

INVERSE GAS CHROMATOGRAPHIC EVALUATION OF THE EXTENT OF CROSS-LINKING OF RESINS IN GRINDING TOOLS

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SUMMARY

Production of abrasive materials includes the stages: covering of abrasive material with wetting agent, addition of binder, i.e. the filler with the binding material, mixing of the components, stabilization to achieve homogeneity of composition, and hardening. The most important processes affecting the properties of the final product are: the coverage of the abrasive materials, mixing, and proper hardening. The quality of abrasive materials strongly depends on their wettability [1]. Ensuring the homogeneity of the mixture of precursors increases the quality of the final product. The effectiveness of the hardening process depends on the temperature programme used.

Although determination of the wettability of abrasive materials is relatively simple, controlling the hardening process is much more complicated. The objective of the work discussed in this paper was evaluation of an inverse gas chromatographic (IGC) procedure for determination of the extent of cross-linking of the resins used in abrasive articles. The results showed that IGC is a simple and suitable method for qualitative estimation of the extent of cross-linking in grinding tools and for checking the homogeneity of the precursors of the product.

INTRODUCTION

Grinding tools consist of the abrasive, the filler, and the binder. Different types of aloxite are used as the abrasive. Silicon carbide, carbides of such elements as tungsten or zirconium, and artificial diamond (super-hard tools) may also be used as the abrasive raw material. Fillers are inorganic compounds such as pyrite (FeS_2), cryolite (Na_3AlF_6), lithopone ($\text{ZnS} + \text{BaSO}_4$), iron oxide red, and slag after-copper. Ceramic or organic

(e.g. phenolic resins) materials may be used as the binding material. Ceramic binding materials give stable and high-quality products but the process used to manufacture such grinding tools involves large consumption of energy – the precursors must be hardened at above 1000°C. Manufacture of grinding tools containing phenolic resin is more economical, because the resin cross-links at 180°C.

Novolak resin is obtained by polycondensation, in an acidic medium, of a mixture of formaldehyde and phenol with a deficiency of formaldehyde [2,3]. In the presence of a divalent metal salt (usually zinc acetate) regular ortho-novolaks are formed. Novolak resin is cross-linked by use of urotropin, which reacts with phenolic resins at temperatures as low as 60–80°C. The first cross-linking process starts at 120°C and the fundamental process of cross-linking occurs at 180°C. Proper cross-linking of novolak resin in grinding tools is of great importance technologically. Weak cross-linking of the resin leads to an unstable product which cracks when used. This is especially important when working with grinding wheels at very high speed.

Examination of the extent of cross-linking of a phenolic resin is difficult [4,5]. It is especially complicated for grinding tools, because of the presence of inorganic species – fillers and abrasive materials. The simplest method – the swelling method – is useless for novolak because this type of polymer is, after cross-linking, resistant to all solvents, even very aggressive reagents. For this reason inverse gas chromatography (IGC) has been used to study the cross-linking of this polymer in grinding tools.

IGC is an extension of conventional gas chromatography [6,7]. In this method the examined material is placed in the chromatography column and its properties are determined on the basis of the retention behaviour of carefully selected test compounds. In this work the Flory–Huggins term, χ_{12}^{∞} , was used to express the magnitude of the interactions between the test compound and the material studied [8,9]. This is a new application of χ_{12}^{∞} . Comparison of the values of χ_{12}^{∞} determined for non-hardened material and the material after hardening may indicate the efficiency of the cross-linking process.

EXPERIMENTAL

In this paper two types of precursor were studied. One, denoted M448, with very good properties, is used to manufacture high-quality cut-

ting-off grinding wheels – very thin, highly productive tools. The other, denoted M470, has poorer properties and is used for mass production of cheaper grinding tools. The abrasive used in both materials is aloxite, but of different granulation and type – M448 contains 60-mesh (250–300 μm) monocrystalline aloxite (denoted M60) whereas M470 contains 36-mesh (500–600 μm) black aloxite (denoted 95A36). Phenolic resin – resol – was used as the wetting agent. Non-aqueous resol was used for M448 and resol S containing approximately 5% water was used for M470. Another type of phenolic resin – novolak LFR12 – was used as the binding material in both products, although the phenolic resin used for production of M470 contains less urotropin as setting agent. Mixtures of different inorganic compounds were used as fillers. The compositions of these two materials are compared in Table I. Binders are mixture of fillers and novolak; they were denoted B448 for M448 and B470 for M470.

Table I

The composition of the products examined

Product	Aloxite used	Resol used	Novolak used	Filler used
M448	M60	Non-aqueous resol	LFR12	Mixture of inorganic compounds
M470	95A36	Resol S	LFR12	Mixture of inorganic compounds

Four samples of M448 were tested, all from one mixing. After mixing the precursors were sifted to achieve even granulation and put into boxes for further stabilization. The Flory–Huggins term, χ_{12}^{∞} , was determined for the materials:

- precursor M448 – four samples from one mixing after sifting from different boxes in which they are stabilized, denoted M1, M2, M3, and M4
- precursor M470
- binder B448 – LFR12 + fillers
- binder B470 – LFR12 + fillers
- novolak resin LFR12.

The measurements were made by use of a Chrom5 gas chromatograph equipped with a flame-ionisation detector (FID). Helium was carrier gas at flow rate of 15 mL min⁻¹. The temperature of the injector and the

detector was 200°C. The test compounds, selected to enable investigation of the effects of different types of intermolecular interaction, were pentane, hexane, heptane, octane, acetone, methanol, ethanol, 1,2-dichloroethane, and diethyl ether. Test-solute vapour (1 µL) was injected on to the chromatographic column to achieve the infinite dilution region.

The materials tested were placed in packed columns 2 m long and 4 mm i.d. The materials were conditioned overnight before measurement. Values of χ_{12}^{∞} were determined before hardening and after hardening at 120°C and 180°C. The first retention data for the test solutes were collected at 30°C. After completion of the IGC experiment the sample was heated to 120°C, held at this temperature for 3 h, then cooled to 30°C, with subsequent IGC measurement. During the first heating step preliminary hardening occurs. The next step of the experiment was heating at 180°C for another 3 h, during which proper hardening occurred. After this step the sample was again cooled to 30°C and examined by IGC.

Determination of the Flory-Huggins term, χ_{12}^{∞}

χ_{12}^{∞} was estimated by use of the equation:

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

where R (8.314 J mol⁻¹ K⁻¹) is the gas constant, p_1° (Pa) the vapour pressure of the test compound at the temperature of measurement, V_g (m³ g⁻¹) the absolute retention volume, M_1 (g mol⁻¹) the molar mass of the test compound, T (K) the temperature of measurement, V_1° (m³ mol⁻¹) the molar volume of the test compound, and B_{11} the second virial coefficient, calculated by use of the equation:

$$B_{11} = V_c \left[0.25 - 1.5 \left(\frac{T_c}{T} \right) \right] \quad (2)$$

where V_c (m³ mol⁻¹) is the critical molar volume of test compound and T_c (K) the critical temperature of the test compound.

RESULTS AND DISCUSSION

Two precursors, the binders and the novolak resin used for their manufacture, were examined by the same procedure. Comparison of the χ_{12}^{∞} values obtained for the initial sample, for the sample after initial hardening at 120°C, and for the sample after final hardening at 180°C enabled evaluation of the different material properties resulting from the hardening process. Knowledge of the value of χ_{12}^{∞} enables estimation of the magnitude of the interactions between the examined material and the test solute. Low (i.e. close to zero) or negative values of χ_{12}^{∞} indicate the presence of relatively strong interactions between the test compound and tested material. Weakening of these interactions results in an increase of χ_{12}^{∞} . Hardening of the precursor should cause an increase of the value of χ_{12}^{∞} , because it is known that interactions between cross-linked materials and any test compounds are definitely weaker. The values of χ_{12}^{∞} for samples of precursors M448 (M1) and M470 (at 30°C, and after hardening at 120°C and at 180°C) are presented in Figs 1 and 2, respectively.

Values of χ_{12}^{∞} increase after hardening at 120°C and a further increase is observed after the second hardening at 180°C. Although χ_{12}^{∞} values vary among test solutes, the trend is the same, irrespective of the nature of the test solute, i.e. its tendency to participate in non-polar, polar, or hydrogen-bonding interactions. Precursor M448 (M1) is characterized by significantly higher χ_{12}^{∞} values after hardening compared with precursor M470 (Fig. 2). This means that M448 is better hardened than M470, which leads to better properties (e.g. wear resistance, working speed, cutting distance, durability) of the products obtained from these materials.

It is quite possible that the behaviour of the precursor during the hardening process depends on the properties of the binder. This assumption is supported by comparison of χ_{12}^{∞} for binders B448 and B470 (Fig. 3). χ_{12}^{∞} values for B448 are higher than those for B470. These two binders differ from each other only in the filler used. It can be concluded that the type of filler affects the hardening process of the binder. The greater differences between χ_{12}^{∞} values for the precursors (Fig. 2) than for the binders (Fig. 3) indicate that the type of electrocorundum and the type of resol also affect the hardening process. It is worth noting that differences between χ_{12}^{∞} for these two binders are relatively small for initial samples

(30°C) but increase after the first hardening and increase further after the second hardening at 180°C.

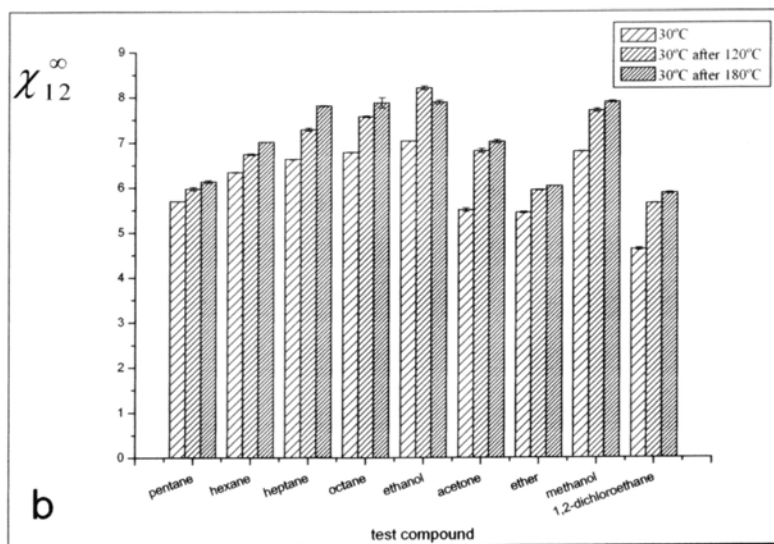
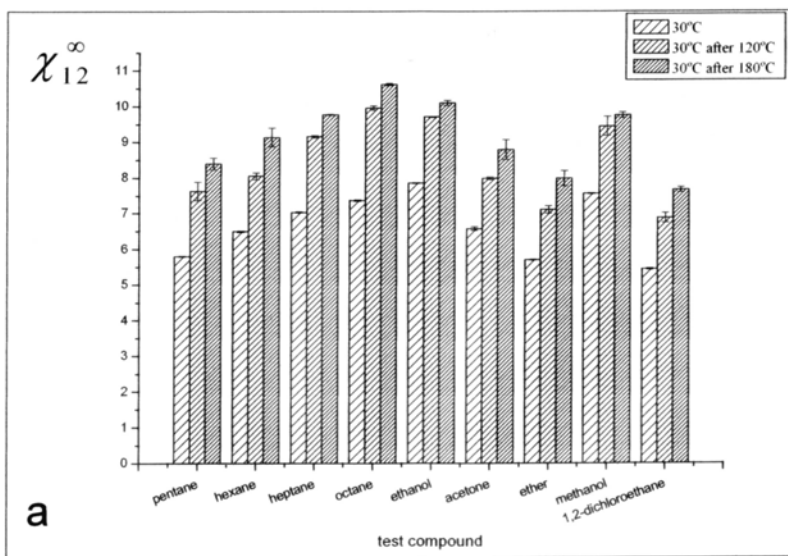


Fig. 1

Values of χ_{12}^{∞} for (a) M448 (M1) and (b) M470 before and after hardening at 120°C and 180°C

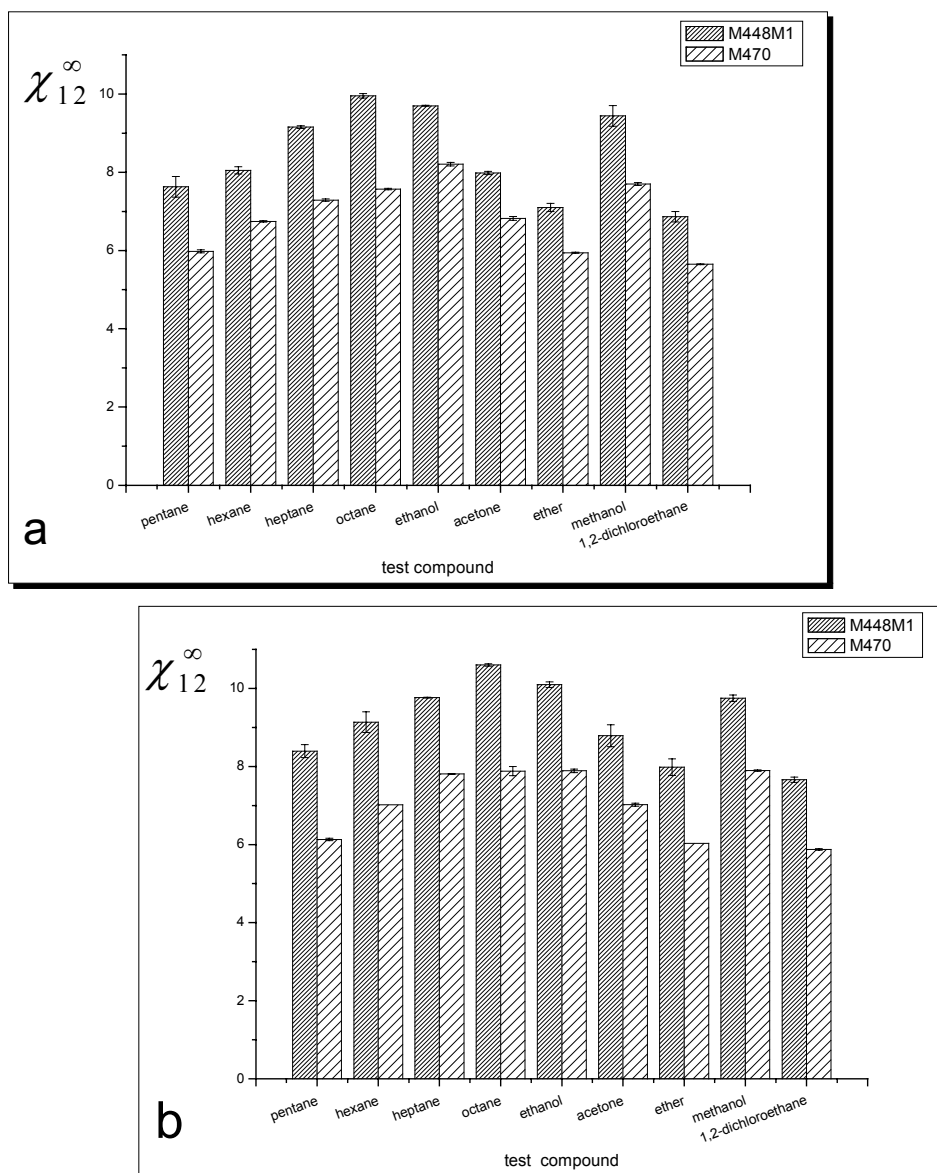


Fig. 2

Comparison of χ_{12}^{∞} values for precursors M448 (M1) and M470 (30°C) after hardening at (a) 120°C and (b) 180°C

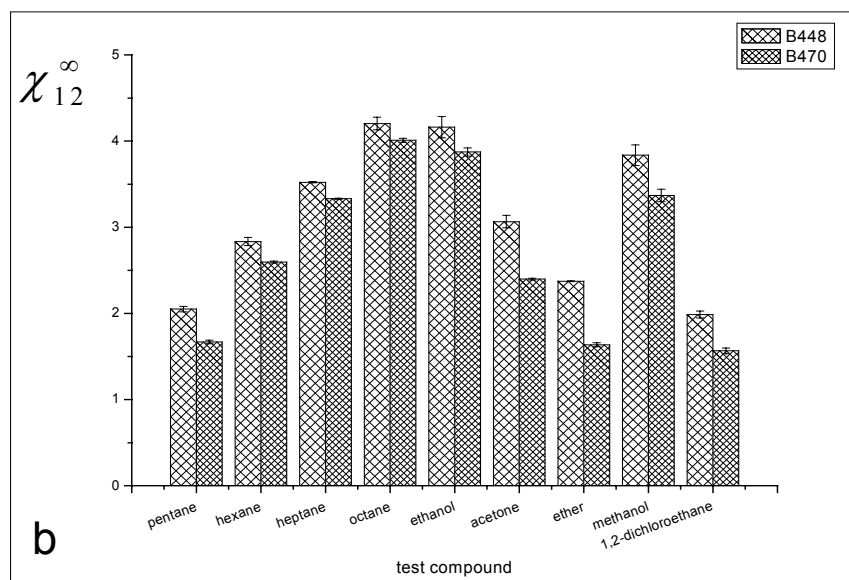
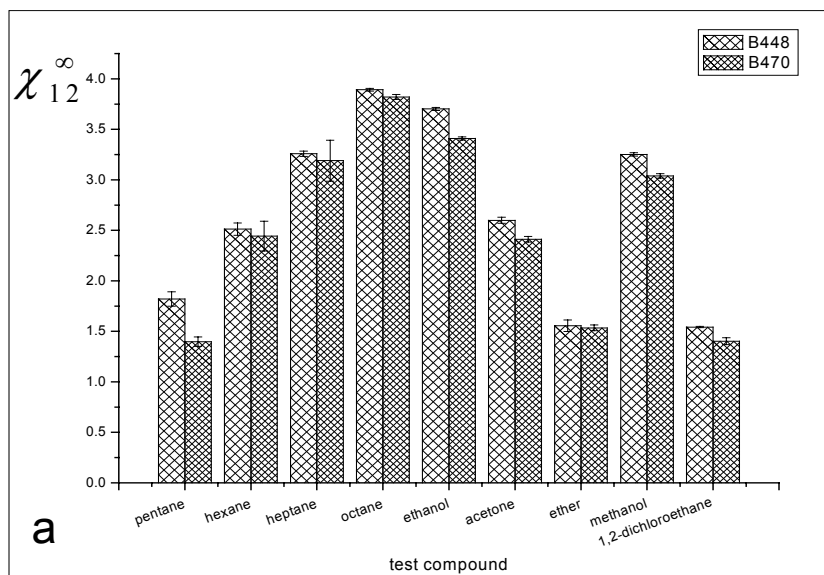


Fig. 3
 Comparison of χ_{12}^{∞} values for binders B448 and B470 (30°C): (a) initial and (b) after hardening at 120°C

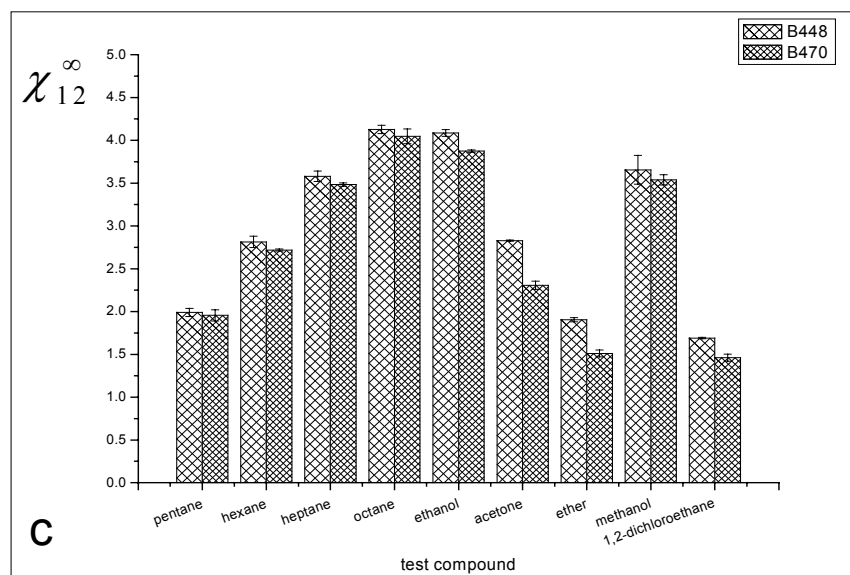


Fig. 3 (continued)

Comparison of χ_{12}^{∞} values for binders B448 and B470 (30°C): (c) after hardening at 180°C

Comparison of the properties of the precursor with those of novolak and binder (Fig. 4) shows the strong effect of aloxite. The values of χ_{12}^{∞} are definitely lower for novolak and binders than for the complete precursors.

χ_{12}^{∞} can be used for evaluation of the homogeneity of the batch or, better, the reproducibility of the precursor. M448 samples from different boxes in which the precursor was stabilized after mixing and sifting were compared (Fig. 5). It is clear that these four samples have different properties – they are not homogenous and their processing will lead to products of different usefulness. They are, in principle, homogenous at 30°C (Fig. 5a). Even small differences between the properties of the initial samples affect the hardening process, however. The differences between these samples increased after hardening at 120°C (Fig. 5b) and were even larger after hardening at 180°C (Fig. 5c).

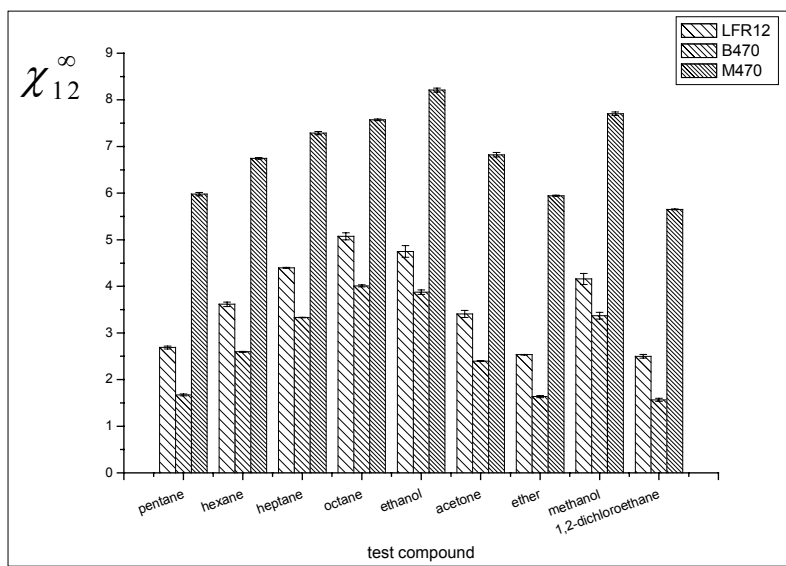


Fig. 4

Comparison of the values of χ_{12}^{∞} for novolak LFR12, binder B470, and precursor M470 at 30°C and after hardening at 120°C

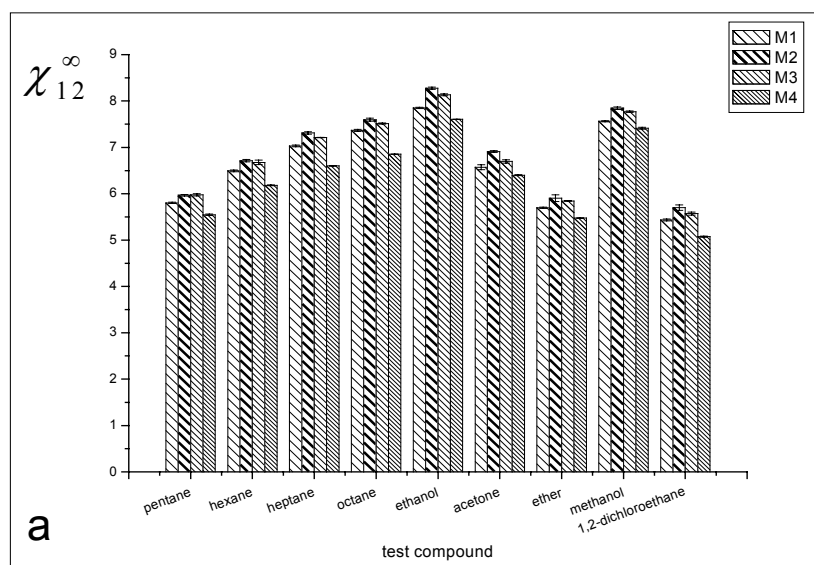


Fig. 5

Comparison of the values of χ_{12}^{∞} for precursor M448 (M1, M2, M3, and M4) (30°C): (a) initial

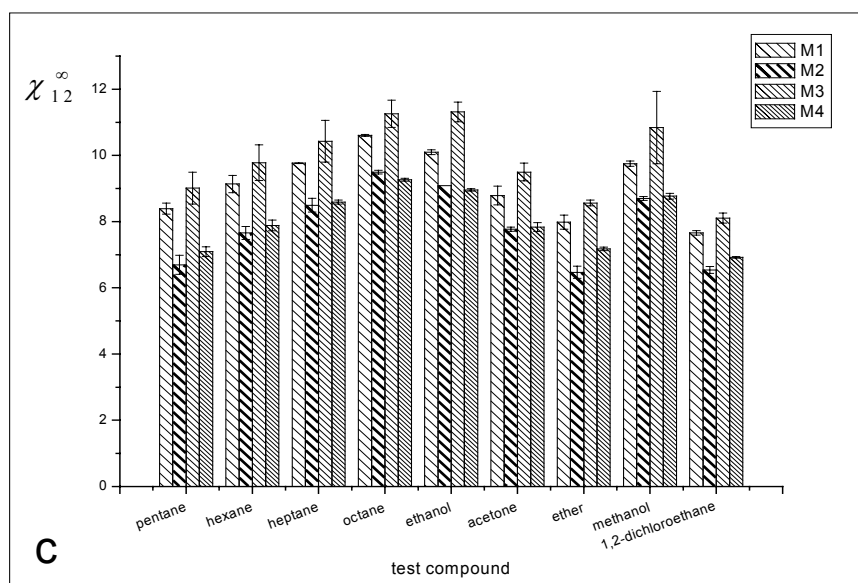
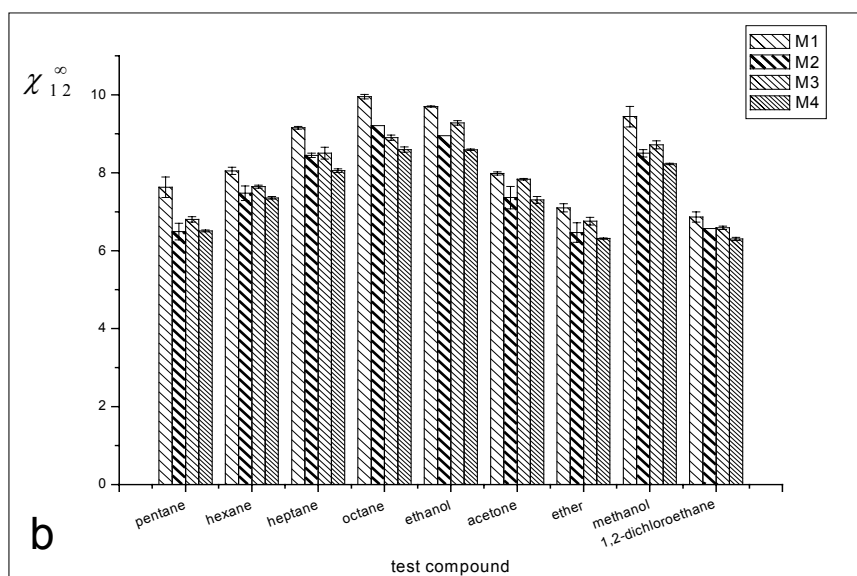


Fig. 5 (continued)

Comparison of the values of χ_{12}^{∞} for precursor M448 (M1, M2, M3, and M4) (30°C): (b) after hardening at 120°C and (c) after hardening at 180°C

The process of mixing of the precursors must be very brief, because of the high temperature at which it is performed. The high temperature can cause unfavourable melting of the resin. Short mixing time might be the reason for the inhomogeneity of the precursors – our results show that the precursor mixtures are not homogenous even after sifting. This affects the hardening process. It should, however, be taken into account that the observed inhomogeneity does not significantly reduce the good mechanical properties (wear resistance, cutting distance) of M448.

CONCLUSION

It has been shown that χ_{12}^{∞} can be used for evaluation of the extent of hardening of precursors during the manufacture of grinding tools. Comparison of χ_{12}^{∞} for the precursor before and after hardening reflects the progress of hardening. Hardening of the precursor (cross-linking of the resin) results in weakening of its interactions with test compounds, which in turn is reflected by an increase in χ_{12}^{∞} . The extent of cross-linking depends on the presence of all the components of precursor mixture and cannot be concluded from the behaviour of the isolated resin (novolak) alone. The fundamental significance of the type of aloxite to the process of hardening has also been shown.

χ_{12}^{∞} can be successfully used for comparison of different batches of precursor and to monitor their homogeneity. Further processing of precursors with more cross-linking leads to final products with much more useful mechanical properties (wear of the articles, working speed, cutting distance, durability). It must be emphasized, however, that these results are only qualitative. Quantitative description will be presented in a forthcoming paper.

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REFERENCES:

- [1] K. Woźniak, *Abrasive Articles: Production and Properties*, WNT, Warsaw, 1982, pp. 223–290 (in Polish)
- [2] M.P. Stevens, *Introduction to Polymer Chemistry*, PWN, Warsaw, 1983, pp. 303–313 (in Polish)
- [3] A. Gardziella, L.A. Pilato, and A. Knop, *Phenolic Resin*, 2nd edn, Springer, Berlin, 2000, pp. 24–51
- [4] H. Janik, *Elastomery*, **3**, 16 (2001)
- [5] P.J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943)
- [6] A. Voelkel, *Crit. Rev. Anal. Chem.*, **22**, 411 (1991)
- [7] H.P. Schreiber and D. R. Lloyd, *Overview of Inverse Gas Chromatography*. In: D. Arnould and R.L. Laurence (Eds) *Inverse Gas Chromatography*, American Chemical Society, Washington, DC, 1989
- [8] K. Milczewska and A. Voelkel, *J. Chromatogr. A*, **969**, 255 (2002)
- [9] J. Fall, K. Milczewska, and A. Voelkel, *J. Mater. Chem.*, **11**, 1042 (2001)