Synthesis and characterization of membrane from high molecular weight polyeugenol

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Abstract. High molecular weight polyeugenol was synthesized by cationic polymerization, using the \( \text{H}_2\text{SO}_4 - \text{CH}_3\text{COOH} \) catalyst, and further characterized. Furthermore, the polymers were determined to be heterotactic using \(^1\text{H}\) measurement, while the membrane produced from a combination of PVC / DOP (32:38) and DOP was liquid, with polyeugenol alone generating solid. The result of Scanning Electron Microscopy (SEM) analysis indicates a pore size of 42.3 - 127 μm in polyeugenol membrane and the potential for application in the filtration of yeast cells, bacteria, and oil emulsions.

1. Introduction
Eugenol (4-allyl-2-methoxyphenol) comprises approximately 80–90% of the clove oil weight and is primarily grown and produced in Indonesia. The compound generally has a molecular formula of \( \text{C}_{10}\text{H}_{12}\text{O}_2 \) containing allyl (\(-\text{CH}_2\text{-CH}=\text{CH}_2\)), phenol (\(-\text{OH}\)), and methoxy (\(-\text{OCH}_3\)), instigating the possibility for application as a raw material in the synthesis of more valuable compounds [1–4]. The synthesized high molecular weight polyeugenol possesses strong antibacterial and antioxidant activity [5]. Current developments in polymers with similar characteristics prompt the need to search for intrinsic functions, including tacticity and ensure appropriate membrane characterization. Kiswandono et al. [6] previously studied the membranes of low molecular weight polyeugenol, created by mixing carrier compounds, plasticizers, and supporting polymers in a solution, followed by printing in molds to form a thin, stable, and flexible film. The resulting product is known as Polymer Inclusion Membrane (PIM) [6], potentially used as a carrier compound [7]. Another study shows the application in liquid membranes, in combination with plasticizers, and supported by plastic polymer (polyvinyl chloride, PVC) [8]. Furthermore, the carrier compound being a facilitator in the membrane phase, plays an important role as a determining factor in the separation performance. The target compound is transported via a diffusion process in the boundary layer, involving absorption, transition, desorption, and re-diffusion of the target compound at the source, source-membrane interface, membrane, membrane-receiving interface, and receiving phases, respectively [7].

The rapid development in the last few decades has yielded several technical and economic advantages, hence applying the separation and purification of substances in a research laboratory and industrial scale. Also, there have been numerous benefits in the form of minimal energy requirement, simplicity, practicality, and ease of application without the need for additional chemicals. The material to be separated, ligands in organic solvents, and bases as the release agents are contained in the donor, membrane, and acceptor phases of the liquid membrane transport system. Besides, the applied ligand
requirements include high molecular weight, lipophilic characteristics and a structure enabling complex formation. A study by Febriasari et al. [9] used poly(eugenol), polyvinylchloride (PVC), and dibenzyl ether (DBE) as carrier, base polymer, and plasticizer, correspondingly. This present research uses high molecular weight poly(eugenol) to produce membranes, followed by the determination of morphological features and the subsequent application of dioctyl phthalate (DOP) as a plasticizer.

This study aims to determine the tacticity and type of membrane produced from poly(eugenol)/PVC DOP, poly(eugenol)/DOP, and high molecular weight poly(eugenol). Furthermore, the morphological structure of the material was evaluated, resulting in beneficial information.

2. Experimental

2.1 Material and Methods

The materials used include eugenol (99.99% purity, obtained from Happy Green Co.), concentrated sulfuric acid, glacial acetic acid, diethyl ether, n-hexane, anhydrous sodium sulfate solids, distilled water, polyvinylchloride (PVC), dioctyl phthalate (DOP), tetrahydrofuran solvent (THF) (technical grade). In addition, poly(eugenol) with high molecular weight was prepared by polymerizing eugenol with \( \text{H}_2\text{SO}_4-\text{CH}_3\text{COOH} \) [5].

2.2 General procedure

2.2.1 Manufacture of membranes from Poly(eugenol) [9] Two variations of Membrane Inclusion Polymers (PIM) were formulated. The first involved mixing poly(eugenol), polyvinylchloride (PVC), and dioctyl phthalate (DOP) as carrier compound, base polymer, and plasticizer, respectively, at a quantity ratio at 10: 32: 58. These were incorporated into ± 15 mL tetrahydrofuran (THF) solvent, with a total PIM mass of 3.5 grams. Meanwhile, the second was created by mixing poly(eugenol) with DOP at a quantity ratio of 70:30 into ± 15 mL diethyl ether solvent, with a total PIM mass of 3.5 grams. Furthermore, the mixture is homogenized with the stirrer for 30 minutes, and the PIM is then molded using a petri dish before drying for 72 hours. For membrane poly(eugenol), 3.5 grams of poly(eugenol) was dissolved with ± 15 mL THF and then put into a petri dish and allowed to dry for 72 hours.

2.2.2 Structure of Surface Morphology of Poly(eugenol) Scanning Electron Microscope (SEM) is used to analyze the surface morphological characteristics of poly(eugenol) by evaluating 5 x 5 mm cut samples with HITACHI FLEXSEM 1000. The energy conditions were adjusted following the physical and thermal resistance of polieugenol, to obtain a complete photo.

2.3 Detection Method

The tools used include analytical balance, magnetic stirrer, glassware, 500 mL separating funnel, 9 cm diameter petri dish, universal pH paper, and Scanning Electron Microscopes (SEM) JEOL JSM-5610 microscope (7kV voltage). The \(^1\)H NMR spectra were recorded in chloroform-d (CDCl3) on a JEOL EX-400 spectrometer.

3. Results and Discussion

3.1 Tacticity of poly(eugenol)

The chiral C atom, with a crystal-like shape and bound to the main structure, shows the tacticity of poly(eugenol). This polymer property is the chiral centre's relative stereochemistry adjacent to the main structure, determined by the \(^1\)H NMR spectral peaks distribution. The data collected is essential because of the close relationship with crystallinity, strength, elongation, modulus, toughness, melting point, solubility, and other physical polymer properties [10]. Figure 1 shows the \(^1\)H NMR analysis of poly(eugenol) structure.
Figure 1. Structure of Polyeugenol with High Molecular Weight

Figure 2. $^1$H NMR of Polyeugenol with High Molecular Weight

Figure 2 shows the $^1$H NMR of results on polyeugenol synthesis. The tacticity obtained is heterotactic, a combination of isotactic and syndiotactic, indicated by the CH$_2$ spectrum peaks, shorter with isotactic. Previous research also indicates a similarity between the $^1$H NMR spectrum of high molecular weight polyeugenol and polypropylene heterotactic.

3.2 Fabrication membranes from Polyeugenol

Several researchers have attempted membrane fabrication [11-20], but this is the first study conducted with high molecular weight polyeugenol, and PIM (Membrane Inclusion Polymers) (PIM) was formulated using two varied techniques. The first involves mixing the polyeugenol, polyvinylchloride (PVC) and dioctyl phthalate (DOP) with a THF solvent, followed by homogenization with a stirrer for 24 hours. It is then closed with aluminum foil to ensure complete dissolution and prevent THF evaporation and produce good quality yield. The product is subsequently printed on a 9 cm diameter petri dish and reserved for 72 hours (3 days) to ensure complete evaporation of THF, thus generating a light brown liquid membrane. A study by Febriasari et al. [9] involved the combination of low BM polieugenol with polyvinylchloride (PVC) as a base polymer, and dibenzyl ether (DBE) as a plasticizer, yielding a porous solid membrane. However, the liquid membrane characteristics obtained in this current research was due to the different types and molecular weights of PVC, plasticizers, and polyeugenol used. The second variation was a mixture of polyeugenol and dioctyl phthalate (DOP) plasticizer with diethyl ether solvent. These materials were homogenized for 30 minutes and covered with aluminum foil to prevent the solvent from losing steam. Therefore, they were printed on a 9 cm diameter petri dish and reserved for 72 hours (3 days), to ensure complete evaporation, yielding a light brown liquid membrane. Table 1 shows the overall results obtained.
Table 1. The Result of Fabrication Membrane from Polyeugenol

| No | Composition           | Type of membrane |
|----|-----------------------|------------------|
| 1  | Polyeugenol/PVC/DOP (10:32:58) | Liquid Membrane  |
| 2  | Polyeugenol           | Solid Membrane    |
| 3  | Polyeugenol/DOP (70:30) | Liquid Membrane  |

Figure 3. Surface morphology of polyeugenol membrane measured by SEM

Figure 4. Pore size membrane polyeugenol membrane measured by SEM
3.3 Morphological Surface Structure

Figure 3 shows 100, 300, 500 and 1000 times magnification of polyeugenol, used to determine the surface morphology. Figure 4 indicates the pore size of 42.3 - 127 μm or 0.042 - 0.127 nm within the microfiltration membrane, where the usual range is 10-100 microns. Also, the compound possesses numerous advantages, including the ability to filter yeast and bacteria cells, as well as oil emulsions. For example, liquid membranes comprising polyeugenol as the carrier compounds can filter water polluted with chemicals, e.g., phenols, which transit based on the principle of like dissolves like [7].

4. Conclusions

Based on the results and discussion, tacticity of high molecular weight polyeugenol was determined to be heterotactic. The membrane-type obtained from a mixture of polyeugenol/PVC/DOP, polyeugenol/DOP, and high molecular weight polyeugenol were liquid, liquid, and porous solid, respectively. The morphological structure evaluation showed a pore size of 42.3 - 127 μm for polyeugenol with high molecular weight.

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