Surface & Coatings Technology 239 (2014) 70–77

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Atmospheric plasma torch treatment of polyethylene/boron composites: Effect on thermal stability

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ARTICLE INFO

Article history:
Received 16 August 2013
Accepted in revised form 9 November 2013
Available online 18 November 2013

Keywords:
Composite materials
Thermogravimetric analysis
Surface properties
Thermal properties
Epoxy resin
Boron

ABSTRACT

Low density polyethylene (LDPE) and its boron composites (LDPEB) are typically used as coatings with functional nuclear properties. However, they present low surface energy and adhesion problems. Atmospheric pressure plasma torch (APPT) processes improve polymer wettability. The main objective of this work is the evaluation of the effect of APPT on the thermal stability of LDPE and its composites reinforced with 15 and 30% (by wt.) of boron. Physical and chemical changes on the surface of treated materials are analysed using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The influence on thermal stability is evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. The decomposition rate is measured by means of the Kamal equation, and the activation energy of the reaction is calculated from an Arrhenius equation and the Kissinger method. Results show that the APPT treatment is adequate to treat these materials (LDPE and its boron containing composites), as it does not degrade the material, but it modifies the chemistry and nanoroughness of the surface, increasing its wettability.

1. Introduction

Polyolefins are a family of thermoplastics with a good balance of physical and chemical properties. Due to their low cost, light-weight, easy processing and recycling characteristics, they are suitable for the manufacture of composites. Low density polyethylene/boron composites (LDPEB) are highly efficient neutron shielding materials: polyethylene (PE), due to its high hydrogen content, and boron due to its neutron absorption ability [1–3]. Depending on boron amount, LDPEB can be used in different components, from capture-gamma radiation applications (5% boron) [4] to radioactive waste immobilization [5] (when boron ranges from 30 to 50%).

However, the application of polyolefins and their composites is sometimes restricted by their poor wettability, which causes adhesion problems. Plasma techniques are fast and environmentally friendly processes that significantly increase surface energy (γ_s) and therefore, the adhesion properties of polymers [6].

In particular, atmospheric pressure plasma torches (APPT) [7,8] are non-local thermodynamic equilibrium plasma devices which produce cleaning and surface activation by means of the breakdown of pollutants and the introduction of different moieties of polar nature [9–11]. The advantages of APPT on PE to improve wettability and adhesion properties of the substrate have been demonstrated [10]. But it is necessary to assure the thermal stability of those materials after treatment to use them in nuclear plants.

These polar groups are ($C{=}O$, $C-O$, $N-O$, $B-O$, etc.) active species on the polymer surface. According to Mueller and Jakob, these species sometimes can accelerate the degradation process at high temperature [12]. The ageing process occurs as a consequence of diverse phenomena such as cross-linking and free radical formation.

Sanchis et al. have demonstrated that low pressure oxygen plasma changes PE thermal transitions [13], appearing an additional peak in differential scanning calorimetry (DSC) curve at 65–95 °C, possibly related to an increase in the crystallinity of the polymer [14]. This will also accelerate the degradation process of PE. Corona discharge [15] and other low-pressure plasma processes [16] may increase the crystallinity of the polymer due to the high temperatures achieved during surface treatment.

Unfortunately, there is no evidence in the literature about the influence of the polar moieties created by APPT [10] on the degradation of LDPE. The main objective of this work is to determine the influence of APPT and the addition of boron in the chemical and thermal properties (melting temperature, enthalpy of fusion, crystallinity and decomposition temperature) of LDPE.

The study evaluates not only the changes in thermal properties, but also the mechanism, the rate and the activation energy of decomposition reactions. This calculation provides information on possible

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http://dx.doi.org/10.1016/j.surfcoat.2013.11.020

changes that may occur in the LDPE by the addition of boron and APPT, dramatically important for its thermal stability and safe thermal destruction.

2. Experimental procedure

2.1. Composites preparation

LDPE and LDPEB composites were prepared using commercial grade LDPE powder (0.92 g/cm^3 density) and boron amorphous powder (2.34–2.37 g/cm^3 density, 0.4–0.7 μm particle size, from Strem Chemicals Inc. Bischheim, France). LDPE and boron particles were blended in a Rheodrive 5000 from Haake Fision, Waltham, MA, USA. Different concentrations of boron powder (15 and 30% by wt.) were used, being materials labelled as LDPE15B and LDPE30B respectively. Uniform mixtures were prepared at 130 °C, using a screw speed of 50 rpm for 6 min. Precursors were compression moulded in a two hot-plate press at 170 °C and 5.5 MPa (Remtex, Barcelona, Spain). For each formulation 1-mm thick films were prepared. Neat LDPE was processed in the same way for comparison purposes.

2.2. Atmospheric pressure plasma torch (APPT) treatment

An APPT device from Plasmatreat GmbH (Steinhagen, Germany) was used to treat both LDPE and LDPEB. The setup operated at a frequency of 17 kHz and a high tension discharge of 20 kV, and it was provided with a rotating torch ending in a nozzle (1900 rpm) through which plasma was expelled. The system contains an electronically speed-controlled platform where the samples were placed. The air plasma was generated at a working pressure of 2 bars inside the rotating nozzle by a non-equilibrium discharge and expelled through a circular orifice onto the samples. The speed of the platform was set at 10 m/min, and the distance between the sample and the plasma nozzle was fitted to 6 mm. The size of the treated samples was 3 × 2 cm^2.

2.3. X-ray photoelectron spectroscopy (XPS)

APPT treated samples were analysed with a VG Scientific Microtech Multilab (VG Scienta, Hastings, United Kingdom) spectrometer using a Mg-K$_\alpha$ X-ray source (1253.6 eV) operating at 15 keV and 300 W. The take-off angle was 45°. The analysis was performed on the surface of 1 × 1 cm^2 samples at a residual pressure below 5×10^{-8} Torr. A survey scan encompassing the 0–1200 eV region was obtained for each sample. High resolution spectra were obtained in a 20 eV range. All binding energies were referred to as the C 1s core level spectrum position for C–C and C–H (hydrocarbons) species at 285.0 eV. Atomic concentrations were calculated using VGX900-W system.

2.4. Atomic force microscopy (AFM)

The AFM studies were performed using a MultiMode Nanoscope® IV (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA, USA). The AFM measurements were carried out at room temperature, operating in the tapping mode, employing silicon tips with a force constant of about 40 N/m and a resonance frequency close to 300 kHz, recording simultaneously height and phase images.

2.5. Thermal characterization

Differential scanning calorimetry (DSC) was used to evaluate the melting temperature and crystallinity in all materials. Heating dynamic cycles between −40 and 200 °C at 10 °C/min was carried out, followed by cooling at 20 °C/min. The first one was done to remove the thermal history effects, and the measurements were done in the second run. The equipment used was a DSC822 Mettler Toledo (Greifensee, Switzerland), using nitrogen (80 ml/min) as a purge gas.

Thermogravimetric analysis (TGA) was carried out to evaluate the decomposition temperature and residue in all materials. A dynamic cycle between 50 and 600 °C was carried out at 5, 10 and 20 °C/min (non-isothermal decomposition). The equipment used was a TGA/SDTA851e Mettler Toledo (Greifensee, Switzerland), under nitrogen (60 ml/min). Three samples were tested for each condition.

2.6. Kinetic analysis

In the thermal degradation of a system, the reactions are considered irreversible and the kinetic parameters can be determined from the non-isothermal thermogravimeric data. In order to analyse the degradation mechanisms of LDPE and LDPEB, kinetic parameters such as the activation energy (E), the pre-exponential factor (A) and the conversion function $f(\alpha)$ or $\alpha(T)$ were evaluated from TGA curves at different heating rates.

A differential kinetic equation (Eq. (1)) of n-order can be applied, where α is the advance degree of reaction ($0 < \alpha < 1$) at time t, n is the order of reaction, and k is the rate constant (defined by the Arrhenius expression, Eq. (2)). From Eqs. (1) and (2), Eq. (3), a differential kinetic equation which combines E and α, can be obtained. In those equations, T_p is the decomposition temperature (in K), corresponding to the inflection point in TGA curve (maximum decomposition rate), R is the gas constant (J·mol^{-1}·K^{-1}).

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

$$\ln k = \ln A - \frac{E}{RT_p} \tag{2}$$

$$\frac{d\alpha}{dt} = A \exp\left(-E/RT_p\right) f(\alpha). \tag{3}$$

From Eq. (3), Kissinger [17] defined Eq. (4), which allows calculating the activation energies from TGA at different heating rates (β) in K/min, being C a constant. This method has been applied to other polymers, such as polyester/polycarbonate systems [18].

Furthermore, an autocatalytic mechanism can be taken into account in the kinetic equation (Eq. (5)), being n and m order of reactions. The Kamal equation (Eq. (6)) [19] reflects the n-order (Eq. (1)) and the autocatalytic mechanisms (Eq. (5)).

$$\ln\left(\frac{\beta}{T_p{}^2}\right) = -\frac{E}{RT_p} + C \tag{4}$$

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \alpha^m \tag{5}$$

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^n + k_2(1-\alpha)^n \alpha^m. \tag{6}$$

In Eq. (6), k_1 is the rate constant of the n-order reaction, k_2 is the rate constant of the autocatalytic reaction and n and m are the reaction orders. Eq. (6) is used in thermoset polymers to calculate the kinetic parameters in the curing reaction [20–22]. In this way, the activation energy (E) can be determined through various analytical methods: it can be obtained from the slope of the plots of ln k (Eq. (2)) or $\ln(\beta / T_p{}^2)$ (Eq. (4)) vs. the inverse of T_p.

The activation energy is the parameter used to estimate the lifetime of a material at different temperatures for quality control purposes or for the specification of a material. Although there are numerous methods to calculate E [23–27], ASTM E1877 or ASTM E1641 standards suggest the use of Eq. (1), being the decomposition an n-order process, with n = 1. This implies that only one species is involved in the reaction, with only one mechanism of decomposition taking place. This approach is very similar to that of Kissinger (Eq. (4)).