Polymer Degradation and Stability xxx (2015) 1–8

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Thermal degradation of γ-irradiated PVC: I-dynamical experiments

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ARTICLE INFO

Article history:
Received 8 December 2014
Received in revised form
6 March 2015
Accepted 25 March 2015
Available online xxx

Keywords:
PVC
Dynamical thermal degradation
Kinetics
Radio-oxidation
FTIR

ABSTRACT

Polymers used in nuclear industry are important constituents of nuclear wastes. In case of fire during waste transportation, package temperature could rise markedly. Within this context, the objective of this work is to analyze the thermal degradation of irradiated polymers. The dynamical degradation of radio-oxidized poly(vinyl chloride) was investigated by thermogravimetry coupled with mass spectrometry and by thermodesorption coupled with gas chromatography–mass spectrometry. Additive-free and plasticized PVC was pre-aged using γ-irradiation under air at room temperature. Pre-irradiation induces a decrease of the initial degradation temperature and leads to an early formation of HCl and benzene. Although dehydrochlorination remains the predominant degradation process within the temperature range used in this study, others processes contribute to the mass loss such as dehydration and desorption of degradation molecules resulting from radio-oxidation.

1. Introduction

Polymers are widely used in nuclear industry (electric cables, plastic bags, filters…) making them important constituents of the Long Lived and Intermediate Level Waste packages. Materials present in nuclear waste package are exposed to high level radiation in air. Then within the context of nuclear waste transportation, the thermal degradation of radio-oxidized polymers has to be investigated in detail. In point of fact, in case of fire, the interior of the package can be subjected to a temperature peak that can reach 150 °C. After the accident, the temperature could remain above 80 °C several days. Temperature increase can have an influence on the degradation of these materials and has then to be considered.

This study focuses more particularly on the analysis of the thermal decomposition of irradiated poly(vinyl chloride) (PVC). Degradation mechanisms and kinetics are investigated. The aim of this work is twofold: acquire data intended to be used in the specific context of transportation of nuclear waste containing polymers and to study the influence of chemical defects on the thermal stability of polymers. The latter point is fundamental since the thermal degradation is often controlled by labile groups initially present in the material.

PVC is, by far, the most common thermoplastic material used in industry. For this reason, its degradation has been intensively studied since the 1930s. PVC degradation, leading to the formation of toxic or harmful compounds, has been the subject of detailed analyses in different conditions, using a full range of analytical techniques. In 1985 and 2008, Jerzy Wypych published a synthesis combining the whole knowledge of thermal, photolytic and radiolytic degradation of PVC [1,2]. It is generally accepted that thermal degradation proceeds through three major stages [3–12]. The first one, in the temperature range between 180 °C and 360 °C, corresponds to dehydrochlorination (DHC) process, with the consecutive formation of HCl and benzene resulting in the formation of polyenes [6,12–16]. The second stage, corresponding to a condensation process, occurs between 360 °C and 500 °C and corresponds to the formation of aromatic hydrocarbons obtained by cyclization of conjugated structures. Above 500 °C, a new stage is

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http://dx.doi.org/10.1016/j.polymdegradstab.2015.03.014
0141-3910/

Please cite this article in press as: Boughattas I, et al., Thermal degradation of γ-irradiated PVC: I-dynamical experiments, Polymer Degradation and Stability (2015), http://dx.doi.org/10.1016/j.polymdegradstab.2015.03.014

defined as fragmentation and involves hydrocarbon structure destruction and char formation [3,7,13–16].

In the following we will focus on DHC process. It is described as a chain reaction and the initiation step involves radical, ionic or molecular species [12]. The relative importance of these processes will depend on the presence of additives or impurities and on external conditions: ionic mechanism is possible in presence of polar solvents or acidic additives whereas the radical mechanism is promoted by irradiation or at temperatures above 250 °C. Below this temperature or in the presence of HCl, the molecular mechanism is favored [12]. For example, Fisch and Bacaloglu studied the DHC process at a temperature lower than 200 °C. They suggested that DHC is initiated by a molecular mechanism associated to allylic chlorine, because of the higher reactivity of this group rather than tertiary chlorine [17].

Thermal decomposition of PVC was also studied by varying different parameters such as atmosphere and pre-irradiation. The acceleration of HCl formation in the presence of oxygen is attributed to side reactions with the oxidation products and more particularly to thermal degradation of hydroperoxides formed by the reaction of oxygen with macroradicals [12]. Moreover, the presence of HCl in the environment promotes PVC degradation [18,19]: whatever atmospheric conditions are, HCl plays the role of autocatalyst and accelerates the thermal degradation of PVC. The authors show that HCl reacts with polyenes and leads to an increase of HCl production [1,2,20–23]. To our best knowledge, pre-irradiation was studied only by Salovey et al., who analyzed the thermal degradation of pre-irradiated PVC under inert atmosphere by dynamical and isothermal measurements under nitrogen and oxygen atmosphere [24,25]. They showed that only the initial degradation temperature is affected by irradiation, and decreases from 200 °C for non-irradiated polymers to 160 °C for a pre-irradiated sample at 522 kGy. Moreover, pre-irradiation enhances isothermal degradation at 150 °C. This result is attributed principally to tertiary chloride and to allyl chloride formed during irradiation.

Different kinetic models were developed to describe PVC thermal degradation [5,6,26–29]. Due to the complexity of the chemical reactions and physical processes involved, the models generally use a limited number of pseudo-chemical reactions. Pre-exponential factors, activation energies and reaction orders are variously adjusted [27,28]. According to numerous authors, the DHC process can be described as a single-step degradation reaction with an order close to 3/2 and with an activation energy around 140 kJ mol^{-1} [12,26–28,30–32]. Bockhorn et al. determined an activation energy of 136 ± 5 kJ mol^{-1} and attributed this value to the formation of HCl by the scission of C–Cl by a radical chain process. Pre-irradiation under inert atmosphere induced a decrease of the activation energy of HCl formation but does not modify the reaction order [25]. The global activation energy variation as function of the conversion degree $(\alpha)E_a^{\infty}$ can be obtained from dynamical measurement analysis, as proposed by Ozawa [33].

Numerous studies have been performed on the effect of plasticizers on thermal degradation formulated PVC. No simple relationship between polymer thermal stability and the concentration of plasticizers has been found. Their presence can increase or decrease the thermal stability of PVC. Thermogravimetry (TG) is generally not a suitable method because it does not differentiate HCl loss and plasticizer evaporation or degradation.

In the present paper, we studied the thermal degradation of radio-oxidized additive-free PVC and of plasticized PVC. We have investigated dose effects using TG dynamical experiments, the radio-oxidation degradation molecules have been identified by thermodesorption (TD) coupled with gas chromatography–mass spectrometry (GC–MS) and the chemical evolution of the polymer has been characterized by in-situ Fourier transform infrared spectroscopy (FTIR). Thermal degradation kinetic of irradiated PVC was investigated using Ozawa's method [33]. Isothermal measurements at 120 °C and 150 °C and a general reaction scheme for the low temperature degradation step, *i.e.* the DHC step, in a radio-oxidized PVC will be presented in details, in a forthcoming paper.

2. Experimental

2.1. Materials

For a better understanding of thermal degradation mechanism, the study was, first, carried out on additive-free PVC, supplied by Plastunion (grade K75) in the form of powder. Industrial PVC, hereafter referred to as plasticized PVC, supplied by Plastunion in the form of sleeves (300 μm thick) was also investigated to analyze the influence of additives and plasticizers on thermal degradation. Its composition of industrial PVC was: 63 wt% PVC resin (grade K70 and K75), 31 wt% of diisononyl phthalate (DINP), 1.4 wt% of heat stabilizer and 2.25 wt% of others additives.

2.2. Preparation and pre-irradiation of samples

Additive-free PVC films 50–70 μm thick were prepared by compressing the powder in a mold at 170 °C under a pressure of 4 tons during 30 s. Plasticized PVC films were reduced at 50 μm to ensure a homogenous oxidation. During γ-irradiations, films were hung on a glass stick, keeping enough space between them to allow a homogenous oxidation process. They were then introduced into pillboxes and then placed in aluminum baskets. Pillboxes were then covered with a Kapton film to avoid ambient pollution.

γ-Irradiations were performed at IONISOS (Dagneux, France) using a ^{60}Co γ-source. Samples were irradiated at room temperature under air, at a dose rate between 0.51 and 0.62 kGy h^{-1}. The water equivalent absorbed doses were 260, 500, 756, 1015 kGy (±6%). Dosimetry was performed using radio-chromic (Red Perspex) dosimeters. No correction was made to take into account the electronic density difference between water and PVC.

After irradiation the color of the samples turned from white-transparent to black. As a consequence, UV–visible spectroscopy could not be used to monitor the formation or the development of polyene sequences.

It is known that PVC samples continue to suffer DHC processes for a long time after irradiation. Nevertheless, at such high doses used in this work, PVC samples are so degraded that post-irradiation DHC process is negligible compared to irradiation DHC process. Nevertheless, precautions have been taken before their thermal treatment: pre-aged samples were stored under nitrogen atmosphere away from the sun light.

2.3. FTIR characterization

After irradiation, some films were characterized by FTIR. Spectra have been collected on a Brucker Tensor 27 spectrometer in transmission mode. For each spectrum, 64 scans were registered and averaged with a resolution of 4 cm^{-1}. For comparison, FTIR spectra were normalized according to the film thickness.

2.4. Thermogravimetry coupled to mass spectrometry (TG-MS)

Thermal and gas analyses were performed using a NETZCH model STA 449 Jupiter coupled with a QMS 403 D Aëolos® quadrupole mass spectrometer. For each measurement, 5 mg of the sample were placed in an alumina crucible in the thermobalance. Analyses were carried out under dynamic helium atmosphere at a

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