Melt Stabilisation of High-Density Film-Grade Polyethylene

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Summary: The thermoxidative degradation of a high-density polyethylene stabilised either with standard and novel kinds of antioxidants was examined at many different temperatures. The aim of this work was to investigate the degradation response (crosslinking or chain-breakage) on the polyolefin molecular structure in terms of low shear rate melt viscosity increment and oxidation induction time both studied through steady and dynamic shear flow tests performed in a rotational rheometer. Lactone type antioxidants, especially the one containing P-EPQ phosphite component, exhibit the lowest thermoxidative degradation at high temperatures. Vitamine E, used in blend with a phosphite, appears to be a good stabiliser only at 230°C, but at high aging time

Introduction

Thermomechanical and thermoxidative degradation of high density polyethylene have been studied[1-12] extensively.

Molecular weight increase and scission reactions occur simultneously and dependent from both temperature and unsaturation (vinyl end-groups)[1-3]. Rideal et al.[2] proposed a reaction scheme to explain changes in molecular weight following which, at high melt temperature (>290°C), decreases in melt viscosity and narrowing of molecular weight distribution were observed, while at lower melt temperatures, molecular enlargement (i.e. melt viscosity increase) appeared to take place in both shear and thermal degradation. The addition of phenolic antioxidant (free radical scavenger) raises the temperature at which net degradation response is observed[2,4]. The presence of oxygen significantly accelerates the degradation reaction. Thus, air present in an extruder triggers oxidation. Melt viscosity at low shear rate and under extensional deformation are significantly affected[5]. In the present work we consider the degradation of high density polyethylene at low shear rate thermomechanical stress. The influence of different type of stabilisers on the rheological behaviour of the resin was also investigated.

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Experimental

The material used is a high density polyethylene produced in a gas-phase plant with a chromium catalyst (Base Resin in Table 1). It has the following physico-chemical characteristics:

$\rho_{(T=23°C)}$= 0.9412 g/cm^3, $MFI_{(190°C/5kg)}$= 0.55 g/10', M_w= 195000, M_w/M_n= 17.6, [η]= 2.03 dl/g. All tests were performed on the HDPE stabilized by the formulations shown in Table 1. The additives (kindly supplied by CIBA) were dry blended with the polymer powder before extrusion. A different method was used to deposite Vitamine E, which has a viscous-oil appearance, in the compound preparation. The additives were solubilised in heptane; the heptane solution was then added to a base resin dispersion in hexane and mixed for one hour. After having stripped the solvents by means of a vacuum pump, the final resin formulation was dried under vacuum in an oven at 90°C for two hours.

Table 1- Material preparation

Material Code	Antioxidant Type	Quantity (ppm)	Antioxidant TradeName*	Antioxidant Composition	
Base Resin	-	-	-	-	
A	Phenol-Phosphite	3000	B911	Irganox 1076 : Irgafos 168	1: 1
B	Phenol-Phosphite-Lactone	3000	HP 2921	Irganox 1076 : Irgafos 168 : HP136	2: 3: 1
C	Phenol-Phosphite-Lactone	3000	XP 490	Irganox 1076 : Irgafos P-EPQ : HP136	3: 2: 1
D	Vitamine E – Phosphite	1800	-	Irganox E201 : Irgafos 168	1: 5

* CIBA

The base resin and the compounds were processed using a Clextral co-rotating twin-screw extruder having L/D= 36 and D= 25 mm. All the extrusion were performed under air atmosphere; the temperature profile used was 150, 200, 210 and 220°C, the rotational speed was 400 rpm and the flow rate was 6 kg/h.

The rheological behaviour was studied using a rotational rheometer for dynamic time sweep tests in shear flow regime and for steady state tests to determine low shear rate viscosity. The time sweep tests, i.e. the complex viscosity vs. time, were carried out at different temperatures (170-270°C), using a Rheometrics Dynamic Spectrometer (RDS), version 800, equipped with dynamic parallel plate 25 mm radius. An evaluation of molecular weight modification was

obtained via steady state rate sweep tests at 230°C using the same rheometer equipped with 25mm radius and 50 μm gap cone and plate.

Results and Discussion

The rheological investigation has shown that thermo-mechanical degradation, studied by multiple passes through an extruder, is negligible.

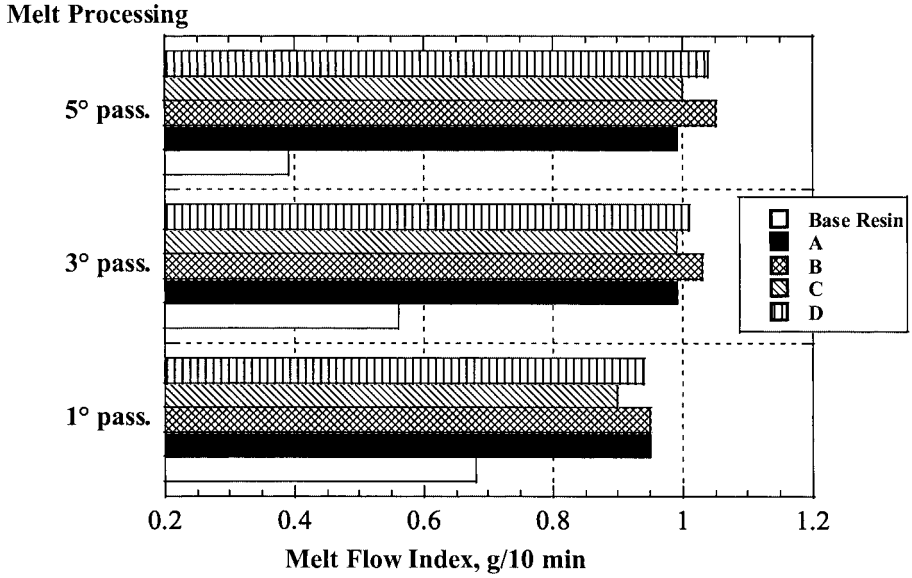

Figure 1. Melt processing stability for the base resin and the blend.

The behaviour of $MFI_{190°C/5kg}$ as a function of the number of passes through a twin screw extruder (Figure 1) indicates that, except for the base resin for which a significant MFI decrease is observed, the other blends exhibit a small decrease in viscosity such that thermo-mechanical degradation can be considered negligible. To separate the effect of thermo-oxidative degradation from thermo-mechanical one, tests were performed at different temperatures keeping a low level of deformation (2%) by means of a rotational rheometer. This kind of degradation was analysed via the increment of complex viscosity η^* as a function of time in a time sweep test. In Figure 2, η^* vs time curves are shown for the base resin at different temperatures (from 170 to 270°C). It is clear from Figure 2 that η^* is nearly constant at 170 and 190°C; higher temperatures are accompanied by large changes in viscosity. The increase in melt viscosity arises from a molecular enlargement, i.e. crosslinking

or long-chain branching, which is more important than chain scission event[2], as already shown in literature[2].

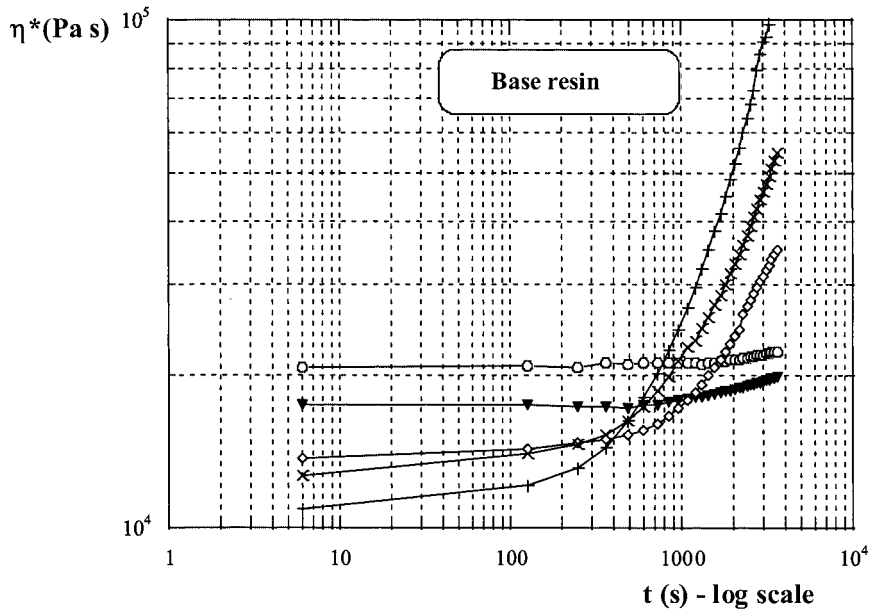

Figure 2. Dynamic complex viscosity vs time curves at different temperatures for the base resin; O =170°C;▼=190°C; ◇ =230°C; ×=250°C; +=270°C.

To better evaluate viscosity increments, the derivative of η* vs time was calculated. As an example, in Figure 3, dη/dt relevant to the data shown in Figure 2 at three different temperatures, are shown. The effect of increasing temperature on the plot is clear: at 190°C the values of dη/dt are small and constant, while at 230°C they reach a plateau value after about 1000 seconds. At the highest temperatur, a plateau was not detected over the time interval investigated.

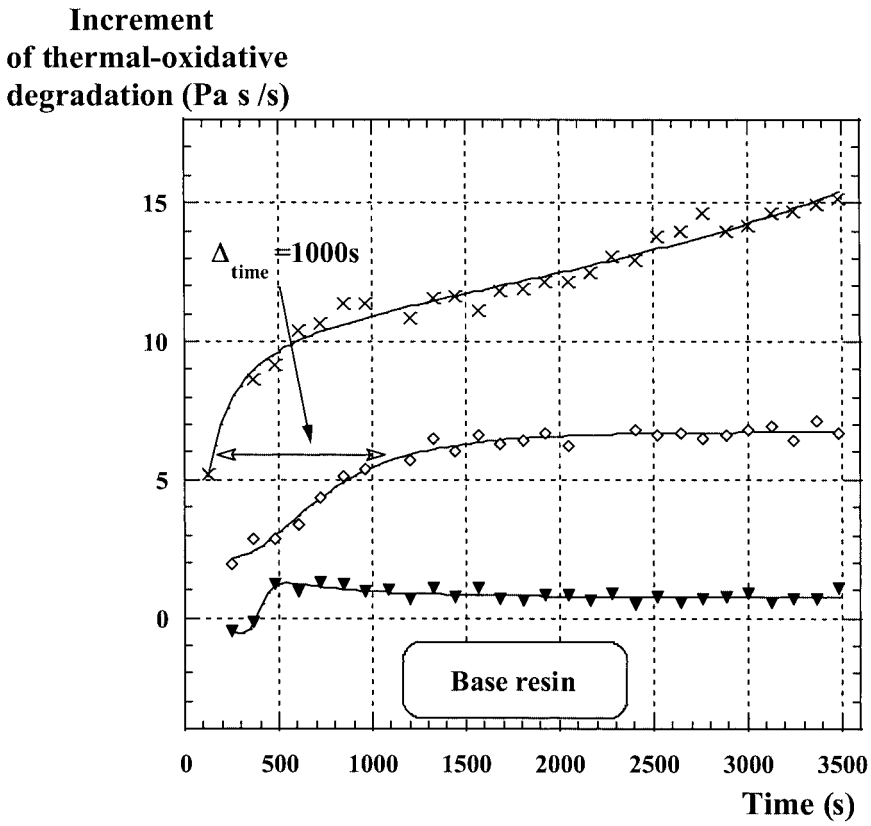

Figure 3. Derivative of complex viscosity (dη/dt)vs time at different temperatures for the base resin: ▼=190°C; ◇ =230°C; ×=250°C.

Moreover the time taken to observe a viscosity increment, and subsequently, to have a structure modification, is lower as the temperature increase. For example, an increment from 230°C to 250°C leads to a reduction of 1000s to reach the same increment of thermal-oxidative degradation (see Figure 3). The same approach was used to evaluate the effect of additives on melt stabilisation of the base resin. Figure 4(a-d) show the increment of thermal-oxidative degradation as a function of time at 190, 230, 250 and 270°C, respectively. In each figure the base resin curve is shown alongside curves obtained with resins A, B, C and D. It is clear from these figures that the presence of additives reduces the extent of changes in thermal-oxidative degradation (if any) at 190°C (Figure 4a) with respect to the base resin. At 230°C, a typical temperature at which the resin is normally processed, the D blend shows lower induction times to viscosity increases.

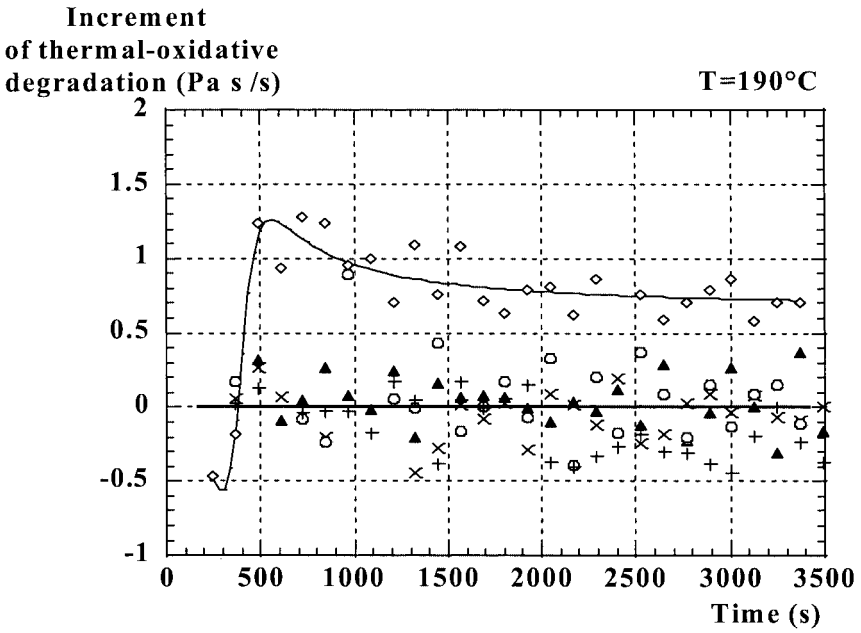

Figure 4a. Increment of thermal-oxidative degradation at 190°C: ◇ =Base Resin;▲ =Blend A; ×=Blend B;○ =Blend C; +=Blend D.

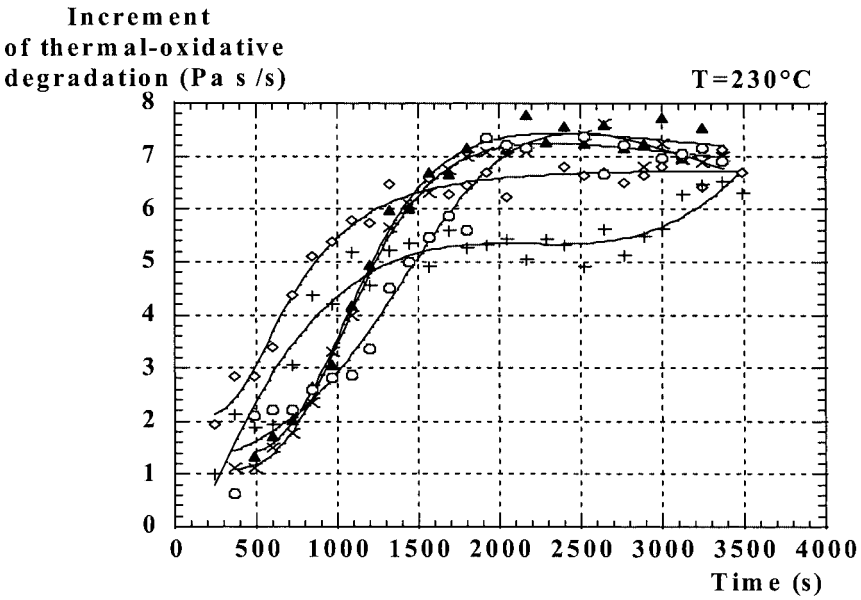

Figure 4b. Increment of thermal-oxidative degradation at 230°C; legend as in Figure 4a.

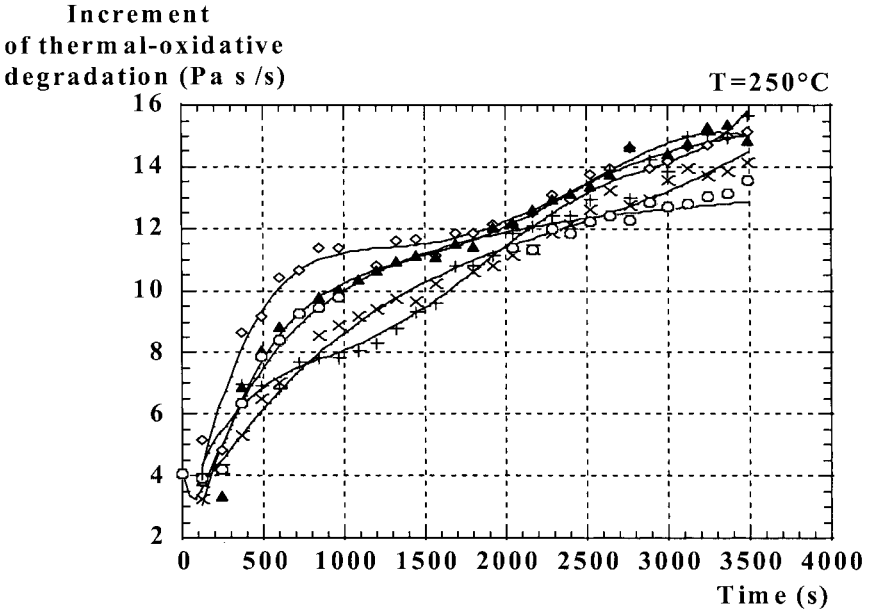

Figure 4c. Increment of thermal-oxidative degradation at 250°C; legend as in Figure 4a.

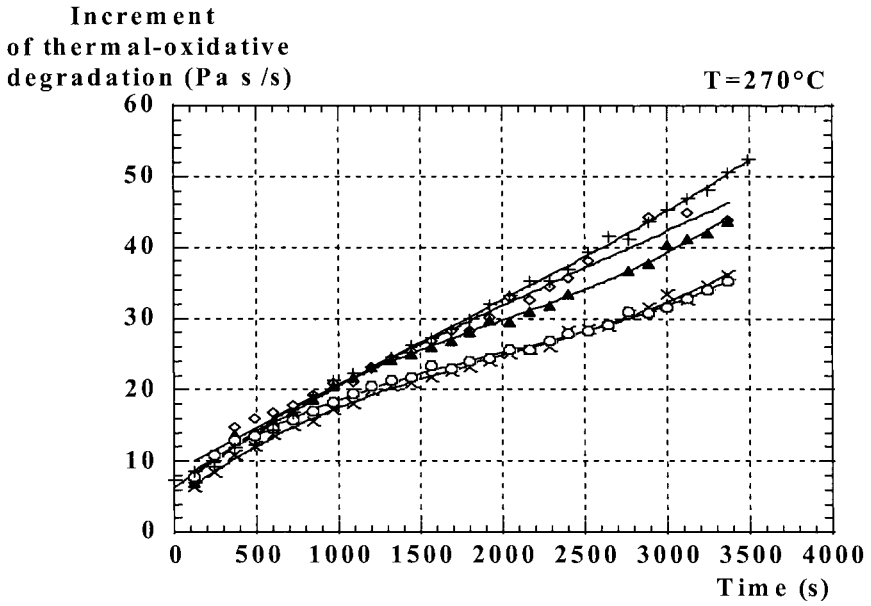

Figure 4d. Increment of thermal-oxidative degradation at 270°C; legend as in Figure 4a.

It is clear from Figure 5 that the time taken by blend D to show a 20%increase in viscosity is about 1000 s. This time is higher than that of the base resin induction time (800 s) but is much lower than what observed for the other antioxidants (blends A, B and C) which show an induction time of about 1400 s. Moreover at 230°C (Figure 4b), blend D shows thermal degradation that begins at lower times but appears to proceed at a lower rate at intermediate times (1500-3000 s). The same behaviour can be recognised also at 250°C (Figure 4c), albeit shifted to shorter times. The smaller increment of thermal-oxidative degradation is exhibited by blend D between 1000 to 2000 s, while at longer times the lactone-type antioxidants, B and C, appear to behave better as stabilizers.

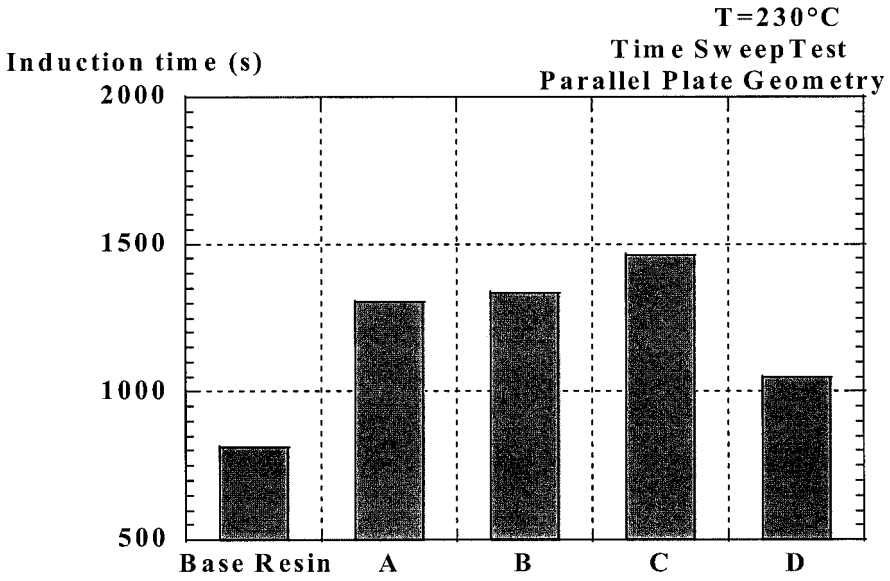

Figure 5. Induction time to have 20% viscosity increment at 230°C.

At 270°C (Figure 4d) we observe that the effect of Vitamine E (D blend) is negligible because of its well known volatility, while the difference between lactone-type antioxidant and B911 effect is more pronounced. The effect of thermal-oxidative degradation on molecular structure can be seen through the determination of the viscosity η at low shear rate. The same specimens aged and tested in the dynamic test at 230°C were analysed in a cone and plate steady state tests. In Figure 6, the viscosity η at shear rate 0.01 s^{-1} was considered for different

times of aging (900, 1500 and 2400 s). The same test was also performed on the unaged material (indicated as 0 s in Figure 6).

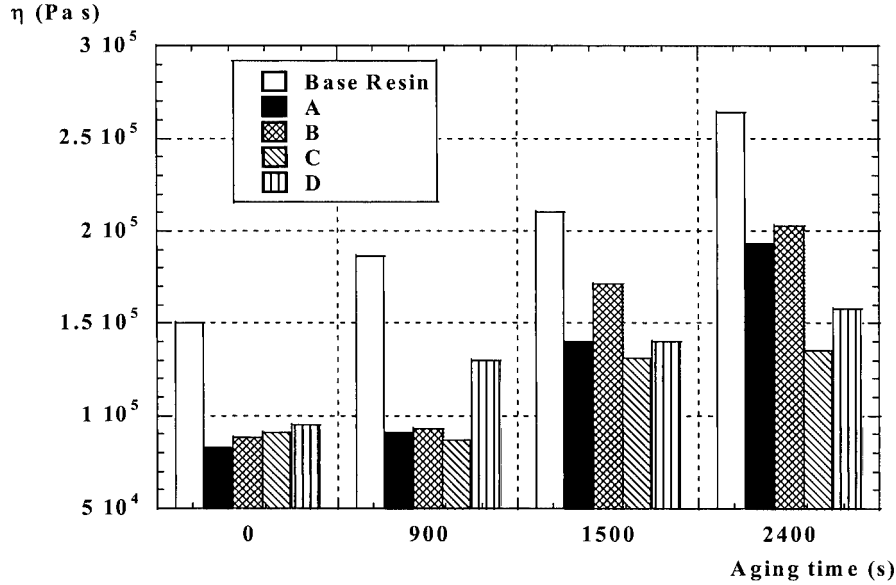

Figure 6. Viscosity (η) as a function of the aging time at shear rate 0.01 s^{-1} and 230°C from a cone and plate steady state test.

We can observe that Vitamine E (blend D) is less stable than other blends at 900 s. At higher times, blend C seems to behave better than others showing the lowest viscosity. This is probably due to the presence in XP 490 of P-EPQ phosphite-component which is more effective at this temperatures.

Vitamine E (blend D) instead shows the lowest rate of increment of viscosity with respect to aging time at least at this temperature. This behaviour can be easily correlated with the increment of thermal-oxidative degradation already shown in Figure 4b.

Conclusions

The experimental data reported in this work confirm that the calculation of derivative of complex viscosity as a function of time is a good quantitative method to evaluate the thermal-oxidative degradation of polyolefines. This type of degradation has an obvious effect on the molecular structure, as can be seen from a melt viscosity increase at very low shear rate. The following observations emerge from the present study.

Thermal-oxidative degradation at high temperatures is lower for blends (B and C) containing lactone antioxidants

1. At 230°C, and at all aging times studied, the combination of the lactone antioxidant and P-EPQ phosphite brings about the smallest change (increment) in viscosity at very low shear rate, i.e. the lowest increase in molecular weight
2. Vitamine E, at least in the blend used in this work, seems to be a good antioxidant only at certain temperatures (230°C) and time of exposure to the oxigen ($1200<t<2500$).

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