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Chromatography for Sustainable Polymeric Materials

Renewable, Degradable and Recyclable

Springer

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Volume Editors:
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Preface

Polymeric materials, both "inert" and degradable, constantly interact with the surroundings. Because of this interaction changes take place in the polymer matrix and small molecules are released to the environment. Reliable methods for testing biodegradability and environmental interaction of renewable resources and biodegradable polymers are required to answer the remaining questions concerning the environmental impact of these future materials. In the case of degradable polymers multiple factors affect the degradation process and small changes in the chemical structure or product formulation may change the susceptibility to degradation or cause different degradation product patterns, rendering the product less environmentally adaptable. Development of sustainable polymeric materials also demands the development of more migration-resistant polymer additives. Chromatographic techniques especially gas chromatography and liquid chromatography preferentially coupled to mass spectrometric detection are ideal tools for studying these low molecular weight compounds and polymer–environment interactions.

In the first chapter of this volume chromatographic fingerprinting and indicator product concepts are presented as tools for evaluating polymeric materials. These concepts have great potential in evaluation of degradation state and life-time/service-life of polymeric materials, evaluation of anti-oxidant or pro-oxidant systems, degradation mechanism and processing parameters as well as rapid comparison and quality control of materials. The solid-phase microextraction technique has rapidly found applications in numerous fields. The second chapter reviews the extraction of polymer degradation products and additives, monomer-rests, odour compounds, migrants from packaging and medical products as well as extraction of polymer additives from environmental samples and biological fluids by solid-phase microextraction demonstrating the high versatility and potential of this technique also in polymer analysis. In the third chapter the possibilities and limitations in the headspace extraction of volatiles from solid polymer matrixes are discussed. Examples of the use of multiple headspace extraction to remove matrix effects are shown and finally the application of headspace analysis for early degradation detection and quality control of recycled materials is presented. The fourth chapter summarises the literature on chromatographic analysis of degradation products from the most common aliphatic and aliphatic–aromatic polyesters. Espe-

cially the effect of macromolecular architecture and copolymer composition on the resulting degradation mechanism and degradation product pattern is discussed. The last two chapters deal with the analysis of polymer additives. The fifth chapter overviews different extraction techniques and aspects of analyzing antioxidants in polymeric materials. The sixth chapter discusses the migration of monomeric and polymeric PVC plasticizers with the focus on migration from medical products and food packaging. Especially the possibilities of improving the migration resistance and plasticizing properties of polymeric PVC plasticizers through the right plasticizer design are presented.

The interest in degradable and/or renewable materials is increasing rapidly. Degradation of these materials is still often studied only by measuring the weight loss or changes in molecular weight, which can be misleading. Especially in the case of bioresorbable materials the knowledge of degradation products is a crucial point for biocompatibility of the materials. As an example we have in chapter four presented results showing the influence of macromolecular design on the formation of acidic degradation products, a possible cause of negative impacts in the body. We have also shown that copolymer composition influences the stability, degradation mechanism and amount of degradation products formed during radiation sterilization. Hopefully these chapters will inspire more extensive use of chromatographic techniques for polymer analysis and result in increased understanding of polymeric materials, which in turn will provide tools for the development of sustainable future materials.

Stockholm, April 2008

Ann-Christine Albertsson
Minna Hakkarainen

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Indicator Products and Chromatographic Fingerprinting: New Tools for Degradation State and Lifetime Estimation

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Abstract The demands on polymeric products are growing both with respect to their function and purity. There is a need for new high-throughput characterisation tools for rapid quality control and evaluation of materials. Precise control over degradation rate and service-life are also prerequisites for successful use of degradable polymers in an increasing number of applications. The chromatographic fingerprinting and indicator product concepts, presented in the current paper, are novel and attractive alternatives for rapid evaluation of the product quality, degradability, durability and service-life. The sensitivity of these techniques allows for detection of small initial changes in the materials and signs of early degradation. The possible applications include evaluation of different pro-oxidants or antioxidants, optimisation of processing parameters, evaluation of long-term properties or storage stability and lifetime prediction. The same principal could also be applied to process control and monitoring, acceptance or rejection of raw materials, intermediate and final products. The usefulness of indicator products and chromatographic fingerprinting is shown for estimation of the degradation state of degradable polyethylene. In addition, chromatographic fingerprinting together with multivariate data analysis is utilised to classify degradable polyethylene materials based on their incorporated pro-oxidant systems.

Keywords Chromatographic fingerprinting · Degradation · Indicator products · Lifetime prediction · Long-term properties

Abbreviations

ATD	automated thermal desorption
ATR-FTIR	attenuated total reflection-Fourier transform infrared spectroscopy
CL	chemiluminescence
CP	conducting polymers sensor
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC-MS	gas chromatography mass spectrometry
HDPE	high density polyethylene
LLDPE	linear low density polyethylene
LSE	liquid-solid extraction
MALDI	matrix-assisted laser desorption ionisation
MDA	multivariate data analysis
MFI	melt flow index
MOS	metal oxide semiconductors
MOSFET	metal oxide semiconductors field effect transistor
MS	mass spectrometry
NIR	near infrared reflection spectroscopy
PC	principal component
PCA	principal component analysis
PCL	polycaprolactone
PCR	principal component regression
PLLA	poly (L-lactic acid)
PLS	partial least squares regression
SEC	size exclusion chromatography
SPE	solid phase extraction
SPME	solid phase microextraction

1 Introduction

Throughout their life cycle, polyolefin's suffer oxidative degradation promoted by heat, UV-radiation and mechanical stress. The degradation is associated with irreversible changes in the chemical structure of the polymer. It influences the physical and chemical properties, such as morphology, molecular weight, tensile strength, elongation at break and colour. The new methods presented in this review for classification and rapid degradation state estimation are valuable tools for evaluation of polyolefin long-term properties and further for development of tailored polymer materials.

Degradable materials are desirable in various applications ranging from disposables, decreasing the amount of litter, to mulch films improving growth conditions for grain. Therefore, several different degradable polyethylene materials have been developed and are on the market today. The susceptibility of polyolefins to degradation can be varied by additives or by copolymerisation. Transition metal ions, e.g. iron, manganese and copper, catalyse the decom-

position of hydro peroxides in thermal and photo-oxidation, see Eqs. 1 and 2 [1], and are used to enhance the degradation at low temperatures of otherwise relatively stable polymers such as polyethylene [2]. The products of the catalysed decomposition of hydro peroxides are similar to the products from un-catalysed oxidation processes [3].

Catalytic decomposition of hydro peroxides.

$$ROOH + M^n \rightarrow RO^{\cdot} + OH^- + M^{n+1} \quad (1)$$

$$ROOH + M^{n+1} \rightarrow ROO^{\cdot} + H^+ + M^n \quad (2)$$

The use of transition metals as pro-oxidants in polyethylene gives degradable cost effective materials with good technical performance. Pro-oxidant systems may also contain natural polymers, such as starch, or unsaturated polymers [4–6]. The ability of materials to degrade by thermal oxidation and UV radiation as well as controlled degradation rate are crucial for their application. It is therefore important to investigate the degradation process during the early stages of oxidation to be able to produce materials for specific applications and for different degradation rates.

A good example of a class of materials with specific stability and degradability criteria are mulch films for corn production as seen in Fig. 1. They should protect the crops at the beginning of the season but be brittle enough

Fig. 1 Corn production with and without mulch-film

after 4 to 6 weeks for the crops to puncture the films without being damaged. However, the films must also be sufficiently resistant so that they are not torn into pieces by wind and normal weather conditions during the time when the plants are still small. With such demands it is crucial to understand and to have control over the degradation process during the early stages. To be able to detect small changes in the material would be very valuable for the development of rapid classification methods based on the initial stages of degradation. This would provide further tools for the development of improved degradable polyethylene materials and for making the right choices between the already existing ones.

Early degradation state detection is also a key issue in the field of stabilised materials [7]. The evaluation of long-term efficiency of antioxidants under non-accelerated conditions takes too much time to be practical. The accelerated tests currently in use are often made under unrealistic physical conditions leading to unreliable results [8–10]. Accelerated aging at high temperature is frequently used even though the degradation and stabilisation reactions taking place at high temperatures are different from those taking place at low temperatures. Sensitive techniques for early degradation detection are, thus, essential components in the effort to reduce the acceleration needed to reach practical test times.

2
Evaluation of Long-Term Performance of Polyethylene

Polymer degradation can be analysed at macroscopic, macromolecular or molecular scale, Fig. 2. The detection of early degradation and small differences in degradation behaviour between different materials requires an

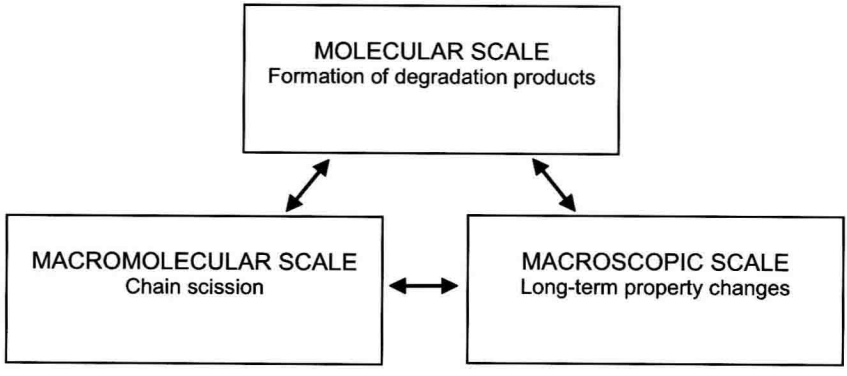

Fig. 2 Degradation of polymers can be analysed at macroscopic, macromolecular or molecular level

analytical technique with high sensitivity. Macroscopic scale properties are less sensitive parameters for early degradation detection and degradation state evaluations than the changes taking place at the molecular level, e.g., the formation of degradation products. The most common techniques used today to monitor the degradation of polymers are Fourier transform infrared spectroscopy (FTIR), where a carbonyl index is used as a measure of the oxidation induction time and degradation rate, size exclusion chromatography (SEC) to follow the changes in molecular weight [11, 12], differential scanning calorimetry (DSC) to follow the changes in crystallinity [13], and mechanical testing of changes in strength and brittleness. As an example loss in mechanical properties occurs first when the molecular weight of the polymer has decreased to a critical value [14].

2.1 Evaluation Based on Changes at the Molecular Level

Degradation products can usually be detected, identified and quantified long before the mechanical performance of the material changes. Degradation products also give information regarding the degradation mechanisms beyond these changes. FTIR is a useful technique that provides information at a molecular level but compared to chromatographic techniques there are limitations in how detailed the information is that is obtained. Carbonyl compounds account for most of the oxidation products and they are seen in the FTIR spectra in the region between 1680 and 1780 cm^{-1} as overlapping bands corresponding mainly to acids (1712 cm^{-1}), ketones (1720 cm^{-1}), aldehydes (1730 cm^{-1}), esters (1743 cm^{-1}) and lactones (1785 cm^{-1}) [15, 16]. Because of the overlapping of the bands, derivatisation, using for example NO and SF_4, is necessary for quantification of the functional groups. [17]. During the 1970s and 1980s Albertsson et al. followed the degradation of polyethylene by measuring the CO_2 emission from the polymers using a ^{14}C technique with liquid scintillation spectrometry [18–20]. The labelling assured that the CO_2 containing ^{14}C came from degrading polymers. Chemiluminescence (CL) is a newer technique that has mostly been used for evaluation of stabiliser efficiency, but that today is sensitive enough for early degradation detection and classification of degradable polyethylene materials [21]. The counted photons emitted from the oxidising polymer correlate with the amount of hydro peroxides in the material, i.e. the initial degradation products during oxidation [22, 23]. CL has been shown to detect oxidation earlier than FTIR [21] in degradable polyethylene, even when looking at the range of the hydro peroxide detection in the FTIR spectra. However, good degradation state estimations are prevented by a non-linear increase in the luminescence intensity versus the degradation time.

2.1.1 Evaluation Using Gas Chromatography

FTIR is a valuable technique for obtaining information of the various product groups. However, identification of the individual degradation products gives more insight into the degradation mechanisms [24]. Gas chromatography (GC) in combination with selective extraction method and mass spectrometric detection are the ideal tools for identification of volatile and semi-volatile products. Since the early 1980's Albertsson et al. have used chromatographic analyses of low molecular weight degradation products to study the long-term performance of polymers [25, 26]. Their latest works on degradable polyethylene have focused on the development of rapid and informative tools to provide a greater understanding within this area. Reliable extraction methods are vital for the correct chromatographic analysis of long-term performance of polymers. The choice of extraction technique depends on the analytes, on the surrounding media and on the purpose of the extraction. The development of several extraction methods utilising liquid-solid extraction (LSE), solid phase extraction (SPE) and solid phase microextraction (SPME), made it possible to identify over 200 degradation products and product fingerprints to clarify the complex degradation patterns of polyethylene [27–32]. The most abundant groups of degradation products were mono- and dicarboxylic acids, but alkanes, alkenes, ketones, aldehydes and alcohols were formed as well.

2.1.2 Multivariate Data Analysis for Optimised Information Extraction

The amount of data that can be obtained from, for example chromatographic and spectrometric techniques, has increased dramatically. Wold [33] introduced the principle of multivariate data analysis (MDA) in the mid-1970s as a way to obtain as much information as possible from these analyses. Estimates based on many variables have in addition the advantage of being more robust than estimates from a few measurements since the first are decided with higher degrees of freedom [34].

Principal component analysis (PCA) is a qualitative method where the X-data can be studied without any knowledge of the Y-data. A score plot of the X-data gives an overview of possible patterns in the data and is therefore a useful tool for classification. The X-data are explained using uncorrelated vectors in pairs called principal components (PC). The first principal component (PC1) is in the direction of the largest variation in the multidimensional X space, Fig. 3. PC2 is in the direction of the second largest variation perpendicular to PC1 etc, all orthogonal to each other. The two-dimensional plane containing two principal components, e.g. PC1 and PC2, is called a score plot. The number of components to be included in the model is chosen on the basis of the amount of variation in the data that each of