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Assessment of the chemical changes during storage of phenol-formaldehyde resins pyrolysis gas chromatography mass spectrometry, inverse gas chromatography and Fourier transform infra red methods

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ABSTRACT

The chemical changes occurring in the phenol-formaldehyde resins (resol and novolac type) during their storage were investigated. In this paper the FT-IR, py-GCMS and inverse gas chromatography methods were applied for assessment of the changes occurring during storage of the phenolic resins. We have found that during storage some examined resins occurred partial curing. The results from all techniques applied are consistent. Py-GCMS is useful technique for screening the storage processes but IGC seems to be most sensitive one.

1. Introduction

Phenol-formaldehyde resins, resol and novolac resins are commonly used for production of abrasive articles [1,2]. Resol is used as wetting agent while novolac as a binder.

Resol is a liquid resin obtained in the reaction of phenol with formaldehyde in the basic environment by using excess of formaldehyde (Fig. 1). The nucleophilic phenolic ion (Fig. 1a) undergoes the electrophilic substitution by formaldehyde (Fig. 1b). Due to high reactivity of phenol the mixture of hydroxymethylphenol, bis(hydroxymethyl)phenol and tris(hydroxymethyl)phenol is formed. These hydroxymethyl derivatives of phenol react at higher temperature to resol. The methylene bridges joining the aromatic chains are obtained in the condensation reaction (Fig. 1c). The methylene bridges can arise also in the Michael addition (Fig. 1d). Consequently, the resol is a complex mixture (Fig. 2) which might be cured at elevated temperature.

Novolac is a powder resin obtained in the reaction of phenol with formaldehyde in the acidic environment by using excess of phenol. In this case the structure presented in Fig. 2b is obtained.

Novolac resin differs from resol by the absence of CH_2OH groups. Due to the absence of hydroxymethylene groups novolac is cross-linked only after addition of the extra volume of formaldehyde, paraformaldehyde or urotropine (Fig. 3).

The most advantage of phenol-formaldehyde resins is their low price. The main disadvantage of these resins is their instability during storage. The aging of resol causes the increase of its viscosity. The resol with too high viscosity does not cover abrasive grains evenly. Thus, viscosity of resol is very important parameter [3]. Aging of novolac causes change of its color (from creamy to yellow) and deterioration of mechanical properties.

In order to inhibit aging process of resins it is important to know what chemical changes cause these unfavorable physical changes.

Inverse gas chromatography (IGC) can be used for evaluation of the chemical changes occurring during the resins storage. IGC is an extension of the classical gas chromatography [4–7]. IGC characterizes the surface of any material which is placed in the chromatographic column. Carefully selected test compounds, with known physicochemical properties, are injected into the column. Retention data are suitable to calculate parameters describing surface properties [8–10] as well as bulk properties of polymer such as

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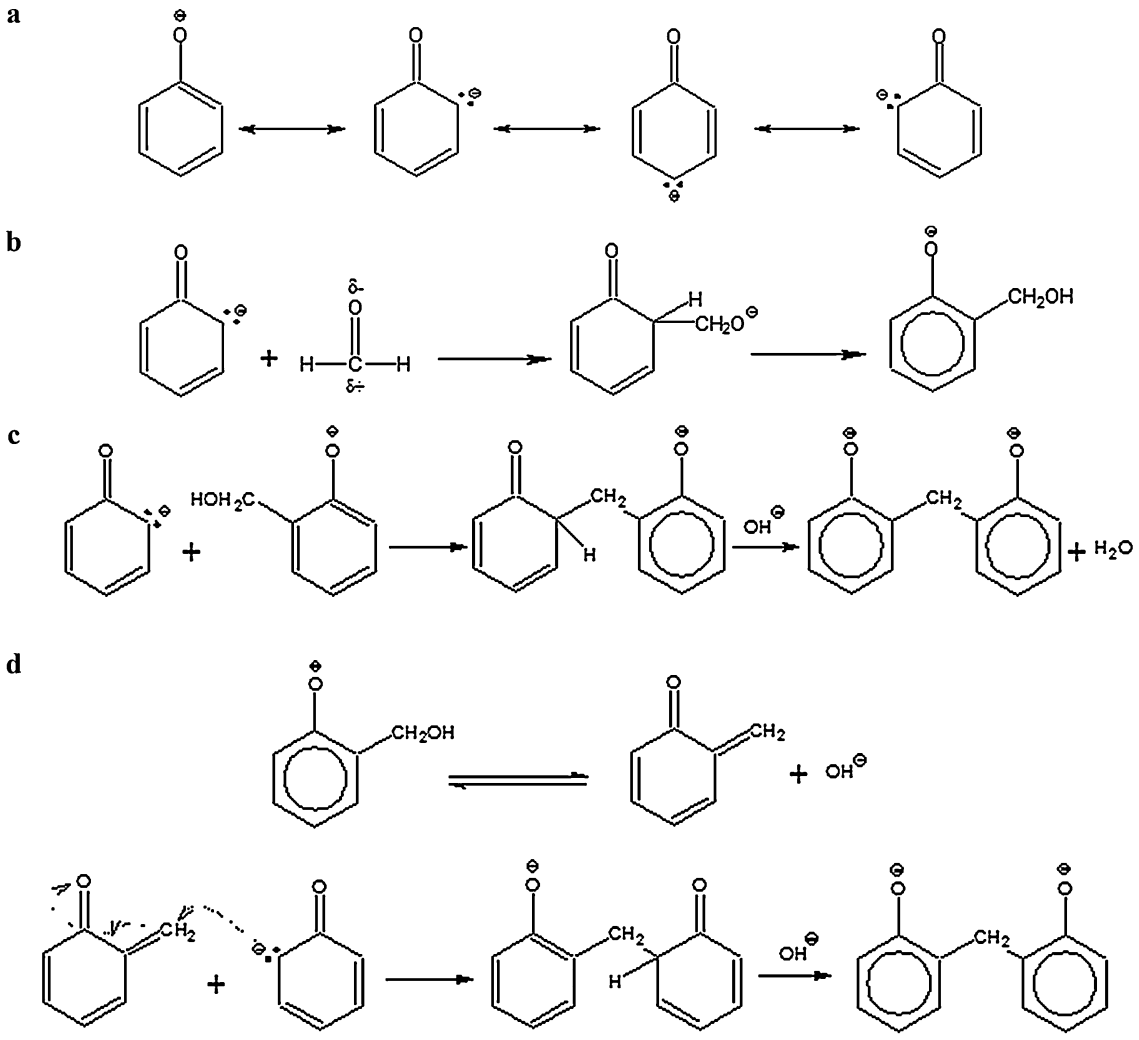

Fig. 1. Reactions occurring during curing of resols: (a) the formation of nucleophilic phenolic ion, (b) electrophilic substitution of phenol by formaldehyde, (c) formation of the methylene bridges joining the aromatic chains by the condensation reaction and (d) formation of the methylene bridges joining the aromatic chains by Michael addition.

solubility parameter [11] or glass temperature of polymers [12]. In our research the Flory–Huggins parameter, χ_{12}^{∞}, was used for evaluation of physicochemical changes during the storage of resins. χ_{12}^{∞} parameter expresses the magnitude of the interactions between the examined material and test compounds of different character. During the storage of resins chemical changes can occur. These changes will be reflected in the different magnitude of interactions between resin and test compounds for new and aged resins. Flory–Huggins interaction parameter as an important factor of miscibility of polymer blends and solutions has been determined by a number of methods (e.g. SANS, DSC, IGC) and reported in different papers. The way of determination of χ_{12}^{∞} and its application in the description of characterization of polymeric materials was recently presented in the review paper [4]. The equations used in this paper are presented in Section 2. The aim of this paper was the estimation of the changes occurring in the composition and properties of resol and novolac resins during the storage at room and lowered (cooler) temperature. In these studies Fourier transform infrared spectroscopy (FTIR), pyrolysis GC–MS and inverse gas chromatography were used. Application of py-GCMS technique in such examination is justified. One may expect that the changes occurring during the aging of resins will result in the changes of the composition of pyrolitic derivatives of the examined materials. Three techniques used should submit complementary data on the processes occurring in the stored resins.

2. Experimental

2.1. Materials

Two types of resol resins and one of novolac were studied. Resol resins were aqueous (10% of water) and non-aqueous (10% of furfuryl alcohol) marked as S and BW, respectively. Novolac resin contained 8% of hexamine as cross-linking agent. All resins were supplied by Organika-Sarzyna. The resins were studied as received just after delivery (marked as new) and after six months of storage at "room" condition (RH about 40% and temperature about 20 °C) – marked as aged.

2.2. FTIR

FTIR analysis was carried out using Vertex70 spectrometer, Bruker Optics. Liquid resol was studied as liquid film. It was placed between NaCl plates. Solid novolac and cross-linked resins were studied as KBr tablets.

2.3. Py-GCMS

Pyrolysis-GC/MS analysis was carried out using AutoSystem XL gas chromatograph coupled with TurboMass Gold quadrupole mass spectrometer, PerkinElmer, USA equipped with DB-35MS capillary