



Non-isothermal degradation kinetics of Ethylene-Vinyl Acetate Copolymer nanocomposite reinforced with modified Bacterial Cellulose Nanofibers using advanced isoconversional and master plot analyses



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ARTICLE INFO

Keywords:

Thermal degradation
Master plots
Ethylene-vinyl acetate copolymer (EVA)
Nanocomposite

ABSTRACT

The non-isothermal degradation kinetics of Ethylene-Vinyl Acetate (EVA) Copolymer containing modified Bacterial Cellulose Nanofibers (MBC) was reported to determine its service temperature. The apparent activation energies are estimated using advanced isoconversional and various model-free methods, which indicate the two-stage degradation mechanism. The kinetic mechanisms are determined using the differential $f(\alpha)$ and combined $Z(\alpha)$ master plots by comparing the experimental plot with the theoretical master curves. The results on 'FZ master plots' reveal that the degradation proceed via $D2$ mechanism in the range of $(\alpha \leq 0.3)$ exhibiting that the simultaneous acetate groups and MBC degradations is controlled by two-dimensional diffusion of the volatiles. However, for $(\alpha \geq 0.3)$ there is a gradual change to $F1$ mechanism that means the scission of the residual main chains of EVA is performed by random nucleation with one nucleus on the individual particle. The calculated kinetic triplets are used to predict the lifetime.

1. Introduction

Research in thermal degradation mechanism of thermoplastic polymer substances has received considerable attention due to the extensive utilize of these materials as structural applications, coatings, electrical insulators, adhesives, and matrices in reinforced composites [1]. The knowledge about the long-term behavior of high-performance polymers for their applications in high-temperature environments is too important. Therefore, decomposition kinetic of these materials effectively assists in probing degradation mechanisms, defining the thermal stability and choosing their utility areas. In this regard, thermogravimetry analysis (TG) is an outstanding technique which is broadly used to get useful information on kinetic parameters and solid-state degradation kinetic model [2]. The thermal properties of polymeric nanocomposites have also been an area of interest for numerous investigators. Ethylene-vinyl acetate copolymer (EVA) has a widespread range of industrial applications and among the numerous ethylene copolymers, owing to its versatile properties depending on its vinyl acetate content, EVA has converted to one of the most beneficial copolymers in the different industries as an insulator, hot melt adhesive, coating, packaging and barrier sheets, etc [3]. While, the flammable characteristics of EVA limit its usage in some cases. Hence the flame

retardation of EVA has been broadly investigated [4]. From this point of view, it is important to determine the thermal stability of EVA for determining their durability and how they are used. On the other hand, the utility of natural nanofibers as reinforcement in polymer composites have attracted attention and now they obtain opportunities for various commercial applications. The natural nanofibers such as cellulose nanofibers owing to their very high specific surface areas and high surface-to-volume ratio exhibit unique properties in the resultant composites [5]. Despite the numerous benefits of natural nanofibers, when nanocomposites are manufactured they expose less effectively with respect to thermal properties owing to low thermal stability of the natural nanofibers. To overcome this challenge, the surface modification of natural nanofibers is inevitable [6–8]. The impact of wood fiber content and particle size on the thermal degradation of EVA copolymer/wood fiber composites was addressed by Diboke and Luyt [9]. The outcome demonstrated that the wood fiber size do not have much influences on thermal behavior of composites. Ahmed and Luyt have synthesized sisal fiber/polyethylene composites. They reported that the thermal stability of the composites decreases in comparison to the neat matrix, whereas the treated fiber composite exhibited marginal improvement in thermal stability than the untreated fibers [10]. Silvyia and co-workers investigated the mechanical and thermal properties of

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EVA/banana derived celluloses composites their results showed that the EVA/celluloses composite has superior thermal stability when compared with pure EVA and cellulose [11]. Also, Sonia et al. have fabricated EVA/cellulose microfibers composites. The consequences demonstrated that the onset temperatures of decomposition for composites was increased compared with pure EVA [12]. The crystallization kinetic of EVA/BCNs nanocomposites was successfully described in our recently published article [13]. Typically, the so-called ‘model-free’ isoconversional methods, through several heating rates, can provide reliable predictions of the kinetic triplet, namely the pre-exponential factor (A), the activation energy (E_a), and the kinetic model $f(\alpha)$. The parameter of kinetic model is an algebraic expression that is related with the physical model that defines the kinetics of a reaction [14]. There are various model-free isoconversion methods which can be used for computing activation energy of thermally activated reactions. The most extensively applied model-free methods are those developed by Kissinger [15], Flynn–Wall–Ozawa [16,17], Kissinger–Akahira–Sunose [18], Friedman [19], Vyazovkin [20], and advanced isoconversional [21]. However, these methods do not directly produce the reaction kinetic model. The fitting of numerous reaction models with the kinetic data, which are known as model-fitting approaches, are approved by several investigators. Criado and Malek suggested master plots for the detection of the proper kinetic mode that permits the comparison of the experimental master curves to theoretical ones [22]. Master plots are reference theoretical curves which related to the kinetic model based on both differential $f(\alpha)$ and integral $g(\alpha)$ function but are independent of the kinetic parameters A and E_a [23]. However, the degradation pathway and determination the appropriate kinetic model of polymers is a complex phenomenon, and despite the abundant deal of study implemented on this subject, high argument still remains. It should be noted that are some reports on the thermal degradation of EVA [24] but only a few published works have been conducted on the thermal degradation mechanism of EVA nanocomposites [25]. A sequence of surveys on EVA’s thermal oxidative degradation performed by Allen et al. [26] that revealed the degradation pathway for EVA include the initial loss of acetic acids followed by oxidation and the breakdown of the main chains. Wang et al. examined the thermal decomposition of EVA composites containing hydrotalcite (LDH) and red phosphorus (RP) by thermogravimetric analysis. They computed activation energy from different methods and results indicate that the addition of LDH and RP affects mainly the first thermal degradation stage of EVA [27]. Besides, to the best of our knowledge there is not any published work in literature on prediction of mechanism and durability during degradation using kinetically modelling and master plots of the EVA nanocomposites degradation process. Therefore, the main objective of this study is to kinetically investigate thermal degradation process of EVA nanocomposite containing modified bacterial cellulose nanofibers (MBC) and to obtain its kinetic triplet parameters. Knowing kinetic parameters, thermal behavior during degradation can be described as a phenomenological process instead of difficult mechanistic investigation. For this purpose, the kinetic analysis of the non-isothermal TG data was accomplished within the framework of a multi-step solid-state process at multiple heating rates considering several differential and integral kinetic functions. Moreover the kinetic triplet parameters on the degradation reaction were determined by means of advanced isoconversional method followed by master plots which compares the plots of experimental data with the master curves of theoretical kinetic models. The main objective is to obtain an insight into the mechanism of thermal degradation process as well as thermal durability of EVA/MBC nanocomposite.

2. Experimental

2.1. Materials

Ethylene-vinyl acetate copolymer (EVA) containing 18 wt% vinyl

acetate used in this study is of commercial grade (melting point of 84 °C) supplied by Honam Petrochemical Co. (South Korea) with melt flow index (MFI) of 2.5 g/10 min. Bacterial cellulose nanofibers gel (BCNs) 2.5 wt% having a purity of 99% and average diameters of 40 nm were procured from Nano Novin Polymer Co. (Sari, Iran). Sulphuric acid (95–97%), toluene, and acetic anhydride solutions were acquired from Sigma Aldrich Inc. Acetic acid, acetone, and ethanol (96%) was obtained from Merck Co.

2.2. Nanofibers surface treatment

In this study chemical modification of bacterial cellulose nanofibers was carried up by using acetic anhydride. This will aid in better mechanical bonding between the nanofibers and polymer. Acetylation treatment causes to introduction of acetyl group into the BCNs resulting in plasticization of BCNs. This modification decreases the hygroscopic nature of the cellulose fibers causing enhanced dimensional stability. Before modifying the surface, specific amount of BCNs was activated into a mixture of sulfuric acid (3%) and acetic acid (25%), which was stirred for 40 min at 60 °C. The remains were extracted through centrifugation and decanting. Then, the activated BCNs was poured to a reaction flask comprising 5 mL of acetic anhydride (2.5 wt%) and 20 mL of acetic acid. The suspension was refluxed for 4 h at 100 °C. After acetylation, the treated fibers were washed thoroughly with acetone and ethanol (2:1 by volume) by centrifuges to remove unreacted acetic anhydride and acetic acid by product. In order to achieve a homogenous dispersion of polar BCNs in non-polar toluene the solvent was exchanged four times from ethanol and acetone to toluene by centrifugation.

2.3. EVA nanocomposite preparation

The EVA nanocomposite containing 5 wt% modified BCNs was fabricated according to the solution casting technique. At first, 3 g of EVA (containing 18 wt% vinyl acetate) was dissolved in 25 mL of toluene through heating at 100 °C for 4 h while being stirred strongly. In order to prevent evaporation of solvent a reflux condenser was used. As well as a specific amount of the acetylated BCNs was suspended in toluene followed by stirring for 4 h. The suspension was further homogenized by ultrasonic treatment for a period of 40 min. Then, the dispersed solution of acetylated BCNs was introduced to the previously prepared EVA solution and the mixture was kept at 100 °C under reflux for 30 min while being stirred. The prepared specimen was poured into a glass mold and allowed to dry at room temperature over the course of 48 h. The film was 0.5 mm in thickness. In this study the amount of acetylated BCNs was chosen to be 5 wt% of the total mass of the composition which are designated as EVA/MBC.

2.4. Thermogravimetric (TG) analysis

Thermogravimetry measurements were carried out with a thermogravimetric analyzer (Mettler Toledo TGA/DSC 1). The analysis were conducted under dynamic mode from room temperature to 600 °C in a nitrogen atmosphere (60 mL min⁻¹). Data are taken at different heating rates 5, 10, 15, and 20 K min⁻¹. Small specimens of EVA/MBC 5 wt% (10 mg) were used in order to minimize mass and heat transfer phenomena. The sample was placed in alumina crucibles. An empty alumina crucible was used as a reference.

2.5. Theoretical background

Lately, ICTAC Kinetics Committee has been developed some recommendations that offer specific advice for reliable evaluation of kinetic parameters (the pre-exponential factor, the activation energy, and the reaction model) from the data obtained by means of thermal analysis methods [28,29]. Isoconversional approaches are independent

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