تركيب متشابكة جديدة من بولي ثنائي الفينول أيثر ديجليسيدل (بولي BADGE) كحامل في نقل الفينول

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الملخص

يوضح البحث أنه تم تركيب توليفة جديدة من بولي ثنائي الفينول أيثر ديجليسيدل (Poly-BADGE) عن طريق تفاعل بولي أيوجينول وثنائي فينول أثير ديجليسيدل في الدايوكسين تحت ظروف قلوية. تم تمييز المُنتج باستخدام تحويل الأشعة تحت الحمراء (FTIR) وتحليل العناصر. أظهر تحليل FTIR لبولي BADGE فقدان مجموعة الفينيل النموذجية للايوجينول (v 995 cm^{-1}). يشير البحث إلى اختبار المُنتج لبيان قدرته كمركب حامل لنقل الفينول باستخدام طريقة غشاء تضمين البوليمر (PIM). تم تقييم ثبات غشاء PIM تجاه NaOH باستخدام FTIR والمسح المجهري الالكتروني (SEM). أظهرت الدراسة أن الأغشية المتضمنة بولي BADGE تتسم بالثبات والقدرة الكبيرة على نقل الفينول، ولذا يمكن استخدامها كناقلات فينول فعالة.

Synthesis of a new crosslinked Poly-Bisphenol A Diglycidyl Ether (Poly-BADGE) as a carrier in Phenol transport

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Abstract

A new crosslinked poly-bisphenol A diglycidyl ether (poly-BADGE) has been synthesized by the reaction of polyeugenol and bisphenol A diglycidyl ether in dioxane under alkaline conditions. The product was characterized using fourier-transform infrared spectroscopy (FTIR) and elemental analysis. FTIR analysis of poly-BADGE showed the loss of the typical vinyl group of eugenol (v 995 cm^{-1}). The product was then tested for its capability as a carrier compound in phenol transport, using the polymer inclusion membrane (PIM) method. The stability of the PIM membrane towards NaOH was evaluated using FTIR and scanning electron microscopy (SEM). The study shows that membranes containing poly-BADGE have great ability and stability to transport phenol; therefore, they may be used as efficient phenol carriers.

Keywords: Phenol transport; PIM; poly-BADGE; polyeugenol.

1. Introduction

Phenols are among the most common forms of chemical pollutants in wastewater and their discharge to aqueous systems may produce an unpleasant smell and can be detrimental to human health. Phenols and their derivatives are often present in aqueous effluents from various manufacturing processes, including the products of dyes, paints, synthetic resins and pharmaceuticals. While there are many methods available for the removal of organic compounds including phenols from industrial wastewater, liquid membrane processes have been regarded as one of the most effective methods (Benosmane *et al.* 2018; Gherasim *et al.* 2011). Commonly used liquid membranes to separate phenols include bulk liquid membranes (Djunaidi *et al.* 2018), emulsion liquid membranes (Rosly *et al.* 2018), supported liquid membranes (Bhatluri *et al.* 2015; Shimoyama & Neha, 2014) and polymer inclusion membranes (PIM) (Kiswandono *et al.* 2013; O'Bryan *et al.* 2017). Compared to other waste-water treatment methods, i.e. those that are based on adsorption and coagulation, membrane-based techniques are more effective and can be used continuously, which saves time and energy (Sun *et al.* 2017; Thilagavathi *et al.* 2015).

Transporting a target compound using a liquid membrane method usually requires supplementary materials and plasticizers. The PIM system contains a polymer and a chemical carrier, which is intended to extract or transport chemical species (ions or molecules) from aqueous solutions. Carriers used in PIM are generally complexes of ion exchangers, which can interact with chemicals in aqueous solutions and transport them across PIM. On the other hand, plasticizers are used to improve membrane properties (Benosmane *et al.* 2018; Kiswandono *et al.* 2012)**.** Previously, we have used a PIM method employing a copoly-eugenol-divinyl benzene (co-EDVB) carrier for phenol transport and found that concentration of phenol decreased with increasing percentage of the amount DVB (Kiswandono *et al.* 2012).

To transport phenol optimally, carrier compounds used in the PIM methods should have appropriate functionalities (active sites). Hydroxy groups, which can form hydrogen bonding, may assist a phenol transport process, whereas benzene rings may assist phenol transport through π-π interactions (Kiswandono *et al.* 2012)**.** In addition, the capacity of a carrier compound may be improved by polymerization, as the products would have higher molecular weights and contain more active sites than the original compound (Kiswandono *et al.* 2012; 2019). The number and the efficiency of the active sites in a carrier compound are determined by the type and the amount of crosslinking agents added to the reaction. Therefore, modifications of the synthesis procedures may increase the

molecular weight and the active sites of a carrier compound, thus improving the quality of the compound.

Bisphenol A diglycidyl ether **(BADGE)** is an epoxide-containing compound that is soluble in water and can be used as the starting material for producing polymers with an extended number of active sites (Oshita *et al.* 2007). Here, we report the synthesis of poly-BADGE, using BADGE and polyeugenol as a copolymer, and the evaluation of the effectiveness of poly-BADGE as a carrier in phenol transport. The synthetic product was tested in a system with PIM-based PVC (polyvinyl chloride) as a basic polymer and DBE (dibenzyl ether) as a plasticizer.

2. Experimental

2.1. Materials

Most of the chemicals, such as eugenol, bisfenol A diglycid ether, diethyl ether ($C_2H_5OC_2H_5$), phenol (C_6H_5OH), 4-aminoantipyrin, $K_4Fe(CN)_6$, tetrahydrofuran (THF), dibenzyl ether (DBE), polyvinylchloride (PVC), and phosphate buffer, were purchased from Merck. Boron triflouride dietyl ether [$BF_3.O(C_2H_5)_2$] was purchased from Sigma-Aldrich. Other reagents, including sodium hydroxide (NaOH), chloric acid (HCl), methanol (CH_3OH), chloroform, NH_4OH, Na_2SO_4 anhydrate, K_2HPO_4, KH_2PO_4, and demineralized water, were purchased from Bratachem (Indonesia).

2.2. Instrumentation

The instruments used in this study were a pH meter, analytical balance (Mettler Toledo AB54-S), UV-Vis spectrophotometer (772 Spectrophotometer), SEM Hitachi SU8000, and a Shimadzu infrared spectrophotometer

Prestige-21 IR model with a KBr magnetic pellet holder 0016-008. 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.

2.3. Synthesis of polyeugenol

Eugenol (5.8 g) was transferred into two three-necked flasks, then $BF_3O(C_2H_5)_2$ (1.0 mL) was added as a catalyst (Kiswandono *et al.* 2012). The mixture was stirred overnight and the reaction was quenched by adding MeOH (1.0 mL). The red gel formed was dissolved in Et_2O and then washed with ddH_2O to a neutral pH. The organic layer was dried with anhydrous Na_2SO_4 and decanted. The solvent was evaporated in a rotary evaporator at 40 °C and the product was then characterized using FTIR (Tables 1 and 2).

2.4. Synthesis of poly-BADGE

Polyeugenol (3.28 g, 0.02 mol) was mixed with BADGE (1.7 g, 0.005 mol) in dioxane (29 mL) and NaOH solution (1 M, 40 mL). The mixture was refluxed at 60 - 70 °C for six h. The solid product was washed with ethanol and ddH_2O to neutral pH, filtered using Whatman filter paper #42, then the solid was dried in an oven at 40 °C. The product (see Table 1) was smoothed and sieved (250 mesh) and then characterized by the FTIR (see Table 2), the proposed chemical structure is in Figure 1. Polyeugenol was prepared from eugenol by treating the compound with Lewis acid, $BF_3O(C_2H_5)_2$, overnight to give a red brown material (Kiswandono *et al.* 2012).

a
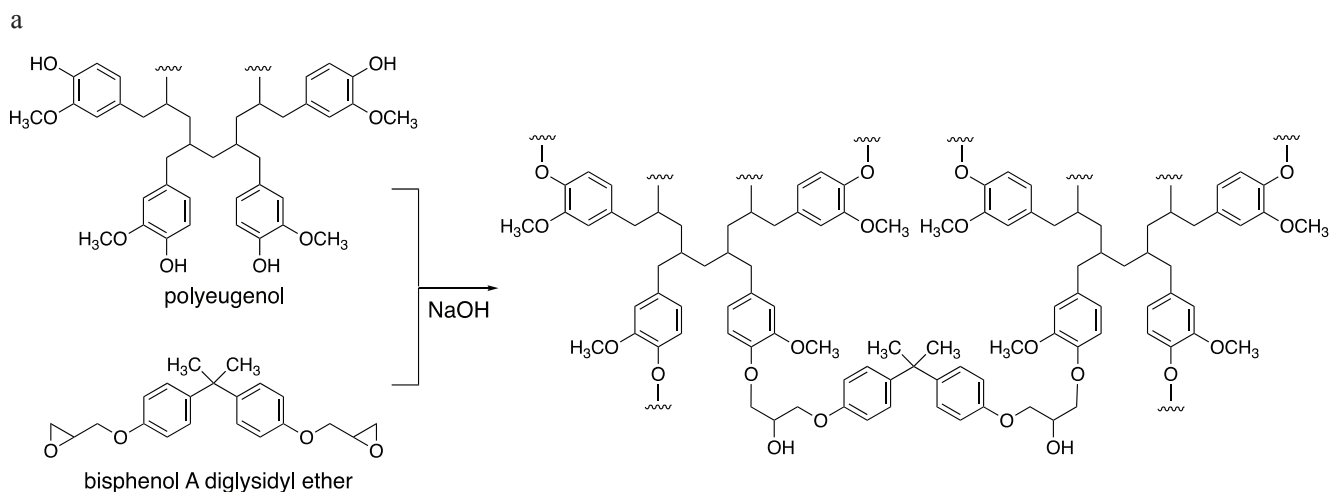
**Fig. 1.** Synthesis of poly-BADGE and its proposed chemical structure

Poly-BADGE was synthesized by refluxing polyeugenols and BADGE in dioxane under an alkaline condition (Pitchai *et al.* 2014). The crosslinking reaction was carried our under alkaline conditions to facilitate the bimolecular (SN_2) nucleophilic substitution reaction. Crosslinking between the hydroxy groups of polyeugenol and the epoxide of BADGE resulted in the formation of ether bonds.

2.5. Preparation of PIM membranes and evaluation of their ability to transport carrier compounds

The preparation of PIM membranes was carried out according to the procedure described in the previous paper (Kiswandono *et al.* 2012). Briefly, the PIM membrane was printed/prepared in a mold with the ratio of poly-BADGE (as a carrier compound), PVC (as a basic polymer), and DBE (as a plasticizer) 10:32:58. Tetrahydrofuran (THF) (10 mL) was used to homogenize the mixture in the mold. The mold was kept for three days to let the solvent evaporate naturally.

The source phase contains a phenol solution (50 mL, 60 ppm) and the receiving phase contains a NaOH solution (50 mL, 0.25 M). The rate of transport was measured under various conditions, such as variations of pHs of the source phase, NaOH concentration in the receiving phase, membrane thickness and transport time. The experiment was repeated several times using the same PIM membrane, but each time the source phase and the receiving phase were replaced with fresh phenol and NaOH solutions, respectively. Phenol concentrations in both phases were analyzed using the 4-aminoantipyrine colorimetric method (Benosmane *et al.*2018).
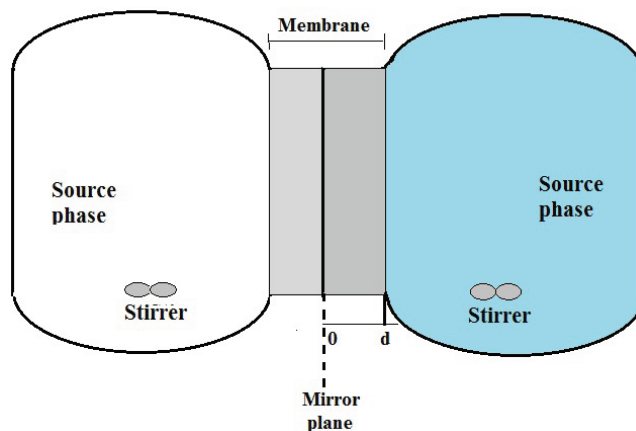
Fig. 2. Schematic diagram of the membrane extraction system used in this study (d: half of the thickness of the membrane) (Nghiem *et al.* 2006)

3. Results and discussion

3.1. Properties of Poly-BADGE

Poly-BADGE was obtained as a white, brown-green, or grey powder, depending on the molar ratios of polyeugenol and BADGE used in the reactions (Table 1). The compound is not soluble in water or chloroform. The melting points of poly-BADGE (>380 °C) are significantly higher than polyeugenol (80.3 – 83.7 °C), indicating a much higher degree of complexity of the products compared to the starting material (Kiswandono *et al.* 2012). It is expected, therefore, to have a high thermal stability and chemical resistance.

Table 1. References and physico-chemical properties of poly-BADGE powders

Sample	Color	Melting Point (°C)	Jumlah (g)	Elemental Analysis (%)			Solubility in chloroform
				C	H	O	
Polyeugenol	Brown	80.3 – 82.7	5.169				Yes
Poly-BADGE 2:1	White	> 380	4.897	71.33	7.07	21.60	No
Poly-BADGE 4:1	Brown-green	> 380	3.108	70.92	7.20	21.88	No
Poly-BADGE 6:1	Grey	> 380	3.630	71.83	7.11	21.06	No
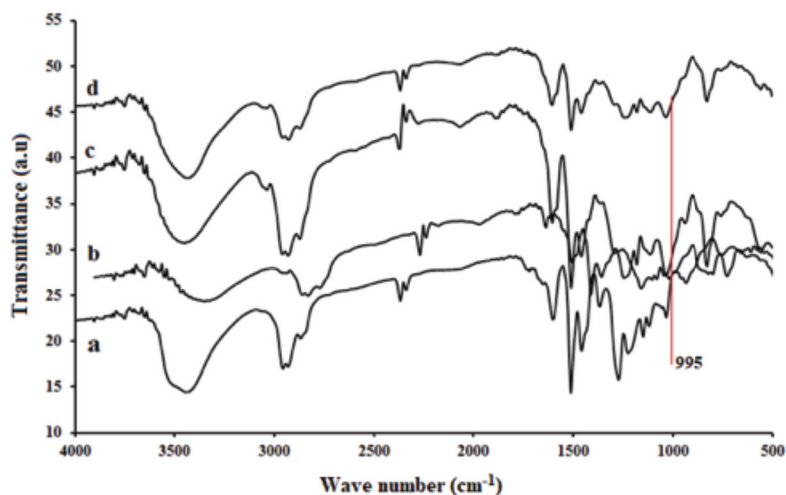
Fig. 3. IR spectra of (a) polyeugenol; (b) poly-BADGE 2:1; (c) poly-BADGE 4:1; and (d) poly-BADGE 6:1

Table 2. Infrared spectra analysis of polyeugenol and poly-BADGE

No	IR absorption type	Wave number (cm^{-1})	
		Polyeugenol	Poly-BADGE
1.	O-H strain	3448	3425
2.	C-H sp^3 strain	2931	2931
		2846	2870
3.	Aromatic absorption 1,4-disubstituted	None	2059
			1774
4.	Ar-H strain	1604	1604
5.	C=C aromatic bending	1512	1512
		1458	1458
6.	–OH bending in the plane	1365	None
7.	Sharp strain of aromatic ether (aril-O-CH$_2$)	1273	1234
		1226	
8.	Medium strain of aromatic ether (aril-O-CH$_2$)	1033	1033
9.	Aromatic absorption 1,2,4-trisubstituted	887	825
		794	717

To confirm the identity of the synthetic products and to evaluate their functional groups, the compounds were analyzed by FTIR (Figure 3). Based on the polyeugenol spectra and poly-BADGE images, it can be seen that there are differences in spectra between the two. The difference in spectra in terms of peak area and the occurrence of a shift in wavelength at a –OH peak stretching vibration indicates that the crosslinking reaction of BADGE-polyeugenol has occurred. 1.4 uptake of the substituted on typical poly-BADGE is seen at 2059 cm^{-1}-1774 cm^{-1} (Figure 2b-d where this absorption is not present in the polyeugenol (Figure 3a). Absorption in wave numbers 1365.32 cm^{-1} is bending -OH vibration in the polyeugenol spectra and its intensity is lost in the poly-BADGE spectra especially at Poly-BADGE 4: 1; this is because the -OH polyeugenol group reacts with the BADGE epoxide group to form an ether group, so the ratio of the absorbance of the ether group to the IR spectra after crosslinking is different. In addition, in the IR spectra before and after crosslinking there is also a shift in the wave number of the 1,2,4-substituted benzene group bending

(884 cm^{-1} - 794 cm^{-1}) widened on the polyeugenol, whereas in the poly-BADGE, the aromatic group is a substituted BADGE will cause sharp absorption at 825.53 cm^{-1} in poly BADGE 4: 1 and 6: 1 and 717 cm^{-1} in poly-BADGE 2: 1. Table 2 presents a complete analysis of polyeugenol and 4: 1 polyeugenol-BADGE spectra.

3.2. Phenol transport evaluation

3.2.1. Effect of source phase pH on phenol transport

It has been reported that pH can affect phenol transport (Benosmane et al. 2018). To determine the optimum pH for phenol transport in the poly-BADGE system, five different solutions of phenol (60 ppm) with pH values (3.5, 4.5, 5.5, 6.5 and 8.0) were tested. The pH was adjusted with NH$_4$OH and HCl solutions, where the addition of NH$_4$OH and HCl solutions was kept to a minimum to avoid undesired effects of other ions. The results showed that the optimal phenol transport was reached at pH 4.5 (Figure 4). Interestingly, at a lower pH the concentrations of phenol in both the source phase and the receiving phase were also low, indicating that most of the compound resided in the membrane. It may be hypothesized that in a highly acidic solution most of the phenol exists in its molecular form, which partitions more effectively to the organic phase (the membrane) than the water phase. Compared to the recovery of phenol (phenol transported to the receiving phase) at pH 4.5, which is 40%, the recovery of phenol at pH 3.5 was only 11%. Nevertheless, this number is still better than that showed in the co-EDVB system (Kiswandono et al. 2012), indicating that poly-BADGE is more effective in transporting phenols than co-EDVB. The results also showed that at high pH (>4.5), the effectiveness of the transport process significantly diminished, mainly due to the formation of more phenolic ions which tend to stay in the aqueous source phase and have less interactions with the carrier compound (Figure 4).
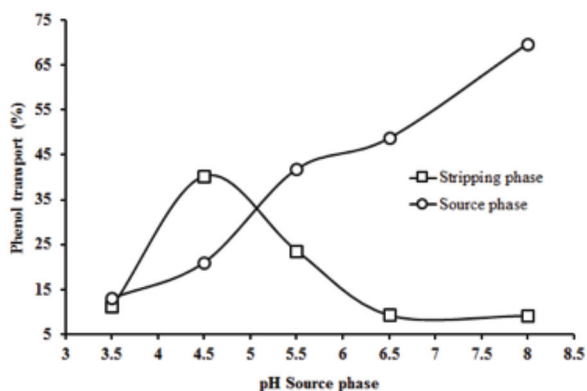
Phenol transport through carrier compounds occurs through a transport mechanism that depends on phenol concentrations gradient between the source phase and the receiving phase. This transport process may take place through hydrogen bonding and/or π-π interactions between phenol and the membrane/carrier compound. The more phenol being transported across the membrane is interpreted as the more effective functional groups in the membrane that can move phenols from the source phase to the receiving phase. In principle, this can occur in both directions. However, reverse transport of phenol to the membrane cannot occur due to the presence of NaOH as a stripping agent in the receiving phase. NaOH converts phenol to sodium phenolate, which will stay in the aqueous receiving phase. The pH difference between the acidic source phase and the basic receiving phase may also contribute to the increase in phenol transport process.

3.2.2. Effect of NaOH concentration on phenol transport

In addition to the pH of the source phase, NaOH concentration in the receiving phase may also affect the phenol transport process (Benosmane et al. 2018). Therefore, to investigate the effect of NaOH in phenol transport by poly-BADGE, five different NaOH concentrations (0.01, 0.05, 0.15, 0.25 and 0.50 M) in the receiving phase were tested. The experiments were carried out using a phenol solution (60 ppm) as the source phase and a NaOH solution as the receiving phase.

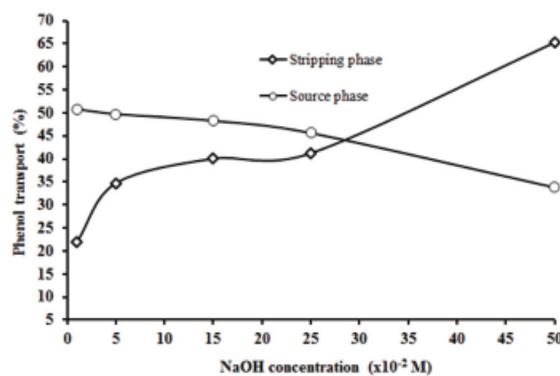**Fig. 5.** Effect of NaOH concentration on phenol transport

Both phases were stirred at room temperature for 24 h. Subsequently, phenol concentrations in both phases were analyzed using the 4-aminoantipyrine colorimetric method. The results show that the concentration of NaOH in the receiver phase positively affects phenol transport (Figure 5). The higher the concentration of NaOH the better phenol transport process was observed.

Fig. 4. Phenol transport with pH variations in source phase.

3.2.3 Effect of membrane thickness on phenol transport

To investigate the effect of membrane thickness on phenol transport, membranes varying in their weight and thickness were obtained with different compositions i.e., T_{27} (contains carrier compound (27 mg), PVC (864 mg), and DBE (1566 mg), T_{54} (contains carrier compound (54 mg), PVC (1728 mg), and DBE (3132 mg), and T_{108} (contains carrier compound (108 mg), PVC (3456 mg), and DBE (6264 mg). The optimum pH and NaOH concentration obtained in the previous sections were used in these experiments.
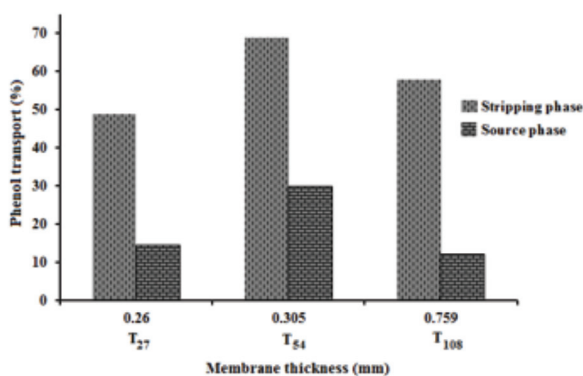

Fig. 6. Effects of membrane thickness on phenol transfer

The thicknesses of the membranes obtained from formulas T_{27}, T_{54}, and T_{108} were 0.260 mm, 0.305 mm and 0.759 mm, respectively. The results showed that phenol transport in the membrane generally increased with the thinner membrane. Membranes containing poly-BADGE even though the optimum phenol transport is found in the thickness of the T_{54} membrane with a thickness of 0.305 mm, but when viewed from the value of phenol removal (meaning that phenol has been transported even though it has not reached the receiving phase) the T_{27} membrane gives the optimum phenol transport (Figure 6). This is because transport through the membrane is affected by the thickness and surface area of the membrane itself (de San Miguel *et al*. 2011; Kiswandono *et al*. 2012).

The poly-BADGE T_{27} membrane was able to transport 49% phenol from the source phase to the receiving phase. However, this is lower than the ability of the T54 membrane to transport phenol (69%). In the T_{27} membrane, the diffusion of solutes through the membrane appears to be very fast but the low amount of the carrier compounds makes the interaction with phenol become less optimal, and phenol is only trapped inside the membrane without being transported to the receiving phase. In fact, the phenol concentration in the T_{27} membrane phase reached 37%.

3.2.4. Effects of crosslinking agents

In a liquid membrane method, the carrier compound plays an important role and is considered to be a determining factor in transporting the target compound. To evaluate the effect of the ratio of crosslinking agents used, on the efficiency of phenol transfer, three crosslinked Poly-BADGE polymers were prepared from different mole ratios (2:1, 4:1, and 6:1) of polyeugenol and BADGE. Polyeugenol alone was used as a control. The experiments were performed under an optimal condition at pH 4.5, the receiving NaOH concentration of 0.5 M, and the polymer thickness of 0.305 mm.
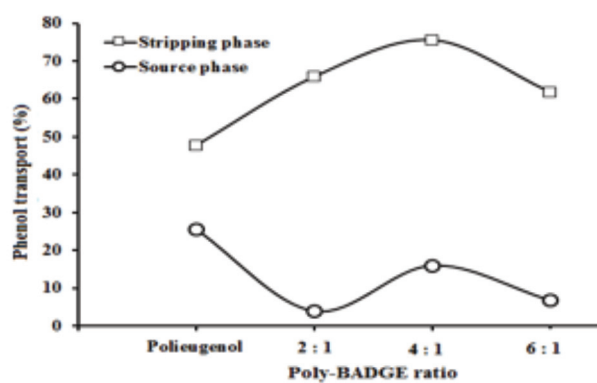
Fig. 7. Effects of polyeugenol-BADGE ratio on phenol transfer

The results showed that the ratio of crosslinking agents in the membrane has an effect on phenol transport (Figure 7). Poly-BADGE 4:1 appears to be the most effective carrier, reaching 75% of phenol transfer. It may be hypothesized that the 4:1 ratio of polyeugenol – BADGE would produce a polymer that contains a higher number of active sites than the others. Figure 7 shows that the peak area of –OH in poly-BADGE 4: 1 is larger (broad) than poly- BADGE 2: 1 and 6: 1, so that with the high peak area of –OH groups in 4: 1 poly-BADGE the concentration of phenol transported is also increasing.

3.2.5 Effects of transport time

The time needed for phenol to pass through a membrane is one of the variables that must be considered. Previously, Zidi *et al*. (2010) have observed the effects of time on phenol transport efficiency and kinetics using Accurel® PP as a supporting polymer and TBP (20%, v/v) in kerosene as the organic phase.
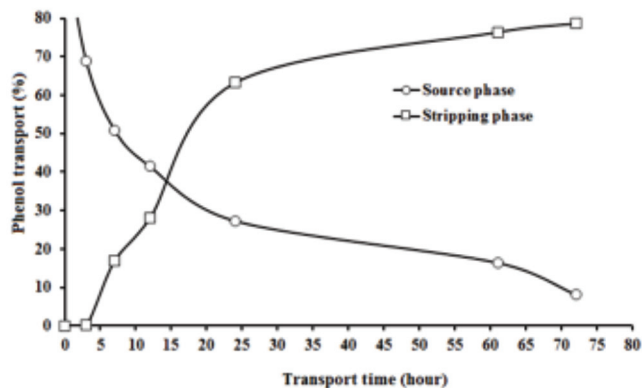
Fig. 8. Effects of time on phenol transport

In this study, the effects of transport time on phenol transport efficiency was evaluated by carrying out the experiments at different time intervals. The study was done under an optimal condition as described above using poly-BADGE 4:1 as the carrier. Analysis of the phenol concentration at different time intervals in the receiving phase revealed that the phenol concentration increased with time and reached a plateau after 72 h (Figure 8).

3.3. Characterization of PIM membrane

One of the important properties of membranes/carrier compounds to be used in PIM is their chemical stability towards a high concentration of NaOH solution, which is used in the receiving phase. To evaluate the stability of the poly-BADGE membrane towards NaOH solution, the membrane was subjected to SEM imaging. As shown in Figure 9a, there was no significant damage observed on the surface of the poly-BADGE membrane exposed to 0.5 M NaOH solution in the receiving phase, indicating that NaOH does not appear to negatively affect the poly-BADGE membrane or change the solubility of the carrier compound. On the other hand, 0.25 M NaOH solution in the receiving phase was enough to cause a significant damage to a membrane containing coEDVB as a carrier compound (Figure 9b).

Structurally, coEDVB contains phenolic hydroxyl groups (as its active functional groups), which are slightly acidic and can react with NaOH to form sodium phenolates that are more water soluble and may be leached out from the membrane. On the other hand, poly-BADGE mostly contains allylic hydroxyl groups (as its active functional groups), which are unreactive with NaOH.
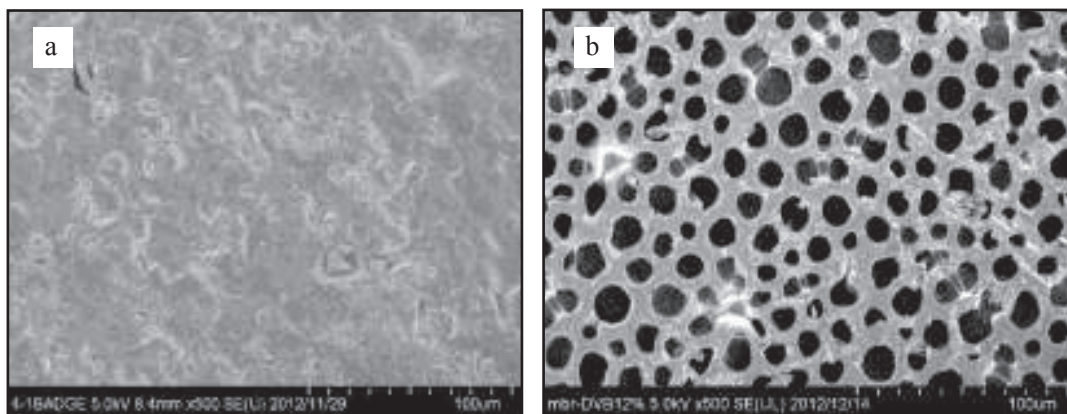

Fig. 9. SEM images of poly-BADGE- and co-EDVB-containing membranes. (**a**) image of a membrane containing poly-BADGE carrier compound (0.5 M NaOH), (**b**) image of a membrane containing co-EDVB as a carrier compound (0.25 M NaOH) (Kiswandono *et al.* 2013).
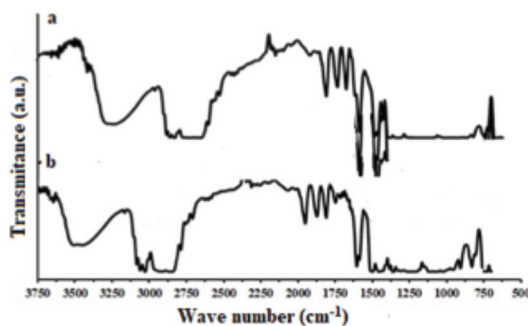

Fig. 10. IR spectra of polyBADGE membrane. (a) After transport (b) Before phenol transport.

The presence of pores or cavities on the surface of the membrane may also be due to the inhomogeneity of the constituents of the membrane when it is made. This can lead to defect or damage to the membrane, so that when the cavity transport process is covered by sediment from the constituent components of the membrane and salting out of $NaNO_3$ takes place.

To further evaluate the poly-BADGE membrane's stability, the membrane was analyzed with FTIR before and after the transport experiment was performed (Figure 10). The results showed that the membrane was relatively unchanged. Before the membrane was used for phenol transport (Figure 10b), there were a number of peaks in the IR spectrum indicating the presence of -OH stretching (3522 cm^{-1}), –C–H aromatic stretching (3062– 3026 cm^{-1}), –C–H alkane stretching (2911–2844 cm^{-1}), and –C=C aromatic stretching (1602 cm^{-1}). The 1,4-disubstituted benzene group frequency at 829.76 cm^{-1} was used as an indicator for the presence of poly-BADGE as one of the constituents of the membrane. After the membrane was used for phenol transport, the absorption at this frequency was still visible but with a low intensity because it had been saturated with water (Figure 10a).

Comparative results from the two spectra showed that the functional groups at the frequency of 400 - 1500 cm^{-1} relatively did not experience a shift or difference in intensity. The small change in the intensity of the –OH group in the spectra was also observed, where the increase in the intensity and widening of the peak showed a reduction in –OH groups. This indicated that there was an interaction between the carrier compound and the active site of the membrane during the transport process. Phenol and the carrier compound are two compounds which have the same -OH group, so that it was possible to interact in the form of hydrogen bonds between the two -OH groups.

4. Conclusions

A new derivative of polyeugenol, namely poly-BADGE, has been synthesized by crosslinking polyeugenol and bisphenol A diglycidyl ether in dioxane under an alkaline condition. The product was confirmed by FTIR and elemental analysis. Poly-BADGE can be used as a carrier to transport phenol in the polymer inclusion membrane (PIM) method. For the optimal phenol transport the pH of the source phase is 4.5, and the optimal concentration of NaOH in the receiving phase is 0.5 M. A maximum of 79% of phenol transfer can be achieved after 72 h

transport time. Poly-BADGE appears to be stable towards 0.5 M NaOH solution used in the receiving phase, making it a better alternative to co-EDVB as a carrier compound in PIM.

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