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4 Synthesis and characterization of co-edaf and its application test as a carrier membrane for phenol transport using polymer inclusion membrane (PIM)

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Abstract

The development of a new compound derived from polyeugenol as carrier compound in phenol transport has been successfully performed. The compound of copoly(eugenol-dialyl phthalate) or co-EDAF was synthesized by reacting eugenol and dialyl phthalate agent through a polymerization process using boron tri-fluorodiethyl ether as a catalyst. The obtained compound was then tested for its ability as a carrier compound in phenol transport using polymer inclusion membrane (PIM) method. The synthesized compound was characterized by using FTIR, SEM and TG-DTA analytical methods.

Based on the results of characterization, it was shown that co-EDAF has been successfully obtained. The loss of the absorbance band at the wavenumber of 995.27 cm⁻¹ suggests that the unsaturated vinyl group (-CH=CH₂) in eugenol has undergone successful polymerization process. The TG-DTA data also support the success of the polymerization process as indicated by the differences in temperature T_{5%}, T_{20%}, T_{50%} and T_{max} in co-EDAF from those of the control compound polyeugenol. Furthermore, the carrier test in phenol transport has also demonstrated that the membrane containing the co-EDAF can effectively serve as a carrier compound as shown by its ability to transport phenol repeatedly.

Keywords: Carrier, co-EDAF, Phenol, PIM, Polyeugenol

Introduction

Liquid membrane methods especially PIM (Polymer Inclusion Membrane) can be used and applied to various fields such as in analytical chemistry and outside analytical chemistry¹. Researchers are able to use this method for many purposes, among them are metal separation²⁻⁶, gold purification⁷, separation of strontium from radioactive waste⁸, continuous clean-up of thiocyanate from gold mine tailings water⁹ as well as the separation of organic wastes such as dyes¹⁰ and phenol¹¹⁻¹³. The transport of a targeted compound using a liquid membrane method always involves a carrier compound^{3, 14} that acts as a compound facilitating the target compound from the source phase to the receiving phase.

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Various carrier compounds using the PIM method have been reported in previous studies such as di(2-ethylhexyl)phosphoric acid (D2EHPA)¹⁵, aliquat 336¹⁶, LIX84I (2-hydroxy-5-nonylacetophenone oxime)⁵, di(2-ethylhexyl) phosphoric acid¹⁷, bis(2-ethylhexyl) phosphate (B2EHP)¹⁰, and copoly divinyl benzene (co-EDVB)^{18, 19}. The co-EDVB is a compound resulting from polymerization between eugenol and divinyl benzene (DVB). This compound can be used as carrier in the separation of phenols.

Separation of phenol using a liquid membrane requires a carrier compound which facilitates the successful process of the transport of the target compound. The active side available in the carrier compound determines the success of the transport of targeted compound^{11, 13, 18}. Phenol as the target compound in this study has a hydroxyl group in its structure. This functional group as the active site of the targeted compound becomes main consideration in searching, synthesizing and designing a new carrier compound so that the new carrier compound has the active site that matches with that of targeted compound. The goal in designing new carrier compound is that the transport process of targeted compound can run smoothly and continuously.

The transport process is the transfer of target compound through the surface of the source phase which diffuses through the membrane phase, further forming the complex between the target compound and the carrier compound, finally the target compound is released to the receiving phase^{2, 9, 20}. The main requirements of carrier compounds which can be used in membrane phases containing species with high molecular weight are that it is lipophilic and has a structure that allows the formation of bonding, interaction or complex with the compound to be transported. One example of the natural materials that is potential to be developed into the type of the polymer is eugenol obtained mainly from clove leaf.

Structurally, eugenol is a compound having double vinyl bonds that can be polymerized into polyeugenol²¹. Polyeugenol derivatives can also be further produced by polymerization processes using a cross-linking agent^{18, 19, 22}. One of good cross-linker agents that can be used in copolymerization process is dialyl phthalate (DAF). This cross-linker is a diene compound which can undergo addition polymerization. The double bond of the diene species is quite reactive so that the crosslinking synthesis can

be performed at room temperature. The copolymerization process always produces newly derived compounds that have higher molecular weight than that of their original compounds.

Hence, the newly derived compound is intended to have more active sites. The increase ⁴ in the number of active sites normally will be followed by the increase in its transportability¹⁸. The number and transportability of the active sites are defined by the type and number of crosslinkers added during the copolymerization process. Modification of the synthesis process in this way is an alternative technique to increase the molecular weight and the active site of a targeted carrier compound so as to improve the transportability of the membrane.

Therefore, the purpose of our study is to synthesis a new potential carrier compound by reacting eugenol and crosslinking agent of dialyl phthalate using polymerization technique. The resulting polymer is then tested as a carrier compound for its ability to transport phenol using PVC (polyvinyl chloride)-based PIM as base polymer and DBE (dibenzyl ether) as plasticizer.

Material and Methods

Experimental protocol adopted in this study is analogous to the experimental conditions that have been reported by Kiswandono et al¹⁸, consisting of transport equipment, membrane composition, membrane printing and phenol transport procedures.

Materials: Eugenol was supplied by PT Indesso Aroma, Purwokerto, Indonesia. Dialyl phthalate, bisphenol A diglisidyl ether (BADGE), 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 all purchased from Merck with pure analysis grade. Boron trifluoride diethyl ether [$BF_3O(C_2H_5)_2$] was obtained from SIGMA Aldrich. Other reagents including sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (CH_3OH), chloroform, methanol, NH_4OH , anhydrous Na_2SO_4 , K_2HPO_4 , KH_2PO_4 , and demineralized water were purchased from Bratachem company.

Instrumentation: The instruments used in this study are pH meters (Mettler Toledo AB54-S), analytical balance (Mettler Toledo AB54-S), UV-Vis spectrophotometer (772

Spectrophotometer), SEM Hitachi SU8000, infrared spectrophotometer Shimadzu IR model Prestige-21 with magnetic KBr pellet holder 0016-008. Transport equipment consisted of two chambers which are separated by a membrane. The volume of each chamber is ³ 50 mL. The effective diameter of the chamber which is directly in contact with the phenol solution is 2.5 cm, this area is the center of the transport process.

Synthesis of eugenol-crosslinked dialyl phthalate (co-EDAF): The polymerization conditions were carried out in accordance with those reported by Kiswandono et al¹⁸. Eugenol 23.2 g was put into four-round flasks (5.8 g each). Then, into the three-round flasks were added 2, 6 and 12% by weight of dialyl phthalates to the weight of eugenol used. One of the remaining round flasks was set without the addition of crosslinking agent (polymerization results of eugenol without the crosslinker is called polieugenol). Then, into each round flask was added 1.0 mL $BF_3O(C_2H_5)_2$ as a catalyst. The polymerization reaction was carried out in one night and it was stopped by the addition of 1.0 mL of methanol. The formed red gel was dissolved in diethyl ether and then washed with distilled water until neutral pH was obtained.

The organic layer containing anhydrous Na_2SO_4 was ¹ then decanted. The solvent was evaporated using rotary evaporator at 40 °C and the obtained residue is stored in the desiccator. The polymer compound formed was weighed to determine the yield. The product was then subjected to elemental analysis melting point determination. Finally, the sample was subsequently characterized using SEM, FTIR and TG-DTA analytical methods. The prediction of polieugenol and co-EDAF structures based on the characterization results are given in fig. 1a and 1b.

Preparation of PIM membrane and transportability of the new synthesized compound: PIM membranes were made and printed in a mold with the ratio of carrier compound (co-EDAF), base polymer (PVC), and plasticizer (DBE) of 10:32:58. Tetrahydrofuran (THF) of 10 mL was added to the mold for each PIM membrane to homogenize the mixture. The mold was allowed to stand for three days in room temperature to evaporate the solvent naturally. The membrane obtained was then tested for its ability in transporting phenol using the chamber as shown in fig. 2. The transportability test was performed in three replications by using the same membrane and procedure.

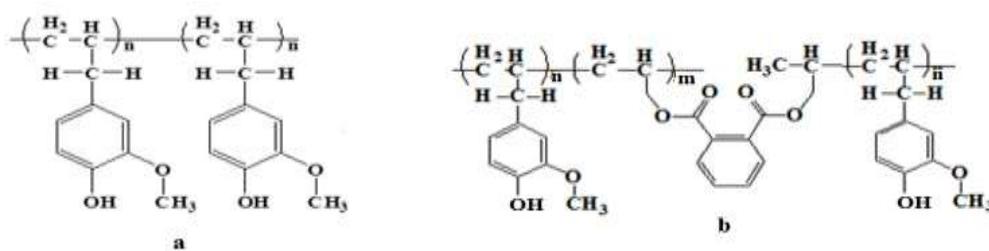


Figure 1: Predicted structures (a) Poly(eugenol) and (b) a crosslinked polieugenol derivative using DAF

The transport experiment is carried out by the following procedure. Source phase was filled with 50 mL of phenol solution (60 µg/ml) and the receiving phase was filled with 50 mL of 0.25 M NaOH. Each chamber was then stirred at room temperature for 24 hours. This transport experiment is repeated three times for each condition and at every repetition, the phenol and NaOH solutions in each chamber were replaced with freshly prepared solutions but using the same membrane. Then, the phenol concentration in both the source phase and the receiving phase was analyzed for its phenol content using the 4-aminoantipirin method^{18,23}.

Solution absorbance was measured with UV-Vis spectrophotometer at a wavelength of 450 nm. The PIM membranes before and after transport experiment were characterized using IR spectrophotometer (Shimadzu Prestige-21) in KBr pellet (magnetic KBr pellet holder 0016-008) and scanning electron microscope (SEM) (Hitachi SU8000).

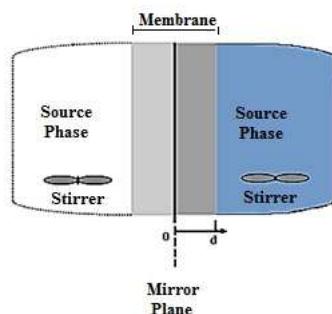


Figure 2: Experimental set-up chamber

Results and Discussion

Synthesis and Characterization of co-EDAF: The new carrier compounds of co-EDAF were synthesized using eugenol as base material and dialyl phthalate agent with $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ as catalyst. The synthesized materials are in the form of powder with almost the same color of brown-orange and all materials are soluble in chloroform. The properties of co-DAF (Figure 1b) are compared with those of polyeugenol (Fig. 1a). Similar to DVB study previously reported by Kiswandono et al¹⁸, DAF is a diene compound having an allyl group i.e. a group which plays an important role for the success of the polymerization reaction. This polymerization is a cationic addition copolymerization

reaction because the DAF vinyl group undergoes addition reaction. As expected, this copolymerization reaction took place through the three stage of polymerization consisting of initiation, propagation and termination.

The initiation stage is the stage in which the carbocation ions are formed in the eugenol and dialyl phthalate structures. A catalyst of $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ used in this synthesis is a salt formed from a Lewis acid and base. BF_3 is a Lewis acid and therefore it is an electron-pair acceptor, while $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$ is a Lewis base i.e. an electron pair-donating compound. The presence of electron releasing groups in eugenol structure and the properties of catalyst used which is consisting of electron acceptor and donator have driven the formation of cationic species of eugenol so that the copolymerization process can start. On the other hand, the empty orbitals of BF_3 are able to bind to DAF forming a carbocation. This situation favours the formation of copolymerization process.

The resulted polymer from the synthesis was then characterized for its yield, melting point and solubility in chloroform (Table 1).

Table 1 shows that the increase in the amount of DAF added leads to the increase in the melting point of the resulted co-EDAF and the increment of the increase in melting point is directly proportional to the added amount of DAF. The rise in the melting point clearly indicates that the carbon chain of the polymer is getting longer; hence it is anticipated that the molecular weight of co-EDAF also increases. The increase in molecular weight is important because it is also an indication of the multiplication of the -OH active sites.

From the table 1, it is also clearly shown that high yields of the synthesis are accompanied by a low melting point of the resulted polymer. It means that there is a correlation between the difficulty of the copolymerization process and the resulting yield of polymer. This suggests that not all materials in the reaction mixture produce the desired product during the copolymerization process. Hence, it can be understood that the addition of polymer chains in this copolymerization process probably gives rise to the slower reaction and eventually the product yield is lower than those of the other two copolymerizations.

Table 1
Yield, physico-chemical properties and elemental analysis of polyeugenol and synthesized co-EDAF

Compounds	Cross-linker (mMol)	Yields (%)	Color	Melting Point (°C)	Solubility in Chloroform	Elemental Analysis (%)		
						C	H	O
Polyeugenol	0	88.93	Brown	80.3 - 82.7	Soluble	71.36	7.06	21.58
Co-EDAF								
2% (w/w)	0.5	93.85	Brown	81.2 - 86.5	Soluble	71.02	7.04	21.94
6% (w/w)	1.4	89.07	Brown	87.2 - 91.4	Soluble	70.85	7.08	22.07
12% (w/w)	2.8	85.97	Brown	90.0 - 93.7	Soluble	71.17	7.15	21.68

To determine the ratio of carbon, hydrogen and oxygen atoms contained in the synthesized polymer, the elemental analysis has been conducted. The purpose of this analysis is to determine carbon, hydrogen and oxygen content in the polymer because these data correspond directly to the number of active sites, chains and melting point of the polymers.

The increase in the molecular weight of polymers corresponds to the increase in the number of atoms in the polymers, so that the increase in the ratio of hydrogen to carbon (H/C) atoms can empirically show the length of the polymer chain or the molecular weight of the polymer, meaning that the H/C ratio can give an idea of the melting point of the resulting polymer. If we examine closely the H/C and H/O ratio in table 1, it can be observed that the highest H/C ratio is found in 12% co-EDAF e.g. 10.05% and the highest H/O atomic ratio is also found in 12% co-EDAF i.e. 32.97%. So, these calculation results support the data of melting point of polymer as summarized in table 1.

Furthermore, it is noted that the result of eugenol polymerization using BF_3 as catalyst without the addition of cross-linker agent is polyeugenol while the polymerization between eugenol and the DAF cross-linker results in co-EDAF. Accordingly, the polyeugenol derivative of co-EDAF that acts as a carrier compound has an active site of -OH, therefore FT-IR characterization becomes important as the data can provide information about the success of the synthesis process. Figure 3 gives the FT-IR spectra of eugenol, polyeugenol, co-EDAF 2, 6 and 12%. Based on the fig. 3, it is obviously observed that there are spectral differences among eugenol, polyeugenol and co-EDAF. Fig. 3 shows the comparison of IR spectra of eugenol, polyeugenol and co-EDAF 2, 6 and 12%. The eugenol

spectra (Fig. 3a) have a typical group of 1,2,4 substituted aromatic compounds. The existence of aromatic compounds is usually indicated by the $900 - 800 \text{ cm}^{-1}$ absorption band¹⁸. In this study, the spectra of the aromatic group exhibit absorption at 817.82 cm^{-1} . The absorption of the allyl group ($\text{C}=\text{C}$) is found in the 1636.5 cm^{-1} which is amplified by the absorption band at $650 - 900 \text{ cm}^{-1}$ (out of plane $\text{C}=\text{C}$) while the unsaturated group (vinyl, $-\text{CH}=\text{CH}_2$) is observed at 995.27 cm^{-1} absorption. Absorption at 3448.72 cm^{-1} indicates the presence of the -OH stretching group¹⁸. The rise of double peaks in the $3500-3200 \text{ cm}^{-1}$ region indicates that the sample is a polymer. Therefore, it can be concluded that polymerization and copolymerization in this study have occurred successfully.

Moreover, bands in the $3000-2800 \text{ cm}^{-1}$ region indicate the presence of methylene and methyl groups. This is supported by the bands in the range of 1450 and 1370 cm^{-1} i.e. the methyl group ($-\text{CH}_3$) shown by the absorption band at 1365.60 cm^{-1} and the presence of the methylene group ($-\text{CH}_2$) indicated by the band at 1435.04 cm^{-1} . The obvious differences that can easily be seen by comparing the IR spectra of eugenol and co-EDAF is the loss of allyl $\text{C}=\text{C}$ (1636.5 cm^{-1}) and vinyl ($-\text{CH}=\text{CH}_2$) (995.27 cm^{-1}) groups.

Another clear proof is the disappearance of absorption in the region of $1000-650 \text{ cm}^{-1}$ indicating that there has been an addition reaction to the double bond of eugenol, suggesting that eugenol polymerization and copolymerization of co-EDAF have been successfully formed. The rise of 2931.8 cm^{-1} absorption in the IR spectra of the synthesized polymer clearly confirmed the presence of CH_{sp^3} . On the other side, the presence of -OH groups is shown in the band of 3510.42 cm^{-1} and the aromatic $\text{C}=\text{C}$ groups in benzene are indicated by the band at 1604.77 cm^{-1} .

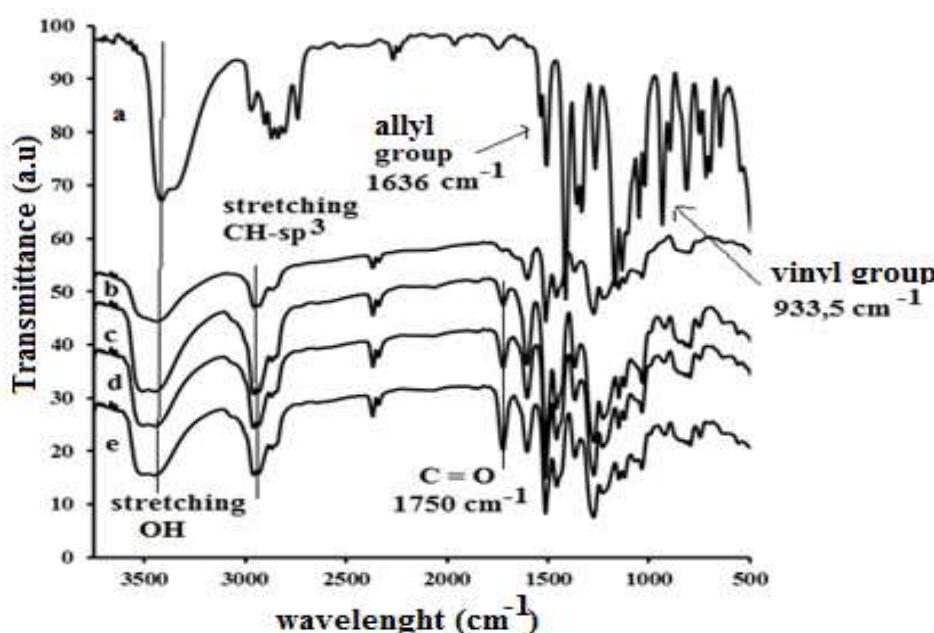


Figure 3: FTIR spectra of (a) eugenol, (b) polyeugenol, (c) co-EDAF 2%, (d) co-EDAF 6% and (e) co-EDAF 12%

Fig. 3 is the IR spectral overlay of polyeugenol (3b) and co-EDAF 2, 6 and 12% (3c, d, e). The spectra show that polyeugenol and co-EDAF exhibit almost the same pattern of spectra, these are because of no new group or clusters appear or disappear in these two compounds, so the type of the functional groups in polyeugenol and the co-polymers are the same except for the absorption at 1750 cm^{-1} which belongs to typical of C=O of co-EDAF whereas polyeugenol does not have this carbonyl group. These differences may be further analyzed from the point of view of the area of the spectra and the intensity ratio of each absorption.

Co-EDAF has a greater intensity and peak area ratio than polyeugenol because the crosslinker polymer has much greater number of identical group clusters than polyeugenol and it was recorded in the IR spectra and therefore gives relatively stronger absorption band. Hence, the higher absorption strength of the IR spectra can be taken as indication that the two crosslinked polymers have more functional groups than polyeugenol. The stronger absorption is observed not only in the band of -OH group, but also in almost all spectra, therefore it can be concluded that copolymerization has been successfully accomplished.

The characterization of the obtained polymer was further carried out by using scanning electron microscope (SEM; SU-8000). The SEM data provide useful information related to the physical properties of the material, especially the surface morphology of the material under investigation. For such purposes, some researchers have also used high stereoscopic and magnetic SEM techniques (> 100000 times)^{24, 25}. Fig. 4 shows the co-EDAF surface morphology with magnification of 500 times (Fig. 4a) and 2000 times (Figure 4b). It is seen from figure 4 that the polymer exhibits almost the same morphology and they are basically uniform, have a solid-shaped chunk and mutually exclusive. The solids on the co-EDAF appear as solid and solid, similar to the SEM results that have been reported on polyeugenol²². At 2000 magnification (Fig. 4b), no other information can be obtained except for solid and solid powdered batches.

Further characterization has been done by using thermogravimetry (TGA) and differential thermal analysis (DTA). This thermal analysis is performed with the purpose

of determining the temperature as well as occurrence of the decomposition reaction that causes changes in the sample weight and physical properties of the co-EDAF polymers. The sample that has been characterized by TGA and DTA is co-EDAF 6% with the initial weight of 0.60 mg. The sample was heated at a constant rate i.e. $10\text{ }^{\circ}\text{C}/\text{min}$ in the temperature range of $30 - 900\text{ }^{\circ}\text{C}$.

Results of TGA analysis given in figure 5 show a process causing decrease in weight occurs at $37.2 - 546\text{ }^{\circ}\text{C}$. From DTA analysis it can be understood that the process is exothermic. Moreover, it is also observed that the sample undergoes an undershooting at a temperature of $25.9 - 37.2\text{ }^{\circ}\text{C}$, a state in which the sample does not decrease in weight or weight constant at a certain time interval until the sample begins to decompose continuously²⁶.

Detailed examination of figure 5 reveals that there are three main processes of weight loss. The first weight change occurs at temperature range of $37.2 - 361\text{ }^{\circ}\text{C}$. This weight change is associated with the dehydration of the sample and release of water content (evaporation) into the atmosphere. The high content of hydroxyl groups in co-EDAF polymer makes the weight loss in this process quite high e.g. 22.7%. The second thermal change is detected on the TGA curve at the $361 - 408\text{ }^{\circ}\text{C}$, giving weight loss of 14.8%. Comparing with the DTA curve, it is clearly seen that the process is an exothermic change. The last process of weight loss occurs at a fairly step of weight change of around 19.1% at the temperature range of $350-529\text{ }^{\circ}\text{C}$. This weight loss has been commonly associated with the dissociation of CO and OCH₃.

Further analysis can be done by comparing glass transition temperature (T_g) between polyeugenol and co-EDAF. Table 2 summarizes the data of decomposition for both polyeugenol and co-EDAF. It is clearly seen from the table that polyeugenol has the lower glass transition temperature (T_g) compared to that of co-EDAF. This indicates the increase in the formation of branch in the polymer backbone of co-EDAF as well as the number of benzene rings available in the polymer²⁷.

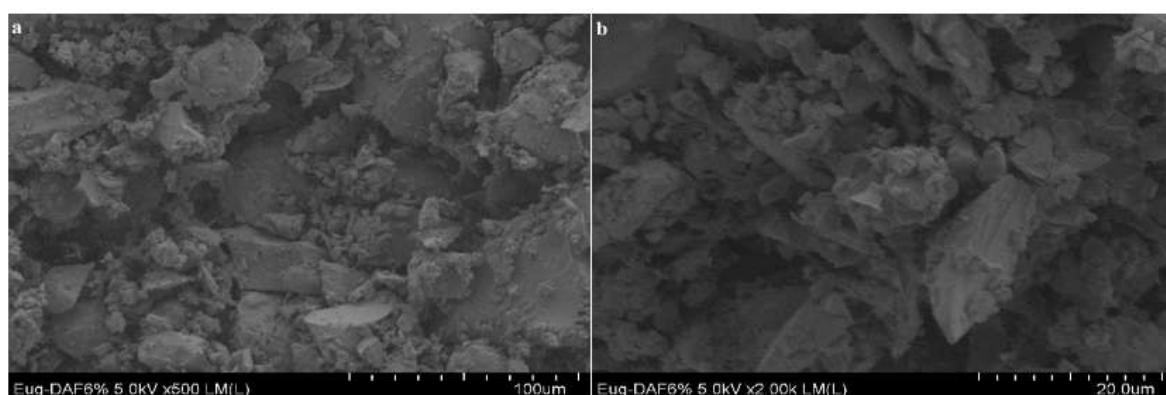


Figure 4: SEM Morphology of co-EDAF powder (a) 500x (b) 2000x

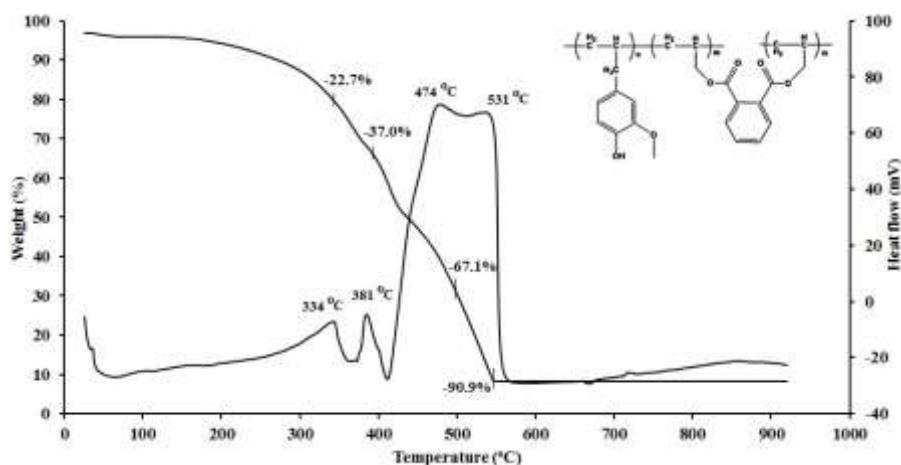


Figure 5: DTA and TGA curves for co-EDAF 6% powder

The obtained Co-EDAF polymer is expected to have more branched substituent groups and therefore possesses higher polarity because theoretically the increase in polymer branch and polarity will induce the higher T_g . The higher glass transition temperatures may also be generated by the differences in the number of benzene rings. Hence, it is easily understood that co-EDAFs have higher T_g because it contains more benzene rings. According to Stevens²⁷, aromatic polymers have a rigid structure and thus characteristically have high glass transition temperatures, high melt viscosity and low solubility. Several factors have been well understood to affect the glass transition temperature; among them are addition of branching, polarity properties, hydrogen bonding and the addition of benzene rings.

The characteristic differences of the synthesized polymers can also be observed from the temperatures at which the decomposition of the sample occurs by 5% ($T_{5\%}$), 20% ($T_{20\%}$), 50% ($T_{50\%}$) and maximum temperature (T_{max})^{22, 28}. Table 2 shows the temperature differences in $T_{5\%}$, $T_{20\%}$, $T_{50\%}$ and T_{max} . The significant differences in the temperature of $T_{5\%}$, $T_{20\%}$, $T_{50\%}$ and T_{max} between polyeugenol and co-EDAF suggest that the two polymers are mutually different. Furthermore, the differences of these two polymers can be assessed from the energy amount required for the heat flow and the weight loss that occurs in the first weight change at temperatures below 350 °C. This weight change is associated with the dehydration of this sample or evaporation of the water containing the sample.

Obviously, it is observed that the two types of polymer, although both have hydroxyl groups but the weight loss in the process of water release has different percentage values e.g. 20.5% (polyeugenol) and 22.7% (co-EDAF), indicating that the two polymers are structurally different.

The fact that the profile of the TGA-DTA curve between the two polymers as discussed above confirms that the co-polymerization process has been successfully conducted. Although the elimination temperature of H_2O for three

samples of polymers is almost the same, there is significant difference of changes after temperatures above 350 °C; therefore, it can be concluded that the two polymers differ from one another.

Test of transport capability of Co-DAF as a carrier compound: The transport test has been conducted by PIM membrane method containing co-EDAF as a carrier compound. This experiment was conducted in order to know the capability of the carrier compound in separating phenol. Membranes containing co-EDAF are used repeatedly for once, twice and three times to check the endurance of PIM membrane. The ability of phenol transport and the degree of membrane liquid (ML) loss (loss of membrane constituent components) obtained from this experiment are presented in fig. 7.

From fig. 7, it appears that the percentage of transported phenol found in the receiving phase generally decreases with the increase in repeated use of membrane from once, twice and three times. This is possibly due to the leaching of membrane components, in particular co-EDAF as a carrier compound into the solution at the first application, second and so on. This assumption is characterized by the data of high ML loss as given in fig. 7 (b). This ML loss results in the reduced number of active sites of the membrane so that the $\pi-\pi$ interactions and hydrogen bonds that can be formed between phenol and membrane carrier compound also decrease. As a result, the percentage of phenol transport for the second and third applications decreases. The existence of the loss of membrane components can also be clearly detected by examining the IR spectra of the membrane after 3rd application (Fig. 8).

Fig. 8(b) shows that the intensity of OH group vibration of PIM IR spectra after 3-time repeated use significantly decreases compared to that of initial IR spectra of the membrane (before use). The vibration of OH group as the active site of the membrane that is responsible for phenol transport no longer exists in the spectra as compared to the OH group vibration of initial membrane spectra (Fig. 8a).

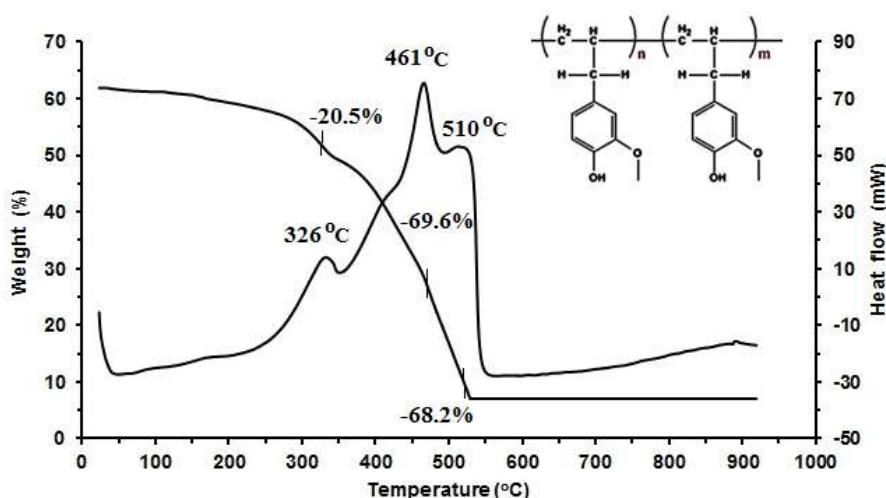


Figure 6: DTA and TGA curves of polyeugenol powder

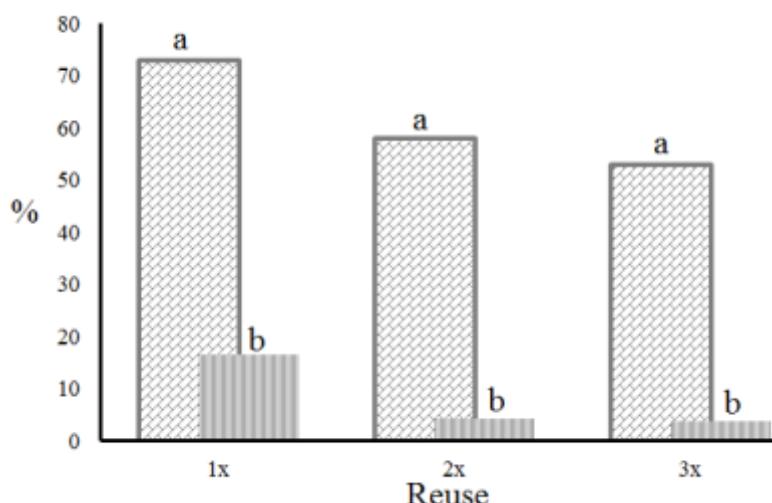
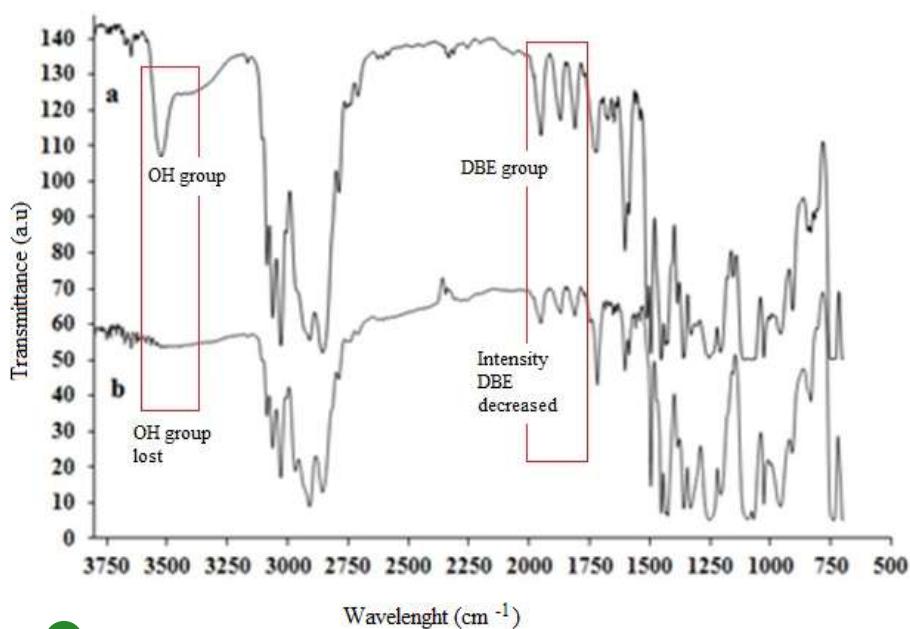
Figure 7: The ability of phenol transport with repeated use of PIM membranes.
(a): percent transport phenol (b):% ML lossFigure 8. ⁴IR spectra for PIM membrane (a) before transport (b) after 3rd transport

Table 2

Temperature of decomposition at T_{5%}, T_{20%}, T_{50%}, and T_{max} and T_g Temperatures of Polyeugenol and Co-EDAF

Samples	T _{5%} (°C)	T _{20%} (°C)	T _{50%} (°C)	T _{max} (°C)	Interval Temperature T _g (°C)	Temperature T _g (°C)
Polyeugenol	222.0	344.8	457.4	529.2	95.5 – 104.8	100.2
Co-EDAF	242.8	351.9	444.5	546.3	113.0 – 116.7	114.5

T_{5%}: temperature conditions where the sample decomposes by 5% of the number of samples used.

T_{20%}: temperature conditions where the sample decomposes by 20% of the number of samples used.

T_{50%}: temperature conditions where the sample decomposes by 50% of the number of samples used.

T_{max}: temperature conditions where the sample has maximum decomposition

This indicates that the amount of co-EDAF as a carrier compound in the membrane has decreased significantly, resulting in the lower percentage of transport. The percentage of membrane loss on each transport decreases with the increase in the number of repeated uses of the membrane. The percentage of membrane loss was calculated by weight differences between initial and final weight of the membrane after application. The decrease in the percentage of membranes loss in second and third applications is possibly caused by relatively huge loss of membrane components in the 1st application so that the second and third use induce only a little of component loss.

The occurrence of membrane component loss in phenol transport can also be observed by examining the results of SEM analysis (Fig. 9). The SEM image of membrane surface recorded following the transport process presented in fig. 9 shows clearly the existence of both open and closed pores of the membrane. The presence of the open membrane pores indicates the occurrence of the leaching process (soluble) of membrane component during the process of phenol transport.

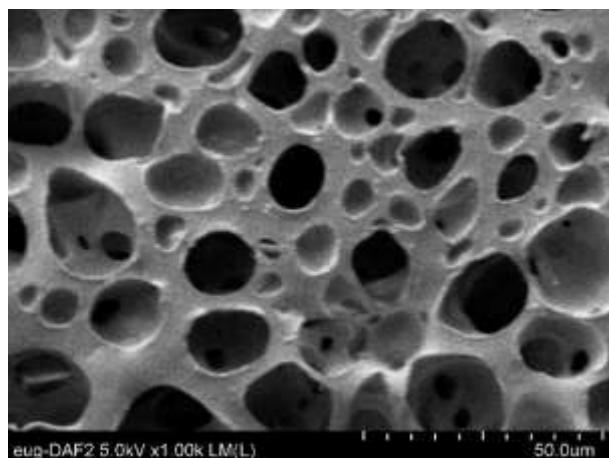


Figure 9: SEM image of PIM membrane after phenol transport

Conclusion

Preparation of new compounds, co-EDAF derived from polyeugenol has been successfully carried out using polymerization techniques. The success of synthesis has been proved by the significant differences in the profile of FT-IR spectra and TG-DTA curves. Test of phenol transport

by PIM membrane containing co-EDAF demonstrated that the compound can be applied as a carrier compound in phenol transport. The transportability of phenol is indicated by the high percentage of phenol that can be transported through PIM membrane containing co-EDAF.

The capability test of membrane transport also provides information about the existence of membrane liquid (ML) loss and indicated by the difference in weight of the membrane before and after application. This ML loss has also been confirmed by the SEM image showing the availability of open and closed pores of the membrane after being used for the phenol transport.

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