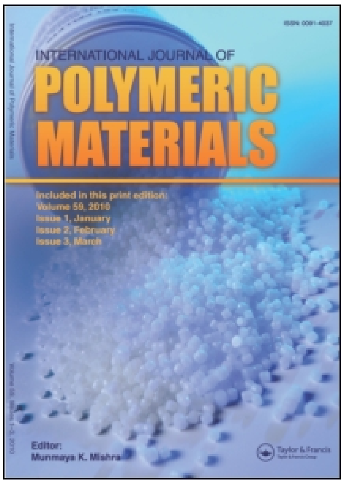

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Koleva, Dimitrina , Atanassov, Atanas and Nedelchev, Nedelcho(2008) 'Nonisothermal Degradation Kinetics of Ultra-High Molecular Weight Polyethene Composites Filled with Carbon or Aramid Fibers', International Journal of Polymeric Materials, 57: 9, 841 — 851

To link to this Article: DOI: 10.1080/00914030801963440

URL: http://dx.doi.org/10.1080/00914030801963440

International Journal of Polymeric Materials, 57:841–851, 2008

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030801963440

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The thermal degradation in static air of three types of composite materials based on ultra-high molecular weight polyethene with unmodified and modified carbon fibers or aramid fibers have been investigated under nonisothermal conditions at a heating rate of 10 K min^{-1}*. The Coats–Redfern method was used to determine the kinetic parameters. The analysis of the result obtained by the Coats–Redfern method shows that the thermal degradation process of these composites corresponds to a diffusion-controlled reaction (*D_5 *mechanism, three-dimensional diffusion described by Zhuravlev–Lesokhin–Tempelman equation). It was found that the composites with unmodified and modified carbon fibers or aramid fibers possess the highest thermal stability at 3 mass % fiber content. The activation energy, frequency factor and the changes of entropy, enthalpy and Gibbs energy for the active complex of the composites were also measured.*

Keywords: aramid fibers, carbon fibers, composite materials, kinetic parameters, ultra-high molecular weight polyethene

Received 17 January 2008; in final form 6 February 2008.

The authors wish to express their gratitude to Prof. K. Gjurova for the thermogravimetric analyses.

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INTRODUCTION

Polymer degradation of various polymers and composite materials (CM) based on them is known to be a very complex phenomenon comprising several elementary reactions which are difficult to analyze separately, and their quantitative contribution to the global degradation process is virtually impossible to assess. This is the reason why mathematical models are developed. A mathematical model for thermal decomposition reactions is useful for the understanding and verification of the validity of the assumptions implied by such reactions.

Data on the mechanism and kinetics and mechanism of polymer thermal degradation can be obtained from the TG-curves recorded under dynamic heating conditions. To achieve the proposed goal, it is necessary to use different mathematical methods which may predict the various kinetic parameters. These methods are: Horowitz–Metzger [1], Coats–Redfern [2], McCallum–Tanner [3], Madhusudanan–Krishnan–Ninan [4,5], Dharwadkar et al. [6], Reich–Stivala [7], classic differential model [8] and the analytical method [8].

Despite the great efforts devoted to the kinetics of the thermal decomposition of polyolefins in recent years, the authors found only one publication for thermal degradation of ultra-high molecular weight polyethene (UHMWPE) stabilized with natural and synthetic antioxidants at low (around 0.3%) concentrations [9]. Some authors have reported experiments with low-density polyethylene (LDPE) high-density polyethene (HDPE), and some composites based on them, but the values of the kinetic parameters vary widely from one publication to another [10–12]. According to Sinfronio et al. [10], the results obtained by the Coats–Redfern method showed that the model that best describes the process of thermal decomposition reaction in solid state LDPE and HDPE is the R_2 mechanism (phase boundary reaction), with activation energy for HDPE degradation at heating rates of 5, 10 and $20\,\mathrm{K\,min^{-1}}$ in steady flow of nitrogen being 202.36, 208.27 and $247.44\,\mathrm{kJ\,mol^{-1}}$, respectively. Other authors used the dynamic method [11]. The values of the activation energy of thermal destruction had been found to be 333.2–343.2 for HDPE and 187.5–199.1 $\mathrm{kJ\,mol^{-1}}$ for LDPE. Yet another publication on the activation energy of thermal degradation of HDPE in a nitrogen medium, determined by the Flynn and Wall methods, reported values of $238.4 \pm 3.7\,\mathrm{kJ\,mol^{-1}}$ [12].

In our previous work [13] we investigated the kinetic parameters and the possible reaction mechanism of the thermal degradation of UHMWPE and its CM with fiber monocrystals. It has been found that composites with fiber monocrystals degraded by two concurrent mechanisms (D_3 diffusion and A_1, F_1 mechanism, see Table 1), and

TABLE 1 Algebraic Expressions of Functions g(α) and f(α) and their Corresponding Mechanism

No.	Symbol	Name of the function	g(α)	f(α)	Rate-determining mechanism
I Chemical process or mechanism noninvoking equations					
1.	$F_{1/3}$	One-third order	$1-(1-\alpha)^{2/3}$	$(3/2)(1-\alpha)^{1/3}$	Chemical reaction
2.	$F_{3/4}$	Three-quarters order	$1-(1-\alpha)^{1/4}$	$4(1-\alpha)^{3/4}$	Chemical reaction
3.	$F_{3/2}$	One and a half order	$(1-\alpha)^{-1/2}-1$	$2(1-\alpha)^{3/2}$	Chemical reaction
4.	F_2	Second order	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$	Chemical reaction
5.	F_3	Third order	$(1-\alpha)^{-2}-1$	$(1/2)(1-\alpha)^3$	Chemical reaction
II. Acceleratory rate equations					
6.	$P_{3/2}$	Mampel power law	$\alpha^{3/2}$	$(2/3)\alpha^{-1/2}$	Nucleation
7.	$P_{1/2}$	Mampel power law	$\alpha^{1/2}$	$2\alpha^{1/2}$	Nucleation
8.	$P_{1/3}$	Mampel power law	$\alpha^{1/3}$	$3\alpha^{2/3}$	Nucleation
9.	$P_{1/4}$	Mampel power law	$\alpha^{1/4}$	$4\alpha^{3/4}$	Nucleation
10.	E_1	Exponential law	$\ln\alpha$	α	Nucleation
III. Sigmoidl rate equations or random nucleation and subsequent growth					
11.	A_1, F_1	Avrami-Erofeev eq.	$-\ln(1-\alpha)$	$(1-\alpha)$	Assumed random nucleation and its subsequent growth, n = 1
12.	$A_{3/2}$	Avrami-Erofeev eq.	$[-\ln(1-\alpha)]^{2/3}$	$(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth, n = 1.5
13.	A_2	Avrami-Erofeev eq.	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth, n = 2
14.	A_3	Avrami-Erofeev eq.	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth, n = 3
15.	A_4	Avrami-Erofeev eq.	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	Assumed random nucleation and its subsequent growth, n = 4
16.	A_u	Prout-Tomkins eq.	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$	Branching nuclei

(Continued)

TABLE 1 Continued

No.	Symbol	Name of the function	g(α)	f(α)	Rate-determining mechanism
IV. Deceleratory rate equations and Phase boundary reaction					
17.	R_1, F_0, P_1	Power law	α	$(1-\alpha)^0$	Contracting disk
18.	R_2, $F_{1/2}$	Power law	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Contracting cylinder (cylindrical symmetry)
19	R_3, $F_{2/3}$	Power law	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Contracting sphere (spherical symmetry)
V Based on the diffusion mechanism					
20.	D_1	Parabola low	α^2	$1/2\alpha$	One-dimensional diffusion
21.	D_2	Valensi eq.	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	Two-dimension diffusion
22.	D_3	Jander eq.	$[1-(1-\alpha)^{1/3}]^2$	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	Three-dimensional diffusion, spherical symmetry
23.	D_4	Ginstling–Brounshtein eq.	$1-2\alpha/3-(1-\alpha)^{2/3}$	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion, cylindrical symmetry
24.	D_5	Zhuravlev–Lesokhin–Tempelman eq.	$[(1-\alpha)^{-1/3}-1]^2$	$(3/2)(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion
25.	D_6	anti-Jander eq.	$[(1+\alpha)^{1/3}-1]^2$	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	Three-dimensional diffusion,
26.	D_7	anti-Ginstling–Brounshtein eq	$1+2\alpha/3-(1+\alpha)^{2/3}$	$(3/2)[(1+\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion,
27.	D_8	anti-Zhuravlev–Lesokhin–Tempelman eq.	$[(1+\alpha)^{-1/3}-1]^2$	$(3/2)(1+\alpha)^{4/3}[(1+\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion

incorporation of this filler can increase the thermal stability of the composite material obtained.

The main purpose of this work is to study the probable mechanism of degradation of UHMWPE composites with carbon or aramid fibers. The kinetic parameters of these composites were calculated by the Coats–Redfern method due to its wide applicability in the thermal decomposition of polymeric materials.

EXPERIMENTAL

Materials

UHMWPE with melt index 0.001 g/10 min (temperature 463 K, load 21 kg) and molecular weight 1.8×10^6 was used, product of Lukoil Neftochim Bourgas Co. The carbon fibers (CF) used had the following characteristics: diameter 7.5 μm, linear density 0.8 dtex, tensile strength 3900 MPa and elongation 3.3% (NCV, France). The aramid fibers (AF) used were Kevlar-49, produced by DuPont (USA), with the following characteristics: diameter 12 μm, linear density 1.61 dtex, tensile strength 1600 MPa and elongation 17.0%. For the preparation of the composites, CF and AF with aspect ratio L/D from 30 to 60 were used. The amount of fibers in the composite materials ranged from 0 to 6 mass%.

Preparation of Modified Carbon Fibers

Initial carbon fibers (unmodified CF) were subjected to thermal oxidation in air at 1073 K for 60 min and the products obtained were designated as modified CF.

Preparation of UHMWPE Composites and Materials Characterization

The homogenization and preparation of the composites based on UHMWPE with CF and AF have been described earlier [14]. The mass loss and the thermal properties of the CM obtained were measured using OD-102 derivatograph (Hungary) in static air at a heating rate of $10\,\mathrm{K\,min^{-1}}$. Alumina crucibles with an initial sample mass of 50 ± 1 mg were used.

The diameter of the single CF or AF and their length were determined on a scanning electron microscope BS 380 TESLA (Czech Republic) under regime of secondary electrons at acceleration of 20 kV.

Method of Coats–Redfern

The kinetic parameters of the thermal degradation of UHMWPE composites with carbon or aramid fibers were determined by applying the Coats–Redfern method.

The Coats–Redfern method [2] uses the equation

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{q_A^E} - \frac{E_A}{RT} \tag{1}$$

where T = sample temperature, A = pre-exponential factor, R = gas constant, q = heating rate, E_A = activation energy.

According to Eq. (1), the activation energies (E_A) and pre-exponential or frequency factors (A) for each g(α) function can be calculated at a constant heating rate from the fitting of $\ln g(\alpha)/T^2$ vs. $1/T$ plots. If the correct g(α) function is used, the plot of $\ln g(\alpha)/T^2$ against $1/T$ should give a straight line with a high correlation coefficient of the regression analysis.

The algebraic expressions of the functions in differential and integral form often used for thermal degradation during reactions in the solid state ($f(\alpha)$ and $g(\alpha)$), depending on the kinetic model, are reported in [15–17]. Table 1 presents the most common kinetics models and their algebraic expressions.

RESULTS AND DISCUSSION

Table 2 shows the main temperature characteristics of the UHMWPE composites obtained—initial temperature of degradation (T_d^i), temperatures at 10, 25 and 50 mass % mass loss (T_{10}, T_{25} and T_{50}), maximum rate of decomposition (T_d^{max}) and end temperature of

TABLE 2 Temperature Characteristics of UHMWPE Composites Containing Different Amounts of CF or AF

	Content of fillers, mass%								
	Unmodified CF			Modified CF			AF		
Characteristics*	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0
T_d^i, K	633	653	653	633	653	663	653	653	663
T_{10}, K	683	688	688	663	683	683	663	693	688
T_{25}, K	713	713	718	703	701	718	708	728	725
T_{50}, K	733	738	748	743	743	743	743	753	753
T_d^{max}, K	746	743	763	743	743	753	753	763	763
T_d^f, K	783	783	783	783	783	783	783	783	783

*T_d^i, T_{10}, T_{25}, T_d^{max}, and T_d^f of pure UHMWPE were assumed to be 653, 668, 703, 723, 728 and 765 K, respectively [13].

decomposition (T_d^f). More or less clearly distinguishable was the tendency of the values of these parameters (except for T_d^f) to increase along with the increase in the content of unmodified and modified CF and AF up to 6 mass%.

The E_A and A (Eq. (1)) for each g(α) function can be calculated at a constant heating rate from the fitting of $\ln g(\alpha)/T^2$ vs. $1/T$ plots. With the properly selected expression of the g(α) function, straight lines with high values of the linear regression correlation coefficient R^2 can be obtained. The slope of the straight line gives the value of E_A and the cut-off from the ordinate—the pre-exponential factor A.

Determining the mechanism of thermal degradation of the CM obtained with unmodified and modified CF or AF, the highest correlation coefficient ($R^2 = 0.9726$–0.9959) was observed for the D_5 diffusion mechanism according to the following formula (see Table 1):

$$\ln\frac{(3/2)(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}}{T^2} = \ln\frac{AR}{q_A^E} - \frac{E_A}{RT} \qquad (2)$$

The Zhuravlev–Lesokhn–Tempelman equation describes the kinetics of processes limited by the diffusion of the reagents/products through the layer of the forming product. It is usually applicable in studies on the kinetics of pyrolysis of organic and bioorganic materials in oxidative media. In these cases, oxygen should diffuse through the layer formed by pyrolysis products to the core of the initial substance while the gaseous products of the pyrolysis should diffuse back through the newly formed layer to the environment. In one case, for instance, the authors found that the pyrolysis of rice husks is limited by diffusion processes and is better described by the similar Ginstling–Brounshtein equation [18].

The values of E_A, R^2 and $\ln A$ for this mechanism calculated by the Coats–Redfern method are presented in Table 3. It can be seen that E_A had a maximum at 3.0 mass % contents of the three types of fillers used. This was probably due to the fact that at 1.5 mass % filler content of unmodified or modified CF or AF, the polymer structure had been disturbed before the fibers exerted their stabilizing effect. This effect can be observed as low as 3.0 mass % content of unmodified and modified CF or AF, which means that the materials containing 3.0 mass % unmodified and modified CF or AF possess higher resistance to thermal degradation. Besides, the activation energy of thermal degradation of these composites was significantly lower than that of the initial UHMWPE and its composites with inorganic filler of fiber monocrystals observed along the D_3 mechanism, 343.3 and 361.1–402.9 kJ mol^{-1}, respectively [13].

TABLE 3 Mechanism of Degradation and Kinetic Parameters of UHMWPE Composites Containing Different Amounts of CF or AF

Content of fillers, mass %	D_5 mechanism								
	Unmodified CF			Modified CF			AF		
	R^2	E_A, kJ mol^{-1}	ln A	R^2	E_A, kJ mol^{-1}	ln A	R^2	E_A, kJ mol^{-1}	ln A
1.5	0.9901	168.7	22.3	0.9788	123.3	14.0	0.9831	129.3	15.7
3.0	0.9914	209.9	29.3	0.9864	225.5	31.9	0.9903	170.5	22.1
6.0	0.9952	157.0	20.0	0.9726	184.8	24.7	0.9959	155.3	19.8

The relationship between E_A and A of heterogeneous reactions is often described by a compensation equation [16]:

$$\ln A = \ln k_{\text{iso}} + \frac{E_A}{RT_{\text{iso}}} \tag{3}$$

This equation implies the correlation of E_A, as a parameter influencing and indicating the system reactivity, with the parameters that compensate its influence (A and temperature interval in which the reactions take place).

The dependence of $\ln A$ vs. E_A for the composites based on UHMWPE with unmodified and modified CF or AF calculated along the D_5 mechanism is shown in Figure 1. The three linear dependencies obtained for the three types of composite materials confirmed the occurrence of the D_5 mechanism of thermal degradation for the composites.

The other kinetic parameters of the process can be calculated using the fundamental theory of the activated complex (transition state) and Eyring equation [19]:

$$k = \frac{e\chi k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{E_A}{RT}\right) \tag{4}$$

where χ = the transition factor, which is unity for monomolecular reactions, k_B = Boltzmann constant, h = Planck's constant, $e = 2.7183$ and $\Delta S^{\neq}$ is the change of entropy for the activated complex formation from the reagent.

Taking into account Eq. (4) and the pre-exponential factor from the Arrhenius equation, the following expression is obtained:

$$A = \frac{e\chi k_B T_P}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{5}$$

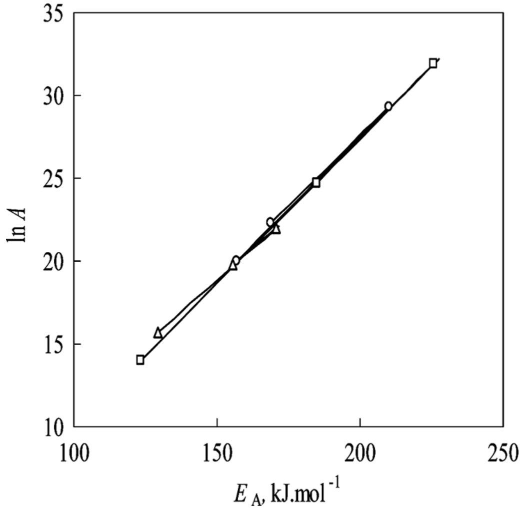

FIGURE 1 Dependence of ln A vs. E_A at thermal degradation of UHMWPE composites along mechanism D_5 with different contents of unmodified (○) and modified (□) CF or AF (Δ).

and $\Delta S^{\neq}$ can be calculated according to the formula:

$$\Delta S^{\neq} = R \ln \frac{Ah}{e\chi k_B T_P} \tag{6}$$

where T_P is the peak temperature from the DTG curve. Since

$$\Delta H^{\neq} = E - RT_p \tag{7}$$

the changes of the enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ for the activated complex formation from the reagent can be calculated using the well known thermodynamic equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T_p \Delta S^{\neq} \tag{8}$$

The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were calculated at $T = T_P$, since this temperature characterizes the highest rate of the process and, therefore, is its important parameter.

The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for UHMWPE and its composites with CF or AF calculated at the compositions rates used in the experiments are presented in Table 4.

It can be seen that $\Delta H^{\neq}$ also had a maximum at 3.0 mass % fiber content. The negative values of $\Delta S^{\neq}$ determine the higher degree of arrangement of the activated complex [20]. Table 4 shows also that

TABLE 4 Values of the Changes of Entropy, Enthalpy and Gibbs Free Energy of UHMWPE Composites at Different Contents of CF or AF

	D_5 mechanism								
	Unmodified CF			Modified CF			AF		
Content of fillers, mass %	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
1.5	162.5	−109.4	244.5	117.0	−173.5	248.3	123.1	−164.1	245.8
3.0	203.8	−51.1	241.6	219.4	−29.1	240.9	164.2	−111.1	248.4
6.0	150.7	−128.4	248.0	178.5	−89.7	245.7	149.9	−130.7	248.1

the positive values of $\Delta G^{\neq}$ obtained were quite close for the CM based on the three types of fibers at fiber content 1.5–6.0 mass %. It means that the processes of thermal degradation of CM obtained were not spontaneous.

CONCLUSIONS

The mechanism of thermal decomposition of composite materials based on ultra-high molecular weight polyethene with unmodified and modified carbon fibers or aramid fibers was studied by the Coats–Redfern method in static air. It was found that the D_5 mechanism describes well the thermal destruction of the composites. The activation energy, change of entropy, enthalpy and Gibbs energy of the three types of composites were calculated.

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