



Short communication

Study of new macroamorcors and grafted copolymers by ozonisation of poly(vinylidene fluoride)

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ABSTRACT

We studied the synthesis of a macroamorcors containing poly(vinylidene fluoride) (PVDF) obtained by an ozonisation reaction. On one hand, we optimised the reaction in order to control the rate of oxidation and on the other hand the ozonised polymer was also proportioned, which enabled us to determine the rate of active oxygen $T(0^\circ)$ and the rate of peroxide and hydroperoxide. We noticed an average of $5.5 \times 10^{-6} \text{ mol g}^{-1}$, a relatively lower rate $T(0^\circ)$ compared to those obtained for polyethylene (PE) and the poly(vinyl chloride) (PVC), respectively of 5.6×10^{-5} and $28 \times 10^{-5} \text{ mol g}^{-1}$. With regard to these two products, the presence of CH and C–Cl bonds sensitive to the action of powerful agents of oxidation such as ozone makes it easy to obtain compounds of oxidation of peroxides type and hydroperoxides compared to the PVDF for which the C–F bond which has proven to be stronger. In the same way, this study showed that the technique of ozonisation of the powder PVDF, despite of the insufficient rates of oxidation to which it leads, remains the most adequate adapted because it leads to a reduced increase in mass of the product.

We studied the graft of various monomers using the techniques in solid and in solution. From this study we deduce that solid graft technique, besides its easy way of making, leads to better efficiency rates of graft with relatively short time reaction in comparison with those carried out in solution.

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1. Introduction

The ozonisation reaction of organic compounds, such as polymers has been intensively investigated, since it represents an interesting method for oxygenated functions introduction in molecular structures, and by the way it enables the creation of carbonyl C–O bonds. The main inconvenient of this technique being the formation of a multiple components mixture, difficult to separate. For example, the oxidation of tetradecane (a relatively simple molecule), achieved at 40°C in the presence of O_2/O_3 gas mixture, leads to the formation of a mixture ketones, acids, alcohols (with various carbon numbers) and of water [1,2].

Concerning the various polymers reported in literature and overviewed here, it is worth noticing that different behaviors mainly are obtained which depend on the chemical structure [3].

2. Experimental

2.1. Determination of macroinitiators decomposition constant

The determination of k_d consists of introducing a diphenyl picryl hydrazine (DPPH) dose into a given quantity of active oxygen $T(0^\circ)$ at a given time of an ozonised PVDF sample maintained at a temperature $T(0^\circ\text{C})$. For this, we have prepared a DPPH solution in the DMFF at $15.4 \times 10^{-5} \text{ mol l}^{-1}$ and containing a mass (m) of ozonised PVDF. The solution was heated at different temperature (60, 70, 80 and 90°C) for a period of time t_∞ . To monitor the reaction as a function of time, small quantities of the product (5 cc) were taken. These quantities were first soaked in liquid nitrogen then diluted in (25 cc) of isopropanol in order to precipitate the PVD. The filtrates obtained were then dosed by calorimetric at 520 nm. By using a calibrated curve made previously [4–6], we calculated the instantaneous values of $T(0)$.

3. Results and discussion

In order to distinguish various ozonised samples and to determine their activation rates, we have managed to put forward a

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Table 1
Results obtained during the ozonisation of polyethylene (PE).

Time (min)	Peroxides rate present in the polymer ($\times 10^5 \text{ mol g}^{-1}$)		
	Temperature: 20 °C	Temperature: 40 °C	Temperature: 50 °C
30	–	3.3	4.75
60	0.8	5.0	6.25
90	1.6	–	–
120	2.0	6.1	7.75

method that allows undertaking qualitative doses of peroxides and hydroperoxide formed during treatment by ozone. For this, two methods were applied N doses by iodometry and one dose by calorimetry.

In our case, we used powders whose particles diameter is between 100 and 300 μm that can be easily obtained by cryogenic crushing.

3.1. The study of polyethylene (PE)

This investigation is related to the most interesting polymer. Many grades of polyethylene were possible, however we decided to choose only one PE of fluidity index (FI) equals to 70 because samples with higher FI index have weaker softening temperature.

These tests show that the maximum concentration that can be achieved on this kind of polyethylene is $8.0 \times 10^5 \text{ mol}$ of the peroxide of polymer at a temperature of 50 °C (Table 1).

Longer periods of time lead to a yellow colour and degradation. The short periods of time less than 30 min have not been considered since at the end of the reaction, the reactor was washed during 20 min using air flow in order to eliminate residual absorbed ozone. Similar studies carried out by Sarraf [7] on another type of polymer in a bigger reactor show that:

At low temperature, the ozonised product contains 60% of hydroperoxides, however for higher temperatures (i.e. 50 °C), this concentration decreases to a half for an ozonised polyethylene, the value of the Mn starts by decreasing (from 17,700 to 15,400) for a concentration of $1.6 \times 10^{-5} \text{ mol}$ of peroxides g^{-1} then increases if the concentration reached $7.5 \times 10^{-5} \text{ mol}$. This corresponds to a chain cuts at the beginning of the reaction (peroxides cut) then at the start of reticulation in due course or the formation of inter-molecular peroxides.

This study allows synthesising several grafted copolymers used as emulsifying agent.

3.2. The study of poly(vinyl chloride) (PVC)

This was exposed to same ozonisation test, carried out under similar conditions and with a product free from any stabilising, plastifying or any other additive. A similar study has been carried out by Castaneda et al. [8] but with different working conditions, giving below:

Ozone concentration = 16 g/h; pressure = 6 bar.

The values obtained show that we can achieve very high rates of peroxides functions than those obtained in the case of PE (Fig. 1).

The rate of $27.1 \times 10^{-3} \text{ mol}$ of total peroxides g^{-1} of polymer is the maximum value that can be reached since beyond this, PVC degrades, which ends by carbonisation and a form of compact mass. As a result, we have followed the proportioning of the overall peroxides rate that exists in the ozonised PVC sample. These results show that at 18 °C, the concentration of peroxides and hydroperoxides functions decreases slowly within a larger time scale, these results are close to those obtained by Michel and Monnet [9] in the case of polypropylene for which the concentration decreases significantly then increases subsequently and slightly, the same researchers,

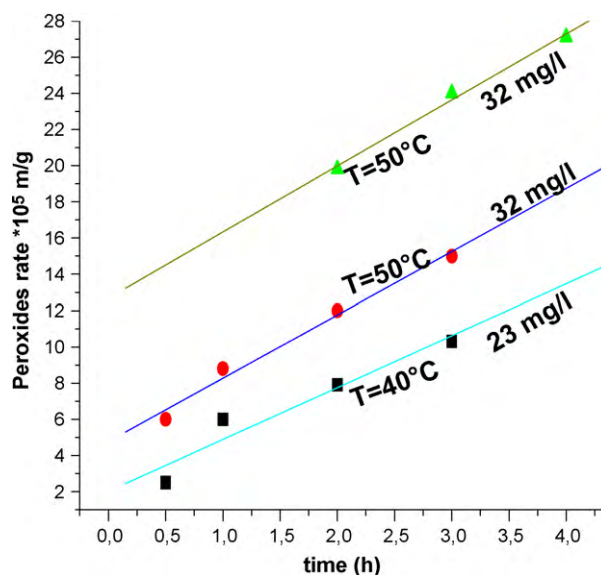


Fig. 1. Results obtained during the ozonisation of PVC.

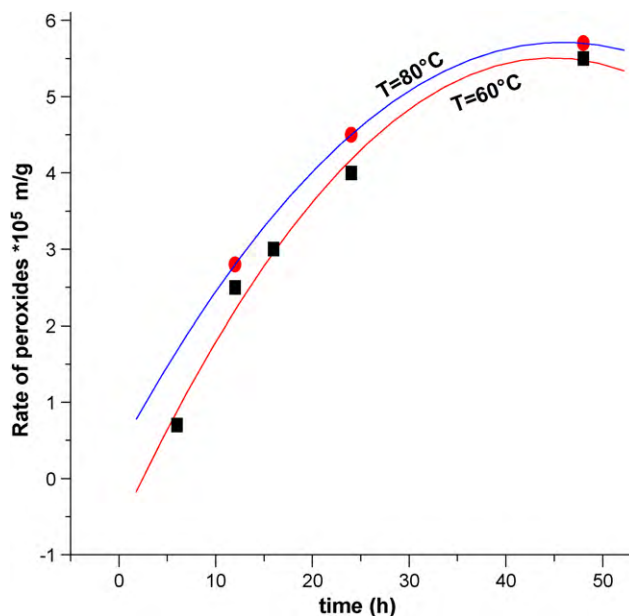


Fig. 2. Results obtained during the ozonisation of PVDF.

on the other hand, have studied the products of decomposition of ozonised PVC and showed that diacids are mainly obtained.

3.3. The study of poly(vinylidene fluoride) (PVDF)

In parallel to the work carried out on two polymers with weak oxidation resistance, we have considered the case of a very stable polymer PVDF.

The results obtained show that we can get very weak activation material even after a long time exposure [4,10]. Also, an overall peroxide rate of about $5.5 \times 10^{-5} \text{ mol g}^{-1}$ is obtained at 60 °C in 60 min and at 80 °C in 120 min, respectively (Fig. 2). It is obvious to notice the difference in the behaviour between basic polyolefin (PE) and chloride polyolefin (PVC) on one hand and a fluoride polymer, on the other hand.

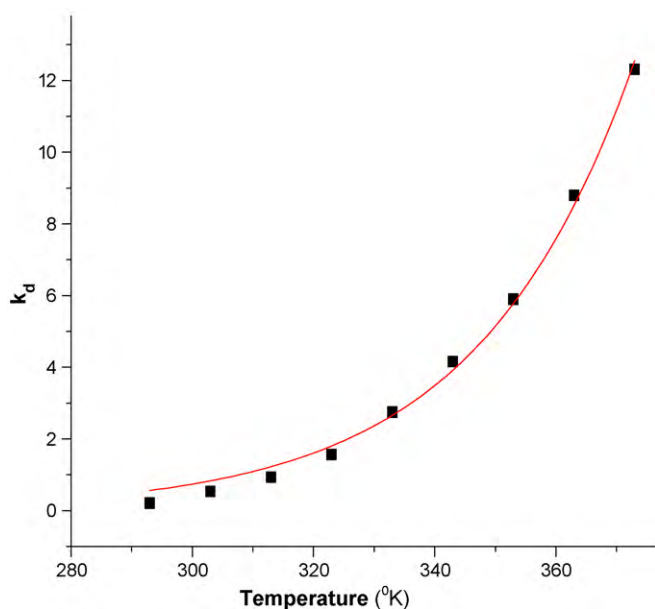


Fig. 3. Effect of the k_d on the temperature.

3.4. Kinetic study of different copolymers

Half-lifetimes of active species at different temperatures have been deduced also from Fig. 3 using the following relation:

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

Table 2 summarises the k_d values at different temperatures and the corresponding half-lifetimes.

We notice that the half-lifetimes ($t_{1/2}$) at room temperature is around 9 h, which is relative by short that allows deducing that the storage in the long term of ozonised PVDF remains impossible. To check this, we introduced doses of DDPH into ozonised PVDF and kept it at room temperature in open atmosphere. After 10 days we noticed a reduction in the rate of active oxygen of the order of 8% in comparison with the initial rate [11]. It can be deduce that the high values of k_d can be explained by the fact that the thermal decomposition is made easy by the presence of DDPH or when the decomposition of ozonised PVDF occurs in absence of a radical detector (DDPH) but in the presence of oxygen from open atmosphere, the latter reacts with the formed radicals to give again peroxide functions and hydroperoxides, it is interesting to consider the similar results obtained by Sarraf et al. [12] in the case of low density polyethylene (EPLD):

- High values of k_d .
- Short half-lifetimes.
- Activation energies of the same order of magnitude ($E_a = 52.5 \text{ kJ mol}^{-1}$).

We can conclude that although the activation energy of ozonised PVDF is low in comparison with that of ozonised (EPLD), the species obtained are thoroughly identical, also, for (EPLD), the ozonised

Table 2

The determination of half-lifetimes at different temperature.

	T (K)									
	293	303	313	323	333	343	353	363	373	
$t_{1/2}$ (h)	9.10	3.56	2.00	1.20	0.70	0.46	0.32	0.20	0.15	
$-\ln k_d$	10.75	0.54	0.93	1.56	2.75	4.16	5.90	8.80	12.31	

Table 3

Mass grafting of styrene on the PVDF or a reaction time of 14 h and a PVDF/S mass ratio = 1 and variation of resisting torque of ozonised PVDF during styrene grafting: 1—non-ozonised PVDF+S; 2—ozonised PVDF; 3—ozonised PVDF+S at 130 °C; 4—ozonised PVDF+S at 110 °C.

Temperature (°C)	$T(0) (\times 10^5 \text{ mol g}^{-1})$	ζ (%) molar	
		1st method (%F)	2nd method (%C; %H)
70	2.8	7	7.2
70	4	8.4	8.5
80	2.8	6.2	6.2
80	4	7.6	7.6
110	2.8	13.5	13.85
110	4	16.6	16.5
130	2.8	11.8	12
130	4	15.6	15.6

PVDF can be stocked at room temperature for several days without losing significantly its activity.

3.5. Synthesis of copolymer poly(VDF-g-S)

The grafting of the styrene (S) was carried out in mass and in solution, in both cases the cancelling of the homopolymer (PS) was made by washing in acetone. The quantity of grafting styrene is found by a basic analysis of carbon, hydrogen and Fluor, applying the two methods to calculate the grafting rate previously described. The results of mass grafting and solution grafting rates are shown in Table 3.

We can notice that in solution or in mass, the grafting rate increases with active oxygen rate of activated PVDF when the reactional temperature is reduced.

As far as the restoring remote torque monitoring, during the grafting reaction is concerned, we notice similar features as that of MMA grafting [13], that is a torque increase with reactional time then it reaches steady state when total grafting is reached. This happens in 30 min of reaction at 130 °C. Whereas this happens only in 70 min at 110 °C. As in the case of grafting of MMA on PVDF, the reaction carried out in mass leads to better efficiency rates than that carried out in solution and this almost in a ratio of 2.

3.6. Synthesis of copolymer poly(VDF-g-MAGLY)

The methacrylate of glycidyle (MAGLY) has been also grafted in mass and solution.

The homopolymer (PMAGLY) is separated from copolymer by washing the latter in a homopolymer solvent (Acetone) and the quantity of grafted monomer was determined from the basic analysis of C, H and F elements contained in the synthesised copolymer. The results obtained are summarised in Table 4. We notice that in both cases, MAGLY grafting leads to important rates (up to 50% for mass grafting and 20% for solution grafting) in comparison to other monomers considered and that mass grafting led to a reticulate.

3.7. Synthesis of copolymer poly(VDF-g-AA)

The reaction of acrylic acid (AA) grafting was carried out in mass and in suspension. The suspension grafting was made in water

Table 4Grafting of MAGLY and acrylic acid (AA) ozonised PVDF containing 4.2×10^5 mol of peroxides per gram and for a ratio of PVDF/MAGLY = 1.

Grafting method	T (°C)	ζ (%) molar		ζ (%) molar	
		1st method (%F) [MAGLY]	2nd method (%C; %H) [AA]	1st method (%F) [AA]	2nd method (%C; %H) [MAGLY]
In solution	60	21.0	–	–	21.3
	80	16.0	–	–	16.0
In suspension	70	–	13.0	13.0	–
	80	–	12.3	12.5	–
In mass	90	51.0	12.4	12.0	51.2
	110	48.0	11.0	11.6	47.8

acrylic acid mixture to which small quantities of sulphate and iron were added in order to prevent further formation of PPA homopolymers [14,15]. The process of grafting acrylic acid in mass is the same as that of MMA grafting and styrene. In both cases of grafting, the quantity of grafted acid was determined by analysis of C, H and F elements on the treated copolymers. The results obtained are summarised in Table 4. In this case, no significant change was noticed in the grafting rate with temperature change. We notice equally that regardless of the process of grafting in mass or in suspension; the grafting rates obtained are similar. These observations show a particular behaviour of acrylic acid during its grafting and this in comparison with styrene and methacrylate of methyl.

In fact, regardless of the temperature and grafting mode we obtain a grafting rate near 12%, this is total at 110 °C in the first 35 min whereas, it is total in 80 min at 90 °C.

We notice that the ratio of PVDF homopolymer, the solubility of copolymer (PVDF-g-AA) in the DMF at room temperature is increased by about 55 g l^{-1} .

4. Conclusion

We have studied the polymerisation of different monomers initiated by ozonised PVDF. We have determined the decomposition constant of macroamorcors at different temperatures and their different half-lifetimes. On one hand, we have shown that this reaction satisfies the first order reaction rules and that the values of k_d

obtained are of the same order of magnitude as those found for the PE and the ozonised PVC at the same temperature.

We have deduced that “in mass” grafting technique beside its simplicity and its functioning and this with relatively short reaction times in comparison with those involved in grafting “in solution”. Finally, we notice the particular behaviour of acrylic acid, which in the contrary to all other monomers gives as good results in mass as in solution.

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