Polymer Bulletin 45, 531–538 (2001)

Polymer Bulletin

Application of different kinetic models for determining thermal stability of PA 66/HDPE blends

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Received: 2 March 2000/Revised version: 9 November 2000/Accepted: 10 November 2000

Summary

The thermal decomposition of Polyamide 66 (PA)/High-Density polyethylene (HDPE) blends at different compositions was studied. The results for activation energy show that when Polyamide 66 with HDPE blends are processed within the range of the compositions being studied, it is possible to obtain a material with similar thermodegradative properties than those corresponding to PA. These blends would represent an economically viable alternative, because a material would be obtained with low cost/property ratio. Of the presented results, it is inferred that the composition of 20% of HDPE is the one that presents greater thermal stability.

Introduction

Polyamide (PA) is one of the polymers most used in engineering applications. To improve deficiencies that limit its use, such as fragility, high humidity absorption, poor thermal stability and poor impact strength, PA is mixed with other polymers. Numerous studies (1) deal with blends of PA with polyolefins.

High Density Polyethylene (HDPE) rigid containers have been used for packaging household products such as bleach and detergent. High quality, low cost packaging is also required for many additional products such as paint thinners, solvents, insecticides and pharmaceuticals. In these cases, the solvent barrier alternative to HDPE includes the polyethylene/polyamide blends.

Almost all polymers have decomposition reactions at any stage of their life cycle, i.e. during manufacturing, storing, processing, or final usage of the product. Factors related to polymers, to production and manufacturing processes, and the environment are among the possible causes of decomposition.

Calahorra et al. (2) concluded that there might be interactive reactions competing with the processes of decomposition during the degradation of a binary blend.

The degradation of polymers is a complex phenomenon, involving many simple reactions that are difficult to analyze separately. The quantitative contributions of these reactions to the degradation process are impossible to evaluate. For this reason, though the global mechanism does not agree with the real mechanisms, it is useful as an indicator to quantity the global velocity of the reaction, to acquire further knowledge of the structure of polymers, and to analyze the behavior of the finished product.

Therefore, this work is aimed at studying thermal decomposition of PA 66/High-Density Polyethylene (HDPE) blends at different compositions. The technique used for this analysis

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was dynamic thermogravimetry (TGA). The results obtained were analyzed using the Coats-Redfern (3), Van Krevelen (4), Horowitz-Metzger (5) and Romero-García (6) models and activation energy values were determined. To determine possible decomposition mechanisms, Romero-García (6) and Criado-Dollimore (7) models were used.

Theoretical Background

In kinetic studies of decomposition, the concentration of the reactants and the products is one of the main factors. Reactions are considered irreversible, and the velocity depends on the activation energy and order of the reaction. When we combine the reaction velocity and the Arrehenius expression, we have the following basic expression:

$$\frac{d\alpha}{dt} = f(\alpha)A\exp(-\frac{E_a}{RT}) \qquad (1)$$

Where: T is the temperature (K), α is the reacted fraction at the time t, $d\alpha/dt$ is the velocity of reaction (t^{-1}), $f(\alpha)$ is a function of α depending on the reaction mechanism, E_a is the activation energy (kJ/mol), A is the pre-exponential factor and R is the gas constant. While, the conversion is equal to $\alpha = \frac{w_0 - w}{w_0 - w_f}$. Where: w_o is initial mass of the sample (g), w is mass of the sample to a given temperature (g) and w_f is final mass of the sample (g).

With the integral method of Coats and Redfern (3), the expression is as follows when $n \neq 1$ (n: reaction order):

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{BE}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \qquad (2)$$

Where B is the rate of heating (degree/time)

When n=1, the expression becomes:

$$\log\left(-\frac{\log(1-\alpha)}{T^2}\right) = \log\frac{AR}{BE_a}\left(1-\frac{2RT}{E_a}\right) - \frac{E_a}{2.3RT} \qquad (3)$$

Van Krevelen (4), using the same methodology as Coats and Redfern, obtained, for n≠1:

$$\ln\left(\frac{(1-\alpha)^{1-n}-1}{1-n}\right) = \ln\left(\frac{A}{B}\left(\frac{0.368}{T_n}\right)^{\frac{E_a}{RT_n}}\left(\frac{1}{\frac{E_a}{RT_n}+1}\right)\right) + \left(\frac{E_a}{RT_n}+1\right)\ln T \qquad (4)$$

Where T_n is the temperature at the maximum rate (K)

When n=1, the expression becomes:

$$\ln(\ln(1-\alpha)) = \ln\left(\frac{A}{B}\left(\frac{0.368}{T_n}\right)^{\frac{E_a}{RT_n}}\left(\frac{1}{\frac{E_a}{RT_n}+1}\right)\right) + \left(\frac{E_a}{RT_n}+1\right)\ln T \qquad (5)$$

The Horowitz and Metzger method (5) is a simplification of that of Coats and Redfern. Where the characteristic temperature is defined as $\theta = T - T_s$, T is temperature at any time and T_s the TGA differential curve peak temperature.

For n≠1 the following expression is obtained:

$$\ln(1-(1-\alpha)^{1-n}) = -\frac{E_a\theta}{RT_s^2} + \ln(1-n) \qquad (6)$$

When n=1, equation (4) becomes:

$$\ln(-\ln(1-\alpha)) = \frac{E_a\theta}{RT_s^2} \qquad (7)$$

Those classical models used in the kinetic analysis of this kind of reactions study the simultaneous influence of temperature and conversion. However, the effect of temperature can mask that of conversion or viceversa. The Romero-García model (6) tries to separate both effects; therefore experimental data at different heating rates is needed.

The Romero-García equations are:

-At constant temperature:

$$G(\alpha) = \frac{RT_a^2 A}{(T_1 - T_o)E_a}\left(1 - \frac{2RT_1}{E_a}\right)\exp\left(-\frac{E_a}{RT_1}\right) \qquad (8)$$

-At constant conversion:

$$\mathrm{Ln}\frac{B}{RT^2} = \mathrm{Ln}\frac{A}{EG(\alpha)} - \frac{E_a}{RT} \qquad (9)$$

Where T_o is the initial temperature of the reaction (K), G (α): function that depends on the reaction mechanism and T_1: temperature to which the study is carried out at constant temperature (K).

The equation of the differential Criado-Dollimore (7) is:

$$\frac{\left(\ln\left(\frac{d\alpha}{dT}\right)\right) - (\ln F(\alpha))}{(\ln(1-\alpha))} = -\frac{E_a}{R}\frac{\left(\frac{1}{T}\right)}{(\ln(1-\alpha))} \qquad (10)$$

Where F (α): function that depends on the reaction mechanism

Experimental

PA 66 (MFI: 22.5 g/min) with HDPE (Altaven, MFI: 0.40g/ 10 min) were mixed in an extruder at 10, 20, 30, 40 and 50% concentrations by weight of HDPE. It should be noted that mixtures above 50% concentrations by weight of HDPE were not obtained, since the aim is to effect favorable changes in the behavior of PA66 through the action of HDPE. Then the samples were dried and analyzed in a thermogravimetric analyzer (TGA, Dupont 951) to produce the decomposition process. Thermograms were obtained under the following conditions: the samples were heated to a temperature of 773 K at different rates 5, 10 and 15 degrees/minute, in nitrogen atmosphere. Subsequently, the blend was kinetically examined using different models in order to determine the global energy of activation and reaction mechanism. The models used to study the kinetic parameters are applicable in the range from the beginning of the fall in the weight loss versus temperature to the final descent. This is done in order that the discussion of the values of activation energy obtained may be compared using the proposed models.

Results and Discussion

The analysis of the kinetics of degradation of PA 66, HDPE, and their mixtures, is based on thermograms obtained in TGA. In the thermograms, three zones were obtained. The initial region that starts from room temperature up to the range 623-643 K, depending on the blend, characterized by a low velocity of having loss in weight that depends in particular on each system, not being bigger than 15%. In the PA 66 and in the mixtures with a composition of this above 70%, the velocity of loss of weight in this stage is bigger than for the rest of the compositions, which is basically due to the loss of humidity absorbed by the Polyamide, since it is hygroscopic. The second stage of the thermogram is understood from 643-758 K. In this interval the reaction or reactions of decomposition occur. In general, the percentage of having loss in weight is from 5 to 90%. At 773 K it is assumed that the decomposition is almost complete since the residuals were inferior to 8%.

In Figure 1, the variation of the conversion with temperature, α versus T, is shown for the blends and the neat polymers. The curves obtained suggest that the reaction decomposition is possibly a catalytic process. Since, according to Garner et al (8), these curves present an initial induction period corresponding to a nucleation phenomenon. The formed nuclei are active centers that accelerate the decomposition. Due to this, three stages are observed in Figure 1. The first stage of induction corresponds to the prenucleation, which is a period when the nucleus formation velocity is slow. This process of prenucleation corresponds to the formation of the first radicals. In the second stage, these nuclei accelerate the decomposition process, this behavior being similar to that of a catalytic process. In the last stage, the reaction velocity slows down, since active nuclei do not exist.

Decomposition processes in polymers initially occur via the formation of CH^* radicals, From these, whether in the presence or not of oxygen, occurs the stage of propagation of decomposition which, according to the polymer may involve crosslinking and/or rupture of chains that allow the formation of gels and/or carbonyl groups. It is possible to infer from the curves in Figure 1 that once the decomposition process is complete, almost all the material is transformed in volatile material and the remaining residue (less than 8%) is crosslinked material and/or additional additives to the polymer during its synthesis or for its preservation against environmental agents.

On this basis, we may infer that the HDPE in its initial decomposition phase presents crosslinking and later the breakdown of chains predominates.

One explication as the formation of the crosslinking reactions was carried out by Chapiro (9) in studies on irradiated HDPE, a similar technique on the effect of temperature on these materials. According Chapiro, initial crosslinking can be explained based on the destruction of the crystallites, which act as "physical crosslinks"; whereas at higher radiation doses, the increase in the crosslinking density compensates for the further loss of crystallinity. When almost all crystals have been destroyed, density rises as a result of the structural changes in the polymer, i.e. the formation of the double bonds and crosslinks, which bind the molecules more closely together and lead to a tighter packing of the polymer chains. Similar results were obtained by Albano et al. (10).

The above leads us to think in a change in the reaction mechanism or in simultaneous mechanisms in the alone polymers or their mixtures, but this can not be confirmed although it is possible through an analysis of the results obtained applying the models of Criado-Dollimore and Romero-García to determine the possible reaction mechanisms predominant in the decomposition process of these materials.

It is worthwhile to point out that polymers show typical characteristics of thermal decomposition of the solid-gas reactions that occur via free radicals. The former reactions are affected by the diffusivity of the volatile reaction products and the reaction mechanisms. This leads to the conclusion that the decomposition takes place via a very complex mechanism, since each reaction has its activation energy. Therefore, the results obtained show the global activation energy of the real mechanism of decomposition.

In Figure 2, the values of the initial and maximum temperature of decomposition are presented for the polymers alone and the mixtures. The initial temperature of decomposition determines the upper temperature limit at which polymers can be processed or manufactured. The value of this temperature could indicate the beginning of the decomposition process.

In figures 2 and 3 it may be observed that on comparing the initial decomposition temperature of HDPE and PA66, that they present values of 715 and 690 K, respectively. This would indicate that the previously mentioned nucleation process begins at lowers temperatures in the case of the PA66. In the case of the mixtures, this temperature has values close to that of the PA66, from which we may infer that PA66 affects the beginning of decomposition of HDPE in the mixtures.

During the process of decomposition, the temperature to which the velocity of loss of weight is the maximum temperature of decomposition and it represents a measure of the long-term stability of the polymer. In Figure 2, it is observed that an increase of both temperatures occurs in the range of 20-40% of HDPE and then it descends, with regard to the values presented by the PA 66. From these results it can be inferred that up to 40% of HDPE in the mixtures, retard the degradation process. On the other hand, the feasibility of processing the mixtures to slightly superior conditions of temperature to that of the PA 66 is established.

The different values of activation energy obtained through the several methods used in PA/HDPE are shown in Table 1. The methods used in the experiments were those of Coats-Redfern (C–R), Horowitz-Metzger (H–M), and Van Krevelen (K). Although each model used presents its own suppositions especially the expression f(α), which does not correspond to the systems formed by macromolecules. They do report interesting values, since these models indicate similar tendencies between themselves. For the three used methods a similar behavior is observed in the variation of the activation energy, which verifies the obtained results (Table 1). For this reason, a satisfactory discussion is feasible insofar as comparing the activation energy values obtained for the different mixtures activation under study is concerned.

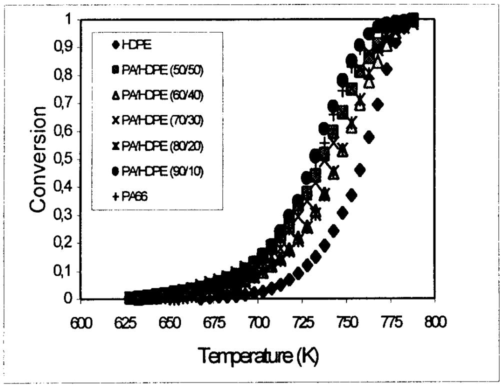

Figure 1: Conversion versus temperature, at different compositions.

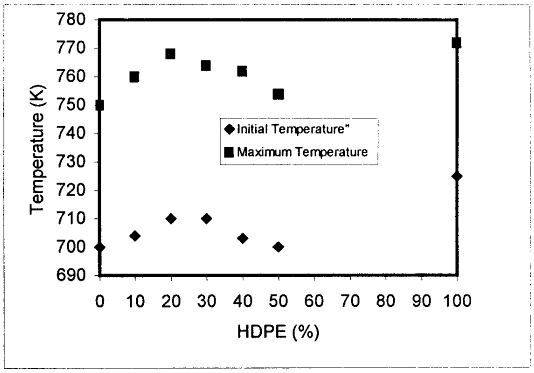

Figure 2: Dependence of the initial and maximum temperatures of decomposition of the blends, at different compositions.

HDPE (%)	C-R (kJ/mol)	H-M (kJ/mol)	V-K (kJ/mol)
0	200	237	225
10	174	214	223
20	194	230	237
30	159	199	183
40	167	208	192
50	168	117	191
100	252	286	278

Table 1: Global activation energy for the PA 66, HDPE and their blends

In general, the tendency of the calculated activation energy, in the present work, for the different methods is adjusted to the established ones by other researchers such as Carrasco (11) and Albano *et al.* (12).

As far as the activation energy of the pure polymers is concerned (Table 1). PA 66 shows values that vary between 200 and 237 kJ/mol. Albano *et al.* (13) obtained values for the PA 66 between 224 kJ/mol and 249 kJ/mol, for these integral methods,. The values obtained in the present work are slightly lower than those presented by Albano *et al.* (13), which is related to the thermal stabilizer present in the sample of PA 66.

The activation energy of mixtures of PA66 with HDPE presents values lower than those of pure components (Table 1), being the 20% of HDPE composition the one which has a value of E_a closest to that of Polyamide.

In Table 2, the values of activation energy are presented both for the HDPE and the PA 66 as for their mixtures, at different conversions using the Romero-García method. The activation energy for the PA 66 increases with the increase in the conversion level. From these results it can be inferred, according to the pattern of Romero-García, that the degradation of the PA 66 occurs under the control of more than a stage of decomposition where one or several mechanisms of decomposition can be present, so that the values of global activation energy presented in Table 1 for this polymer depend on each individual stage and of the relative effect of this to the different conversion or temperature levels. The E_a for the HDPE and their mixtures with PA 66 tend to a unique value as it increases the conversion, the value for each blend being different.

When the activation energy varies with the level of conversion, Budrugeac et al. (14) propose the following equation:

$$E_a = E_o + E_1 Ln(1-\alpha) \tag{11}$$

where E_0 and E_1 are constant and specific to the material.

In Table 3 the values of energy of activation average are presented for the PA 66 obtained for each conversion level by the equation of Brudugeac et al. (14). It can be observed that these values are approximately inside the range determined by Romero-García of maximum and minimum conversion to constant temperature and conversion (Table 3), 136 and 219 kJ/mol, respectively. It is inferred of these values that, although the activation energy changes with the conversion, it is possible to use this kinetic model to determine with a good approach the stability of the PA 66.

On the other hand, maximum and minimal activation energy values at constant temperature and conversion shown in Table 4 can indicate that the activation energy is higher in blends with HDPE than for PA alone. Of these E_a results, although they are slightly different to

Conv. (α)	Nylon	50/50	60/40	70/30	80/20	90/10	HDPE
0.1	122	156	195	183	191	161	---
0.3	149	135	176	187	222	167	225
0.5	163	159	197	180	215	176	260
0.7	170	161	215	178	178	187	242
0.9	206	170	233	180	202	205	218

Table 2: Activation energy obtained by the method of Romero-García(kJ/mol) for the polymers alone and their mixtures.

Conversion	Ea (kJ/mol)
0.1	137
0.3	149
0.5	165
0.7	190
0.9	213

Table 3: Values of Ea for the PA 66 at different conversion levels

PEAD (%)	Minimum Ea at constant temperature	Maximum Ea at constant temperature	Ea at constant conversion
0	136	219	162
10	204	251	175
20	213	288	208
30	150	198	165
40	149	193	205
50	146	203	176
100	262	317	234

Table 4: Maximum and minimal activation energy at constant temperature and conversion (kJ/mol), using Romero-García method for polymers alone and blends

those obtained by integral methods (Table 1), they lead to the same conclusion with regard to thermal stability of the blends.

Of the values presented in the Tables 1 and 4, it is inferred that the composition of 20% of HDPE is the composition that presents greater activation energy, and therefore it is the mixture that has bigger thermal stability. These studies demonstrate that is possible to use HDPE, and in that way to obtain materials with a thermal stability grater than the obtained with alone PA 66. The using of HDPE is a significant contribution to the finished products.

In Table 5 the obtained reaction mechanisms are presented through the pattern of Romero-García (R-G) and Criado-Dollimore (C-D), both for the polymers alone and their blends. These methods establish that the mechanism of dominant decomposition for the HDPE is the diffusion in its different forms presenting a near correlation index to the unit and a value of the intercept next to zero. Through these models it is obtained that for the blends the mechanism of decomposition that correlate better is diffusion, save some exceptions. From the results presented in table 5, it may be inferred that the model C-D does not allow us to distinguish between the different mechanisms that present a good correlation. On the other hand, the R-G model that is based on various heating velocities may indicate more explicitly which is or are the possible controlling mechanism(s) of the decomposition process. Furthermore, it is possible to conclude that although the PA66 affects the Ti of the process of the mixtures, the HDPE induces the probable mechanism of decomposition of the mixtures. On the other hand, for the PA 66 no mechanism could be determined (Romero-García) because for different values of conversions, a significant change in the activation energy occurs (Table 3); therefore, this is indicative that changes of the mechanism take place with the conversion and the temperature.

% HDPE	Romero-García	Criado-Dollimore
0	---------	Random Nucleation
50	Three-dimensional diffusion	Diffusion
40	Diffusion / Random Nucleation	Diffusion
30	Three-dimensional diffusion	Phase boundary controlled reaction
20	Phase boundary controlled reaction	Diffusion
10	Diffusion	Diffusion
100	Three-dimensional diffusion	Diffusion

Table 5: Reaction mechanisms obtained through the different models.

On the other hand, we may infer that for almost all the mixtures analyzed, the predominant reaction mechanism is diffusion in three dimensions (D_4), although in some mixtures more than one decomposition mechanism is present which are produced simultaneously, since in the thermograms (TG) two changes of slope are not observed and in the TGA (derived from the TG) only one maximum is observed.

Conclusions

The PA affects the initial temperature. of the decomposition process of the HDPE, since the mixtures show values at this temperature close to the Ti of the PA.

The use of models that require more than one heating rate suplí more satisfactory information with regard to the Ea and the decomposition mechanisms. For the HDPE and the mixtures of PA66/HDPE, the predominant decomposition mechanism is that of diffusion.

These results for activation energy show that when PA 6.6/HDPE blends are processed within the range of the compositions being studied, it is possible to obtain a material with similar thermodegradative properties than those corresponding to PA 66. These blends would represent an economically viable alternative, because a material would be obtained with low cost/property ratio. Selecting the proper composition depends on the specific uses, which, in turn, is a function of mechanical, thermal and morphologic properties. Of the presented results, it is inferred that the composition of 20% of HDPE is that which presents greater thermal stability.

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