



Inverse gas chromatography investigation of oxidized polyolefins: Surface properties



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ABSTRACT

Oxidized polyolefins were obtained in processes with the use of air or oxygen as oxidizing agent. The oxidation process caused partial polymer degradation and the change of the surface properties of examined materials. The magnitude of these changes was estimated by means of inverse gas chromatography. All oxidized materials were found to exhibit slightly acidic character. Surface properties strongly depend on the content of oxygen functional groups (oxidation degree) and type of initial material. The most active surfaces were found for oxidized polypropylene and polyethylene wax. The use of principal component analysis allowed to select four parameters offering complete information on the physicochemical character of examined materials (γ_S^D), acid volume or saponification number, K_A or K_D and K_A/K_D .

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1. Introduction

Polyolefins have excellent properties, low price, and easy processing. These are the most frequently used polymers produced in large-quantity production. However, their nonpolar nature causes some limitations in their adhesion properties. Therefore, different physical [1–3] or chemical [4–6] methods for the modification of the polarity of polyolefins have been investigated.

The oxidation with air or oxygen is mainly used in industry. Depending on the type of used polyethylene oxidation process can be carried out in melt [7], in aqueous dispersion [8,9] or in solid phase [10,11]. The obtained oxidized polyethylene (PE) or PE wax can be used in formation of aqueous emulsions, widely used as floor and leather polishes, or as additives for textile and paint applications [12]. Polar polypropylene is obtained generally by reaction with anhydrides, especially maleic anhydride (PP-g-MA) [13]. The polar functionality in these materials facilitates printability, paintability and receptivity to adhesives in the case of extruded and moulded products [14].

1.1. Inverse gas chromatography

The term *inverse gas chromatography* indicates that the material of interest is placed in a chromatographic column and the behavior

of selected test solutes is studied. Retention parameters and the shape of chromatographic peak of these solutes are affected by the nature and magnitude of their interactions with the examined material.

Retention of test solutes on the column filled with studied material is the result of both dispersive and specific adsorbate-adsorbent interactions. The free surface energy consists of two components, dispersive, γ_S^D , and specific, γ_S^S [15,16]:

$$\gamma_S = \gamma_S^D + \gamma_S^S \quad (1)$$

The magnitude of dispersive interactions between adsorbent and adsorbate can be measured by using non-polar alkanes as test compounds and expressed by the value of the dispersive component of the surface free energy, γ_S^D [mJ/m²].

Schultz et al. [17] proposed to calculate the dispersive component of surface free energy according to the following relationship:

$$RT \times \ln V_N = 2Na_p \sqrt{\gamma_S^D \gamma_L^D} + C \quad (2)$$

where V_N —net retention volume of the test solute, a_p —the area occupied by the adsorbing molecule of the test solute, γ_L^D —dispersive component of surface free energy of adsorbent, R —gas constant, T —temperature of the column [K], C —constant, N —Avogadro's number.

The procedure is based on the determination of a linear relationship between left-hand side of Eq. (2) vs. $a_p \times (\gamma_L^D)^{1/2}$ for the series of *n*-alkanes and calculation of γ_S^D from the slope value.

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Table 1
Oxidation conditions.

| No. | Sample | Experiment conditions | | | |
|-----|------------------------------|-----------------------|----------------|----------|--|
| | | Temperature [°C] | Pressure [MPa] | Time [h] | Additional information |
| 1 | HDPE | – | – | – | – |
| 2 | Oxidized HDPE solid phase | 121 | 0.1 | 30 | Air, 1% _{w/w} DCP |
| 3 | Oxidized HDPE solid phase | 121 | 0.1 | 30 | Air, 3% _{w/w} DCP |
| 4 | Oxidized HDPE solid phase | 110 | 0.1 | 35 | Air, 1% _{w/w} DCP |
| 5 | Oxidized HDPE solid phase | 110 | 0.1 | 7.5 | Air, 0.05% _{w/w} acacMn(II) |
| 6 | Oxidized HDPE solid phase | 110 | 0.1 | 7.5 | Air, 0.1% _{w/w} acacMn(II) |
| 7 | Oxidized HDPE solid phase | 121 | 0.1 | 7.5 | Air, 0.05% _{w/w} acacMn(II) |
| 8 | PP | – | – | – | – |
| 9 | Oxidized PP solid phase | 120 | 0.1 | 24 | Air |
| 10 | Oxidized PP solid phase | 110 | 0.1 | 24 | Air |
| 11 | Oxidized PP solid phase | 90 | 0.1 | 24 | Air |
| 12 | Oxidized PP solid phase | 100 | 0.1 | 24 | Air |
| 13 | Oxidized PP solid phase | 110 | 0.1 | 24 | Air, 0.1% _{w/w} acacMn(II), |
| 14 | Oxidized PP aqua | 110 | 0.1 | 5 | Oxygen, ratio PP:water–1:4 |
| 15 | Oxidized PP aqua | 110 | 0.3 | 5 | Oxygen, ratio PP:water–1:4 |
| 16 | Oxidized PP aqua | 110 | 0.5 | 5 | Oxygen, ratio PP:water–1:4 |
| 17 | Oxidized PP aqua | 110 | 0.5 | 5 | Oxygen, 0.5% _{w/w} acacMn(II), ratio PP:water–1:4 |
| 18 | Oxidized PP aqua | 110 | 0.5 | 5 | Oxygen, 2.5% _{w/w} acacMn(II), ratio PP:water–1:4 |
| 19 | PE wax | – | – | – | – |
| 20 | Oxidized PE wax liquid phase | 145 | 0.1 | 2.5 | Oxygen, 0.1% _{w/w} acacMn(II), |
| 21 | Oxidized PE wax liquid phase | 145 | 0.1 | 7.5 | Oxygen |
| 22 | Oxidized PE wax liquid phase | 150 | 0.1 | 7.5 | Oxygen |
| 23 | Oxidized PE wax liquid phase | 145 | 0.1 | 7.5 | Oxygen, 0.1% _{w/w} acacMn(II), |
| 24 | Oxidized PE wax solid phase | 145 | 0.1 | 7.5 | Oxygen, 1% _{w/w} DCP |

DCP – dicumyl peroxide; acacMn(II) – acetylacetonate of manganese(II).

Value of the specific component of adsorption energy ΔG^S is determined as the difference between the adsorption energy of polar compound, ΔG_{polar} , and adsorption energy of hypothetical alkane, ΔG_{ref} , having the same physicochemical properties, e. g. vapor pressure (Papirer method) [18–20], $a_p \times (\gamma_L^D)^{1/2}$ (Schultz et al. method [17]).

The specific component of the adsorption energy of the test solute ΔG^S corresponds to the magnitude of acid–base surface interactions between polar test solute and the examined surface.

Parameters describing acidity (K_A) and basicity (K_D) of the solid polymer surface are related to ΔG^S [20,21]:

$$\Delta G^S = K_A \times DN + K_D \times AN^* \quad (3)$$

where AN^* and DN characterize the test solute ability to act as electron acceptor and donor, respectively.

K_A and K_D are calculated when ΔG^S values are known for several test solutes.

Ratio of K_A and K_D indicates the acid–base character of polymeric surface:

$$S_C = \frac{K_A}{K_D} \quad (4)$$

1.2. Principal component analysis (PCA)

Principal component analysis (PCA) is a well known technique in data analysis for classification [22–27]. The principle is to characterize each object not by analyzing every variable but projecting the data in a much smaller subset of new variables (or principal component scores). These new variables (factors) are linear combinations of the initial variables but highlight the variance within a dataset and remove the redundancies. The linear coefficients of the inverse relation of linear combinations are called the component loadings, i.e. the correlation coefficients between the original variables and the principal components. PCs are uncorrelated and account for the total variance of the original variables. Successive principal components arranged in decreasing order of eigenvalues account for decreasing amounts of variance. The relevant portion of information is carried by the first few principal components

(PC-s). The first principal component accounts for the maximum of the total variance, the second is uncorrelated with (orthogonal to) the first one and accounts for the maximum of the residual variance, and so on, until the total variance is accounted for. For practical reasons, it is sufficient to retain only those components, which account for a large percentage of the total variance. PCA will show which variables and objects (samples, fillers, etc.) are similar to each other, i.e. carry comparable information, and which ones are unique. The algorithm of PCA can be found in standard chemometric articles and textbooks [27,28].

The aim of this paper was the characterization of the properties of several series of non-oxidized and oxidized polyolefins: high density polyethylene (HDPE), polypropylene (PP) and PE wax. The influence of the initial raw material and conditions of oxidizing experiment on bulk and surface properties were examined. Authors were also interested in relations between surface and bulk parameters used for characterization of polyolefines.

2. Experimental

2.1. Materials

Oxidized HDPE were obtained as products from oxidation processes carried out in two-phase (gas–solid) system: below melting point (at 120 °C) using air as oxidizer. The raw material used for these process was HDPE IDEALIS 500 from Braskem (Brazil). To avoid induction period during HDPE oxidation, dicumyl peroxide was used as initiator. PE wax (Type 2T from Euro-Ceras) was oxidized in liquid phase after melt at 140 °C with 1,1'-Azobis(cyclohexanecarbonitrile) (ACCN) as initiator. To avoid crosslinking reaction pure oxygen was used as oxidizer. PP (non-stabilized homopolymer Moplen HP-500J from Basell Orlen Polyolefins Sp. z o.o. Poland) was oxidized below melting point (at 110 °C) in two-phase (gas–solid) system with air as oxidizer. In three-phase system: gas–solid–liquid (aqueous dispersion) oxygen was applied as oxidizing agent. To obtain waxes with different AV and SN, processes were carried out during 1–25 h. Conditions of oxidizing processes are summarized in Table 1. Properties of these materials are shown in Table 2.

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