Journal of Chromatography A, 1441 (2016) 106–115

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Examination of the chemical changes in cured phenol-formaldehyde resins during storage

B. Strzemiecka[a,*], J. Zięba-Palus[b], A. Voelkel[a], T. Lachowicz[c], E. Socha[d]

[a] Poznan University of Technology, Institute of Chemical Technology and Engineering, Berdychowo 4, 60-965 Poznań, Poland
[b] Institute of Forensic Research, Westerplatte 9, 30-033 Kraków, Poland
[c] Jagiellonian University, Faculty of Chemistry, R. Ingardena 3, 30-060 Krakow, Poland
[d] Andre Abrasive Articles, Przemysłowa 10, 62-600 Koło, Poland

ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form 1 February 2016
Accepted 14 February 2016
Available online 2 March 2016

Keywords:
Phenol-formaldehyde resins
Aging
Py-GCMS
FT-NIR
Inverse gas chromatography

ABSTRACT

Chemical changes occurring within cured phenol-formaldehyde resins (resite and novolak type) during their storage were investigated by FT-NIR, py-GCMS and inverse gas chromatography. It was shown that a mixture of resite with novolak was less stable than resite or novolak itself as regards bulk properties. This aging phenomenon is mainly due to reaction of ammonia (product of hexa decomposition) with $-CH_2OH$ groups present in resite. FT-NIR technique seems to be the least sensitive method for assessment chemical changes occurring during cured resins storage. Applications of py-GCMS and IGC method made able to indicate that more significant changes were for bulk samples (py-GCMS results) than on their surface (IGC results).

1. Introduction

The phenol-formadehyde resins resole and novolak resins are commonly used for manufacturing of abrasive products [1,2]. Resole is used as the wetting agent whilst novolak is used as a binder. Resole is a liquid resin obtained in the reaction of phenol with formaldehyde in a basic environment by using excess of formaldehyde. Consequently, resole forms a complex mixture which might be cured at elevated temperature (Fig. 1).

Novolak is a powder resin obtained by the reaction of phenol with formaldehyde in the acidic environment by using excess of phenol. Novolak resin differs from resole due to the absence of CH_2OH groups. Due to the absence of hydroxymethylene groups, novolak is cross-linked only after addition of the extra volume of formaldehyde, paraformaldehyde or urotropine (Fig. 2).

The main advantage of phenol-formaldehyde resins is their low price whilst the main disadvantage of these resins is their instability during storage. The aging of resole results in an increase of its viscosity. However, resole with high viscosity will not cover abrasive uniformly. Thus, viscosity of resole is very important parameter [3]. Also the aging of novolak causes change of its color (from creamy to yellow) as well as a deterioration in mechanical properties.

Inverse gas chromatography (IGC) is a technique for the characterisation of solid state materials can be used for evaluating the chemical changes occurring during the cured resins (resites) storage. The IGC method was used by Chehimi and Abdeljalil for studying the degradation and stability of polypyrrole [4]. IGC is an extension of the classical gas chromatographic method [5–7]. IGC can characterize the surface of any solid state material which is packed in the chromatographic column. Carefully selected vapor phase solutes, with known physicochemical properties, are injected into the column packed with the material of interest. Retention data for these solutes allows the calculation of parameters describing the surface properties of the solid of interest. In this research the dispersive (γ_s^d), acid–base (γ_s^+, γ_s^-) components of the surface free energy were used to evaluate the surface physicochemical changes which occur during the storage of these resins. During the storage of these resins chemical changes can occur on the surface of resites and these can be reflected in changes in the dispersive and acid–base surface properties of these materials. These changes will be reflected in the different magnitudes of interactions between resin and IGC test solutes used for both new and aged resins. The method for the determination of γ_s^d, γ_s^+, γ_s^- parameters has been recently presented in Ref. [8].

* Corresponding author. Fax: +48 616653649.
E-mail address: beata.strzemiecka@put.poznan.pl (B. Strzemiecka).

http://dx.doi.org/10.1016/j.chroma.2016.02.051
0021-9673/

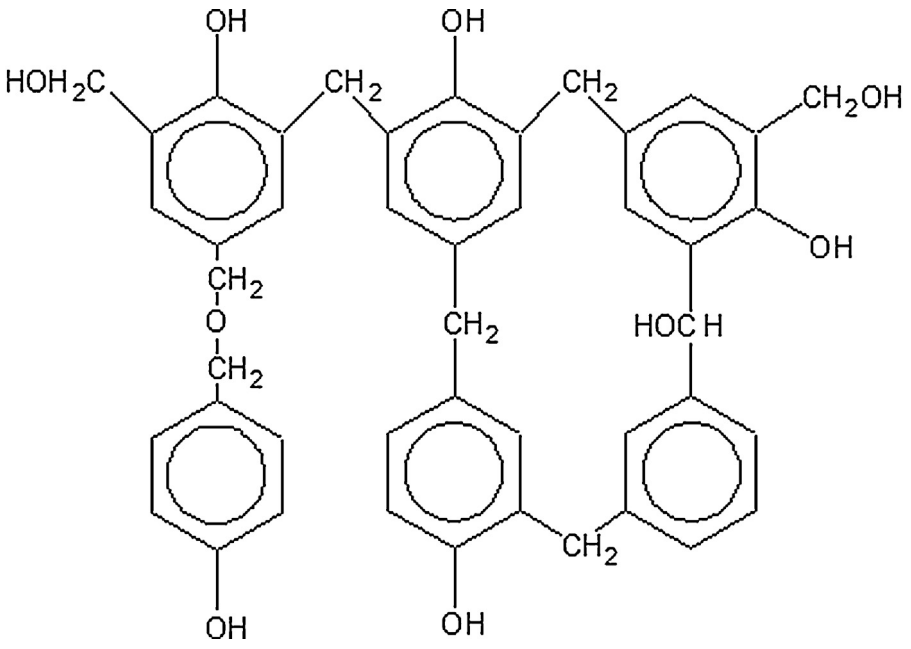

Fig. 1. Cross-linked resole (resite).

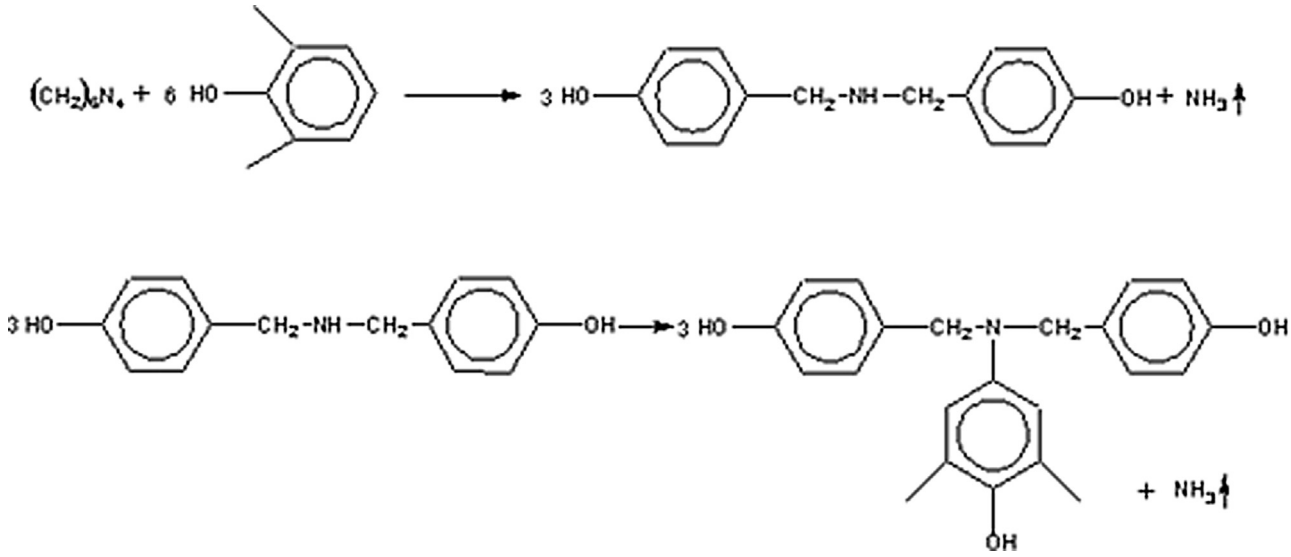

Fig. 2. Cross-linking of novolak resin in the presence of urotropine.

The aim of this paper was to estimate the changes occurring in the composition and the chemical properties of cured resole and novolak resins, as well as their mixture, during the storage at room temperature. The novelty of this paper lies in the detailed description of chemical changes occurring in phenolic resins during their storage that gives useful practical information for abrasive industry how to prevent unwanted product ageing. It was possible thanks to the application of different analytical techniques for the examination of the stability of resin systems such as: Fourier Transform Near Infrared Spectroscopy (FT-NIR), pyrolysis GC–MS and inverse gas chromatography. FT-NIR technique gives information about the chemical groups and thanks to this it was possible to assess the chemical changes in the cured phenolic resins e.g. post-curing reaction, formation of new bondsas a result of e.g. an oxidation reaction. IGC technique makes possible the surface characterization of solid polymers and gives information how chemical changes influence surface properties, surface energy. Thanks to using FT-NIR and IGC techniques it was possible to assess if chemical changes occur on the resins surface or this process is bulk. Py-GCMS technique is more sensitive than FT-NIR and gives information not only about chemical groups but also about chemical structure. It was

Table 1
The parameters of the test probes.

Test compound	a [m^2]	γ_l^d [J/m^2]	γ_l^+ [mJ/m^2]	γ_l^- [mJ/m^2]	Character
Heptane	5.73×10^{-19}	0.0203	–	–	Nonpolar
Octane	6.30×10^{-19}	0.0213	–	–	Nonpolar
Nonane	6.90×10^{-19}	0.0227	–	–	Nonpolar
Decane	7.50×10^{-19}	0.0234	–	–	Nonpolar
CH_2Cl_2 (DM)	2.45×10^{-19}	0.0245	5.2	0.0	Acceptor of electron
Ethyl acetate (EA)	3.30×10^{-19}	0.0196	0.0	19.2	Donor of electron