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Effect of carbon nanotubes on thermal pyrolysis of high density polyethylene and polypropylene

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ABSTRACT

The goal of this work is to analyze the effect of carbon nanotubes (CNTs) on the pyrolysis of either high density polyethylene (PE) or polypropylene (PP) matrices by using both kinetic thermogravimetric analyses (TGA) under non-isothermal conditions and a fixed-bed reactor under isothermal conditions. Under non-isothermal conditions, CNTs increased the beginning of thermodegradation for both matrices with differences as high as 30 °C and 22 °C as compared with neat PP and PE, respectively. This enhanced thermal stability in PP based composites was associated with an increase in the apparent activation energy whereas in PE based composites lower pre-exponential factors associated with reduced conformational entropy, are responsible for the enhanced thermal stability. The thermodecomposition processes were studied by assuming geometrical contraction and nucleation models. The invariant pre-exponential factor and apparent activation energy obtained were quantified for each sample confirming that these values depended on the polymer matrix and concentration of CNTs. These invariant parameters were in good agreement with those obtained by isoconversional analyses allowing the prediction of the thermogravimetric behavior. Our findings clearly showed the strong effect of CNTs on the non-isothermal pyrolysis of polymer materials changing its kinetic and the activation energy. Results from isothermal pyrolysis (450 °C-40′) confirmed the thermal stability by the presence of CNTs as higher condensable (C_9–C_{40}) and lower gas (C_1–C_4) yields in PP-CNTs composites, and a higher amount of unreacted polymer and a lower both condensable and gas yields for PE-CNT, as compared with the pure matrix, were found.

1. Introduction

The growing market of polymeric nanocomposites (PNCs) has raised a great interest thanks to the improvements in thermal, mechanical, electrical, and barrier properties, among others, that nanoparticles confer to the polymeric matrix at low loadings [1–11]. When PNCs were presented to the public for the first time in the 90s [12], a huge market opportunity was forecast and today a demand of c.a 3200 kTons with an approximated value of 15 billion US dollars is estimated in 2020 only for US [13]. Within PNCs, those based on polyolefins are of great importance covering more than 50% of the world demand of plastics, being polyethylene (PE) and polypropylene (PP) the main exponents [14,15]. Among nanoparticles with the highest demand, carbon nanotubes (CNTs) are considered as an unique reinforcement for polymers [16]. In particular, many studies have been carried out expanding the applications of PP and PE by adding CNT to improve the Young's modulus, tensile strength, gas permeability, flame retardancy, and electrical conductivity [8,11,17–21]. However, another important property to be analyzed is the thermal stability as often limits both processing and application of the these nanocomposites [22,23]. For instance, high density polyethylene (HDPE)/CNTs composites presented enhanced thermal stability as compared with pure HDPE using thermogravimetric analysis (TGA) under nitrogen atmosphere and non-isothermal conditions [23]. The weight loss of 5% for neat HDPE occurred at 431 °C while for composites with 3.0 wt% of CNT the same loss occurred at 459 °C. Bocchini et al. [24] found that CNTs dispersed in linear low density PE (LLDPE) delayed approximately 12 °C the thermal degradation respect to virgin matrix. This stabilization is due to both a thin film of CNTs net

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formed by migration at the polymer surface and an accumulation due to LLDPE volatilization. The same tendency was found in PP/CNTs nanocomposites exhibiting superior thermal stability as compared with neat PP under either nitrogen or air atmospheres [7]. Other studies found that, respect to pure PP, the addition of 0.5 and 1% wt of MWCNTs increases 16 °C and 34 °C respectively the onset of thermal degradation [25]. Moreover, Kashiwagi et al. [26] found a significant reduced flammability of PP at 1% wt of MWCNTs due to the formation of a network-structured floccule layer covering the entire sample surface. In general, several explanations for the improved thermal stability in the these systems are reported such as: 1) good matrix–nanotube interaction [21,25,27–29], 2) barrier effect of CNTs on the diffusion of degraded volatile components from polymeric matrix [21,25,30–32], 3) free radical scavenger effect of CNTs due their π-bonds [21,24,25,33], 4) the formation of a superficial protecting nanotube network which is destroyed when increasing the temperature up to a limit value [24,25,27], and 5) improvement of thermal conductivity in the polyolefinic-CNT nanocomposites which allows the spreading of heat uniformly within the composite [4,21,25].

The thermal behavior is also important considering the great consumption of plastic polymers, more than 300 million annual tons [34], demanding novel strategies for feedstock recycling such as the pyrolysis. This kind of chemical recycling has become one of the most attractive method for waste polymer treatment allowing the attenuation of their environmental impact besides the recovery and valorization of its degradation products [14,35–37]. Several studies have been carried out focusing on the products from pyrolysis of HDPE and PP and their potential industrial application [38–40]. For instance, if 1 kg of polyethylene is pyrolized in order to obtain a hypothetical mix of 10%-petroleum gas, 30%-gasoline, 40%-diesel and 20%-wax (residual oil), based on the calorific value of those commercial fuels, the net energy gained is estimated in 42 MJ/kg [41,42]. Assuming the great potential impact of polymer nanocomposites in the market, to understand the effect of nanoparticles on temperature and degradation processes is a very relevant topic in the context of chemical recycling processes.

To our knowledge, there are several reports about the effect of CNTs on the thermal properties of polyolefinic systems [43–49], but combines studies about both isothermal and non-isothermal (or dynamic) pyrolysis are barely found. In this sense, the goal of the present work is to analyze the effect of CNTs on the thermal pyrolysis of PP and HDPE, by means of two complementary approaches. The first one consisting in carried out non-isothermal (or dynamic) pyrolysis by means of thermogravimetric analysis, in order to get information related to the kinetics of the thermodecomposition reactions. This kinetic analysis gives information for the future design of industrial reactors and for in-use lifetime predictions [50–52]. The second one consisting in the analysis of the effect of CNTs on the products generated in a pyrolysis reactor under isothermal conditions in terms of their yield and composition.

2. Kinetic models for non-isothermal pyrolysis

Considering that the shape of thermogravimetric (TG) profiles does not change with time, we can assume that there is no constraints to apply dynamic data for kinetic investigations of a polymeric material [39]. The rate of reaction can be described therefore by using the following equations:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}f(\alpha) \tag{2}$$

where α is the reacted mass fraction at time t, $f(\alpha)$ is a function known as the differential form and it depends on the reaction mechanism adopting various expressions based on the specific model assumed, for instance: nucleation and nuclei growth, phase boundary reactions, diffusion, or order reactions, among others (see Table 1) [53–58]. $K(T)$ is the temperature-dependent rate constant, which has the Arrhenius form $Ae^{-E_a/RT}$, where Ea is the activation energy (kJ/mol), A is the pre-exponential factor of Arrhenius (s^{-1} or min^{-1}), R = gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}) and T is the absolute temperature (K).

If the TG run is carried out under dynamic conditions with a linear heating rate β, eq. (2) becomes:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-E_a/RT}f(\alpha) \tag{3}$$

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_\alpha} e^{-E_a/RT}dT \tag{4}$$

By defining $g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}$ and considering that α will be zero for $T < T_0$ (with T_0 being room temperature), it follows:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha} e^{-E_a/RT}dT \tag{5}$$

$g(\alpha)$ is known as the integral form and it depends on the reaction mechanisms. The term $\int_0^{T_\alpha} e^{-E_a/RT}dT$ is called temperature integral or Arrhenius integral, $I(Ea, T_\alpha)$, which has no analytic solution and numerical or approximate solutions are required [59,60].

The evaluations of the kinetic triplet "Ea, A, $f(\alpha)$" or "Ea, A, $g(\alpha)$" can be performed by using simultaneously two methods: (1) isoconversional methods (or model free methods), where the changes in TG data brought about by variation of heating rate allow to obtain Ea at a given conversion α, even when the functions $f(\alpha)$ and $g(\alpha)$ are not known; and (2) model fitting methods, where different mechanisms ($f(\alpha)$ or $g(\alpha)$) are proven until find the one that better describes the experimental data [51,61]. Keeping into account the ICTAC Kinetics Committee recommendations for thermal kinetic analyses [62,63], here we use two successive methods: (1) Isoconversional consisting in apply these methods to assess the apparent activation energy (Ea_{iso}) as a function of the conversion degree, and (2) Model fitting consisting in consider Ea_{iso} as a reference value meaning that these methods are carried out to assess the possible mechanism and corresponding kinetic parameters.

2.1. Isoconversional methods

The isoconversional procedures can be classified as linear or non-linear methods.

2.1.1. Linear isoconversional methods

The linear procedures can be differential (e.g. Friedman method) or integral (e.g. Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Starink) methods. In the linear procedures such as those named Friedman (FR), Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-