Development of Headspace Gas Chromatography-Mass Spectrometry for Determination of Residual Monomer in Polymer Latex

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Abstract

A full evaporation (FE) and a vapor-liquid equilibrium (VLE) headspace gas chromatography-mass spectrometry (GC-MS) test methods were utilized for the determination of residual monomers in polymer latex such as methyl methacrylate (MMA) and ethyl acrylate (EA). An FE headspace GC-MS was introduced since the sample preparation or solvent extraction did not have to be performed and, a small amount of the latex sample was utilized for analysis as well. With the FE headspace GC-MS, the residual MMA and EA monomers were completely transferred from an aqueous and a solid phase to a vapor phase at a temperature of 120°C within 5 minutes. Therefore, a simple analytical technique for residual monomer determination could be achieved.

Key words: Headspace GC, Full evaporation, Vapor-liquid equilibrium, Emulsion polymerization

Introduction

A polymer latex was produced from emulsion polymerization with polymer particles dispersed in a continuous aqueous phase. The applications of the polymer latex are synthetic rubber, paints, coatings, and adhesive. High conversion of monomers to polymers in the process is desired because it not only improves the efficient production of polymers but also reduces the amount of residual monomers for health and safety concern. Therefore, the method for quantification of residual monomer is of importance because it can determine critical parameter values for process control, modification, and optimization. Monomer conversion can be obtained by traditional method, typically gravimetry. By the evaporation of water, the residual monomer, and any volatile components coupled with weighing the remaining polymer solid, can be calculated from the composition of raw materials. Gas chromatography (GC) is widely used for monomer quantification owing to the high volatility of the monomer. A polymer latex is a multiphase system in that the residual monomers contain both an aqueous phase and a solid polymer particle phase. Therefore, sample preparation is required prior to GC-MS analysis. Solvent extraction and direct sample dilution with a water-soluble organic solvent are common techniques for sample preparation; however, some problems might occur due to the nonvolatile dissolved species deposited on the GC column causing a deterioration in separation performance and considerable damage to the GC column. Thermal desorption technique is a sample preparation method with or without organic solvents for GC analysis. However, the method limited to the quantification of residual monomers in solid samples. An FE headspace GC technique is particularly suitable for liquid sample analysis and requires a few amount of a sample to nearly complete transfer to a vapor phase. However, it is not applicable to a sample with low monomer conversion (high monomer concentration). An equilibration headspace GC technique is a conventionally headspace method for the quantification of high monomer concentration in a sample. Limitation of the method is that the droplet monomers in sample must be completely dissolved in the aqueous phase.

The objective of this work is to demonstrate a simple and accurate FE headspace GC method for the determination of residual acrylate monomers in a liquid latex sample.

Materials and Experimental Procedures

Materials

The monomers used in the experiment were obtained from a commercial source. The

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concentration of two stock standard solutions, a methyl methacrylate (MMA) and an ethyl acrylate (EA) solutions, was 1000 µg/mL (0.1%) which 0.1 g of pure MMA and EA solution was separately poured into 100 mL volumetric flasks and, then, diluted with ultrahigh-pure water (of 18 MΩ·cm resistivity) as a solvent. A working standard solution, the mixed solution of MMA and EA standards, was prepared by diluting the stock solutions with ultrahigh-pure water for 10 times. The concentration of the working standard solution was 100 µg/mL.

The polymer latex was an emulsion polymerization sample. Two polymer latex samples were obtained from a commercial source. The latex sample A was produced from polymerization process of MMA, butyl acrylate (BA) and methacrylic acid (MAA) monomers system. The latex sample B was produced from polymerization process of MMA and EA monomers system.

Sample Preparation Procedure for Headspace GC-MS analysis

A latex sample was weighed inside a 20 mL headspace vial which was immediately capped. The sample was analyzed by automatic headspace GC-MS with the headspace condition as shown below in the subsection of “Apparatus and Conditions”.

Apparatus and Conditions

The GC-MS (QP-2010, Shimadzu, Japan) was utilized for the experiment. The capillary column was DB-5 having a length of 60 m, a diameter of 0.32 mm and a film thickness of 0.25 µm. The column temperature was raised in 3 steps, one at 40°C hold for 10 minutes, second at 40-60°C with a heating rate of 1°C/min and third at 60-180°C with a heating rate of 8°C/min and hold for 2 minutes. The carrier gas used was 99.999% helium gas with a flow rate of 1.4 mL/min. The ion source and interface temperatures of MS detector were at 250 and 280°C, respectively, while the detector voltage was at 7 V, and the scan range of mass-to-charge ratio (m/z) of ion was 33-450. The auto-sampler of GC-MS instrument, AOC-5000 (Shimadzu, Japan), was used for automatic headspace. Temperature and time of the headspace conditions were varied while the syringe temperature was at 70°C. The gas sample injection volume was 1 mL.

The ratio of A2/A1 was used to monitor the completeness of a monomer peak in the chromatogram for the first and second headspace GC analysis. If the ratio of A2/A1 was low, it indicated the near completion of monomer mass transfer from an aqueous phase to a vapor phase. To prevent contamination and remove the residual monomer vapor from the previous headspace extraction process in the first headspace GC analysis, fresh helium purging must be performed after each analysis.

Results and Discussion

FE Headspace GC-MS Optimization Conditions for MMA Quantification in Latex Sample A

The latex sample A was first analyzed to determine the residual monomers remaining. Figure 1 presents the residual monomers in the sample which are butyl acrylate (BA) and methyl methacrylate (MMA) monomers. In this work, only residual MMA monomer was further studied to reveal the effect of temperature and time on quantitative analysis.

Figure 1. Chromatogram of the latex sample A.

Effect of Temperature

The residual monomers in a latex sample were dispersed in an aqueous phase and a polymer solid phase. Therefore, the completeness of residual monomer mass transfer to a vapor phase was obtained when the dissolved residual monomers in an aqueous phase was completely transferred to a vapor phase and, also, residual monomers adsorbed on a polymer solid surface was desorbed from a polymer solid surface to aqueous phase for volatilization in a vapor phase. Temperature is an important parameter that could affect the completeness of residual monomer evaporating to a vapor phase. In this work, the effect of temperature on the complete evaporation of the residual monomers was studied. Temperature for headspace was varied from 60°C to 140°C until the MMA was completely evaporated from aqueous phases to
vapor phases. The condition for helium purging after each analysis was the helium pressure at 200 kPa and the purging time at 45 minutes. The result was shown in Figure 2. With the 70 mg of the latex sample A, the MMA was completely evaporated at 120°C within 5 minutes.

Figure 2. Effect of headspace temperature on the ratio of A2/A1 for MMA quantification.

Effect of Time

In general case, the equilibration times of liquid samples are shorter than those of solid samples, especially aqueous samples with the shortest equilibration time behavior. Equilibration time is a critical parameter, influencing the completeness of residual monomer evaporation. Effect of the holding time of isothermal study is shown in Figure 2. At the temperature of 120°C, the holding time was varied from 5 minutes to 20 minutes. It was found that the MMA was completely evaporated at the temperature of 120°C within 5 minutes (Figure 3).

Figure 3. Effect of holding time for headspace on the ratio of A2/A1 for MMA quantification.

FE Headspace GC-MS Optimization Conditions for EA Quantification in Latex Sample B

Since the latex sample B was the mixture of MMA and EA monomers, the qualitative analysis was first performed to determine the remaining of residual monomers. Consequently, it was found that only EA monomer was detected (Figure 4). Due to the small amount of EA in the sample B, therefore, the sample weight for analysis was increased from 70 mg to 1 g. Under the same temperature (120°C) and holding time (5 minutes), the EA in sample B was fully evaporated to a vapor phase (Table 1).

Figure 4. Chromatogram of the latex sample B.

Table 1. FE headspace GC-MS analysis of sample B.

<table>
<thead>
<tr>
<th>Monomer name</th>
<th>Peak area A1</th>
<th>Peak area A2</th>
<th>A2/A1</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>42,257</td>
<td>0</td>
<td>0</td>
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</table>

Quantitative Analysis of Residual MMA in Latex Sample A by FE Headspace GC-MS

A calibration curve was developed for quantitative analysis of MMA. Five calibration solutions were prepared by varying volumes of 100 µg/mL of the working standard solution; 15, 30, 60, 120 and 240 µL. They were separately transferred to headspace vials. All solutions were analyzed by FE headspace GC-MS with the condition in the subsection of “Apparatus and Conditions” and the headspace temperature at 120°C with a holding time of 5 minutes. The linear relationship between the GC-MS peak area (GC-MS intensity) and the amount of MMA in solution was as the calibration curve with a correlation (R^2) equal to 0.99942 (Figure 5). A standard addition method was used for the quantification of residual MMA in the latex sample A. The latex sample A was divided into 5 portions and 70 mg of the sample was weighed for each portion which was added by the MMA standard solution in various concentrations (1.5, 3, 6, 12 and 24 µg). All prepared solutions were analyzed by FE headspace Linearity of the MMA curve from the standard GC-MS with the conditions used for calibration.
curve method. The linear regression fit of the MMA curve from the standard addition method was obtained with \( R^2 \) equal to 0.9981 (Figure 5).

### Figure 5. The calibration and the standard addition curves of MMA monomer.

With the extrapolation to x-axis, the concentration of residual MMA in the latex sample A was determined and the results were summarized in Table 2. The linear regression fit, an equation, of the standard addition method was shown in Table 2. It was used for quantification of the amount of residual MMA monomer in the latex sample A. At the intercept on the x-axis, the amount of residual MMA (x) containing in the original latex sample was obtained.

Using the calibration curve, the quantification of the amount of residual MMA monomer in the latex sample A could be determined and shown in Table 2. The obtained residual MMA monomer by both standard addition method and calibration curve presented the amount of MMA monomer that could not convert to polymer. The slope of each profile in Figure 5 was slightly different indicating a few interferences from matrix. However, the calculated values of the amount of residual MMA monomer from these two methods were insignificantly different. Therefore, the calibration curve method was still used for quantitative analysis of the residual MMA monomer.

### Quantitative Analysis of Residual EA in Latex Sample B by FE Headspace GC-MS

Based on the results of the quantitative analysis of residual MMA in latex sample A, the quantification of EA monomer in the latex sample B was determined by calibration curve method using FE headspace GC-MS. In this method, the curve showing the relationship between the peak areas and the amount of EA was developed as the calibration curve. The straight-line regression curve with \( R^2 \) equal to 0.9998 was obtained as shown in Figure 6. The amount of EA monomer in latex sample B was calculated using the equation as shown in Figure 6. Using 1 g of the latex sample B, it contained the residual EA monomer of 3.2 μg/g.

### Figure 6. The calibration curve of EA monomer.

### Conclusions

The quantification of residual MMA and EA monomers in the polymer latex could be obtained by FE headspace GC-MS analysis without any sample preparation and solvent extraction. The method is simple and the small amount (in μg/g level) of residual MMA and EA in the latex sample could be detected.

### Table 2. The concentration of residual MMA monomer in sample A.

<table>
<thead>
<tr>
<th>Quantitation method</th>
<th>Standard matrix</th>
<th>Equation</th>
<th>Amount of MMA in sample A (μg)</th>
<th>MMA concentration in sample A (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration curve</td>
<td>MMA solution</td>
<td>( y = 9295 \times + 2069.9 )</td>
<td>5.5 (( y = 56,874 ))</td>
<td>77</td>
</tr>
<tr>
<td>Standard addition method</td>
<td>Sample A + MMA solution</td>
<td>( y = 8627.4x + 5045 )</td>
<td>5.9 (( y = 0 ))</td>
<td>84</td>
</tr>
</tbody>
</table>
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References

