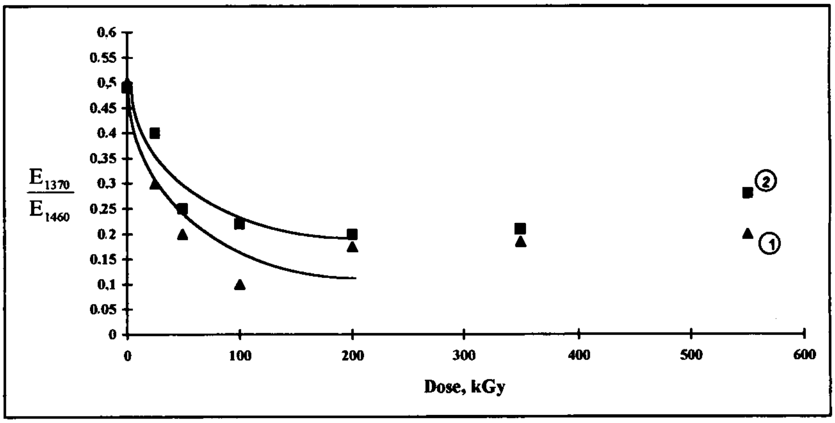


Fig. 3. Development of the content of chlorosulfonic groups as a function of total absorbed dose: 1 - Hypalon 40; 2 - Carom CSM

The development of the band at 1155 cm^{-1} (δ SO_2) cannot be properly used for quantitative evaluation because in the domain of the infrared spectrum from 1200 to 1000 cm^{-1}, the characteristic absorptions belonging to other groups (particularly C-O) are overlapped in spectra of CSM and the determination accuracy is significantly decreased.

At the same time, modification of the bands at 1610 and 825 cm^{-1} assigned to unsaturated units C=C was noticed but their low intensity does not allowed quantitative evaluation. The unsaturation was determined by chemical method (Ref. 7) using the soluble fraction of the irradiated elastomer. The evolution of unsaturation (*Tab. 2*) follows about the same manner for the both CSM samples. Thus, the unsaturation of *Hypalon 40* increases monotonously up to a dose of 50 kGy and after that it decreases to the initial level. *Carom CSM* shows maximum unsaturation at the dose of 100 kGy and then decreases monotonously to a level comparable with *Hypalon* unsaturation, *i.e.* lower than its own initial unsaturation.

Tab. 2. Changes in unsaturation and gel content for irradiated CSM

Absorbed dose, kGy	Elastomer			
	Hypalon 40		Carom CSM	
	Unsaturation, %	Gel, %	Unsaturation, %	Gel, %
0	0.40	0	0.75	0
5	0.63	2.5	0.85	2.3
10	0.67	16.2	0.90	2.7
20	0.73	49.0	0.92	22.7
35	0.81	64.5	1.00	43.0
50	1.60	58.6	1.15	62.6
75	1.30	72.0	1.50	67.0
100	0.90	77.0	2.00	70.2
200	0.80	90.0	1.00	89.5
350	0.70	88.0	0.80	88.0
550	0.60	80.0	0.50	77.0

A somewhat different behaviour for the two kinds of samples was observed for gel content (*Tab. 2*). *Hypalon 40* is almost completely crosslinked at 200 kGy. For the same range of absorbed dose (20 to 200 kGy), *Carom CSM* shows initially a lower degree of crosslinking (lower gel content) and at higher dose its crosslinking becomes comparable with *Hypalon 40*. At higher absorbed dose (350 - 550 kGy) some cleavage of the network occurs for both studied samples and decrease in their gel content was observed. This intricate development of unsaturation and of gel content suggests a complex mechanism involved in radiolysis.

The development of the bands in the region of 750 - 500 cm^{-1} assigned to CHCl groups can not be used for quantitative assessment due to their low intensities. Therefore the changes of sulphur and chlorine content along the radiation exposure was followed by their chemical determination (Ref. 6). *Tab. 3* presents the decrease of chlorine content in the range of 20 - 32 %, while sulphur content decreases within 6.5 - 8 % at maximal absorbed dose.

Tab. 3. Changes in chlorine and sulphur content for irradiated CSM

Absorbed dose, kGy	Elastomer			
	Hypalon 40		Carom CSM	
	Chlorine, %	Sulphur, %	Chlorine, %	Sulphur, %
initial	36.0	1.20	34.0	1.30
5	34.9	1.18	33.5	1.30
10	34.5	1.15	32.8	1.27
20	34.4	1.15	32.6	1.25
35	33.0	1.15	32.5	1.25
50	32.4	1.13	32.2	1.25
75	31.8	1.12	30.4	1.25
100	31.3	1.12	29.9	1.25
200	29.6	1.12	28.5	1.25
350	26.2	1.12	28.3	1.25
550	24.5	1.10	27.2	1.22

The development in chlorine and sulphur content *vs.* absorbed dose, expressed in loss of HCl and SO_2 (*Figs. 4* and *5*), shows similar behaviour of both CSM samples.

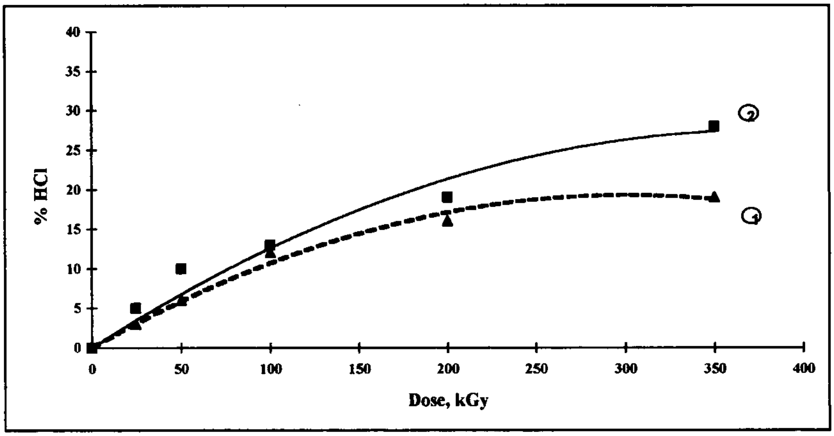


Fig. 4. Loss of hydrochloric acid as a function of absorbed dose: 1 - Hypalon 40; 2 - Carom CSM

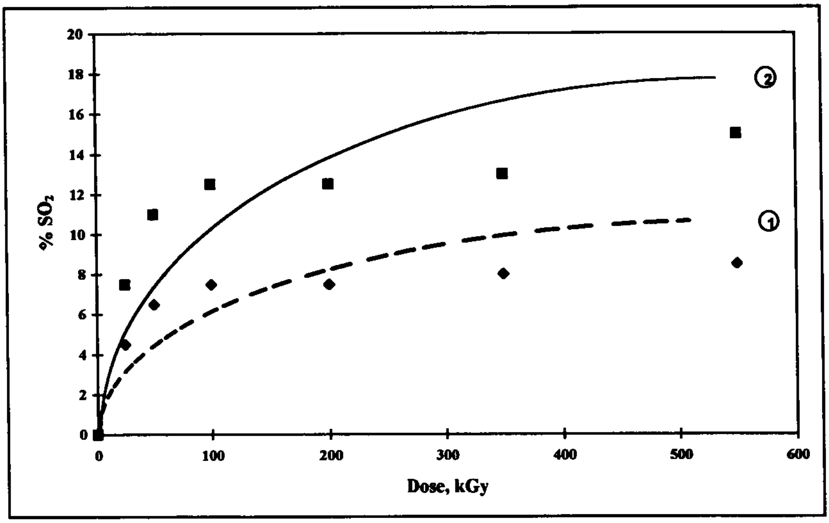


Fig. 5. Loss of sulphur dioxide as a function of absorbed dose: 1 - Hypalon 40; 2 - Carom CSM

The obtained data allowed the calculation of radiochemical yield using the Charlesby equation (Ref. 10). Figures 6 and 7 show the dependence of the yield of HCl and SO_2 splitting from the polymers as a function of the absorbed dose.

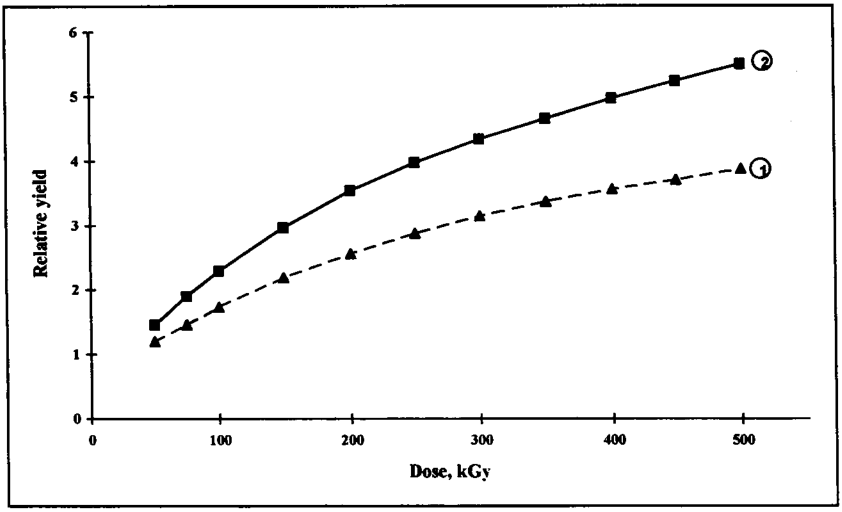


Fig. 6. Change in relative yield of HCl evolved from: 1 - Hypalon 40; 2 - Carom CSM

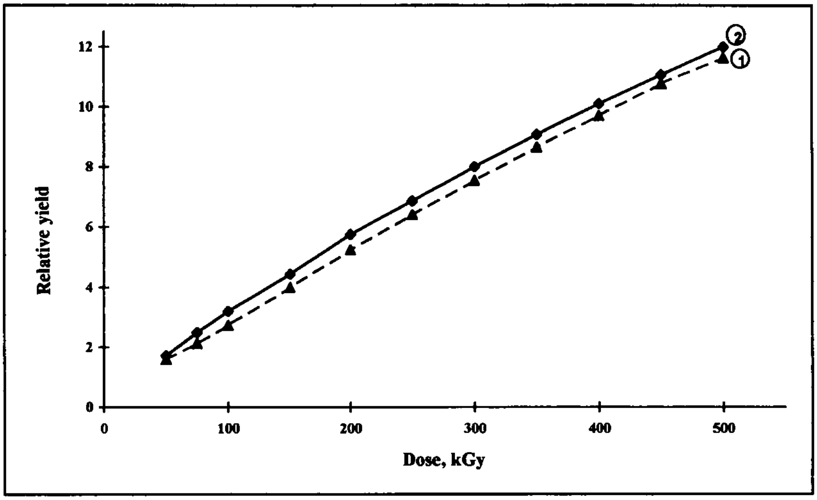
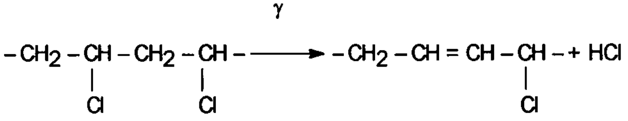
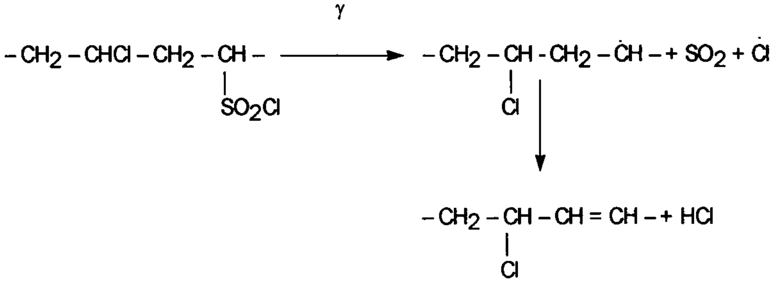


Fig. 7. Change in relative radiochemical yields for SO_2 evolved from: 1 - Hypalon 40; 2 - Carom CSM

When hydrochloric acid is produced, the relative decrease of chlorine content proceeds at lower rate in comparison with the decrease of sulphur content. Reactions (1) - (3) can be assumed to take place as the first steps of radiolytical degradation:



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \xrightarrow{\gamma} -CH_2-CH=CH-\underset{Cl}{CH}- + HCl \qquad (1)$$

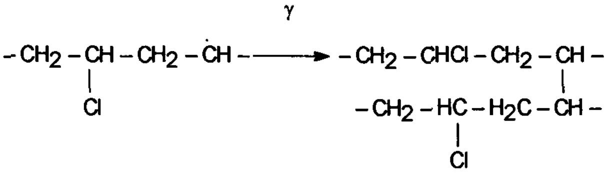


$$-CH_2-CHCl-CH_2-\underset{SO_2Cl}{CH}- \xrightarrow{\gamma} -CH_2-\underset{Cl}{CH}-CH_2-\dot{C}H- + SO_2 + \dot{Cl} \qquad (2)$$

$$\downarrow$$

$$-CH_2-\underset{Cl}{CH}-CH=CH- + HCl \qquad (3)$$

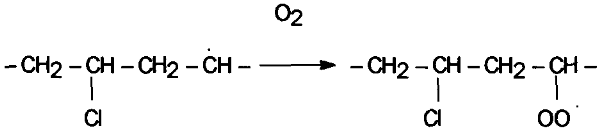
Free radicals resulting in reaction (2) are able to participate in crosslinking reactions (eq. 4):



$$-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\dot{C}H- \xrightarrow{\gamma} \begin{array}{l} -CH_2-CHCl-CH_2-CH- \\ \qquad\qquad\qquad\qquad\quad | \\ -CH_2-\underset{\substack{|\\ Cl}}{HC}-H_2C-CH- \end{array} \qquad (4)$$

leading to an increased gel content up to the complete crosslinking of the polymer. In the radiation field the splitting of polymer backbone takes place simultaneously with the formation of new bonds between macromolecules (Ref. 4).

Because the samples have been exposed to gamma radiation in presence of atmospheric oxygen, the reaction of macroradicals with oxygen has to be also considered (Eq. (5)):



$$-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\dot{C}H- \xrightarrow{O_2} -CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ OO^{\cdot}}}{CH}- \qquad (5)$$

The peroxy radicals formed in the Eq.(5) are very reactive and first of all they are able to extract hydrogen atoms forming macrohydroperoxides and new macroradicals. The oxidative degradation proceeding according to Bolland and Gee's mechanism shows (Ref. 11) that the C=O content is ten times higher than hydroperoxide concentration.

The sequence of increase and decrease of unsaturation level can be considered as typical result of concurent reactions described in Eqs. (1 - 4).

The increase in gel content up to the full crosslinking supports the assessment that reaction (4) is one of the main processes and that the irradiation of CSM would be a suitable technology for industrial crosslinking.

It is well known that by gamma irradiation of the polymers with C-C backbone [like polyethylene and poly(vinyl chloride)] conjugated double bonds would be formed (Ref. 12). By exposure of CSM samples to high energy radiation a dark colour was observed after a dose of 20 kGy was absorbed, but our tentative to determine the content of conjugated double bonds by the published method (Ref. 13) failed.

CONCLUSIONS

The behaviour of chlorosulfonated polyethylene in the field of gamma rays observed at room temperature for an absorbed dose of 5 to 550 kGy renders the following main aspects:

- exposure to high energy radiation leads to cleavage of chlorine and chlorosulfonic groups with formation of hydrochloric acid and sulphur dioxide accompanied by the formation of free macroradicals and unsaturated C=C units;
- resulting free macroradicals are able to react with atmospheric oxygen leading to various oxygen - containing structures;
- simultaneous reactions involving free macroradicals lead to crosslinking of the polymer with/without participation of C=C bonds;
- the hydroperoxides formed during the second step of radiochemical process generate carbonyl derivatives (with a concentration increasing monotonously with absorbed dose) and propagate degradation by other reactions, namely subtraction of hydrogen from the polymer backbone, scission of the main chain of the polymer and so on.

REFERENCES

(1) R. Harrington, *Rubber Age*, **19**, 417 (1963)

(2) B. Hlevca, E. Vâlceanu, T. Memetea, O.Corobchin, *Materiale Plastice*, (Bucharest) **21**, 216 (1984)

(3) B. Hlevca, E. Vâlceanu, T. Memetea, O. Corobchin, *Materiale Plastice*, (Bucharest) **22**, 168 (1985)

(4) V. Gueguen, L. Audouin, B. Pinel, J. Verdu, *European Polymer J.*, **30**, 1157 (1994)

(5) A. V. Podalinsky, *Kauchuk i rezina* No. 10, 10 (1972)

(6) X X X ASTM D 1619 - 83

(7) W. Kimmer, *Kaut.Gummi*, **10**, 606 (1963)

(8) K. Goda, Y. Kusaka, *Nippon Gomu Kyokaishi*, **51**, 737 (1978);
Intern. Polym. Sci. Technol. **6**, T23 (1979)

(9) M. Giurginca, *Materiale Plastice*, (Bucharest) - in press.

(10) A. Charlesby, “Atomic Radiation of Polymers”, Charlesby A. (Ed), Pergamon New York 1960, Chap. 10, p. 142

(11) J. I. Bolland, G. Gee, Tran Faraday Soc. **42**, 236; 244 (1946)

(12) F. Tüdős, T. Kellen, T. T. Nagy, "Developments in Polymer Degradation - 2”, N. Grassie (Ed.), Applied Science, London 1981, Chap. 7, p. 187

(13) J. L. Morand, *Rubber Chem. Technol.* **42**, 1094 (1974)