ON THE EFFECT OF ETHANOL SOLUTION ON MELAMINE TEMPLATE REMOVAL PROCESS

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ABSTRACT

The present communication describes the successful production of molecularly printed polymers with the application of the cooling-heating method. The first step refers to the introduction of melamine to an aqueous solution of ethanol. Methacrylate acid, ethylene glycol dimethacrylate, and benzoyl peroxide are then added as a monomer, a cross-linker, and an initiator, respectively. The solution is stirred at 15°C for 15 min and subsequently transferred to a vial to be cooled at -5°C for an hour. Then the solution is heated for 3 h at 75°C, for another 3 h at 80°C, and for additional 3 h at 85°C. The solid material obtained is then crushed into a powder. The template removal process is carried out through washing with an aqueous ethanol solution. A polymer called MIP is obtained. The FTIR, XRD, HPLC, and SEM characterization results show that the concentration of melamine in MIP is decreased as a result of the removal process. The presence of more cavities in MIP indicates that it can be applied as a membrane sensor.

Keywords: MIP, cooling-heating method, melamine, cavities.

INTRODUCTION

Melamine is obtained in the course of a reaction of phenol with formaldehyde. It is a white colored substance in the form of crystals or a powder. It is an odorless and poisonous chemical of a very low solubility, often used in various products such as tableware, building materials and coatings [1].

The first cases of melamine poisoning are reported in USA, where thousands of animals have suddenly died of an unknown cause in 2007. The subsequent US Food and Drug Administration (FDA) investigation has revealed that the animals have been fed with melamine enhanced fodder mixtures. In 2008 China has faced a public health disaster connected with various infant formulas containing melamine. They have caused kidney stones and/or death of thousands of babies [2]. Melamine's high nitrogen content (66.6 % of its weight) makes it attractive as an additive increasing the protein content of the food products irrespective of its very low solubility [3].

A simple technique of measuring melamine levels refers to molecular imprinting, which provides the production of hollow polymers through the removal of the active substance (template) from the polymerization process. The cooling-heating method [4 - 7] is used. This paper describes the analysis of melamine polymers obtained prior to and after the template removal (MIP). The FTIR spectra and the SEM images recorded show a significant difference providing the assumption that MIP is ready to be applied as a sensor membrane.

EXPERIMENTAL

The polymerization process started with the introduction under stirring of the template, melamine (0.03 g) in this case, to an aqueous/ethanol solution (3:1). Then methacrylate acid (MAA 0.25 mL), ethylene glycol dimethacrylate

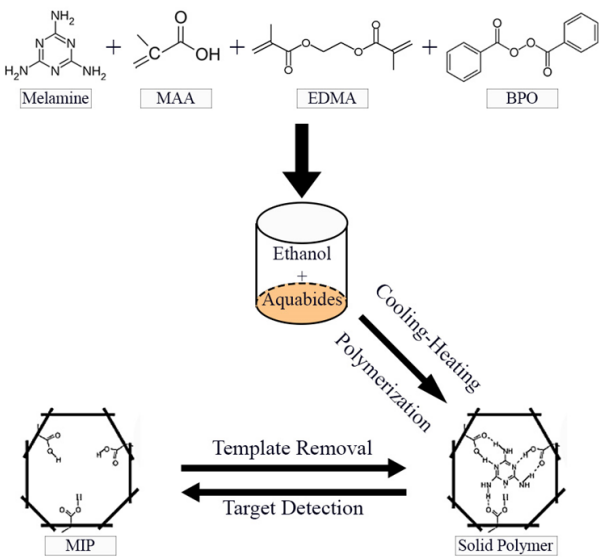


Fig. 1. Melamine polymer and MIP synthesization process.

(EDMA 2.825 mL), and benzoyl peroxide (BPO 0.03 g) were added acting as a monomer, a cross-linker and an initiator, correspondingly. The mixture was stirred for 15 min aiming homogenization. The solution obtained was stored in a vial and cooled for an hour. Then heating was applied by placing the vial in a furnace. The procedure applied included 3 h at 75°C, 3 h at 80°C, and another 3 h at 85°C. The polymer obtained was in a solid state. After subsequent cooling it was crushed into fine particles.

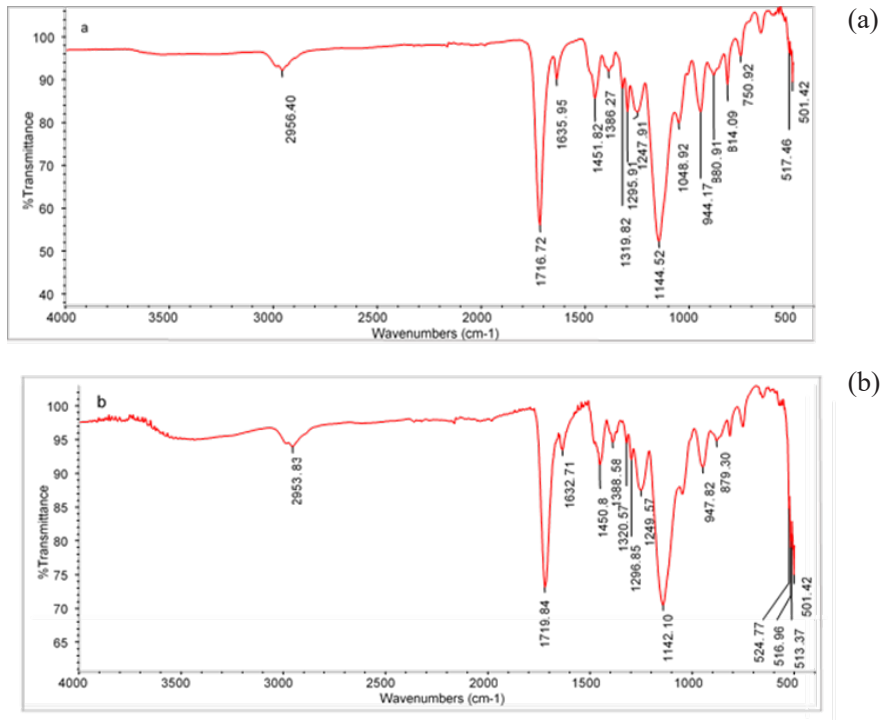
This step was followed by an extraction aiming to draw the melamine out of the polymer powder by using an aqueous solution of methanol and acetic acid (0.625 mL/12.5 mL). This step resulted in a polymer called MIP. It provided the recognition of a target substance (of identical physical and chemical characteristics) [8].

The polymer obtained prior to and after the extraction was characterized. The polymers prior to and after the extraction were analyzed by FTIR (Fortir Hazmat type 360), XRD (Type PW3710), HPLC (Type Ultimate 3000), and SEM (Type Hitachi Flexsem 1000).

RESULTS AND DISCUSSION

FTIR Test

This test is carried out with melamine as a template. The melamine molecule contains N-H and C-N bonds predominantly found in the ranges of 3300 cm^{-1} - 3500 cm^{-1} and 1000 cm^{-1} -1360 cm^{-1}, respectively. The transmittance spectrum charts of the polymers (prior to and following the extraction) are presented in Fig. 2. The data referring to the comparison carried out is presented in Table 1.



(a)

(b)

Fig. 2. FTIR Spectrum from (a) melamine polymer and (b) melamine MIP.

Fig. 2 shows that both charts have the same overall shape as both refer to identical reagents. There are differences in the percentage transmittance as shown in Table 1. The increase of N-H and C-N % transmittance is attributed to a decreased melamine concentration as a result of the extraction process (Fig. 2b).

Table 1 presents a more detailed data derived from the FTIR spectra of the melamine containing polymer (Fig. 2a) and MIP (Fig. 2b).

X-ray diffraction (XRD)

The XRD characterization data reveals peak shifts between MIP and the melamin containing polymer amounting to 15.88° and 16.10°. This is a verification of an interlayer spacing increase [9]. The lower diffraction intensity of the unwashed polymer when compared to that of MIP indicates an interaction between the monomers and the template [7].

The crystal size *L* of both polymers in Fig. 3 is calculated [10] using the Scherrer equation:

$$L = \frac{K\lambda}{B\cos\theta} \quad (1)$$

where K is the Scherrer constant (0.9), λ is the X-ray wavelength, B is the full width at the half-maximum (FWHM), while θ is the diffraction peak.

The XRD data shows that there is a decrease of FWHM value of the unwashed polymer, which is equal to 11.2°, when compared to that of the washed polymer

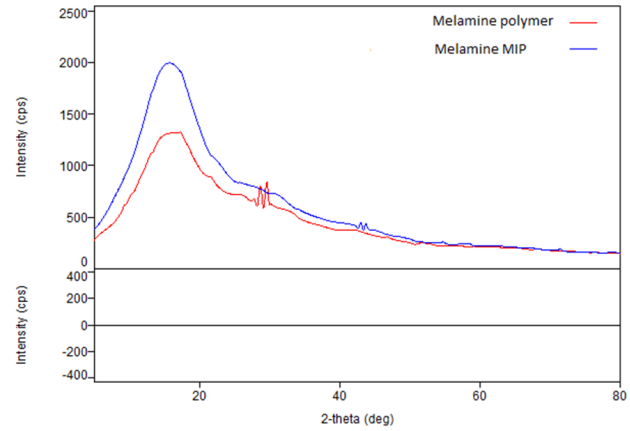


Fig. 3. XRD patterns of melamine-polymer and melamine-MIP.

(MIP), which amounts to 9.06° (Table 2). The smaller FWHM value indicates that the polymer has better properties [11]. Besides, Eq. 1 shows that the smaller FWHM value is connected with a larger crystal size [12]. The latter determines larger diffraction field and higher peak intensity. The data of the XRD analysis is summarized in Table 2.

High Perfomance Liquid Chromatography Analysis (HPLC)

The HPLC analysis is performed to measure the effectiveness of the extraction process in respect to melamine drawing out of the polymer. The obtained data shows that melamine concentration is decreased after the template removal process. This indicates that

Table 1. Transmittance value from melamine polymer and melamine MIP.

No	Wavenumber (cm^{-1})	Functional Group	% Transmittance	
			Polymer	MIP
1	1550-1650	Amine, Carboxylic Acid (C-O; N-H_2)	90,11	93,48
2	1247-1250	Carboxylic Acid, Amine C-O, N-H	82,43	87,48
3	1142-1145	Amine: N-H, C-H	52,31	70,47
4	1000-1100	Amine, Carboxylic Acid (C-O; N-H_2)	79,92	-
5	870-900	Amine (N-H_2)	91,05	94,82
6	810-820	Amine (N- H_2)	89,26	-
7	750-751	Amine (N- H_2)	96,59	-

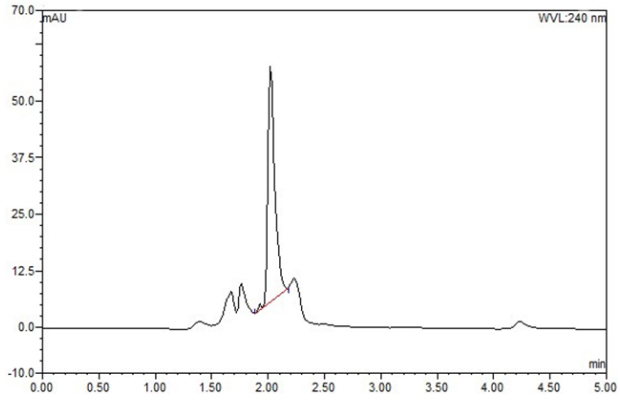
Table 2. XRD Spectrum Analysis for Melamine MIP and Unwashed Polymer.

Sample	2θ (°)	*d-spacing* (Å)	FWHM (°)	*Crystal Size* (Å)
Unwashed polymer	16.10	5.50	11.2	7.168
Melamine MIP	15.88	7.94	9.06	9.2811

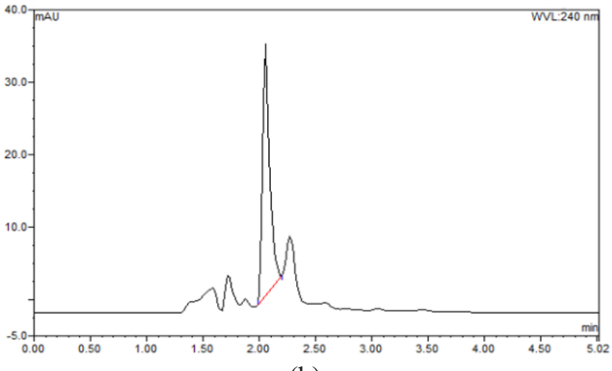
the solvent used provides melamine binding. The visualization of the melamine presence in both polymers is presented in Fig. 4.

The comparison of the melamine concentrations in both polymers is presented in Table 3.

Although the melamine active ingredient is still present in the resulting MIP, the data shows that there is a 34.61 % decrease in its concentration achieved in the course of the extraction. The latter is expected to produce MIP with a sufficient number of cavities.



(a)

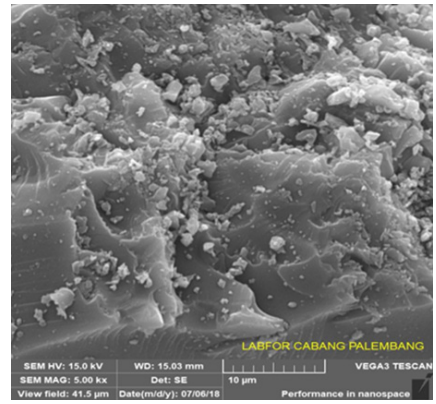


(b)

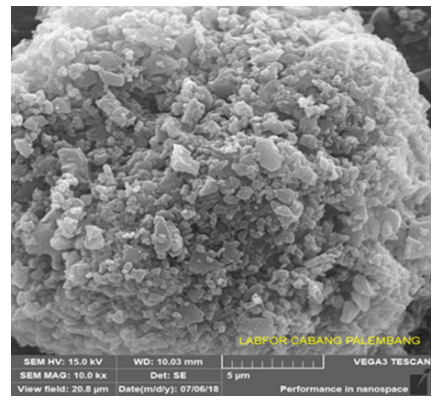
Fig. 4. HPLC Graph of Unwashed Polymer (a) and Melamine MIP (b).

SEM Test

The number of the cavities formed in the course of the extraction process is calculated [13] by analyzing the SEM images with the application of Poredisk software. The results obtained are presented in Fig. 5. The Porediz software analysis illustrated in Fig. 6 shows that MIP has 445 cavities which is essentially greater than that of the initial polymer – the latter number amounts only to 255. This significant increase shows that MIP can be applied as a membrane in a MIP-based working electrode sensor.



(a) Melamine Polymer



(b) Melamine MIP

Fig. 5. SEM Images from melamine polymer and MIP.

Table 3. HPLC Analysis of Unwashed Polymer and Melamine MIP.

Sample	Ret. time (min)	Height (mAU)	Amount (ppm)
Unwashed polymer	2.02	52.053	0.130
Melamine MIP	2.05	34.834	0.085

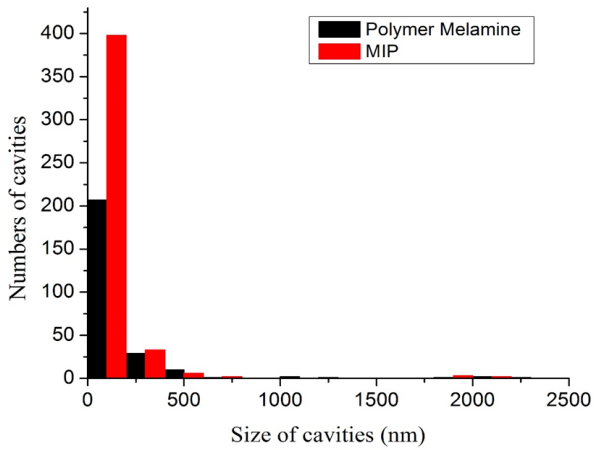


Fig. 6. Cavity size distributions of melamine MIP.

CONCLUSIONS

The FTIR and HPLC results verify that the use of an ethanol solution in the template removal process decreases significantly the melamine concentration of the polymer. The XRD data reveals that MIP has a small FWHM value, while the SEM analysis shows that it has more cavities than the initial polymer - the latter has only 255 cavities, while MIP number amounts to 445. The greater number of cavities suggests that MIP has the potential to be used as a sensor membrane.

Acknowledgements

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