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Copoly Eugenol Crosslinked Dialylphthalate 8% as a Carrier in Phenol and Pb(II) Metal Transport

A A Kiswandono^{1,*}, S Hadi¹, Mudasir², F Sinjia¹, M Y Sari¹ and M Irfan¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lampung, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, North Sekip, Yogyakarta, Indonesia, 55281

Email: agung.abadi@fmipa.unila.ac.id

Abstract. Synthesis of polyeugenol derivatives, copoly-eugenol-dialylphthalate (co-EDAF) through polymerization process between eugenol and diene compounds, dialyl phthalate (DAF) with boron trifluoride diethyl ether ($\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$) as catalyst have been developed. Synthesized compounds were characterized using FT-IR, SEM, and TG-DTA. Furthermore, this compound was applied as a phenol transport carrier compound using the polymer inclusion membrane (PIM) method. The results showed that the co-EDAF compound has been successfully synthesized. The success parameters of the synthesis were indicated by the loss of the vinyl group ($-\text{CH} = \text{CH}_2$) in eugenol at wavenumber 995.27 cm^{-1} and loss of allyl group at a wavenumber of 1636 cm^{-1} . The results also showed that co-EDAF can function as a carrier compound for transporting phenols and Pb (II) metals. Pb (II) metal transport is smaller compared to phenol transport.

1. Introduction

The rapid development of the industrial sector can cause serious environmental problems, because industrial waste, including pollutants of organic compounds, will enter the environment. Phenol is an organic pollutant in waste and is harmful to the environment. This substance can be found in many waste, including chemical installations, hospitals, textile industries, dyes, oil refineries, and pharmaceuticals [1, 4, 11, 15]. Phenol concentrations in industrial waste range between 100-1000 mg/L, refining industrial processes of 6-500 mg/L and the production process of the petrochemical industry, 2.8-1220 mg/L [10, 14].

Several methods have been developed in order to overcome phenol waste, there are adsorption [10], ozonization technique [12], extraction [10], and lately is the liquid membrane method. Liquid membrane-based separation technology is currently attracting more attention from researchers because this technology has a wide application, selective and simple. These advantage is due to the fact that separation with membranes does not require additional chemicals and also the energy requirements are very minimum, simple, practical and easy to apply, so it is making this method as a promising future technology.

Several studies using liquid membrane methods have been developed by several researchers to handle various pollutants, including mercury metal separation [2], strontium separation from



radioactive waste [13], permeation of gas [13], CO₂/N₂ separation [3], arabinitol and perseitol transport [5], cesium transport [6], and phenol transport [7, 8, 16]. Separation using liquid membrane method, one of which is polymer inclusion membrane (PIM) always involves a carrier compound. Some polymers have been used as carrier compounds in the PIM method. One of the carrier compounds based on natural material compounds that can be used is a compound produced from eugenol polymerization. In general, polyeugenols and their derivatives can be produced through direct synthesis using catalysts, boron trifluoro diethyl ether [8], but the synthesized polymer has not been effective, because it has the ability to interact with low target compounds. This is because the polymer produced by this synthesis has a low molecular weight, so the active side is limited. One alternative to increase the active side is by copolymerization using diene compounds, such as diallyl phthalate (DAF). Polymerization by involving diene compounds is carried out with the aim to obtain crosslinked structures in final result [8]. This synthesis polymer is expected to have a large molecular weight, so that it will have more active sides (-OH groups and benzene rings). Increasing the active side of the synthesized polymer is expected to increase transport speed so that the transport process is faster and more efficient. Therefore, this research was synthesized polieugenol derivatives by polymerization technique between eugenol and diallyl phthalate. The amount of diallyl phthalate needed is 8% of the amount of eugenol used. Furthermore, the synthesized compound will be tested for its ability as a carrier compound for phenol and Pb (II) metal separation.

2. Material and Methods

2.1. Materials

Diallyl phthalate, diethyl ether (C₂H₅OC₂H₅), tetrahydrofuran (THF), dibenzyl ether (DBE), polyvinylchloride (PVC), 4-aminoantipirin, K₄Fe(CN)₆, and phosphate buffer were purchased from Merck. Boron trifluoride diethyl ether [BF₃.O(C₂H₅)₂] was purchased from SIGMA Aldrich. Other reagents, including sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (CH₃OH), phenol (C₆H₅OH), chloroform, methanol, diethyl ether NH₄OH, Na₂SO₄ anhydrous, K₂HPO₄, KH₂PO₄, eugenol and demineralized water were purchased from Bratachem.

2.2. Instrumentation

The transport equipment (PIM cell) consists of two cylindrical shaped chambers separated by a membrane. The volume of each chamber is 50 mL and the effective diameter that is directly in contact with the phenol solution is 2.5 cm, this area is the center of the transport process. Other tools used are pH meter, analytical balance (Mettler Toledo AB54-S), UV-Vis spectrophotometer (772 Spectrophotometer), SEM Hitachi SU8000, Shimadzu infrared spectrophotometer Prestige-21 IR model with KBr magnetic pellet holder 0016-008.

2.3. Procedure

2.3.1. Polymerization between Eugenol and diallyl phthalate (co-EDAF)

Polymerization conditions are developed [8]. Eugenol 5.8 g was added into a round flask. Then added diallyl phthalate as much as 8% of the weight of eugenol used. Then in a round flask 1.0 mL BF₃O(C₂H₅)₂ were added as catalyst. The polymerization reaction was carried out for up to 24 hours and was stopped by adding 1.0 mL of methanol. The polymerization results, namely red gel dissolved in diethyl ether and washed several times with aquabidest to neutral. After the solvent is evaporated with a rotary evaporator flask at 40 °C. and the residue is stored in a desiccator. The polymer compounds formed were weighed to determine the yield, then characterized using SEM, FTIR and TG-DTA.

2.3.2. Synthesis of Polymer Inclusion Membrane (PIM) and Transport Capability Test

Standard conditions in membrane printing were developed [8]. The PIM membrane is made in a mold using tetrahydrofuran (THF) as a solvent. Then the membrane was tested for its ability to process phenol transport and Pb (II) metal.

The transport process is done using a pair of chambers. The source phase contains 50 mL of phenol solution and Pb (II) metal with a concentration of 60 ppm while the receiving phase contains 50 mL of 0.25 M NaOH. The transport process is then carried out at room temperature for 12 hours. Phenol concentrations in both, namely the source phase and receiving phase were analyzed using the 4-aminoantipirin method [10, 11].

The absorbance was measured using a UV-vis spectrometer at a wavelength of 450 nm. While the Pb (II) metal concentration was analyzed using MP-AES. Characterization of PIM membrane before and after transport was analyzed using Shimadzu infrared spectrophotometer model Prestige-21 with magnetic KBr pellet holders 0016-008 and SEM Hitachi SU8000.

3. Result and Discussion

3.1. Synthesis of 8% co-EDAF

The synthesis results of the carrier compound, copoly eugenol-Diallyl Phthalate (co-EDAF) 8%, were obtained solid orange powder (figure 1). The powder produced from this synthesis dissolves in chloroform, diethyl ether and Tetrahydrofuran (THF). 8% co-EDAF compounds are then used in the process of making membrane Polymer Inclusion Membrane (PIM).



Figure 1. co-EDAF 8% powder

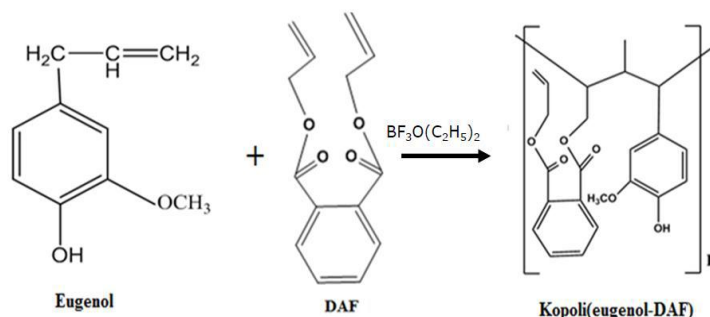


Figure 2. Reaction of co-EDAF synthesis [9]

The synthesis process involving vinyl groups occurs through a cationic addition reaction. This reaction takes place in three stages, namely the stage of initiation, propagation, and termination. The initiation stage is the stage where carbocation formation occurs from these two compounds. $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ is a salt formed from Lewis acids and bases. BF_3 is a Lewis acid, which is an electron acceptor, while $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$ is a Lewis base, which is a compound that gives donors an electron pair. The propagation stage occurs when the carbocation ion will bind to eugenol to form a co-EDAF. The formation of this copolymer will occur continuously. Finally, the termination stage is done by adding methanol which serves to stop the growth of the polymer chain. Prediction of co-EDAF compounds as shown in figure 2.

Synthesis of 8% copoly of Eugenol-Diallyl Phthalate (co-EDAF) is a carrier compound that has an active group of -OH, so characterization using Fourier-Transform Infrared Spectroscopy (FT-IR) needs to be done to determine the success of the synthesis. In figure 3 shows the FT-IR spectra of co-EDAF compounds.

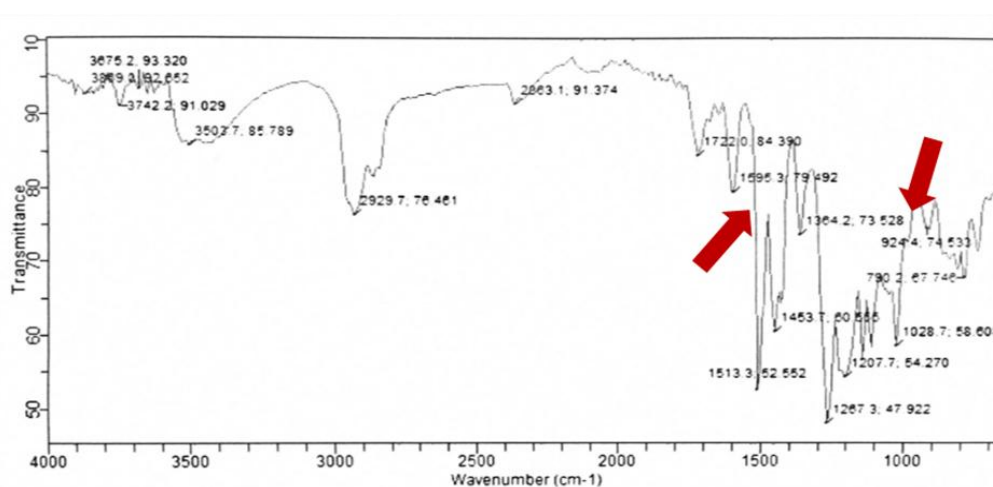


Figure 3. FT-IR spectrum of 8% co-EDAF

Adsorption at 1722 cm^{-1} is a typical absorption of $\text{C}=\text{O}$ belonging to co-EDAF, besides that the adsorption wavenumber at 2929.7 cm^{-1} in the synthesized polymer formed shows the presence of CH sp^3 . The presence of the $-\text{OH}$ group is shown in the uptake of 3503.7 cm^{-1} and the $\text{C}=\text{C}$ aromatic group in benzene is shown in the uptake of 1595.3 cm^{-1} . From the FT-IR spectra (figure 3), shows that no appearance of vinyl groups ($-\text{CH}=\text{CH}_2$) at wavenumber of 995.27 cm^{-1} and allyl groups at a wavenumber of 1636 cm^{-1} , this is a success parameters in this synthesis [8]. Besides that the loss of uptake in the area of $1000 - 650\text{ cm}^{-1}$, also shows that there has been an addition reaction to the double bond in eugenol. Strong absorption at several wavenumbers above shows that copolymerization has been successful [8].

The 8% co-EDAF powder is then characterized by Scanning Electron Microscope (SEM) to find out information related to the surface morphology of the material being tested. figure 4 shows the dominant surface morphology in the form of solid rounded lumps, besides it is seen that polymer powder has almost the same and uniform morphology.

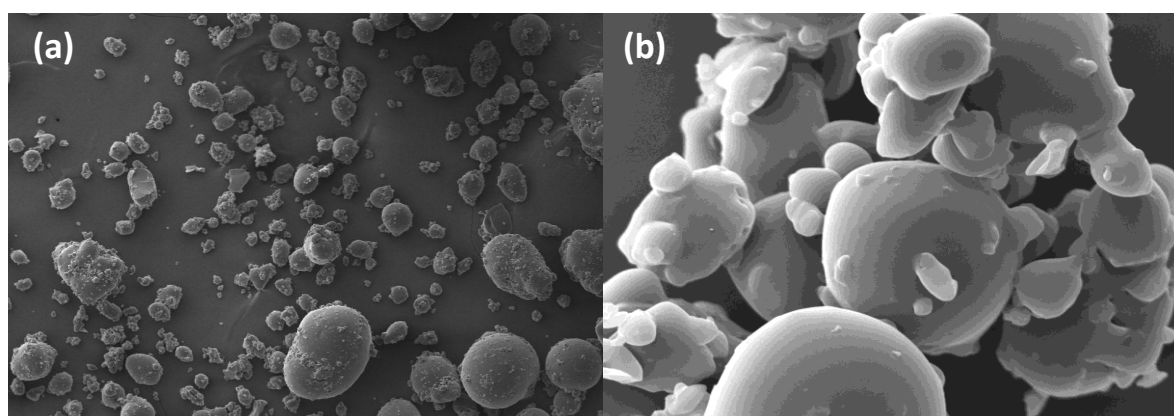


Figure 4. Morphology of co-EDAF powder 8% based on SEM results (a) 100x (b) 500x

The next characterization was an analysis using Thermogravimetry-Differential Thermal Analysis (TG-DTA). This TG-DTA analysis are used for determining the temperature and occurrence of decomposition reactions which cause changes in sample weight and determine changes in mass and physical properties of co-EDAF polymers.

The 8% co-EDAF compound used was 7.940 mg and heated at a constant rate, i.e. at a heating speed of $10^\circ\text{C}/\text{min}$, with a temperature interval between $30\text{--}900^\circ\text{C}$. The TGA curve in figure 5 shows

the changes and weight loss that occurred at 37.2 - 546°C, whereas in DTA it was seen as an endothermic and exothermic process curve. The sample underwent undershooting at a temperature of 50-100°C, which is a condition where the sample does not experience a weight loss or constant weight at a certain time interval until the sample begins to decompose continuously.

Figure 5 shows that at temperatures 150°C there are 1.62% weight loss of the sample. This weight change is thought to be related to sample dehydration, which is the release of water (evaporation) contained in the sample. This is due to the presence of hydroxyl groups contained in co-EDAF as the active side of the compound. Subsequent weight changes were detected at 337°C as much as 20.36%, but almost did not have a trace equivalent to the TGA. The weight loss process in this step is thought to be due to the breaking of bonds or loss of CO and OCH₃ contained in the polymer. Therefore, temperatures high enough with long enough temperature intervals are needed to break bonds and methoxyl groups. Other weight changes were detected on the DTA curve with one small peak at a temperature interval of 337-433°C having a trace equivalent to TGA as an endothermic process. The process of weight loss in this step occurs at higher temperatures with quite long intervals as well. The reason is the termination and decomposition of benzene bonds and the depolymerization of benzene rings, so that the temperature and time required to complete this process is quite long. Then heat (exothermic) release occurs which indicates the preparation of compounds in the sample. When viewed from the sample decomposition in TG-DTA, it can be said that the 8% co-EDAF compound has a fairly high temperature resistance when applied in the environment.

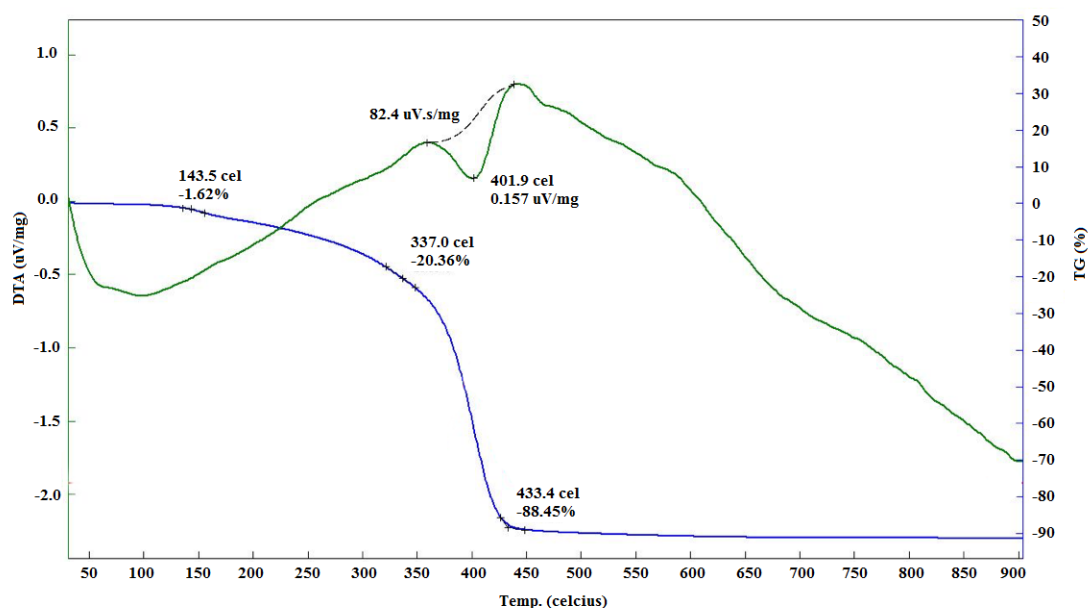


Figure 5. TG and DTA curves for co-EDAF 8%

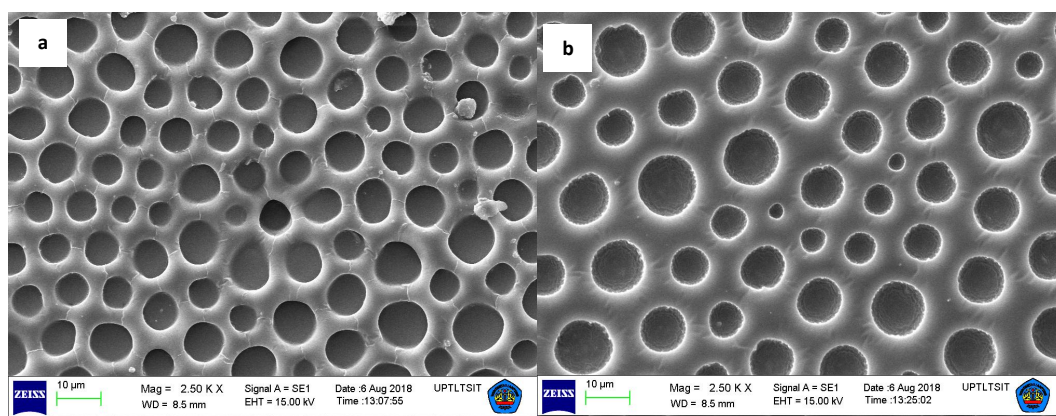
3.2 Transport test of co-EDAF 8% membrane for phenol and Pb (II)

Transport test using PIM membrane was carried out in order to determine the ability of 8% co-EDAF carrier compound in separating phenol and Pb (II). The PIM membrane contains 8% co-EDAF as a carrier compound, PVC as a supporting compound and DBE as a plasticizer. Testing of PIM membrane for phenol transport is carried out with repeated use up to three times. The membrane used is the same membrane, but the phenol solution used is a new phenol solution. As seen in table 1, that membranes containing co-EDAF can translate phenols more than Pb (II) metal

Table 1. PIM transport membrane test for phenols and Pb (II) metals

Substances	Transport capability (12 hours)		
	1st	2nd	3rd
Phenol	15.8%	14.7%	13.06%
	Transport capability		
	3 hours	12 hours	
Pb(II)	0.172 %	0.160 %	

The PIM membrane containing 8% co-EDAF as a carrier compound is capable of transporting phenol up to 15.8%. Although used repeatedly, the PIM membrane can still transport phenols. In addition, that PIM membrane can also be used for Pb (II) metal transport, although the transport capability is smaller compared to phenol transport capability. This is due to the 8% co-EDAF compound containing the active side of hydroxyl which can play an optimal role in transporting phenols through the interaction of hydrogen bonds. Table 1 also shows that the OH group at 3rd use has decreased transport capacity. The -OH group as the active side of the membrane responsible for phenol transport is indicated that, the cluster has decreased so that the transport capability also experiences a decrease. Percentage of membrane components lost in each transport decreased with increasing number of repeated use of membranes. Decrease in the percentage of membrane that is lost in the second and third use times is possible because the use of the first membrane has lost many membrane components so that the second and third use times are lost a little. The loss of membrane components in phenol transport is also supported by SEM results (figure 7). The membrane surface after the transport process in figure 6 shows clearly the presence of open membrane pores and closed pores. The presence of open membrane pores indicates the presence of membrane components that are lost (dissolved).

**Figure 6.** SEM results on membrane a) before and b) after transport

4. Conclusion

Separation with membranes does not require additional chemicals and also the energy requirements are very minimum, simple, practical and easy to apply, so it is making this method as a promising future technology. By developing the Polymer Inclusion Membrane (PIM) method using co-EDAF carrier compounds, it is expected to be used as a solution for phenol waste. This research was carried out by crosslinking the eugenol-diallyl Phthalate compound. Based on the results of FT-IR and TG-DTA, the co-EDAF compound has been successfully synthesized by polymerization techniques. PIM membranes containing co-EDAF as a carrier are able to transport phenols and Pb (II) metals. The ability of phenol transport in the first, second and third repetitions is respectively 15.8%; 14.7%; and 13.06%. While the ability of Pb (II) metal transport is 0.172% (3 hours) and 0.160% (12 hours).

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