

Analysis method

Direct analysis of microstructures of alkyl phenol resin using atmospheric pressure chemical ionization-mass spectrometry



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ABSTRACT

Alkyl phenol resin was directly analyzed using atmospheric pressure chemical ionization-mass spectrometry (APCI-MS). Analysis was performed in both positive and negative ion modes, and product ions were only observed in the negative ion mode. By interpreting the m/z values of $[M - H]^-$ ions, the degree of polymerization, the types of linkages and the types of terminals could be determined. The monomer, dimer, trimer, tetramer and pentamer species were observed. The methylene and dimethylene ether linkages were distinguished. For the terminal types, the methylol, *o*-methylene quinone, hydrogen, and aldehyde were distinguished. Influence of the types of solvents and eluents on the ionization efficiencies were investigated using acetone, chloroform and tetrahydrofuran. Recommendable solvent and eluent system for the analysis of resin using APCI-MS was acetone.

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1. Introduction

As phenolic resins have good properties due to their high thermal stability, excellent resistance to combustion, high dimensional stability, good mechanical properties and high chemical stability, they have been used variously according to the microstructures as bonding agents, tackifiers, crosslinking agents, photo resists, coating materials, reinforcing agents, polymer modification agents and so forth [1–15]. Phenolic resins are synthesized by reaction of phenol derivatives and aldehydes, and their type is determined by the kinds of phenol derivatives and aldehydes [9,12–14,16–22]. Phenolic resins are divided into novolac and resole resins. Novolac is made by excess phenol derivative with aldehyde in acidic conditions, while resole is made by excess aldehyde with phenol derivative in basic conditions. Compared to novolac, the structure of resole is more complicated, having many branched chains and

reactive methylol terminal groups. Sometimes, resole is even more important than novolac in the thermoset resin industry. Alkyl phenolic resins are used for tackifiers (novolac) and crosslinking agents (resole). There are two types of linkages between alkyl phenols of methylene and dimethylene ether. The resoles with methylol substituted to both terminals or with *o*-methylene quinone are used as a crosslinking agent for elastomer compounds [6,23–26].

Properties and application fields of resins are determined by the degree of polymerization, the linkage type and the terminal type. Therefore, microstructural analysis of resins to identify the molecular weight and functional groups is essential for understanding and characterizing the resins. Gel-permeation chromatography (GPC) and high-performance liquid chromatography (HPLC) are useful techniques for measuring average molecular weight of resins [10,11,16,27–31], but chromatography does not give information for absolute molecular weight and chemical structure. Infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) have also been used for the analysis of resins [8,14,30,32], but these methods only give average structures and do not give information for

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molecular weight. Biedermann and Grob [10,11] used gas chromatography/mass spectrometry (GC/MS) for the analysis of resins. However, using GC/MS, only volatile chemicals are analyzed or modification of non-volatile materials is needed, and chemicals with high molecular weight are not analyzed. Schrod et al. [33] analyzed phenolic resoles using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and showed the oligomer distribution of phenolic resoles. The MALDI-MS spectrum of resins can give the degree of polymerization and the number of reactive methylol groups. Sample preparation including the selection of a matrix in MALDI-MS critically affects the analytical results; and drying conditions, temperature and humidity also influence quality of the MALDI-MS spectra.

Atmospheric pressure chemical ionization (APCI) is a soft ionization technique and is a form of chemical ionization that takes place at atmospheric pressure. It can form both positively and negatively charged molecular ion species. In APCI, chemical ionization takes place at atmospheric pressure. The solution containing mobile phase and analyte is sprayed through a heating region and the entire aerosol cloud is introduced to an ionization region of corona discharge. The ionization occurs in the gas phase. In the present work, alkyl phenol resin was analyzed using atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) to identify the microstructures including the degree of polymerization, the linkage types and the terminal types. The analysis was performed in the positive and negative ion modes. Electrospray ionization (ESI) was also used for the analysis of alkyl phenol resin. In general, the quality of APCI-MS spectra is influenced by the kind of solvent to prepare a sample, solution as well as the kind of eluent. Therefore, influence of the kinds of solvents and eluents on the ionization efficiencies of alkyl phenol resin was investigated. Influence of the cone voltage (fragmentor voltage or accelerating voltage) on the ionization efficiencies of alkyl phenol resin was also examined.

2. Experimental

Alkyl phenol resole resin was purchased from Hitachi Chemical Co. Acetone, chloroform and tetrahydrofuran (THF) were purchased from J. T. Baker Co. The resin was dissolved in the solvent and a 50 ppm solution was prepared. Acetone, chloroform and THF were used as the solvents.

A HPLC 1200 chromatograph was coupled to a single quadrupole LC/APCI-MS mass spectrometer of Agilent Technologies Inc. The liquid chromatograph used a binary pump and an injection valve with a 10 μ L sample loop. A sample of 10 μ L was introduced by means of a Rheodyne valve. Acetone, chloroform and THF were used as the eluents, and the flow rate was 1.3 mL/min. MS detection was achieved using a single quadrupole spectrometer equipped with an APCI ionization source. The following instrumental parameters were used for the APCI-MS analysis in the negative ion mode: capillary, 4 kV; cone voltage, 30–150 V; corona current, 15.0 μ A; quadrupole temperature, 100 $^{\circ}$ C; and vaporizer temperature, 325 $^{\circ}$ C. For the positive ion mode, the capillary voltage was -4 kV.

3. Results and discussion

The resin was analyzed using APCI-MS in both the positive and negative ion modes. Besides APCI, the resin was analyzed using ESI as the ionization source. The positive APCI-MS spectra did not display product ions related to the resin, as shown in Fig. 1. The most abundant ion at m/z 117 in the positive APCI-MS spectrum was [Acetone + H] $^{+}$. ESI did not generate the resin ions. The reason for the no resin signal by ESI could be use of less polar solvents such as acetone, chloroform and THF. The resin was not dissolved in highly polar solvents such as water, methanol and acetonitrile. In contrast to the ESI and positive APCI, the negative APCI-MS spectra clearly displayed product ions related to the resin as shown in Figs. 2–4. The formation of negative ions is reasonable because the alkyl phenolic resin has acidic alcohols. Some differences in the mass spectra were found according to the solvents and eluents used.

Notation of the chemical structures of resin includes the degree of polymerization (Mo, Di, Tr, Te and Pe), the linkage types (M and E) and the terminal types (A, Q, H and K). The Mo, Di, Tr, Te and Pe denote the monomer, dimer, trimer, tetramer and pentamer species, respectively. The M and E denote the methylene and dimethylene ether linkages, respectively. The A, Q, H and K denote the methylol, *o*-methylene quinone, hydrogen and aldehyde terminals, respectively. For example, the production at m/z 743 ([M – H] $^{-}$) in Figs. 2–4 has molecular weight of 744 and is an octyl phenol formaldehyde resole resin with the notation Tr-EE-AQ (trimer, two dimethylene ether linkages, and methylol/*o*-methylene quinone terminals). Chemical structures of the principal monomer and dimer species are described in Scheme 1. The ions at m/z 261, 481, 509 and 511 were assigned to Mo-KK, Di-M-AK, Di-E-KK and Di-E-AK, respectively. Scheme 2 shows chemical structures of the principal trimer species. The ions at m/z 727, 729, 743 and 757 were assigned to Tr-ME-KK, Tr-ME-AK (and/or Tr-EE-HK), Tr-EE-AQ and Tr-EE-KK, respectively. Chemical structures of the principal tetramer species are described in Scheme 3. The ions at m/z 901, 915, 931 and 945 were assigned to Te-MMM-AQ

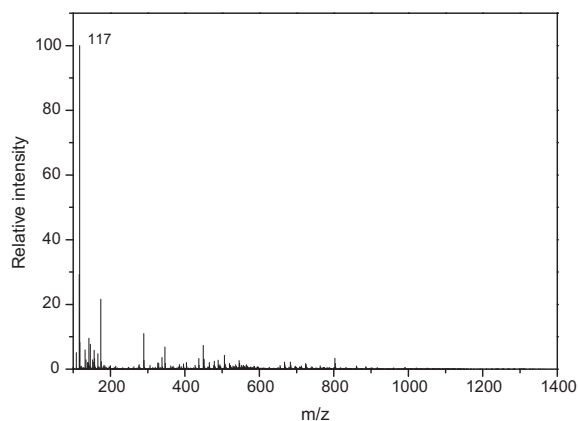


Fig. 1. Positive APCI-MS spectrum of the resin dissolved in acetone. The eluent was acetone and the cone voltage was 90 V.

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