



# Application of inverse gas chromatography in physicochemical characterization of phenolic resin adhesives



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## ARTICLE INFO

### Article history:

Received 29 July 2014

Received in revised form

24 September 2014

Accepted 25 September 2014

Available online 2 October 2014

### Keywords:

Phenolic resins

Degree of hardening

Work of adhesion

Inverse gas chromatography

FTIR

## ABSTRACT

One of the most important stages during production of abrasive tools is their hardening. The degree of hardening is very important and influence toughness of the final product. During hardening process the cross-linking of the phenolic resins, used as a binder, occurs. Nowadays, there is no standard, accurate and simple method for the estimation of the hardening degree of abrasive tools. The procedure of the determination of hardening degree of the binder (phenolic resins) by means of inverse gas chromatography (IGC) was presented in this paper. Results obtained by use of IGC derived method was verified by Soxhlet extraction and by FTIR method. Good agreement was found for results from IGC and Soxhlet extraction whereas those from FTIR were much lower. FTIR method supplies data concerning bulk properties not the surface as in case of IGC and Soxhlet methods. These results indicate that resins are more cross-linked on the surface than inside the material.

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## 1. Introduction

The production of the abrasive materials includes the following stages: covering of abrasive materials by wetting agent, addition of the filler with the binding material, mixing of the components, stabilization of the composition and the hardening. The most important processes influencing the properties of the final product are the coverage of the abrasive materials, mixing and proper hardening [1,2]. The homogeneity of the mixture of semi-product increases the quality of the final product. The effectiveness of the hardening process depends also on the applied temperature programme. Although the determination of wettability of abrasive materials is relatively simple, the controlling of the hardening process is much more complicated. There is no easy standard industry method for controlling the hardening degree of such complex composites [3]. Brinell test is the most commonly used test for assessment of hardness of abrasive tools. This method suffers from several disadvantages. The main disadvantage of this standard method is its very low repeatability and accuracy in case of such composites as abrasive tools. The results depend strongly on the place of ball pressing. Moreover, only final hardness of abrasive tool can be assessed. It is not possible to

monitor the hardening process on-line. Viscoelastic parameters can be also applied for estimation of the degree of hardening. This method needs to use expensive equipment for dynamic rheological measurements. Moreover, it can be applied only for resins without additives or with nano/microfillers. The presence of filler nano/microparticles in resins can influence the rheological parameters significantly.

Inverse gas chromatography is an extension of classic gas chromatography [4–8]. The word “inverse” means that the examined material is placed in the chromatographic column and its properties are determined based on the retention behaviour of carefully selected test compounds. Inverse gas chromatography method is widely used for characterization of polymers and polymer blends [8], surfactants [9,10], biopolymers, solid food and petroleum pitches [1]. Inverse gas chromatography can be divided into inverse gas liquid and inverse gas solid chromatography. The obvious criterion of such discrimination is the state of the examined material placed in the column. The dominating retention mechanism is related to the temperature of IGC experiment. Polymeric materials might be characterized by using both surface parameters (surface free energy, surface acid/base properties and bulk parameters). The pertinence of IGC measurements to surface or bulk properties clearly depends on whether or not the probe molecules can diffuse into the bulk during the experiment. Retention volume measured at the temperature of IGC experiment higher than  $T_g$  of the examined polymer (or blend) results from the sum of surface and bulk sorption. Below  $T_g$  mainly from the adsorption of probe molecules

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on the surface of the stationary phase. Therefore, the surface properties can be determined only below  $T_g$ .

### 1.1. Flory-Huggins parameter - $\chi_{12}^\infty$

Flory-Huggins interaction parameter ( $\chi$ ) reflects interaction between low-molecular-weight solvent and high-molecular-weight polymer, and it has been considered as a Gibbs free energy parameter. According to such assumption interaction parameter  $\chi$  can be divided into enthalpy  $\chi_H$  and entropy  $\chi_S$  components [11]:

$$\chi = \chi_H + \chi_S \quad (1)$$

Deshpande et al. [12] were the first who suggested the use of IGC for studying the polymer blends. Starting from Flory-Huggins expression for the change of free enthalpy of mixing  $\Delta G_{\text{mix}}$  extended to three-component systems, they proposed a method of elaboration of IGC data collected with the use of polymer blend leading to the polymer-polymer interaction coefficient.

The values directly measured by IGC were the retention times of solutes,  $t_R$ , the mass of the stationary phase,  $m_w$ , the temperature of column -  $T$ , and the flow rate,  $F$ . Then the specific retention volume,  $V_g$  can be computed from [11,13]:

$$V_g = \frac{3}{2} \cdot \frac{t'_R \cdot j \cdot F \cdot 273.15}{m_w \cdot T} \quad (2)$$

where  $t'_R = t_R - t_M$ ,  $t_M$  - gas hold-up time,  $j$  - James-Martin's coefficient [14].

At infinite dilution of the probe and for high molecular weight of the stationary phase the Flory-Huggins interaction parameter can be determined from [15–18]:

$$\chi_{12}^\infty = \ln \left( \frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1} \right) - \frac{p_1^o}{R \cdot T} \cdot (B_{11} - V_1^o) + \ln \left( \frac{\rho_1}{\rho_2} \right) - \left( 1 - \frac{V_1^o}{V_2^o} \right) \quad (3)$$

1 denotes the solute and 2 denotes examined material,  $M_1$  is the molecular weight of the solute,  $p_1^o$  is the saturated vapor pressure of the solute,  $T$  is the temperature of experiment [K],  $V_1^o$  is the molar volume,  $\rho_i$  is the density,  $R$  is the gas constant, and  $B_{11}$  is the second virial coefficient of the solute calculated from equation:

$$B_{11} = V_{c1} \cdot \left[ 0.25 - 1.5 \cdot \left( \frac{T_{c1}}{T} \right) \right] \quad (4)$$

$V_c$  - the critical molar volume of test solute [ $\text{m}^3/\text{mol}$ ];  $T_c$  - the critical temperature of test solute [K].

Detailed discussion of the credibility of literature derived physicochemical parameters was presented by Voelkel and Fall [19].

Many authors use simplified form of Eq. (3) [19,20]:

$$\chi_{12}^\infty = \ln \left( \frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1} \right) - \frac{p_1^o}{R \cdot T} \cdot (B_{11} - V_1^o) - 1 \quad (5)$$

Although the determination of wettability of abrasive materials is relatively simple, the controlling of the hardening process is much more complicated. Therefore, the aim of this work was to present the procedure for the determination of the degree of hardening (DH) of the resins applied in the abrasive articles by using inverse gas chromatography (IGC).

## 2. Experimental

### 2.1. Materials

Two kinds of resole resins were studied: aqueous with 10% of water labelled as resole S, and non-aqueous labelled as resole BW.

These two resoles were also tested as composition with different fillers in order to check the influence of fillers on hardening degree of resins. The following fillers were used:

- commonly used in abrasive tools industry: PAF ( $\text{K}_3\text{AlF}_6$  and  $\text{KAlF}_4$ ),  $\text{Mg}(\text{OH})_2$  - powders with granulation about  $50 \mu\text{m}$  (sieve analysis),
- new-generation, ecological aluminosilicates:
  - zeolite micro20, Si:Al ratio based on XPS studies was 6:1;
  - synthetic zeolite marked as Z1-sodium form powder with granulation about  $50 \mu\text{m}$  determined by sieve analysis. The synthesis of Z1 zeolite was described in detail in [9]. The ratio Si:Al based on XPS studies was 24:1;
  - synthetic zeolite marked as Z2-hydrogen form (powders with granulation about  $50 \mu\text{m}$  determined by sieve analysis). The synthesis of Z2 was the same as Z1 but it was modified by 0.1 M  $\text{NH}_4\text{NO}_3$ . The ratio Si:Al based on XPS studies was 24:1.

### 2.2. Procedures

The studied materials were put into the chromatographic column. Resins and their compositions with fillers were put onto glass beads (1% of the weight of the beads). The compositions with fillers were prepared by mixing fillers with resole by weight 0.3:5, respectively.

### 2.3. Hardening

The chromatographic columns with studied materials were placed in the thermal oven type controller P320, Nabertem, Germany. The resins and their compositions with fillers were hardened according to the common temperature programme (heating from  $50^\circ\text{C}$  until  $180^\circ\text{C}$ ; heating rate  $0.2^\circ/\text{min}$  and then heated at  $180^\circ\text{C}$  for 10 h). It is also known that the oven of the GC is itself a real reactor where thermal treatment can be performed [21].

The materials were tested by means of IGC after whole hardening cycle. Resins without fillers were also tested by IGC after some crucial stages of hardening; this means: after hardening at  $50^\circ\text{C}$  for 2 h,  $80^\circ\text{C}$  for 5 h,  $115^\circ\text{C}$  for 2 h,  $140^\circ\text{C}$  for 1 h and  $180^\circ\text{C}$  for 10 h. This allowed to assess the dynamics of hardening process.

### 2.4. IGC experiments

IGC measurements were carried out by using gas chromatograph Varian 430 GC, Perlan Technologies, equipped with flame-ionization detector (FID). Chromatographic Teflon columns (length 50 cm, 3 I.D.), with examined hardened or partially hardened resins (amount of the sample 17 g), were placed in column oven. Measurements were carried out at  $30^\circ\text{C}$ . Carrier gas was helium with flow-rate 15 mL/min. The temperature of injector and FID was  $150^\circ\text{C}$ . The test compounds were heptane, octane, nonane, decane, ethyl acetate, tetrahydrofuran, acetone, chloroform, dichloromethane, acetonitrile and dioxane. Vapours of test compounds were injected in the amount ensuring the achievement of the infinite dilution region. The presence of symmetrical peaks and repeatability of retention times assured the achievement of equilibrium conditions.

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