THERMAL CHARACTERIZATION OF UHMWPE STABILIZED WITH NATURAL ANTIOXIDANTS

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This work presents a study of the thermal degradation of ultra-high molecular mass polyethylene (UHMWPE) stabilized with natural (α-tocopherol and carvacrol) and synthetic antioxidants. Thermogravimetric analysis in dynamic mode was used to determine the apparent activation energies of different samples. The stabilization of UHMWPE with low concentrations (around 0.3%) of α-tocopherol is enough to obtain an efficient thermal performance of the polymer. Carvacrol is also a good stabilizer for UHMWPE, but at higher concentration than in the case of α-tocopherol. The comparison of apparent activation energy between samples with natural and synthetic antioxidants in similar concentration shows that α-tocopherol is a better stabilizer in terms of their thermal performance.

Introduction

It is well known that many different additives, such as plasticizers, antioxidants and ultraviolet (UV) light absorbers, are used to modify and take full advantage of the unique properties of polymers. The type and amount of these additives influence the processing and longevity of fabricated products by providing the necessary properties and protection during manufacturing and end use.

One of the requirements of the materials used in contact with food is a high resistance to oxidation, in order to give a real protection against oxygen to foodstuff. Therefore, compounds with antioxidant character should be added to polymers used in food packaging. Traditional antioxidants are synthetic compounds, mainly phenol derivatives, and in some cases they may change organoleptic food quality and even promote toxicity in case they migrate [1]. The use of natural antioxidants is encouraged in these materials by their similar stabilization properties as well as their non-toxic character. α-tocopherol is a compound with very low toxicity and no harmful effects to foodstuff. The bioactive form of vitamin E, α-tocopherol, was shown to be extremely effective antioxidant for plastics and rubbers, e.g. melt processing conditions in polyolefins [2–4], under long term storage conditions in polybutadiene [5] and fatiguing conditions in natural rubber [5]. It has been stated that the concentration of α-tocopherol needed to yield an efficient stabilization of polymers is very low [6], even at a lower level

than the stabilization afforded by some of the best synthetic hindered phenol antioxidants. Although some amount of stabilizer is consumed during processing, a significant amount may remain in the final material. There are other natural compounds, such as carvacrol [7], thymol, carnosic acid [8], which are known to exhibit antioxidant activity.

Thermal degradation is responsible of serious damage to many polymeric materials during processing and use under high temperature conditions. Therefore, an accurate control of the processing and working conditions of any polymeric system is very important to get a material with good properties and no degradation. Furthermore, a kinetic study of thermal degradation provides useful information for the optimization of the polymer processing [9–11].

Dynamic thermogravimetric analysis (TG) has shown good potential to study the thermal decomposition of polymeric materials [12, 13]. One of its main advantages is the high reproducibility of results in dynamic mode that assures the calculation of precise kinetic parameters. However, classical kinetic methods are being questioned during the last years [14, 15] as it should be considered that the proposed models are generally based on over-simplifications of the chemical reactions involved in the degradation, especially the absence of oxygen [11].

A lot of efforts have been dedicated to the computation of the apparent activation energy of the thermal degradation of polymers, and some reported approaches have become a classic in the scientific litera-

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Table 1 Summary of the three approaches used for the determination of the apparent activation energy of the thermal degradation of polymers

Method	Equation	Plot
Friedman [16]	$\ln\left(\dfrac{d\alpha}{dt}\right)=\ln A + n\ln(1-\alpha)+m\ln(\alpha)-\left(\dfrac{E_a}{RT}\right)$	$\ln\left(\dfrac{d\alpha}{dt}\right)=f\left(\dfrac{1}{T}\right)$
Flynn-Wall [17]	$\Delta\ln\beta=-1.052\left(\dfrac{E_a}{R}\right)\Delta\left(\dfrac{1}{T}\right)$	$\ln\beta=f\left(\dfrac{1}{T}\right)$
Kissinger [18]	$\dfrac{E\beta}{RT_p^2}=An(1-\alpha)^{n-1}\exp\left(-\dfrac{E_a}{RT}\right)$	$\ln\dfrac{\beta}{T_p^2}=f\left(\dfrac{1}{T_p}\right)$

ture. The main parameters of the kinetic methods used in this work [16–18] are summarized in Table 1 and will be used in this research to analyze the degradation behavior of UHMWPE stabilized with different antioxidants. In the present work the following symbols are used: Apparent activation energy, E_a (kJ mol^{-1}); pre-exponential factor, A (min^{-1}); reaction orders, n and m; gas constant, R (8.31 J mol^{-1} K^{-1}); absolute temperature, T (K); time, t (min); degree of conversion, α, and heating rate, β (K min^{-1}).

It should be noticed that some of these approaches do not require the specification of the particular kinetic model for the computation of E_a.

In the present work the study of the thermal degradation of UHMWPE and the influence of the addition of natural and synthetic antioxidants has been carried out with comparison of thermal behavior of the non stabilized polymer.

Experimental

Materials and sample preparation

UHMWPE (ALCUDIA® C-20ORB, Repsol YPF, Spain) was used for the preparation of samples. Each of them consisted of 2 kg (approximately) of UHMWPE mixed with different antioxidants: (±) α-tocopherol 95% (Sigma-Aldrich Química, Spain) in four concentrations 0.1, 0.3, 1 and 2% in mass; carvacrol, 98% (Sigma-Aldrich Química, Spain) 1 and 2% in mass; octadecile 3-(3,5-di-*tert*-butyl-hydroxyphenyl)-propionate (Irganox 1076, Ciba Specialty Inc.) 1 mass% and 2,6-di-*tert*-butyl-4-methylphenol (BHT, Sigma-Aldrich Química, Spain) 1 mass% in separate samples. In addition, a control sample (pure UHMWPE) without the addition of any amount of antioxidant was also prepared. The natural antioxidants were dissolved in ethanol (Merk KgaA, Germany) before their addition to the polymer.

Polymer and additives were mixed in an orbital mixer during 20 min. Then, each mixture was extruded in a twin-screw extruder operated at 25 and 22 rpm at feeding (MD 30 Bausano, Italy) with seven temperature zones. These temperatures were set at 120/130/150/150/155/160/160**°C**. After the extrusion process, the samples were pelletized and thermally analyzed.

Thermogravimetric analysis

Dynamic degradation measurements were carried out using a Mettler Toledo TGA/SDTA 851 instrument (Schwarzenbach, Switzerland). Dynamic tests were run at different heating rates, i.e. 2, 5, 10, 15, and 30°C min^{-1}, from 30 to 700°C. Each test was carried out in nitrogen environment (flow rate 30 mL min^{-1}) to guarantee the constancy of atmosphere for the whole test. Samples were accurately weighed, (between 5 and 6 mg), in a standard aluminum pan without any previous treatment.

Results and discussion

Thermal degradation of UHMWPE stabilized with α-tocopherol

TG data for all samples were obtained in the standard form of mass loss percentage as well as their derivatives as a function of temperature. One example (for the sample with 0.3 mass% α-tocopherol) is shown in Fig. 1 for all heating rates. As expected, the shape of curves is quite similar and the TG curves are shifted
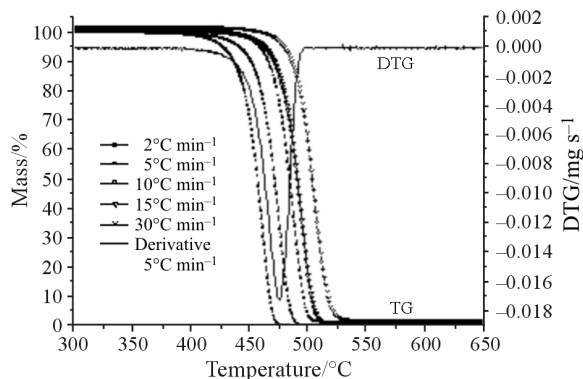

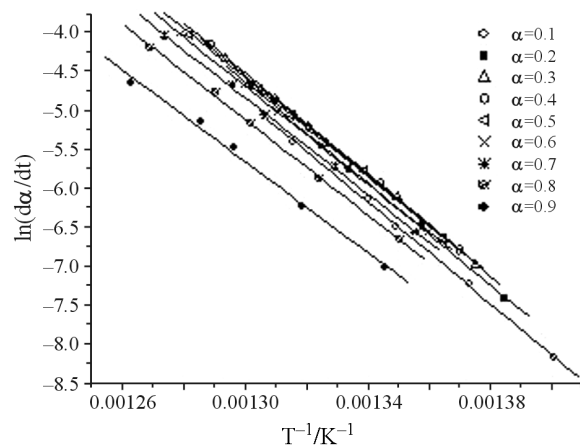**Fig. 1** TG and DTG curves for UHMWDPE-α-tocopherol (0.3 mass%)

Fig. 2a Application of Friedman method to UHMWPE stabilized with α-tocopherol (0.3 mass%)
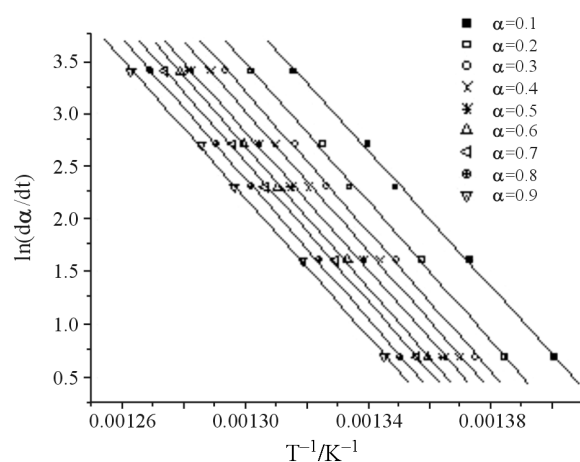

Fig. 2b Application of Flynn-Wall method to UHMWPE stabilized with α-tocopherol (0.3 mass%)

to higher temperatures at higher heating rates. The temperature for maximum degradation in each test can be easily calculated from TG curves. The thermal degradation of all stabilized and non stabilized samples appear to be a one-step reaction represented by a single peak as usual in all polyethylenes.

The calculation of kinetic parameters for the thermal degradation was carried out by using two mathematical methods previously indicated (Table 1). Figure 2a shows the results for the application of the isoconversional Friedman method to UHMWDPE-α-tocopherol (0.3 mass%). A similar plot was obtained by application of the Flynn-Wall method (Fig. 2b).

The linearity of these plots ($r^2 > 0.99$) for every single value of α from 0.1 to 0.9, obtained from dynamic tests at different heating rates, suggests the validity of both approaches for the whole range of temperatures (30–700°C) used in this study. It is to note that both methods can be applied from the very beginning to the end of the conversion degree range. This is

remarkable and caused by the high homogeneity of samples, indicating that the processing method was adequate for this kind of samples.

The reason of the selection of isoconversional Friedman method is the lower amount of simplifications and assumptions from the basic kinetic equation to allow the calculation of the apparent activation energy as a function of the reaction degree [16].

Similar plots can be obtained for all samples including non-stabilized UHMWPE and, consequently, E_a values can be calculated for each conversion degree between α=0.1 and α=0.9. The average value for E_a after the application of the two kinetic methods used in this work was calculated and the results obtained are shown in Table 2. As we could see, the obtained value is higher in those samples stabilized with α-tocopherol but only after the addition of concentrations 0.3 mass% or higher. Those samples stabilized with α-tocopherol 0.1 mass% did not show significant changes in E_a value. Moreover, it can be observed that there are not apparent differences in E_a values after the addition of α-tocopherol 0.3, 1 and 2 mass%. This is very important from the practical point of view, as it seems that the maximum stabilization from the addition of α-tocopherol is obtained at concentrations as low as 0.3 mass% without any further improvement after the addition of higher amounts of antioxidant. This will result in a save of antioxidant (and consequently of money) for those formulations of UHMWPE stabilized with α-tocopherol.

Table 2 Apparent activation energies for the thermal degradation of the non-stabilized and α-tocopherol-stabilized materials

Material	E_a/kJ mol^{-1}	
	Friedman	Flynn-Wall
Non-stabilized	237.0±4.0	234.5±8.9
α-tocopherol 0.1%	224.6±17.2	209.6±14.2
α-tocopherol 0.3%	260.9±8.2	273.6±3.5
α-tocopherol 1%	264.7±5.9	279.3±5.1
α-tocopherol 2%	255.3±13.9	274.2±5.4

Thermal degradation of carvacrol stabilized UHMWPE

Dynamic TG curves at different heating rates of samples stabilized with carvacrol (1 and 2% in mass) show no significant differences with those samples stabilized with α-tocopherol, with a one-step degradation process observed for all samples.

A kinetic study was also performed for these samples, as indicated in the previous section. Table 3 shows the E_a values for carvacrol-stabilized and

Table 3 Apparent activation energies for the thermal degradation of the non-stabilized and carvacrol-stabilized materials

Material	E_a/kJ mol^{-1}	
	Friedman	Flynn-Wall
Non-stabilized	237.0±4.0	234.5±8.9
Carvacrol 1%	242.7±14.3	244.8±10.5
Carvacrol 2%	263.1±4.8	258.0±12.2

non-stabilized UHMWPE. It can be observed that in general, carvacrol can be also considered an adequate stabilizer for UHMWPE as the apparent activation energies for stabilized samples are higher than their value for the non-stabilized sample. However, it must be noted that the amount of carvacrol needed for an efficient stabilization is higher than in the case of α-tocopherol. Stabilization is clearly observed only at concentrations as high as 2%. In addition, this antioxidant has the disadvantage of a very strong phenolic smell, even after mixing with the polymer. This fact is indicative of a certain release of antioxidant from the material and the consequent loss of properties. This leads to a clear drawback for its use as stabilizer of food contact materials. In summary, there are economical and sanitary reasons to consider α-tocopherol a better antioxidant for all food packaging applications.

Comparison between samples stabilized with natural and synthetic antioxidants

The real performance of these natural antioxidants in their use as thermal stabilizers for UHMWPE comes from a comparison with samples formulated with synthetic antioxidants usual in polymer industry and prepared in the same way. A similar TG study was carried out and curves showed the same one-step degradation process as expected.

The value of the temperatures of maximum degradation at different heating rates could be used to evaluate the apparent activation energy by Kissinger method. By using this method $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ is a straight line with slope E_a/R, where T_p is the temperature of maximun degradation. Table 4 shows the values of E_a determined by Kissinger method.

Results observed with this method are in agreement with those obtained with Friedman and Flynn-Wall methods (Tables 2 and 3) showing the validity of this approach for these materials. We observed that the addition of 0.1 mass% α-tocopherol does not increase the E_a value. On the other hand, the addition of just 0.3 mass% α-tocopherol seems to have a significant influence on the stability of the system, without the necessity of higher concentrations (1 or 2 mass%). As re-

Table 4 E_a values obtained with Kissinger method

Sample	E_a/kJ mol^{-1}
Pure	234.6±18.6
α-tocopherol 0.1%	231.2±16.2
α-tocopherol 0.3%	272.7±3.3
α-tocopherol 1%	274.2±21.9
α-tocopherol 2%	268.2±7.2
Carvacrol 1%	251.1±11.1
Carvacrol 2%	263.8±4.2
BHT 1%	263.5±7.9
Irganox 1076 1%	262.3±24.5

Table 5 Apparent activation energies for all samples calculated with Friedman method

Sample	E_a/kJ mol^{-1}
Non-stabilized	237.0±4.0
α-tocopherol 1%	264.7±5.9
Carvacrol 1%	242.7±14.3
BHT 1%	263.2±2.0
Irganox 1076 1%	260.9±7.7

gards the carvacrol, we could see that high concentrations of this antioxidant are necessary for an efficient stabilization. We also observed that the stabilization obtained with α-tocopherol is similar or higher than that observed with synthetic antioxidants.

Table 5 summarizes the apparent activation energy for samples stabilized with 1% in mass of all natural and synthetic antioxidants. It could be seen that values obtained by applying Friedman method are similar for all samples, except in the case of 1 mass% carvacrol, which is a bit lower and similar to the value obtained for the non-stabilized sample. These results indicate that the degree of stabilization of α-tocopherol in UHMWPE is at least similar to stabilization obtained by the addition of synthetic antioxidants, which are extensively used in many applications with polyolefins. It must be also considered that our results are coincident with those reported by Al-Malaika [3, 6] for the stabilization of LDPE and PP with BHT and Irganox 1076. This is an indication of the validity of our approach to determine the thermal stabilization of UHMWPE with all antioxidants used in the present work.

Conclusions

Thermal degradation of UHMWPE stabilized with natural and synthetic antioxidants can be kinetically described in terms of the apparent activation energy (E_a) by using Friedman, Flynn-Wall and Kissinger

mathematical methods [19]. Results show that the addition of 0.3 mass% α-tocopherol yields a sufficient stabilization of UHMWPE, very similar to the stabilization obtained with higher amounts of antioxidant. This will permit to conclude that amounts as low as 0.3 mass% are enough to get the maximum stabilization for these samples. The addition of 0.1 mass% α-tocopherol seems to have no influence in thermal properties of the polymer. In addition, a visual inspection of samples with higher concentrations of α-tocopherol indicated a change in the colour of samples, as described by Al-Malaika [20]. Therefore, the recommended concentration of α-tocopherol in UHMWPE is 0.3 mass% with comparable results to the addition of synthetic antioxidants (BHT and Irganox 1076) at higher concentration. Carvacrol seems to be a good antioxidant for UHMWPE at high amounts but the high price and the eventual release of the additive from samples makes it not useful for food contact materials.

As a final conclusion, it is clear that α-tocopherol is a good alternative to the addition of synthetic antioxidants to polyolefins. However, in order to conclude if this concentration is the optimum for its use in HDPE for food packaging, other properties, such as degradation in an oxidative environment, pyrolysis, mechanical tests and migration should be studied. These studies will be carried out in the next future.

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