



# Insights into the chemical composition and thermo-oxidative stability of novel polyethylene copolymers containing ancillary phenolic antioxidant groups as non-migrating polyolefin stabilizer



Zahra Balzadeh, Hassan Arabi\*

Iran Polymer and Petrochemical Institute, Tehran, Iran

## ARTICLE INFO

### Article history:

Received 2 March 2017

Received in revised form

22 April 2017

Accepted 29 May 2017

Available online 31 May 2017

### Keywords:

Thermo-oxidative degradation

Thermo-gravimetric analysis

Phenolic antioxidants

Non-migrating stabilizer

Plackett-Burman design

## ABSTRACT

The chemical composition and thermal characteristics of a series of novel polyethylene based sterically hindered phenolic antioxidant (PE-SHPA) copolymers were investigated using thermal analysis methods. TGA/DTG curves manifest two distinct degradation events, one at about 250 °C while the second observed at a temperature between 450 and 500 °C under oxygen atmosphere. Oxidation induction time evaluation shows a dramatic increment by increasing the first degradation event weight loss percentage. To find out whether the first degradation event stem from the presence of low molecular weight non-bonding antioxidants or not, PE-SHPA copolymers were extracted. The higher OIT values observed after the extraction confirmed the chemical bonding of SHPA moiety to the polyethylene carrier and the absence of free antioxidant groups in the copolymer. Hence, the weight loss at 250 °C was considered as an antioxidant content index in PE-SHPA to find an appropriate model for the thermal stability of copolymers produced at different conditions.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polyolefins in their pristine state (without stabilizer) are inherently susceptible to degradation in the presence of oxygen, heat and energy during processing to service. Typically, additives such as primary and secondary antioxidants, amine light stabilizers and flame retardants are added during melt blending to avoid the polymer degradation. However, beside the chemical performance of the additives for proper functionality, their physical permanence should be considered for appropriate maintenance throughout the polymer life time [1]. On the other hand, one of the major concerns in environmental issues and safety regulations is the physical loss of alkyl phenols especially from polymers [2–5]. So, problems like additive volatility, migration, blooming and aggregation must be resolved. In this way, the additive diffusion through the polymer matrix should be controlled to reach the lowest possible level. However, homogeneous distribution of the adherently polar ingredient within the polyolefin substrate is substantially

impossible because of the semi-crystalline structure, besides non-polar inherent nature of the matrix.

Polymeric antioxidants based on polyethylene or polypropylene copolymers are benefitted by almost zero migration and high compatibility with the polyolefin matrix [6–8]. In this case, since the antioxidant moiety is tethered into the polyolefin backbone, the migration and extractability is limited or completely restricted [9–12]. In addition, the higher compatibility of the olefin based stabilizer with the polyolefin matrix results in better distribution of the phenolic groups and lower energy consumption during the melt blending. Moreover, since the hindered phenol moiety incorporated in to the polymer backbone, the polymer bulk is modified as well as the surface. Furthermore, utilizing the single site catalysts let the homogeneous introduction of the functional comonomer into the polymer chain, which consequently results in uniform distribution of the stabilizer through the polymer matrix. On the other hand, the amorphous phase is more sensitive to the thermo-oxidative degradation. Notably, by using the aforementioned master batch the crystalline structure of the host polymer may not altered and the thermo-oxidative characteristics are improved, simultaneously [13,14]. Compared to early transition metal catalysts, late transition metals are appropriately suitable

\* Corresponding author. Tel.: 009821 44787024; fax: 009821 44787021.

E-mail addresses: [z.balzade@ippi.ac.ir](mailto:z.balzade@ippi.ac.ir) (Z. Balzadeh), [h.arabi@ippi.ac.ir](mailto:h.arabi@ippi.ac.ir) (H. Arabi).

candidates for olefin-polar monomer copolymerization due to their lower oxophilicity and consequently high tolerance toward functional heteroatom containing monomers [15–17].

To the best of our knowledge, there have been no reports in the literature on the thermal stability analysis of ethylene-phenolic antioxidant copolymers synthesized using late transition metal catalysts. In this work, we have investigated the thermo-gravimetric and oxidative characteristics of macromolecular polyethylene based hindered phenol antioxidant. In order to evaluate the polymerization conditions effect on the thermo-oxidative properties and comonomer incorporation, Stat graphics Centurion XVI was utilized to find out the optimum conditions for the polymer thermal stability. In this case, ethylene pressure, polymerization temperature, concentrations of comonomer, catalyst and cocatalyst, time of comonomer premixing and polymerization in addition to polymerization medium volume were considered as potential affective parameters.

## 2. Experimental

### 2.1. Materials

All air and/or moisture sensitive manipulations were performed under dry nitrogen atmosphere in a continuously purged glow box or in standard Schlenk line system. Industrial toluene (Bandar Emam, Mahshahr) was dried via distillation over sodium and benzophenone. Nitrogen (Roham gas, Arak) and ethylene (Bandar Emam, Mahshahr) were dried by passing through columns containing KOH, silica gel and molecular sieve, prior to entering the reactor. Methylaluminoxane (MAO) (10 wt% solution in toluene, Sigma Aldrich, Germany) was used as received.

### 2.2. Catalyst synthesis method

Bis(N,N'-(2,6 Di iso propyl phenyl) imino) acenaphthene NiBr<sub>2</sub> catalyst was synthesized according to the literature [18,19] (also given in the [supporting info.](#)).

### 2.3. Comonomer synthesis procedure

2,6-di-*tert*-butyl-4-(dec-9-en-1-yloxy) phenol synthesis procedure is the same as our previous work [20] (also given in the [supporting info.](#)).

### 2.4. General copolymerization procedure

The general process was reported in our previous work [20] (also given in the [supporting info.](#)).

### 2.5. Experiment design

A folded Plakett-Burman design was used to investigate the main effects of various factors on the thermal stability of ethylene-phenolic antioxidant copolymer obtained via Ni(II)- $\alpha$ -diimine catalyst.

#### 2.5.1. Factor identification

In this work, some process factors have been identified; polymerization temperature ( $x_1$ ), ethylene pressure ( $x_2$ ), polymerization time ( $x_3$ ), comonomer, co-catalyst and catalyst concentrations ( $x_4$ ,  $x_5$  and  $x_6$ ), respectively, polymerization medium volume ( $x_7$ ) and comonomer premixing time ( $x_8$ ). Considering the effective factors, a full, two-level factorial design ( $2^8$ ) involves a total run

number of 256. Therefore, a folded Plakett-Burman ( $2^8 \times 3/32$ ) type IV resolution design with 15 ° of freedom involving 24 runs was selected. This design is preferred to Plakett-Burman design for its alias structure where the main effects are clearly distinguished from two-factor interactions. The designed experiments are given in [Table 1](#).

#### 2.5.2. Level identification

The high and low levels were assessed after conducting some preliminary experiments to find the proper conditions region in which acceptable thermal stabilities beside catalyst activities were obtained. Polymerization temperature does not exceed 40 °C to avoid thermally induced catalyst deactivation. Furthermore, the lower level was 30 °C for more practical process. The pressure limits were assigned at low ranges (0.5–1 bar of gage) to afford branched polyethylene structures. The comonomer content in the feed stock was varied between 0.25 and 1 mmol since higher amounts of the comonomer showed sever catalyst poisoning and lower contents does not affect the thermal stability of polyethylene.

#### 2.5.3. Response identification

One main response was studied which is proportionate to the weight loss at 250 °C due to its direct correlation with the copolymer thermal stability namely SHPA Index (SHPAI). The polymer weight loss at 250 °C relevance to the thermal stability of the copolymers and SHPAI calculation method will be discussed in detail later.

### 2.6. Characterization of synthesized materials

Thermo-Gravimetric Analysis (TGA) was carried out employing TGA-STA: PL-1500 (UK) device under Oxygen atmosphere at 25–600 °C, to evaluate the thermo-oxidative degradation. Oxidation Induction Time (OIT) was measured via NETZSCH Instruments Co. DSC 200, F3 Maia (Germany) at 200 °C according to ASTM D3895-07. The chemical structure was evaluated using Attenuated total reflectance (ATR) by a Bruker EQUINOX55 equipment on elastomeric samples.

## 3. Results and discussion

### 3.1. Ethylene-antioxidant copolymers synthesis and its structure elucidation

One of the major drawbacks of low molecular weight polar additives such as antioxidants, flame retardants, UV-stabilizers etc. is their diffusion out of the polymer matrix which is accelerated in non-polar mediums like polyolefins. Since, this work focused on the synthesis of a macromolecular antioxidant benefitted by low or even prevented migration from the polymer substrate possessing good compatibility with polyolefins. The main strategy is presented schematically in [Fig. 1](#).

As illustrated the functional groups are anchored on the polyethylene chain which is structurally compatible with the host polyolefin thanks to its inherently non-polar hydrocarbon skeleton. Indeed, branched polyethylene was used as a polymeric carrier for the phenolic antioxidant.

Since late transition metal catalysts are highly tolerant toward polar functionalities and capable of tailoring different topologies of polyethylene containing various levels of branching from dendritic, hyper-branched to linear branched architectures, Ni based  $\alpha$ -diimine catalyst was utilized as an efficient system for phenolic antioxidant bonding to the polyethylene carrier through ethylene-

Download English Version:

<https://daneshyari.com/en/article/5200659>

Download Persian Version:

<https://daneshyari.com/article/5200659>

[Daneshyari.com](https://daneshyari.com)