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Oxidative degradation products analysis of polymer materials by pyrolysis gas chromatography–mass spectrometry☆

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ABSTRACT

Pyrolysis gas chromatography–mass spectroscopy (PGC–MS) has been proved to be a powerful method to analyze both the volatile additives and the macromolecular structure of polymer materials. In this paper, flash evaporation technique was used to analyze the volatile degradation products of polymer materials during natural and artificial aging. In high density polyethylene (HDPE) composites, mainly *n*-alkanes with carbon number from 14 to 29 were detected after natural aging, while no oxidative product was found. Different composites have different *n*-alkane distributions. In contrast, various oxidative products including ketones, alcohols, esters and unsaturated species could be found in aged polypropylene (PP) nanocomposites. Nanoparticles accelerated the chain scission of PP and increased the formation of oxidative products significantly. During thermal oxidation of nitrile rubber (NBR) seal rubbers, heat/oxidation-induced extra crosslinking predominated and no volatile degradation products was detected. The main change happened in the volatiles is the decrease of additives, especially paraffins, antioxidant RD and hindered phenol. This resulted in the hardening of the rubber and the weakening of the protection from oxidation. Furthermore, the additive distribution along the depth was investigated, showing different migration speeds of different additives. From the additive levels remained in the NBR rubber, it is possible to predict the degradation status. In summary, PGC–MS can supply abundant information of polymer degradation and is helpful for mechanism research.

1. Introduction

Pyrolysis gas chromatography–mass spectrometry (PGC–MS) is a simple, fast and reliable analytical method and has been used in analysis of polymers for decades. It combines high temperature pyrolysis of polymers with following separation of fragments mixture and identification. Coupled with flexible pre- and post-pyrolysis techniques such as thermal desorption (TD), solid phase micro-extraction (SPME), flash evaporation and derivatization, PGC–MS can deal with various forms of polymer samples without necessity of complex pretreatment. With strong separation and identification function as well as wide adaptability, it has been used in various polymer research applications including structure identification, qualitative and quantitative determination, thermal degradation kinetics and additive analysis. Many good reviews can be referred in these aspects [1–5].

From its birthday, pyrolysis was designed to break macromolecular chains to small fragments at high temperatures. Therefore, it is naturally suitable for thermal degradation research of natural and synthetic polymers in inert atmosphere at different temperatures and related work have been reviewed in detail [2,3]. However, there are relatively less literature concerning the application of PGC–MS in aging research of polymer materials under natural or artificial weathering conditions. Generally, the concentration of aging-induced oxidation, chain scission and crosslinking are quite low compared to the backbone structure before severe degradation, so the difference between programs of polymer materials before and after aging is so small that it cannot be detected usually or overlapped by the inhomogeneity of samples [6–8]. In contrast, volatile small molecules often present as the chain scission products, and additives such as plasticizers, flame retardants, antioxidants and light stabilizers would migrate out during aging process. These changes can be detected and used to represent the aging status and predict the degradation of polymers. Lattuati-Derieux et al. [9] compared pyrolysis products of natural and artificial aged polyurethane (PU) foams by PGC–MS and volatile degradation products by headspace SPME GC–MS. The results confirmed that hydrolysis predominate the degradation of polyester-based PU (PU-ES),

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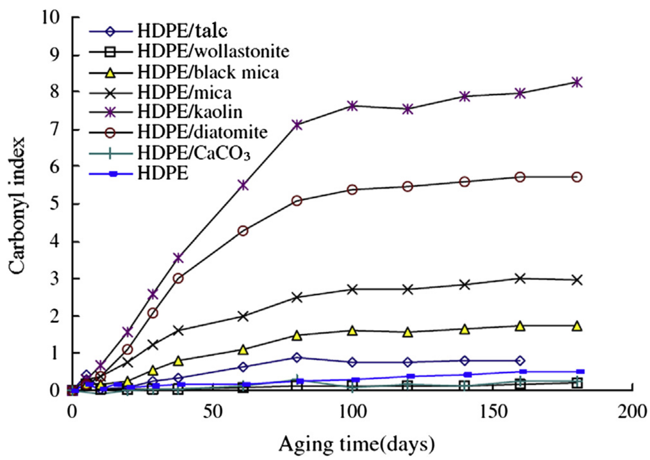

Fig. 1. Carbonyl index changes of HDPE composites with time [18] (Carbonyl index is defined as the absorbance ratio of carbonyl group centered at 1716 cm^{-1} to the reference at 2019 cm^{-1} in IR spectra).

whereas oxidation predominate the degradation of polyether-based PU (PU-ET). Alcohol and acid raw products from PU-ES and glycol derivatives from PU-ET were identified both in natural and in artificial aging. These two groups of volatile products can be considered as degradation markers for PU. Bernstein et al. [10,11] studied the volatile oxidation products of polypropylene (PP) by GC–MS. By isotopic labeling, they clarified the origin of these products and thus elucidated the predominant reaction route of PP. Oxidation mechanism of PP was proposed accordingly. White et al. [12] collected the volatile thermal-oxidative degradation products of nylon 6,6 by SPME and cryotrapping. Evolved CO_2 and NH_3 were analyzed by GC–MS. Their origin was even elucidated by isotopic labeling of ^{13}C, ^{15}N and ^{18}O. Burman et al. [13] extracted small molecular degradation products from linear low density polyethylene (LLDPE) with three kinds of pro-oxidants by solvents and analyzed with GC–MS. Both the type of pro-oxidant system and the state of degradation are predictable from diacid fingerprintings. Wei et al. [14] revealed the difference between volatile components in pigment filled polyvinyl acetate (PVA) before and after UV aging with double-shot PGC–MS, including the formation of acetic acid and the decrease of plasticizers such as diethyl phthalate (DEP) after aging. Meanwhile, the pyrolysis products at 600 °C before and after aging are the same although their relative concentrations are different. The pyrolyzates concentration can be used as indicators for the degradation status of PVA paints.

Another advantage of volatile analysis compared to backbone pyrolysis is that the volatile degradation products can be detected at a very early stage of degradation, far before any significant mechanical or structural changes can be observed. Therefore, it is promising to use volatile degradation products as monitors of degradation state and the lifetime prediction may be carried out accordingly. Hoglund et al. [15] identified eight thermal degradation products of nylon 6,6 by SPME and GC–MS. They found a correspondence between odor, degradation products and tensile properties at the very early degradation stage. Recently, a micro-UV irradiator was incorporated to a PGC–MS system to realize on-line aging and analysis during a short period [16,17].

In most of the above research, volatile degradation products in polymer materials were separated by thermal desorption or solvent extraction and then analyzed by GC–MS. In principle, flash evaporation or temperature programming technique of PGC–MS are straightforward ways to remove volatile components from the polymer matrix without pre-extraction, just by heating samples at temperatures below the decomposition temperature of the polymer. In this paper, flash evaporation PGC–MS was used to study volatile degradation products and additives during natural or artificial aging of polymers.

2. Materials and methods

2.1. Materials

High density polyethylene (HDPE) composites were prepared by mixing and co-extruding HDPE (2100J, Yanshan Petroleum Chemical Co. Ltd, Beijing, China) with 30 wt% inorganic fillers in a single screw extruder at 180–190 °C. The inorganic fillers include black mica (Xichang Institute of Mineral Substances of Sichuan, 800 mesh), mica, calcium carbonate, wollastonite, diatomite, kaolin and talc (Beijing Guoli Powder Making Co., Ltd., 1250 mesh). The composites were hot-pressed at 170 °C to films of about 120 μm in thickness. The natural aging of HDPE composites was carried out outdoors for 6 months.

Polypropylene (PP) nanocomposites were prepared by mixing and co-extruding PP (F1002, Yanshan Petrochemical Co. Ltd, Beijing, China) with 1–5 wt% nano-$CaCO_3$ (15 ± 5 nm in diameter, Beijing University of Chemical Technology) and nano-SiO_2 (*ca.* 40 nm in diameter, Zhejiang Zhoushan Mingri Nanomaterial Co.) in a twin-screw extruder at 200–220 °C. The nanocomposites were hot-pressed to films of about 120 μm in thickness. The natural aging was carried out outdoors for 88 days.

Vulcanized nitrile rubber (NBR) sheets with thickness of 2 mm were supplied by SKF Sealing Solutions, with carbon black, vulcanization package, silane, plasticizer and antioxidant package in the composition. Thermo-oxidative aging was carried out in an air-circulating oven at 60–125 °C for up to 1000 h.

2.2. Method

A PYR-4A pyrolyzer was equipped with a gas chromatography–mass spectrometry (GC–MS-QP5050A, Shimadzu, Japan). Flash evaporation technique was used to separate volatile degradation products from

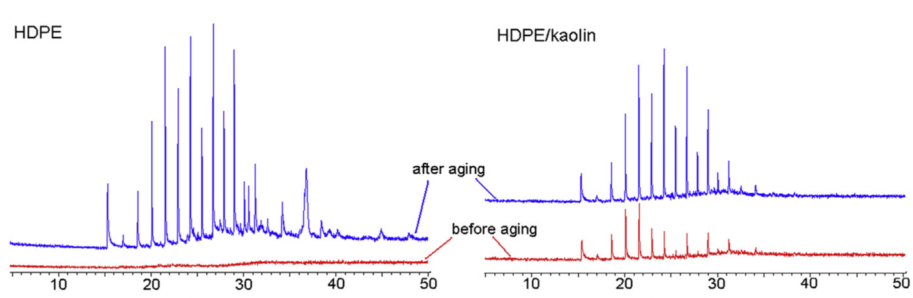

Fig. 2. PGC–MS chromatograms of HDPE and HDPE/kaolin before and after natural exposure for 6 months.

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