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DETERMINATION OF PEROXIDES AND HYDROPEROXIDES WITH 2,2-DIPHENYL-1-PICRYLHYDRAZYL (DPPH). APPLICATION TO OZONIZED ETHYLENE VINYL ACETATE COPOLYMERS (EVA)

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Abstract—The compound 2,2-diphenyl-1-picrylhydrazyl (DPPH) is a stable free radical often used to determine the quantity and the decomposition rate constant of macroinitiators such as ozonized polymers. In fact, DPPH induces the decomposition of hydroperoxides and has no effect on the decomposition of peroxides. Consequently, the hydroperoxides are the only species determined by the method described in the literature. Consequently, the decomposition rate of ozonized polymers measured with this method is wrong. It may be an explanation due to the low activation energy and rapid decomposition rate always found by this method of assay. Using the selective deactivation of hydroperoxides we show that the hydroperoxides are the more numerous initiators in an ethylene vinyl acetate copolymer. They can initiate the polymerization of vinyl monomers. On the other hand, peroxides are in a minority and their decomposition simply carries away a slight degradation by chain scissions.

INTRODUCTION

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) molecule is a stable free radical often used as a polymerization inhibitor. Bawn *et al.* [1] have employed this molecule to measure the decomposition rate of initiators such as tert-butyl peroxide (TBP) and 2,2′-azo-bis-isobutyronitrile (AIBN).

Robin *et al.* [2] also employed this method to determine the peroxides and hydroperoxides brought about by ozonized polymers. Ozone degrades polyolefins and generates functional groups on the chains such as peroxides and hydroperoxides. When treated, the ozonized polymers are able to initiate the radical polymerization of a vinyl monomer. The content of initiators brought about by the ozonized polymers is a fundamental parameter to control the polymerization reactions. Robin [2], Sarraf [3], Serdani [4] and Fahimi [5] used DPPH to determine the quantity and the k_d decomposition rate of the macroinitiators. The decomposition rates follow first order kinetics, which are very rapid with a low activation energy (50 kJ/mol) and an extremely low Arrhenius coefficient (Table 1).

In previous work [6, 7], we studied the decomposition kinetics of an ethylene vinyl acetate copolymer (EVA). We used the ability of the ozonized polymer to initiate the styrene polymerization to calculate the efficiency and the k_d value. The initial concentration of initiators (determined by DPPH) and the polymerization rate are the two parameters used for the calculations. The decomposition rate follows first order kinetics and is rapid with a half-life time of 840 sec at 110°C. On the other hand, the necessary time to reach the stability of the DPPH concentration and the destruction of all the initiators is 10 min at 110°C. Consequently, the half-life time is 90 sec at this temperature. The difference between the two k_d rates might arise from the reactivity of the DPPH, which is the common molecule employed in the two methods. The present article focuses on the study of the validity of the DPPH method to determine the decomposition rate of macroinitiators.

EXPERIMENTAL CONDITIONS

The ethylene vinyl acetate copolymer used in this work is a commercial copolymer and its vinyl acetate content is 22.5 wt%. Its number average molecular weight is 60×10^3 g/mol and its weight average molecular weight is 120×10^3 g/mol compared to polystyrene standards (conditions: eluent = THF at 40°C, flow = 10 ml/min, calibration = polystyrene standards). 2,2-diphenyl-1-picrylhydrazyl (95% free radicals) is a product from ALDRICH. The solvent used is pure O-xylene. It is re-distilled before DPPH determinations.

Ozonisation

The polymer is dissolved n carbon tetrachloride and a O_2/O_3 mixture passes through the solution. The experiment

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Table 1. Examples of activation energy and Arrhenius coefficient of decomposition rate constant of ozonized polymers

References	Ozonised polymer	Method of determination	Activation energy (kJ/mol)	Arrhenius coefficient ln(A)	ΔS (J/mol · K)
Polymer handbook [8]	Usual hydroperoxides and peroxides	—	120–150	27.6–36.8	−25 to +54
Fargere [6, 7]	EVA	Polymerisation rate	46	7.3	−188
Sarraf [3]	PE	DPPH	52.5	10.6	−167
Serdani [4]	PVDF	DPPH	39	5.8	−209
Fahimi [5]	Cross-linked EVA wastes	DPPH	58	11.8	−154

is carried out at an EVA concentration of 30 g/l, solution temperature 25°C, gaseous flow 26.5 l/hr and ozone concentration 60 mg/l of gaseous mixture. The reaction time varies from 30 to 75 min according to the desired content of initiators [5, 8, 9]. The reaction time increases initiator content and polymer degradation. If the time becomes too long, the polymer is completely oxidized and thus unusable.

Polymerisation

Ozonized EVA (2 g) and styrene (3–50 g) are introduced in a reactor equipped with thermometer, condenser and gas entry. The solution is stirred by a magnetic agitator and saturated with argon for 30 min. The reactor is placed in a thermostated oil bath. A slight argon flow is maintained. When the desired reaction time is reached, the reactor is water cooled and the polymer is precipitated with ethanol. The EVA and formed polystyrene are filtered, dried and weighed. The quantity of recovered monomers and the concentration of unreacted monomers [M] is deduced. The solution volume is equal to the monomer volume (density = 0.906 at 20°C) plus the solvent volume, if necessary. The method used to calculate the efficiency and the decomposition rate is described in previous works [6, 7]. The same conditions are applied for the study of the thermal polymerisation using non-ozonized EVA.

Content of initiators

DPPH reacts with free radicals and leads to unreactive products. The final concentration of DPPH depends on the initial concentration of initiators. The decrease in rate of the DPPH concentration depends on the decomposition rate of the initiator. An ozonized EVA sample "m" of 100–200 mg is dissolved in a 20 ml solution of DPPH (0.6 g/l) in redistilled O-xylene. The solution is saturated with argon for 45 min and the reactor is placed in a thermostated oil bath at 110°C for 10 min. The reactor is quickly cooled with cold water and the polymer is precipitated with 160 ml of pure isopropanol. After 30 min without shaking, the solution is filtered through a fine filter (0.45 μm of porosity) and determined by colorimetry at 520 nm. We thus obtain the concentration of residual DPPH "C" in g/l. A blank determination is made under the same conditions without polymer to obtain the concentration "Co" in g/l. When the method is used to determine the decomposition rate constant, this blank determination must be made at all temperatures and reaction times. The content of initiator brought about by a gram of ozonized EVA is [2–5] given by

$$T = ((\mathrm{Co}—\mathrm{C}) \times 180)/(2000 \times 394,33 \times \mathrm{m})$$

in mole of (—O—O—)/g of ozonized polymer.

Separation of the mixture EVA/polystyrene (without grafting)

The polymer mixture (3 g) is dissolved in 50 ml of 2-butanone (MEK) and 37.5 ml of benzylalcohol. The solution is heated to help dissolution. After the solution is cooled, we add 200 ml acetone. The precipitate obtained is EVA and is recovered through filtration. The recovered solution contains the dissolved polystyrene and is precipitated with ethanol. This method is the most rapid and simple for the mixtures used in this work. The purity of each phase is verified by the i.r. method. A peak at 699 cm^{-1} appears in the EVA i.r. spectrum when containing 2% or more of polystyrene in weight. Likewise, a peak at 1740 cm^{-1} appears in the polystyrene i.r. spectrum when containing 0.5% or more of EVA in weight. When the EVA is grafted with polystyrene, it is not possible to obtain pure EVA with this method [1].

Ozonized EVA deactivation

The conditions are the same as for the determination of the initiator content. The quantities are calculated to recover 2–3 g of deactivated EVA. The solution of DPPH and ozonized EVA is heated at 110°C during 10 min and followed by a quick cooling. Dodecylmercaptan is added to the solution to destroy the residual DPPH and the polymer is precipitated with acetone and washed until the rinsing solution runs clear. Acetone is a better DPPH solvent than isopropanol. In spite of these precautions, the recovered polymer is yellow in colour. This colour shows that DPPH is fixed on the deactivated polymer. In comparison, a non-ozonized EVA sample treated under the same conditions is recovered without colour. The deactivated EVA is dried at room temperature. It must be used rapidly or stored for a few days at 4°C in the dark.

Gel permeation chromatography

The ozonized EVA sample and the DPPH are dissolved together and the solution is heated to the desired temperature. Before and during the experimentation, the solvent is saturated with argon to avoid the presence of oxygen. During the reaction, a slight quantity of DPPH is added to set off the loss of DPPH due to the heating effect. At t time, a solution sample is withdrawn with a syringe, diluted and injected in the apparatus (GPC). The eluent used is tetrahydrofuran. The temperature of the columns, the refractometer and the solvent is 40°C and the flow is 1 ml/min. The columns are connected in series and allows the separation of polymers with 3000 to 300 000 apparent molecular weights (Phenogel mixed bed + 10^4 Å + 10^3 Å from Phenomenex).

The columns are calibrated with polystyrene standards. The molecular weight obtained is apparent and must be converted from raw into real results. the Mark–Houwink–Sakurada coefficients used are given by Echarri *et al.* [10]. They are available for EVA with 28% of vinyl acetate by weight in the presence of tetrahydrofuran at 20°C

$$a_{\mathrm{EVA}} = 0.44$$

$$k_{\mathrm{EVA}} = 7.78 \times 10^{-3}.$$

The Mark–Houwink–Sakurada coefficients for polystyrene in tetrahydrofuran at 25°C are the next ones [11, 12]

$$a_{\mathrm{PS}} = 0.71$$

$$k_{\mathrm{PS}} = 1.32 \times 10^{-2}.$$

The real weight average molecular weight of the EVA samples are deduced from the M_{pa} weight average molecular weight measured on the chromatogram using the following equation

$$\ln(k_{EVA}) + (1 + a_{EVA})\ln(\bar{M}_p) = \ln(k_{PS}) + (1 + a_{PS})\ln(\bar{M}_{pa})$$

$\bar{M}_p$: EVA weight average molecular weight
$\bar{M}_n$: EVA number average molecular weight
$\bar{M}_{pa}$: weight average molecular weight from chromatogram (PS standards)
$\bar{M}_{na}$: number average molecular weight from chromatogram (PS standards)
k_{EVA}, a_{EVA}: EVA coefficients
k_{PS}, a_{PS}: PS coefficients.

The polydispersity index of the ozonized EVA used is always around 2.25 [6]. It is possible to deduce the $\bar{M}_n$ number average molecular weight

$$\bar{M}_p/\bar{M}_n = 2.25$$

$$\ln(\bar{M}_p) = \ln(1.442) + 1.187\ln(\bar{M}_{pa})$$

$$\ln(\bar{M}_n) = \ln(1.678) + 1.187\ln(\bar{M}_{na}).$$

The conditions adopted for the present work are slightly different from those of Echarri *et al.* [10] conditions because the vinyl acetate contents of our EVA is 22.5 wt%. Moreover, the columns temperature is 40°C and therefore the coefficients are not exactly the same. However, for the present work, the Echarri's coefficients are employed. These differences give an increase of 10% in the calculated weight average molecular weight. Furthermore, all the subsequent results have not been corrected for this error.

RESULTS AND DISCUSSION

Effect of the DPPH on usual initiators

The results obtained by Bawn *et al.* [1] show that DPPH does not disturb the decomposition rate of peroxides and azo-initiators.

We too used the DPPH method to determine a classical peroxide and a known hydroperoxide. The decomposition rate of these two initiators is well known [13, 14]:

terbutyl peroxide $k_d =$

$$8.95 \times 10^{12}\exp(-130.7(\text{kJ mol}^{-1})/RT)$$

cumyl hydroperoxide $k_d =$

$$7.3 \times 10^{8}\exp(-112(\text{kJ mol}^{-1})/RT).$$

Decomposition kinetics obeys to a first order kinetics and the concentration of residual initiators $[I]_t$ as a function of time and temperature, is given by the following equation

$$[I]_t/[I]_0 = \exp(-k_d t) \qquad (1)$$

$[I]_t$: initiator concentration at t time
$[I]_0$: initial initiator concentration
k_d: decomposition rate constant.

As shown in Table 2, the residual peroxide concentration and the calculated cncentration are the same after 10 min at 110°C. The peroxide decomposition is normal in the presence of DPPH. On the other hand, the residual hydroperoxide concentration is much lower than the calculated concentration for the same time and reaction temperature. Consequently, the hydroperoxide decomposition rate is increased in the presence of DPPH. Whatever the nature of the initiators, we were able to measure the quantity of initiator introduced in the reactor. We can conclude that the DPPH method is available to determine the quantity of radical initiators but it can be used in the kinetics study of usual hydroperoxides.

Effect of the DPPH on the ozonized EVA

Steric hindrances can inhibit the reaction between the DPPH and the heat-sensitive groups brought about by the ozonized EVA. We have shown that DPPH reacts with peroxides and hydroperoxides at different rates and certainly in different ways. Consequently, the DPPH might not react with all the heat-sensitive groups of the macroinitiator.

We have deactivated ozonized EVA samples to identify the nature and quantity of chemical species reacting with DPPH. The deactivation method is the same as a DPPH determination. We can notice that after deactivation the recovered polymer is yellow in colour. This colour certainly shows that DPPH is fixed on the deactivated polymer. In comparison, a non-ozonized EVA sample treated under the same conditions is not coloured.

The initiators which did not react with DPPH are normally able to initiate styrene polymerization. The polymerization conditions have already been used in previous papers [6, 7]. The generated polystyrene quantity is measured by weighing. The results in Table 3 show that the deactivated EVA is unreactive and cannot initiate the polymerization. In the case of a deactivated sample, the weight increase observed can be explained by the styrene thermal polymerization. EVA and polystyrene can be easily separated with the appropriate solvent mixture as for a normal thermal polymerization [6, 7]. If the ozonized EVA is not deactivated, the weight increase is more important and it is not possible to recover the pure EVA while it is grafted with polystyrene. In a previous work, we also showed that there is no transfer reaction between the growing polystyrene chains and the EVA [6, 7].

We can deduce from these results that DPPH reacts with all the functional groups, which are able

Table 2. Comparison between experimental and calculated residual concentration of radical initiators heated in the presence of DPPH

Initiator	Temperature (°C)	Time (min)	Calculated residual initiator ratio (%)	Measured residual initiator ratio (%)
Terbutyl	130	10	94	92.5
peroxide	130	30	83	86
Cumyl	100	5	99.5	22
hydroperoxide	100	10	99	9.5

Table 3. Styrene polymerization in the presence of deactivated ozonized EVA. Experimental conditions: EVA weight = 2 g; styrene weight = 10 g; solvent (O-xylene) = 10 ml; temperature = 130°C; time = 3.5 hr

Polymer properties (content of initiators in mol/g d'EVA)	Styrene conversion rate (%)
Non-ozonised EVA	21
Ozonised EVA No. 1 (1.93×10^{-5})	45
Ozonised EVA No. 1 deactivated by DPPH	18
Ozonised EVA No. 2 (3.48×10^{-5})	47
Ozonised EVA No. 2 deactivated by DPPH	20
Ozonised EVA No. 3 (5.15×10^{-5})	59
Ozonised EVA No. 3 deactivated by DPPH	11

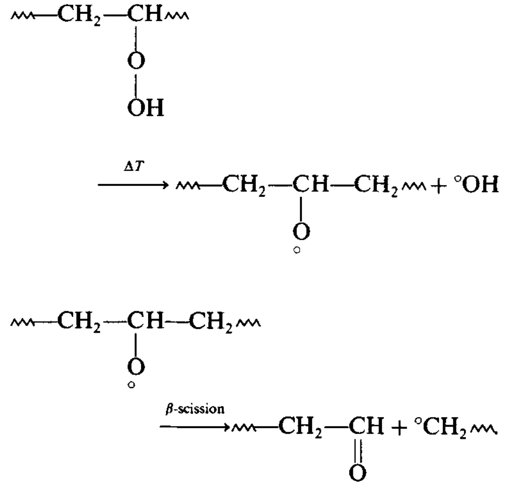
to initiate the styrene polymerization. The steric hindrances change with the nature of the ozonized polymer; consequently, the ability of DPPH to react with the initiators must be verified in each and every case. The deactivation of the ozonized EVA is rapid (10 min at 110°C) and this rate is similar to those obtained with the cumyl hydroperoxide. We now try to estimate the proportion of peroxides and hydroperoxides brought about by the ozonized EVA.

Evolution of the ozonized EVA molecular weight

Thermal decomposition of the ozonized EVA in the presence of DPPH. The reaction between polymer and ozone generates peroxides and hydroperoxides on the polymer chains [2, 15]. The peroxide decomposition always leads to a chain scission

$$R—O—O—R' + 2X \rightarrow R—OX + XO—R'$$

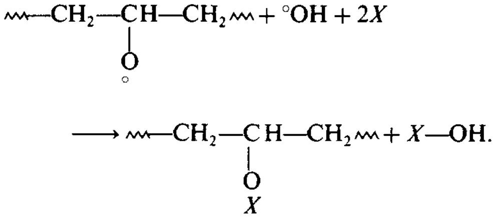
X: free radical inhibitor such as DPPH.
The decomposition of hydroperoxides is more complex because the polymer chain may be cut by a β-scission reaction [15, 16]



$$\sim\!CH_2-\underset{\substack{|\\O\\|\\OH}}{CH}\!\sim \xrightarrow{\Delta T} \sim\!CH_2-\underset{\substack{|\\O\\ \circ}}{CH}-CH_2\!\sim + {}^{\circ}OH$$

$$\sim\!CH_2-\underset{\substack{|\\O\\ \circ}}{CH}-CH_2\!\sim \xrightarrow{\beta\text{-scission}} \sim\!CH_2-\underset{\substack{\|\\O}}{CH} + {}^{\circ}CH_2\!\sim$$

A free radical inhibitor prevents chain scission and changes the reaction mechanism



$$\sim\!CH_2-\underset{\substack{|\\O\\ \circ}}{CH}-CH_2\!\sim + {}^{\circ}OH + 2X \longrightarrow \sim\!CH_2-\underset{\substack{|\\O\\X}}{CH}-CH_2\!\sim + X—OH.$$

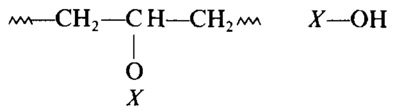
In any case, the average molecular weight of the ozonized polymer must decrease after the thermal decomposition of its peroxides and hydroperoxides. In the presence of DPPH, the polymer is deactivated in 10 min at 110°C; the ozonized polymer molecular weight must therefore remain stable after this time.

Ozonized EVA and DPPH are dissolved together and the solution is heated to the desired temperature. Before and during the experimentation, the solvent is saturated with argon to avoid the presence of oxygen. At t time, a solution sample is withdrawn with a syringe, diluted and injected in a gel permeation chromatography apparatus (GPC).

We notice a slight but significant decrease of the average molecular weight and the thermal decomposition is very slow. So, the working temperature was increased beyond 110°C to accelerate the decrease in the molecular weight (Figs 1 and 2). The molecular weight reaches a plateau after 2 hr at 130°C, 3–4 hr at 120°C and 7–8 hr at 110°C. On the other hand, the molecular weight of a non-ozonized EVA remains stable under the same conditions.

The molecular weight evolution of the deactivated samples was studied in this way. The molecular weight is unchanged before and after the treatment. During the thermal decomposition, the molecular weight decrease of a deactivated sample is similar to the ozonized samples (Fig. 3). The amplitude and the rate of the decrease are the same, so that the two graphs shown in Figs 2 and 3 can be superimposed.

Whatever the temperature, the molecular weight of the ozonized EVA is unchanged after 10 min in a solution of DPPH. Under the same conditions, we showed that the initiators brought about by the polymer are destroyed. We also showed that the hydroperoxides are rapidly degraded in the presence of DPPH. Consequently, the heat-sensitive groups brought about by the ozonized EVA must essentially be hydroperoxides. This assumes that DPPH acts as a β-scission inhibitor and can explain the colour observed on the deactivated EVA. Anyway, we did not yet succeed in isolating the following structures



$$\sim\!CH_2-\underset{\substack{|\\O\\X}}{CH}-CH_2\!\sim \qquad X—OH$$

with X = DPPH.

Number of peroxides and hydroperoxides per chain and decomposition kinetics of peroxides. As the molecular weight of the samples and the content of initiator before the thermal decomposition is known, the average number of initiators per chain can be calculated as follows

$$\bar{N} = T\cdot\bar{M}_{no} \qquad (2)$$

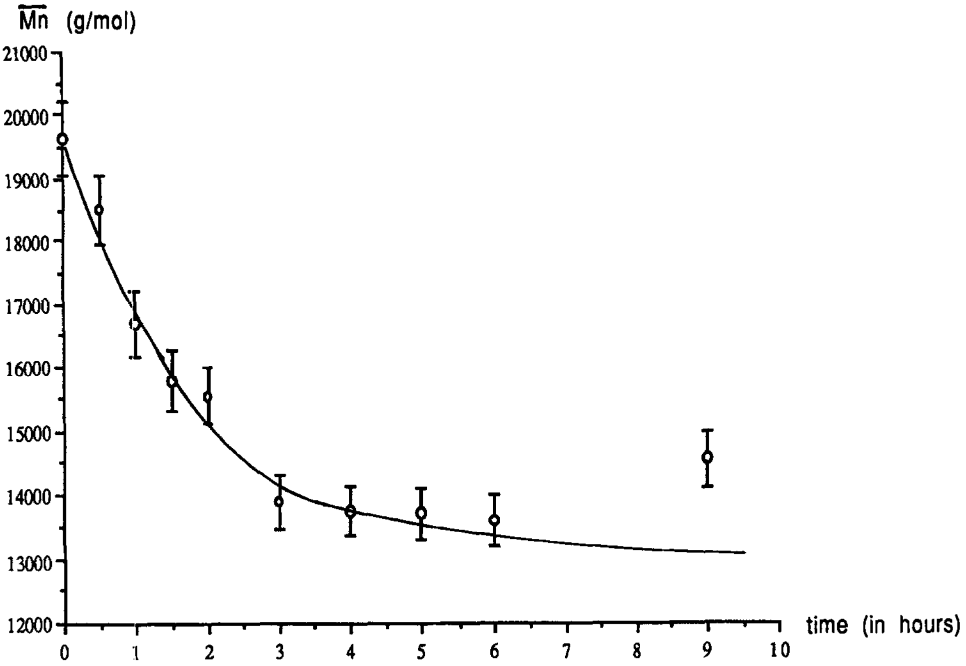


Fig. 1. Molecular weight decrease of an ozonized EVA in the presence of DPPH. Conditions: temperature = 120°C; content of initiators of the ozonized EVA = 7.6 × 10^{-5} mol/g d'EVA. (The molecular weights are not converted.)

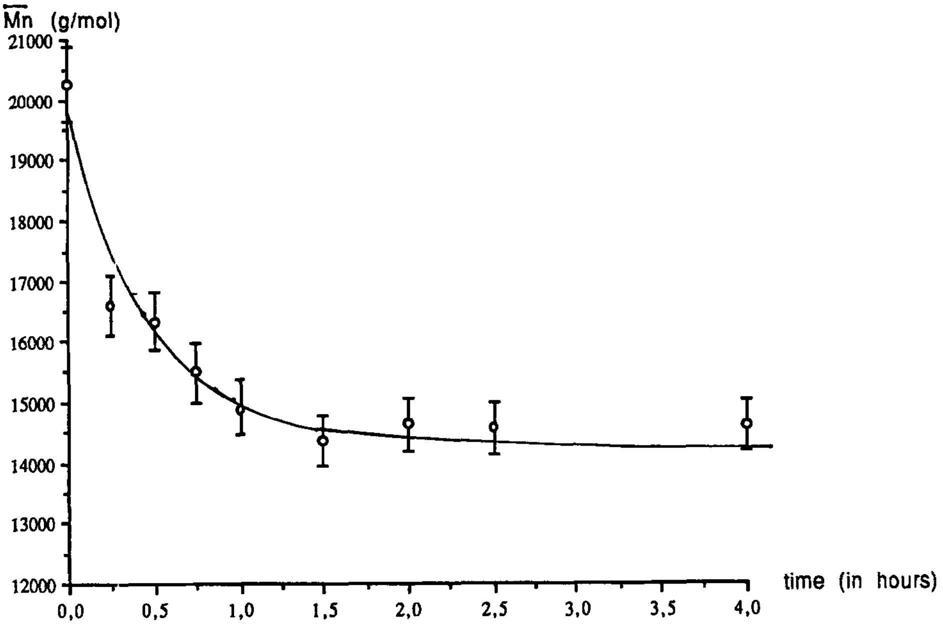


Fig. 2. Molecular weight decrease of an ozonized EVA in the presence of DPPH. Conditions: temperature = 130°C; content of initiators of the ozonized EVA = 5.15 × 10^{-5} mol/g d'EVA. (The molecular weights are not converted.)

Table 4. Comparison between the average number of peroxides per chain (obtained from GPC curves) and the average number of hydroperoxides per chain (obtained from Fig. 4) in terms of content of hydroperoxides of an ozonized EVA (given by DPPH determination)

Content of hydroperoxides measured by DPPH (mol/g of EVA) T	Number average molecular weight $\bar{M}_n$ (experimental results)	Average number of hydroperoxides per chain $(\bar{N} - \bar{X}_m)$	Average number of peroxides per chain $\bar{X}_m$ (±30%)
1.61×10^{-5}	24500 (±500)	4	0.17
3.48×10^{-5}	23250 (±500)	9	0.22
3.71×10^{-5}	22750 (±500)	10	0.37
5.15×10^{-5}	21250 (±500)	13	0.46
7.58×10^{-5}	20000 (±500)	16	0.55

$\bar{N}$: average number of active initiators per EVA polymer chain

T: content of initiators of the ozonized EVA determined by DPPH in mol/g of EVA

$\bar{M}_{no}$: initial number average molecular weight of the ozonized EVA (g of EVA/mol).

The calculations used to convert the experimental results into the form of number average molecular weight need to make some approximations. The $\bar{M}_{no}$ values are important too and the difference reaches 10%. This result has no influence on the conclusions and we employed the $\bar{M}_{no}$ values without any other correction.

As the molecular weight of the samples after the thermal decomposition is known (Fig. 4), the average number of scissions per chain can be calculated as follows

$$\bar{M}_{no}/\bar{M}_{ninf} = \bar{X}_m + 1 \qquad (3)$$

$\bar{M}_{no}$: Initial number average molecular weight before chain scission

$\bar{M}_{ninf}$: Number average molecular weight after chain scission (t-infinite)

$\bar{X}_m$: Average number of scissions per chain (t = infinite).

If we assume that DPPH inhibits the β-scission reactions then peroxides are the only functional groups which cut the chains. The average number of scissions per chain thus represents the average number of peroxides per chain. With $\bar{N}$ and $\bar{X}_m$, we can calculate the number of hydroperoxides per chain. In Table 4, we gathered some results to compare the average number of peroxides and hydroperoxides per chain. Hydroperoxides are in the majority according to what could be expected. The proportion of each kind of initiator does not change with the ozonization treatment (Table 4). Figure 5 represents the variation of the average number of hydroperoxides per chain as a function of the content of initiators. The variation is not linear because the degradation of the polymer is greater than the creation of initiators. The accuracy on the molecular weights measured by GPC reaches ±500 g/mol. The doubt on $(\bar{X}_m + 1)$ reaches 5% and consequently the accuracy on $\bar{X}_m$ is between 15 and 30%. In spite of this poor accuracy on $\bar{X}_m$, the conclusions remain unchanged.

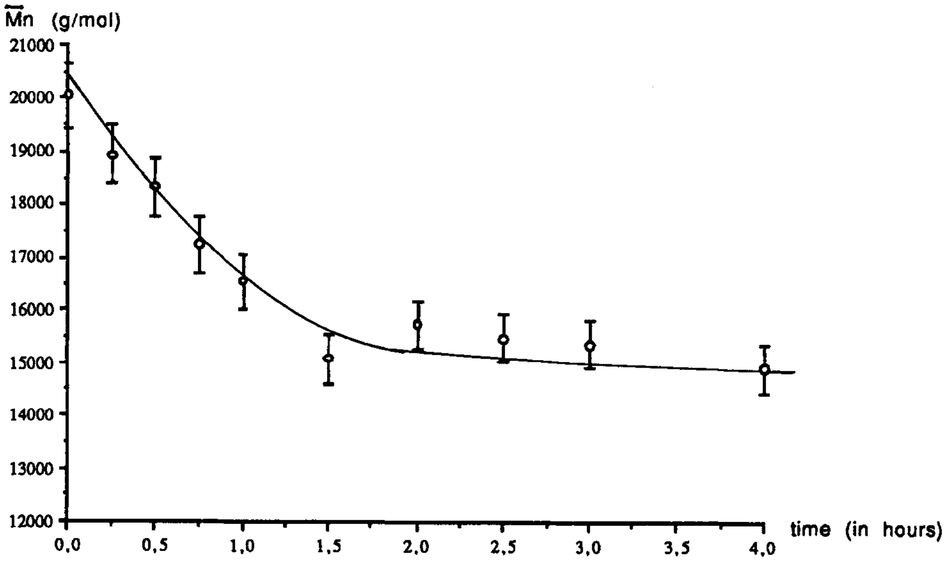


Fig. 3. Molecular weight decrease of deactivated ozonized EVA in the presence of DPPH. Conditions: temperature = 130°C; content of initiators of the ozonized EVA = 5.15×10^{-5} mol/g d'EVA. (The molecular weights are not converted.)

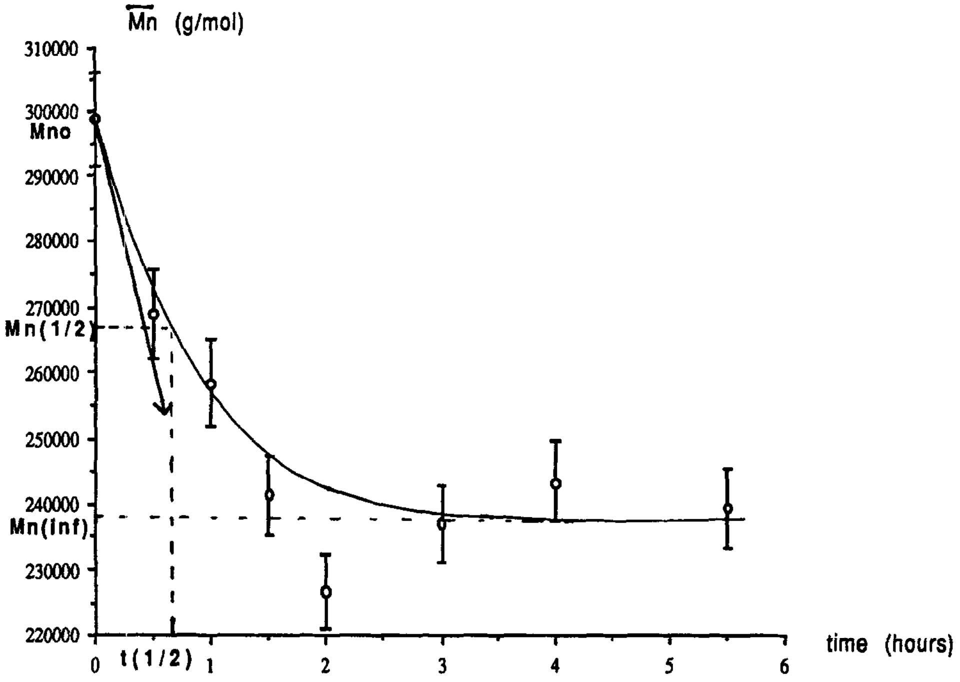


Fig. 4. Example of decomposition rate constant calculation. (The molecular weights are converted in this example.)

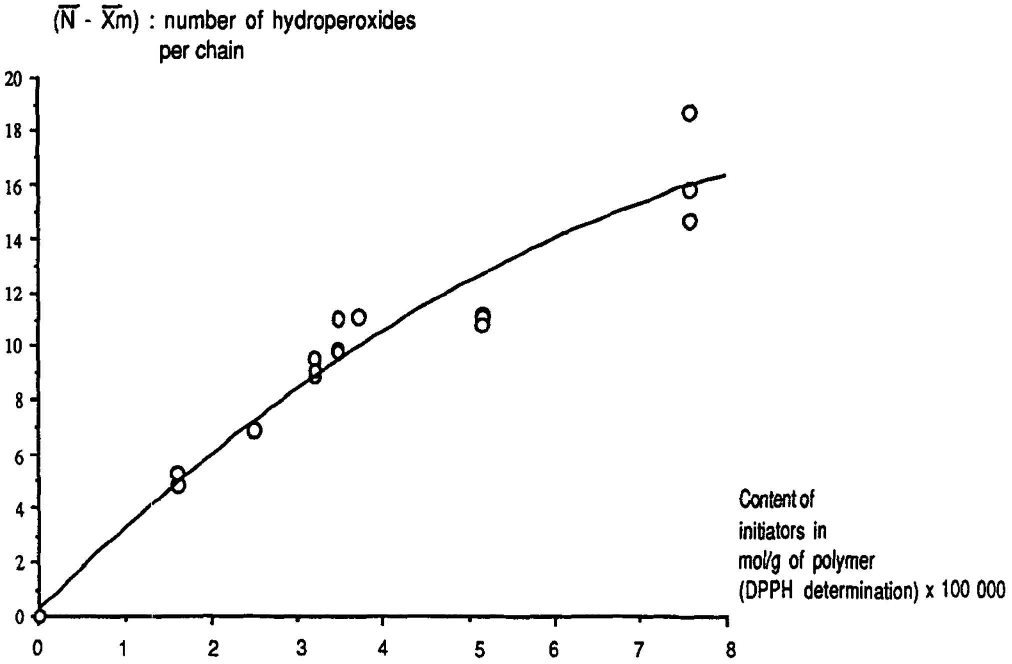


Fig. 5. Increase of the average number of hydroperoxides per chain in terms of content of initiators of an ozonized EVA (given by DPPH determination).

This result is different from the one obtained by Verney *et al.* [15, 16]. The distribution proposed by the authors is 75% hydroperoxides and 25% peroxides on ozonized polypropylene. They obtained these values by comparing two different assays: the determination with iodine and the determination with ferrous ion. But these methods have given results which cannot be reproduced with the ozonized EVA. For example, the ferrous ion method is carried out in an alcohol solution and selectively destroys the hydroperoxides. But, the EVA precipitates on contact with the alcohol solution. Consequently, the ferrous ions may not destroy all the hydroperoxides.

Decomposition kinetics of the peroxides. The variation of the molecular weight can be used to calculate the decomposition rate of the peroxides. If we admit that the peroxide decomposition obeys a first order kinetics, the concentration of peroxides decreases with time [equation (1)]. Assuming that each peroxide decomposition gives a chain scission, the average number of scissions per chain vs time can be given by the following equation

$$\bar{X} = \bar{X}_m(1 - \exp(-k_d \cdot t)). \quad (4)$$

We deduce the variation of the number average molecular weight vs time

$$\bar{M}_n/\bar{M}_{no} = 1 + \bar{X}$$

$$\bar{M}_n = \bar{M}_{no}/((1 + \bar{X}_m) - \bar{X}_m \cdot \exp(-k_d \cdot t)) \quad (5)$$

$\bar{X}$: average number of scissions per chain at t time
$\bar{X}_m$: average number of scissions per chain (t = infinite)
$\bar{M}_n$: number average molecular weight at t time
$\bar{M}_{no}$: initial number average molecular weight ($t = 0$)
t: time (sec)
k_d: decomposition rate constant (sec^{-1}).

There are two ways to measure the decomposition rate constant using equation (5). (1) Initial slopes method: the initial slope of the $\bar{M}_{no}/\bar{M}_n = f(t)$ curve is equal to

$$(\mathrm{d}(\bar{M}_{no}/\bar{M}_n)/\mathrm{d}t)_{t=0} = -\bar{M}_{no} \cdot \bar{X}_m \cdot k_d. \quad (6)$$

(2) Half-life time method: at the $t_{1/2}$ half-live time, the $\bar{M}_{n1/2}$ number average molecular weight corresponds to the $\bar{X}_m/2$ half of the chain scissions, thus we can write

$$t_{1/2} = \ln(2)/k_d \quad (7)$$

at $t_{1/2}$ we have:

$$\bar{M}_{n1/2} = 2 \cdot \bar{M}_{no}/(2 + \bar{X}_m). \quad (8)$$

Knowing $\bar{M}_{no}$ and $\bar{X}_m$ on the curves, we calculate the $\bar{M}_{n1/2}$ value, we plot it on the graph to find $t_{1/2}$ value and thus calculate k_d (Fig. 4).

The uncertainty on the results is important, first due to the choice of the coefficients and second due to the apparatus accuracy. This poor accuracy in the measurements increases the difficulties to draw a single representative curve. Nevertheless using the mathematical expression given by equation (5), a certain number of curves can be drawn in the form of a band within the upper and the lower limits of uncertainties. In spite of all these difficulties to obtain a consistent result, we choose an average representative curve that best fits with the band. We based our results on this average curve and the results are the following:

original slopes method:

$$k_d = 1.6 \times 10^{12} \exp(-121.5(\mathrm{kJ\,mol^{-1}})/RT) \text{ and}$$

half-life time method:

$$k_d = 1.2 \times 10^{9} \exp(-97(\mathrm{kJ\,mol^{-1}})/RT).$$

Although the results are different, we notice that the decomposition rate constant is similar to the usual decomposition rate constants (Table 1). These values are only approximations but they show a different behaviour of the chemical species, which cut the polymer chains. A better accuracy on the measurements of molecular weight will improve this method.

CONCLUSION

The compound 2,2-diphenyl-1-picrylhydrazyl molecule (DPPH) is a stable free radical often used to determine the concentration of free radical initiators or their decomposition rate. This method seems to be the most appropriate with macroinitiators such as ozonized polymers because it gives results which can be reproduced.

However, this method requires some precautions. The DPPH method can be used to determine the quantity of radical initiators. But DPPH increases the decomposition rate of the hydroperoxides and has no effect on the peroxide decomposition. So, this method is not appropriate to calculate the decomposition rate constant of the hydroperoxides. This method does not give the efficiency of initiators. The method using the polymerisation rate constant must be chosen whenever searching the decomposition rate constant and the efficiency are required.

The initiators brought about by the ozonized EVA have two natures. The first species react rapidly with DPPH but do not cut the polymer chains. These initiators initiate the styrene polymerization and the decomposition rate is very rapid in the presence of DPPH. In fact, these initiators react as hydroperoxides. The second species cut the chain. The study of the molecular weight shows that the second species is in a minority (3%) and its decomposition rate is low. We described a method to calculate the decomposition rate using the decrease in molecular weight. This method must be improved in accuracy. The small quantity of the second species cannot initiate the styrene polymerization. These initiators react as peroxides. The ozonized EVA can be considered as a macroinitiator with an important number of hydroperoxide groups.

In previous papers [6, 7], we calculated the decomposition rate constant of the hydroperoxides brought about by the ozonized EVA (in styrene)

$$k_d = 1480 \exp(-46(\mathrm{kJ\,mol^{-1}})/RT).$$

We can notice that this decomposition rate is similar to the rates obtained with other ozonized polymers and with the DPPH method (Table 1). Consequently, it seems that DPPH and styrene have the same effect on the decomposition of hydroperoxides.

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