Combustion and Flame 000 (2015) 1–10

Contents lists available at ScienceDirect

Combustion and Flame

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

Oxidation of crystalline polyethylene

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ARTICLE INFO

Article history:
Received 24 March 2015
Revised 1 July 2015
Accepted 2 July 2015
Available online xxx

Keywords:
Polyethylene
Low-temperature oxidation
Kinetics and thermochemical parameters
Density functional theory

ABSTRACT

Auto-oxidation of polyethylene (PE) is of a common occurrence and could be triggered by several physical and chemical factors. In this study, for the first time, we report a comprehensive theoretical account on the initial oxidation of crystalline PE at low temperatures prior to its melting. We map out potential energy surfaces for large number of reactions, most notably, initial abstraction by O_2 molecules, formation of peroxy- and hydroperoxyl adducts, unimolecular eliminations of HO_2 and H_2O as well as C–C bond fissions. Rate constants have been estimated for all considered reactions over the temperature range of 300–800 K. We have discussed noticeable similarities between the oxidation of PE and that of gas-phase alkanes. Results presented herein provide new insights into the solid-state oxidation of PE and germane crystalline polyolefins/paraffins and pure carbon–hydrogen-type polymers.

1. Introduction

Polyethylene (PE) holds wide range of applications in the society. As a nontoxic low-priced polymer, PE resins have emerged as an important raw material for various industrial uses, frequently deployed, in substantial amount, in medical, automobile, food, pipeline, civil, and domestic sectors [1,2]. The key to the adaptability of PE lies in its adjustable semicrystalline morphology, giving rise to its existence in various forms. Major types of PE include high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and ethylene-vinyl acetate copolymer (EVA) [1,3]. Due to their elevated calorific value and suitable combustion properties [1,4,5], used PE finds outlets in an extensive array of recycling processes, such as thermal energy recovery via incineration technologies, thermolytic conversion into liquid fuels [6-9] and even pyrolytic conversion to low-carbon hydrocarbon gases for application in hybrid rocket propulsion systems [10,11]. Practical applications of thermal degradation of solid fuels often occur in oxidative environment [12], thus, it is important to understand the thermo-oxidative degradation mechanism of PE.

The thermal decomposition of PE arises by homolysis of C–C bond, unzipping, in successive enchained β-scission reactions, yielding monomer from the polymer. The decomposition then proceeds by free radical mechanism involving multistep chain reactions. This consists of consecutive H-abstraction and β C–C scission, intramolecular hydrogen transfer (backbiting) and intermolecular hydrogen shift (random scission). At high temperature under pyrolytic conditions, PE undergoes both backbiting and random scission pathways [6,13–16]. The overall relatively high activation energy for the inert decomposition of PE (150–260 kJ/mol) is linked to a limiting step characterised by the initial random scission [6,12,17–20].

In the presence of oxygen, the reactions proceed differently with lower activation energy of around 80–143 kJ/mol [11,12,20,21]. Experiments on oxidation of low density PE and related polymers usually involve irradiation at low temperature (photo-oxidative accelerated weathering) or a temperature controlled air-circulated operation at moderate temperature of between 373 to 428 K (i.e., thermal ageing) [21–24]. Reactors and/or thermogravimetric analysers serve to perform high temperature oxidation experiments above 473 K (thermo-oxidative degradation) [12,20].

Different pathways exist for the oxidation mechanism of PE [21,22,25–30]. In the most general form, thermo-oxidative degradation begins by formation of radical sites initiated by induced temperature, but UV radiation as well as existence of trace peroxides and hydroperoxides also influence the initiation of photo-oxidative pathways. Oxygen reacts with the chain radical to form a peroxy-radical intermediate during the propagation step:

$$\text{Initiation: } RH \rightarrow R^{\cdot} + H^{\cdot} \quad (a)$$

$$\text{Propagation: } R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \quad (b)$$

The peroxy radical abstracts hydrogen to form hydroperoxide and a radical centre. The former yields an alkoxyl radical via a unimolecular or bimolecular decomposition mechanism. An alkoxyl radical can effectively abstract a hydrogen to form a hydroxyl group.

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http://dx.doi.org/10.1016/j.combustflame.2015.07.007

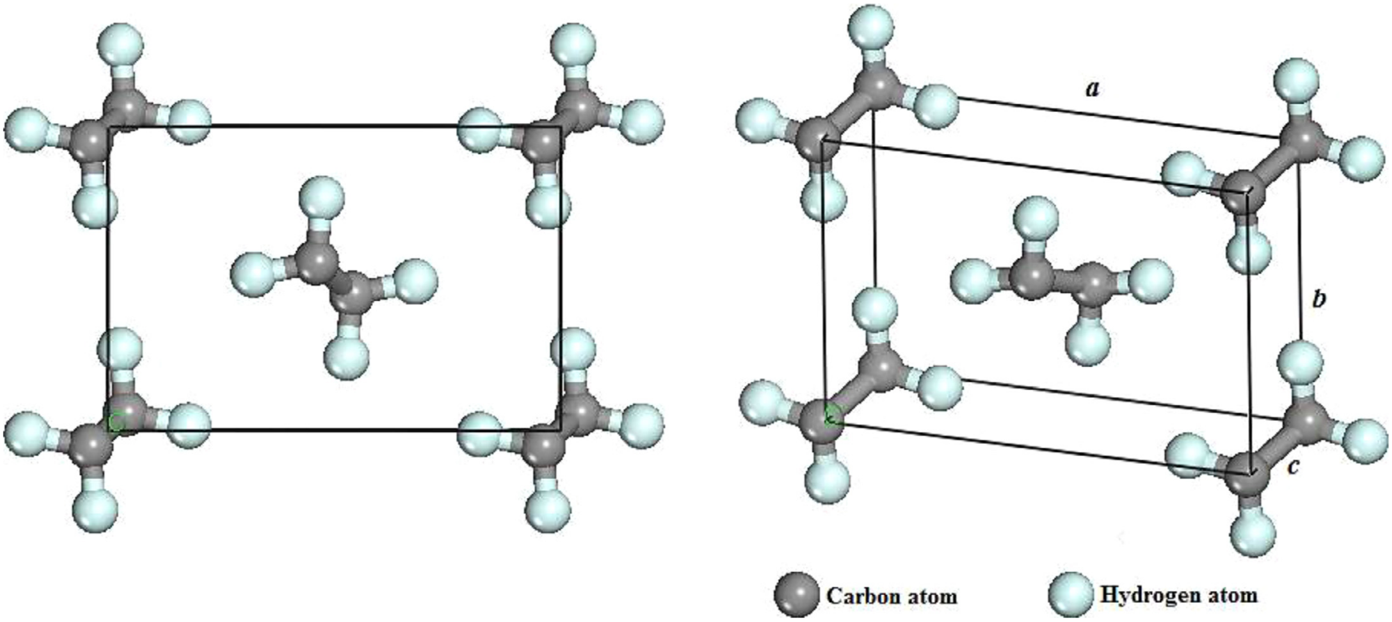

Fig. 1. Unit cell of ideal orthorhombic polyethylene; plan (left) and isometric (right) views.

Intermolecular and intramolecular H-abstractions lead to formation of new radical sites, thereby accelerating the oxidative degradation.

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (c)$$

$$ROOH \rightarrow RO^{\cdot} + OH \quad (d)$$

$$ROOH + RH \rightarrow RO^{\cdot} + R^{\cdot} + HOH \quad (e)$$

$$RH + RO^{\cdot} \rightarrow ROH + R^{\cdot} \quad (f)$$

Amorphous zone of PE has more access to oxygen compared to the densely packed crystalline regions. The amorphous zone oxidises first and then acts as a buffer, protecting the crystalline region from attack during thermal degradation. Therefore, increasing the crystallinity lowers the oxidation rate and increases the sensitivity of mechanical properties of PE towards oxidation [31,32].

While oxidative decomposition of PE mainly occurs in liquid media upon melting, auto-oxidation of solid PE at relatively low temperatures is a common phenomenon that could be triggered by many physical or chemical factors. These factors encompass the presence of structural defects in PE, ultraviolet and ionising radiation, prompt heating, ultrasound, or direct exposure to catalysis, singlet molecular or atomic oxygen and ozone [33].

To this end, the present study deploys the density functional theory (DFT) to investigate initial steps encountered in the oxidation of crystalline PE. We analyse the reaction mechanisms pertinent to thermo-oxidative degradation of PE, and evaluate and compare the kinetic and thermochemical parameters with limited experimental measurements from the literature. Results presented herein provide improved insights into the solid-state oxidation of crystalline polyolefins/paraffins and carbon–hydrogen-type polymers. Such knowledge is instrumental to understand the auto-oxidation process of crystalline PE that underpins its natural ageing mechanism under thermo- and photo-oxidative conditions.

2. Methodology

2.1. Computational details

DMol^3 package [34,35] facilitates all structural optimisations, and serves to calculate all energies and vibrational frequencies. In the optimisation of all stationary points, our theoretical approach comprises the generalised gradient approximation (GGA) as the exchange-correlation potential alongside with the Perdew–Burke–Ernzerhof (PBE) functional. The total energy converges with a tolerance of 1×10^{-6} Ha. The electronic core treatment includes all electrons in the calculations while deploying a double numerical plus polarisation (DNP) basis set [34], and a global cut-off of 4.0 Å. Based on the subsequent thorough benchmarking against analogous experimental and theoretical values from the literature, we have found that, the adopted DFT functional and basis set offer a satisfying accuracy threshold for the system at hand. We carry out integration of the Brillouin zone via automatic generation of $2 \times 3 \times 6$ and $1 \times 2 \times 1$ k-points for the unit cell and periodic slabs, respectively, through the Monkhorst–Pack grid scheme. The average computational cost, for each periodic slab typically amounts to 20 h on a 32 parallel processing cores. Last of all, Tkatchenko and Scheffler's semiemperical dispersion correction scheme [36] offers the necessary measures to validate the compromise between the cost of evaluation of the dispersion terms and the need to improve non-bonding interactions in our system.

2.2. Molecular and crystallographic structural parameter of polyethylene

Crystalline PE exhibits an orthorhombic crystal structure under all but the most exceptional circumstances. Its unit cell contains all crystallographic data needed for a complete crystallite [1,37]. We generated the reference unit cell structure by optimising the orthorhombic crystalline arrangement reported by Avitabile et al. [38]. The primitive cell exhibits a Pnam space group [39,40] that consists of 12 atoms, equivalent to two $-CH_2-$ chains as shown in Fig. 1.

Please cite this article as: I. Oluwoye et al., Oxidation of crystalline polyethylene, Combustion and Flame (2015), http://dx.doi.org/10.1016/j.combustflame.2015.07.007