

Effect of template removal process with methanol solvent on cavities number of melamine molecularly imprinted polymer (MIPS)

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Abstract. A Melamine molecularly imprinted polymer has been successfully produced with cooling-heating method. A melamine as template was entered into methanol and aquabides solvent, then added methacrylic acid (MAA) as monomer, ethylene glycol dimethacrylate (EDMA) as cross-linker and benzoyl peroxide (BPO) as initiator. The pre-polymer solution was then stirred at 40°C temperature for 15 minutes. The solution was then entered into vials. The vials were then cooled in freezer at -5°C temperature for 1 hour. After cooling process, vials were heated in furnace at 75°C held for 3 hours, 80°C held for 3 hours and 85°C held for 1 hour. After vials were heated, the pre-polymerization solution has changed into solid polymer. The solid polymer was then ground to powder. The melamine template was then removed from polymer with methanol solvent. Polymer after template removal process called as MIP. Solid polymer and MIP was then characterized with FTIR and SEM. FTIR result showed that solid polymer has %transmittance is smaller than MIP at wavenumber amines group. FTIR result indicated that melamine level in MIP was decrease. SEM result showed that solid polymer has 247 cavities and MIP has 318 cavities. Cavities in MIP were formed because melamine in polymer has lost.

1. Introduction

Eating is basic human need. But not all substances in food are good for human. The substances contained in human body are very influential on health. On the last year 2008, melamine contained in powder caused some infant death in China [1]. Melamine was added into milk for make fake melamine. With fake protein, infant milk will appear to have high protein [2]. Excessive melamine level in the body can cause dangerous disease. In USA, Food and Drug Administration (FDA) explained that when melamine and cyanuric acid are absorbed in the bloodstream, they concentrate and interact in the urine-filled renal microturbules. The incident can cause kidney malfunction. For more serious cases, excess melamine levels in the body can cause bladder cancer [3].

In order to detect melamine contamination in food, a technology is needed to detect melamine in food. One of them is molecular imprinting technique. Molecular imprinting technique has several advantage among them easy preparation, high sensitivity, inexpensive and its potential application to a wide range of target molecules [4-9]. Previous researchers have been developed sensor technology called as molecularly imprinted polymer (MIPs). MIPs are polymer with cavities where the cavities have same physical and chemical properties with target [4-9]. The polymers are produced with cooling-heating process [5-6]. After the polymers are obtained, melamine in polymers is removed. The



melamine removal process can make the cavities in polymers. MIPs which have many cavities and little melamine contamination called as the optimal MIPs.

2. Material and Method

2.1. Material

The process of making polymer used aquabides and ethanol as solvent, methacrylic acid (MAA) as monomer, ethylene glycol dimethacrylate (EDMA) as cross-linker, Benzoyl Peroxide (BPO) as initiator and melamine as template. Template removal process use methanol as solvent, acetate acid and aquabides.

2.2. Method

Melamine as template was inserted into ethanol and aquabides solvents, then added methacrylic acid (MAA) as monomer, ethylene glycol dimethacrylate (EDMA) as cross-linker and benzoyl peroxide (BPO) as initiator. The polymer solution is then stirred at 40 °C for 15 minutes. The solution was then inserted into vials and vials were closed and inserted into the freezer for 1 hour. The cooling process aims to decrease oxygen level in the vials that can disturb polymerization process [4-6]. Then the vials were inserted into the furnace for 75 °C held for 3 hours then the temperature is raised to 80 °C for 3 hours then the temperature is raised to 85 °C for 1 hour to become a solid polymer. The solid polymer is then ground to a fine powder.

Polymer powder then washed with repeat washing. First step, polymer powder was soaked in 8,5 ml methanol solvent for 16 hours 3 times. Second step, polymer powder soaked again with methanol/acetate acid (10:1) for 1 hour 3 times. Third step, polymer powder soaked again with 3 ml methanol for 1 hour 3 times and fourth step, soaked again with methanol/aquabides (6,275 ml/12,5 ml) for 1 hour. last step, MIP was dried. The scheme for making MIP is shown by figure 1.

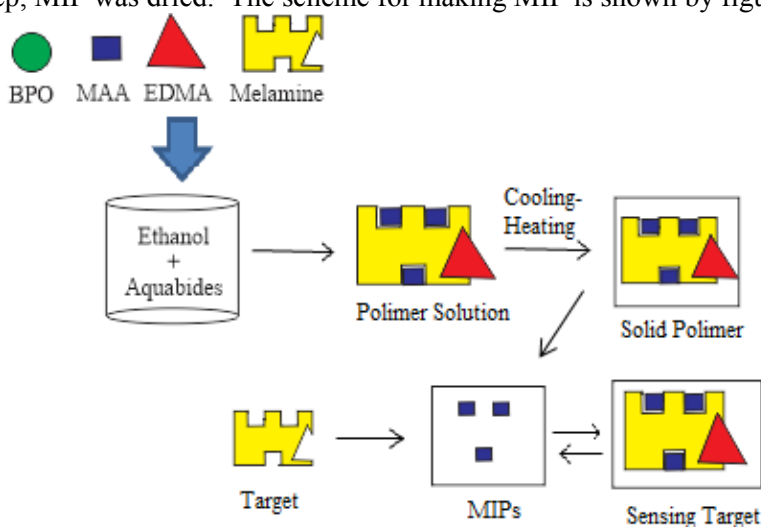


Figure 1. Scheme for making MIP

The schema shown mixture of melamine, MAA, EDMA, BPO and ethanol + aquabides solvent are obtain polymer solution. After cooling-heating process, polymer solution deformed be solid polymer. After template removal process, the polymer has cavities. Polymer with cavities called as MIP. When MIP detect target, target will re-bond with cavities.

3. Result and Discussion

3.1. Fourier Transform Infrared (FTIR)

FTIR work uses Interferometer Michelson Principle. FTIR is used to see functional groups in material [10]. FTIR characterized result MIP, solid polymer and NIP shown in figure 2.

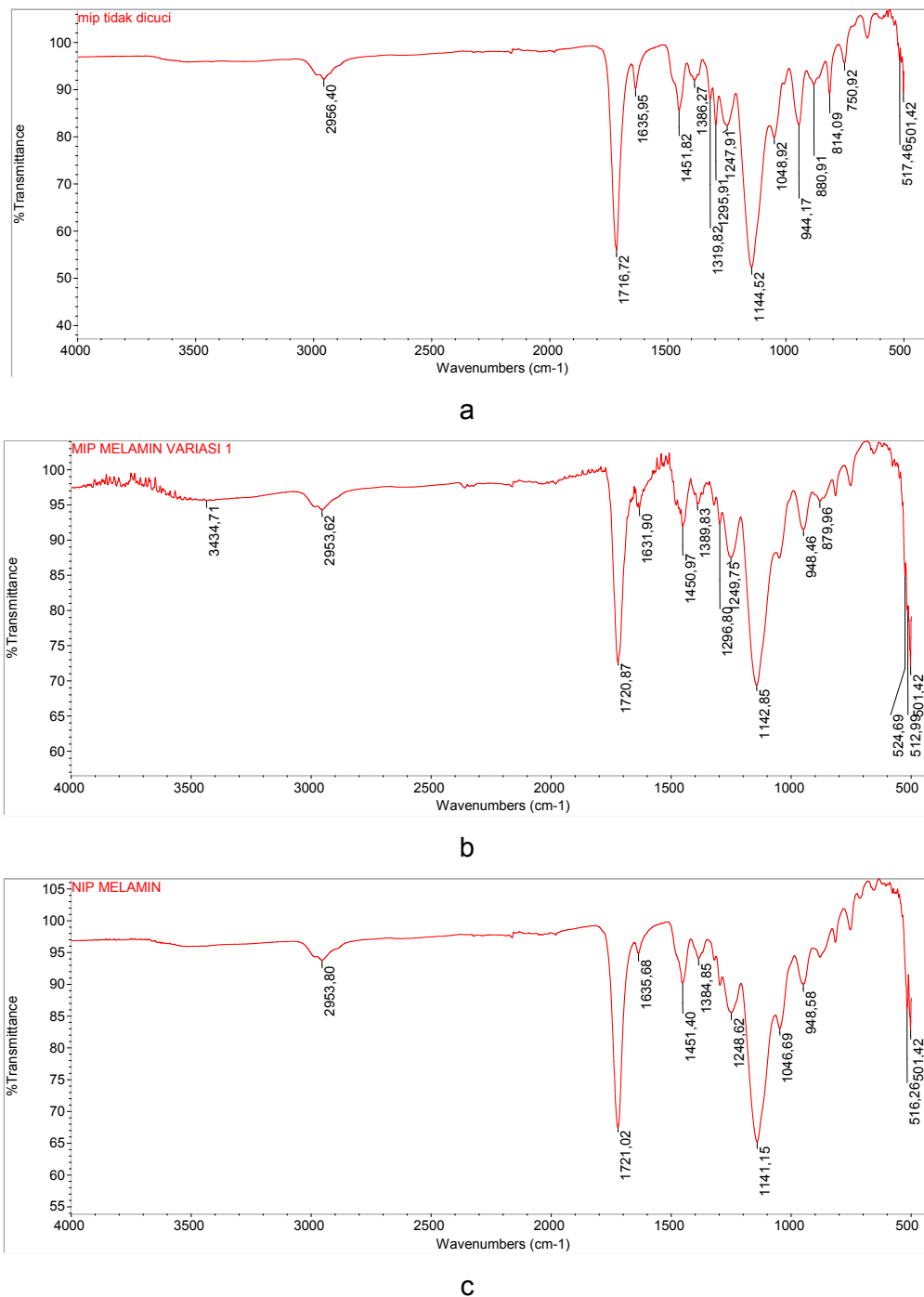


Figure 2. FTIR Result of (a). Polymer, (b). MIPs and (c). NIP

Figure 2.a and 2.b show % transmittance in amines group wavenumber for polymer are less than MIPs. This shows indicated melamine levels in MIPs are decrease. For NIP (Figure 2.c) %transmittance in amines groups are bigger than polymer. This happens because the process of making NIP does not uses melamine. %transmittance in amines group of polymer, MIPs and NIP is shown in Table 1.

Table 1. % Transmittance in amines group of polymer, MIPs and NIP

No	Wavenumber (cm ⁻¹) Range	Wavenumber Amines Group (cm ⁻¹)		
		Polymer	MIPs	NIP
1	1650-1630	90,11	94,44	94,80
2	1250-1247	82,43	87,52	85,55
3	1145-1142	52,31	69,33	65,18
4	1100-1000	79,92	-	-
5	900-870	91,05	95,59	-
6	820-810	89,26	-	-
7	751-750	96,59	-	-

% transmittance in polymer in range 1650-1630 cm⁻¹, 1250-1247 cm⁻¹ and 1145-1142 cm⁻¹ are 90,11 cm⁻¹, 82,43 cm⁻¹ and 52,31 cm⁻¹. For MIPs %transmittance in range 1650-1630 cm⁻¹, 1250-1247 cm⁻¹ and 1145-1142 cm⁻¹ are 94,44 cm⁻¹, 87,52 cm⁻¹ and 69,33 cm⁻¹. This is indicated melamine level in MIPs are decrease after template removal process. Moreover MIPs don't have peak in wavenumber range 1100-1000 cm⁻¹, 820-810 cm⁻¹ and 751-750 cm⁻¹ where wavenumber range 1100-1000 cm⁻¹, 820-810 cm⁻¹ and 751-750 cm⁻¹ belong to the amines group. On MIPs there are still exists peak in wavenumber 900-870 cm⁻¹, but on NIP does not exists. This is indicated melamine is still present in MIPs. It can be said the MIPs after template removal with methanol solvent is not optimal.

3.2. Scanning Electron Microscopy (SEM)

SEM aims to see morphological characteristics of the shape and surface structure of the MIP [11]. In this research SEM useful to find out the number of cavities in MIP. The result of SEM characterized shown in Figure 3 and Figure 4.

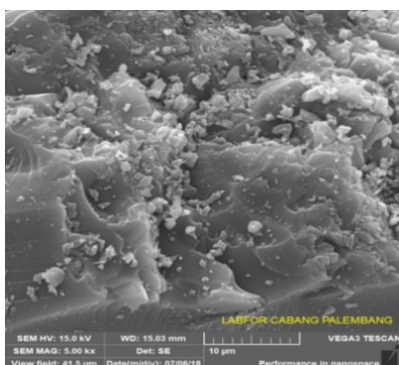


Figure 3. Result of SEM Characterized of Polymer

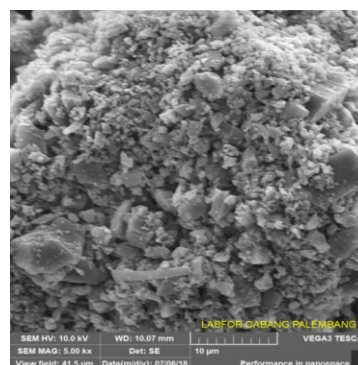


Figure 4. Result of SEM Characterized of MIP

In Figure 3 show number of cavities in polymer are less than cavities in MIP (Figure 4). The cavities in MIP appears because melamine in MIP has been lost. By using porediz program, the number of cavities in polymer and MIPs can be found. The number of cavities of polymer and MIPs shown in Figure 5.

From previous researched, size of melamine is 60 – 710 nm. MIP with repeat template removal process has 318 cavities that same with melamine size. SEM result show MIPs after template removal template have more cavities than polymer.

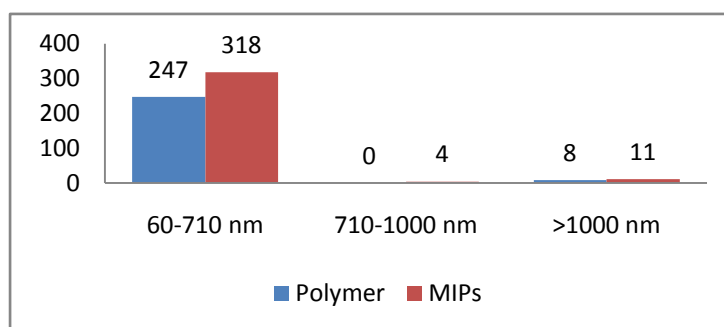


Figure 5. Cavities number distribution of Polymer and MIP.

4. Conclusion

With the cooling-heating method melamine polymer has been successfully made. After removal template process, polymer will have cavities from the loss of melamine. FTIR result show melamine level in MIPs are decrease, but not lost. This can be seen with still peaks on 900-870 nm. SEM result shows MIPs have 318 cavities more than polymers that have 247 cavities.

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