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Estimation of the work of adhesion by means of inverse gas chromatography for polymer complex systems

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ABSTRACT

The usefulness of inverse gas chromatography (IGC) in the examination of complex polymer systems is presented. IGC method was applied for studying resin-bonded abrasive articles. Resin-bonded abrasive articles consist of: abrasive, wetting agent (resol), binder (novolac resin) and filler. IGC technique enabled to characterize one of the most important parameter influencing the quality of final product: adhesion between cross-linked resins and abrasive grains that decide on spalling of the abrasive grains from the binder. The magnitude of adhesion between resin and abrasive grains was expressed by the value of the work of adhesion. Presented in this article the way of estimation of the work of adhesion is quick, simple and can find application e.g. in industry of abrasive articles. The main advantage of this method is the possibility of controlling the quality of raw materials and their influence on the quality of the final product without necessity of manufacturing of trial product.

1. Introduction

Resin-bonded abrasive articles are complex materials. These articles consist of cutting particle (i) very often from electrocorundum, filler (ii) inorganic compound (pyrite or lithopone), binder (iii) novolac resin and wetting agent, resol. The first stage during production of this type of abrasive articles is mixing of different types of abrasive grains. The grains are further covered by liquid resol. Resol and abrasive are mixed shortly (for several minutes) in order to avoid melting and even dieseling of resin. In the next stage the binder and fillers are added to fused alumina covered by resol and carefully mixed. Then, it is placed in the boxes, seasoned and the intermediate-product is transferred into molds. High-pressure molding is the next step of the manufacturing process. Finally, the intermediate-product is hardened according to the temperature program being recommended by the supplier of resin—usually at the temperature range of 120–180 °C. The most important stages during manufacturing of grinding tools are: coverage of the abrasive by wetting agent and proper hardening of semi-product. Authors of this publication proposed innovative application of IGC for studying polymers and their composites used for production of abrasive articles: description of the hardening degree of phenol–formaldehyde resins [1–3], homogeneity of polymer composites and the degree of the coverage of abrasive by resol [3,4].

The two stages during production of abrasive articles meaningfully influence the quality of final product:

(a) the coverage of abrasive grain by resol—it decides about homogeneity of semi-products; it depends on the interactions (adhesion) between resin (resol) and abrasive,
(b) the degree of hardening of the resins binder in the product—it decides about such important parameters as: wear of abrasive articles during work, cutting distance; it depends on temperature and time of hardening process but also on the type of filler [1].

The magnitude of the adhesion between resin and abrasive grains depends on the surface properties of abrasive grain: surface energy. Surface energy of solid consists of dispersive, γ_s^d (resulting from dispersive interactions of the solid surface: long-range forces such as van der Waals forces), and specific component, γ_s^{sp} (resulting from acid–base).

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (1)$$

There are several methods of estimation of the solids surface energy. The contact angle measurement is most often used method for determination of the value of γ_s [5]. The use of different polar and apolar liquids enables the determination of the Lifshitz–van der Waals (γ_s^{LW}) and the acid–base (Lewis) (γ_s^{ab}) components of the solid surface free energy (γ_s). Moreover, the electron-acceptor (γ_s^+) and electron-donor (γ_s^-) parameters of the acid–base component can be determined if the components of parameters of the liquid surface free energy are known. However,

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this method suffers from some limitations, e.g. the diameter of the liquid drop influences the results [6], the solid surface should be smooth [7,8]. Very often the examined solids are powders and it is impossible to prepare flat and smooth surface [9]. The method of surface energy estimation of solid powders is the Washburn method [10] but packing the powder into tubes homogeneously is the main difficulty in this approach [6]. The IGC method seems to be much better for studying powder solids, especially for such solids as, studied in this article, very hard grains of abrasive with 1–0.25 mm diameter. It is impossible to form disk and Washburn method might be inaccurate. Indirect estimation of contact angle is impossible for abrasive grains due to irregular shape and small size of grains. Thanks to IGC it was possible to determine surface free energy of abrasive grains.

Surface energy of connected solid materials determines the strength of adhesion between them. This strength of adhesion can be described by the value of work of adhesion, W_a.

$$W_a = W_a^d + W_a^{ab} \tag{2}$$

where: W_a^d is the dispersive component of the work of adhesion calculated according to equation [11,12].

$$W_a^d = 2\sqrt{\gamma_{s,ar}^d \gamma_{s,r}^d} \tag{3}$$

and

$$W_a^{ab} = 2((\gamma_{s,ar}^+ \gamma_{s,r}^-)^{1/2} + (\gamma_{s,ar}^- \gamma_{s,r}^+)^{1/2}) \tag{4}$$

W_a^{ab} is the component of work of adhesion due to acid–base interactions. In Eq. (3) $\gamma_{s,ar}^d$, $\gamma_{s,r}^d$ denote the dispersive component of the free surface energy of abrasive (ar) and resin (r), respectively. In Eq. (4) $\gamma_{s,r}^+$, $\gamma_{s,r}^-$ are the acidic and basic parameters of the solid surface (resin (r)) describing its ability to electron acceptor and electron donor interactions, accordingly. Symbols $\gamma_{s,ar}^+$, $\gamma_{s,ar}^-$ in Eq. (4) denote the same characteristics of the abrasive (ar). The value of W_a estimated according to Eq. (2) describes the work of adhesion as a result of dispersive (van der Waals) and acid–base interactions between two solids.

It should be mentioned that Eq. (2) does not include polar component of the work of adhesion that is the result of dipole–dipole and induced dipole–dipole interactions. Omitting of polar component of the work of adhesion is justified because Fowkes proved that the polar component of the work of adhesion is negligible [12,13].

All parameters mentioned above, γ_s^d, γ_s^+, γ_s^- can be determined by using Inverse Gas Chromatography.

Inverse gas chromatography (IGC) was discovered in 1967 by Kiselev [14]. The theory and methodology of IGC method was then developed by Smidsrød and Guillet [15] and it is still improved up to now. The popularity of IGC method is due to its simplicity and user friendliness. The necessary equipment is just a standard gas chromatograph [16] although the use of more sophisticated tool is also advised. The word "inverse" relates to the aim of experiment. It is not separation and analysis of injected sample like in classical GC but examination of properties of the material placed in the chromatographic column. Carefully selected test compounds with known properties are injected onto the column containing the examined material. Retention times and the profiles of chromatographic peaks resulting from interactions of studied material with test compound are used for the determination of parameters describing properties of the column filling. IGC makes possible to study polymers and their composites at different temperature and humidity. Examination of polymers below their glass transition temperature, T_g, allows physicochemical characterization of their surface. Determined surface characteristics can be applied for monitoring the changes occurring during chemical modification of polymers surface. For liquid materials in IGC experiment following parameters can be determined: Flory–Huggins interactions parameter (χ_{12}^{∞} and/or χ'_{23}), solubility, δ_2, and three dimensional Hansen solubility parameter. These parameters allow to predict behavior of polymeric materials during technological processes, mutual solubility, miscibility of composite components and/or interactions between them. γ_s^d parameter for abrasive (ar) and resin (r) was calculated according to Schultz–Lavielle method based on the equation [17–21]:

$$RT\ln V_N = 2Na\sqrt{\gamma_s^d \gamma_l^d + C} \tag{5}$$

where R—the gas constant, 8.314 [J/mol K]; T—temperature of measurement [K]; V_N—net retention volume [m^3]; N—the number of Avogadro, 6.023×10^{23} [1/mol]; a—cross sectional area of the adsorbate [m^2]; γ_s^d—the dispersive component of surface free energy [mJ/m^2]; γ_l^d—the dispersive component of the surface tension of the probe molecule in liquid state [mJ/m^2]; C—constant.

Retention data for polar and non-polar test compounds are necessary to quantify acidic and basic properties of the examined surface. These are described by γ_s^+, γ_s^- parameters. γ_s^+, γ_s^- parameters were estimated according to Good–van Oss concept [22] described by the following equation:

$$\Delta G^{sp} = 2N_A a((\gamma_l^+ \gamma_s^-)^{1/2} + (\gamma_l^- \gamma_s^+)^{1/2}) \tag{6}$$

In Eq. (6) γ_l^+, γ_l^- are the electron acceptor and donor parameters of the probe molecules, respectively. ΔG^{sp} is the specific component of the free energy of adsorption of polar compound. The way of determination ΔG^{sp} value is described in many papers e.g. [17,18]. For calculation of γ_s^+, γ_s^- dichloromethane (DM) and ethyl acetate (EA) were used as test compounds. DM is monopolar acid and γ_{DM}^- is 0.0 mJ/m^2. Eq. (6) is condensed to

$$\gamma_s^- = (\Delta G_{DM}^{sp})/(4N_A{}^2 a_{DM}^2 \gamma_{DM}^+) \tag{7}$$

and γ_S^- can be easily calculated. The value of γ_{DM}^+ was established as 5.2 mJ/m^2 on the basis of [23]. Similarly, EA is monopolar base and γ_{EA}^+ is 0.0 mJ/m^2 and from Eq. (8) γ_s^+ parameter for examined solid can be calculated:

$$\gamma_s^+ = (\Delta G_{EA}^{sp})^2/(4N_A{}^2 a_{EA}^2 \gamma_{EA}^-) \tag{8}$$

The value of γ_{EA}^- was established as 19.2 mJ/m^2 [23]. However, in the literature there are different values of the components and parameters of the surface free energy for the test compounds [5]. Van Oss gave the value of γ_l^- for EA equal to 6.2 mJ/m^2 [24] different from this in [23]. Moreover, one cannot find the value of γ_l^- for dichloromethane (DM) but only for chloroform (CH) 1.5 mJ/m^2 therein [24]. In this paper the values of γ_s^+, γ_s^- for studied materials were calculated for the data of γ_l^+, γ_l^- from both these sources. The influence of these physicochemical data on the resulting values of γ_s^+, γ_s^- parameters and further on the values of γ_s^{sp}, γ_s then W_a^{ab} and W_a will be discussed.

The aim of this paper was to estimate the work of adhesion between abrasive grain and resol with the use of γ_s^+, γ_s^-, γ_s^d, i.e. IGC derived parameters.

2. Experimental

The work of adhesion was determined for three types of abrasive grains: M60 (fused alumina, microcrystalline, granulation 60 Mesh), 95A30 (fused alumina, black, brown, granulation 30 Mesh), 95A16 (fused alumina, black, brown, granulation 30 Mesh). All of these types of abrasives were in two forms: calcinated at 850 °C and non-calcinated. Abrasive grains were