

PAPER • OPEN ACCESS

## Effects of percent weight of divinylbenzene as crosslinking agent on the properties of eugenol–divinylbenzene copolymers

To cite this article: N B A Prasetya *et al* 2020 *J. Phys.: Conf. Ser.* **1524** 012089

View the [article online](#) for updates and enhancements.

You may also like

- [A 2-to-2.4-GHz differentially-tuned fractional-N frequency synthesizer for DVB tuner applications](#)  
Meng Lingbu, Lu Lei, Zhao Wei et al.
- [Performance of Differently CrossLinked, Partially Fluorinated Proton Exchange Membranes in Polymer Electrolyte Fuel Cells](#)  
Felix N. Büchi, Bhuvanesh Gupta, Otto Haas et al.
- [Communication—Electropolymerization of Anion-Conducting Polymer Films](#)  
Zi-Ye Xiao, Charles E. Diesendruck, Viatcheslav Freger et al.



The Electrochemical Society  
Advancing solid state & electrochemical science & technology

243rd Meeting with SOFC-XVIII

Boston, MA • May 28 – June 2, 2023

Accelerate scientific discovery!

Learn More & Register



# Effects of percent weight of divinylbenzene as crosslinking agent on the properties of eugenol–divinylbenzene copolymers

N B A Prasetya, N Ngadiwiyana, I Ismiyanto, P R Sarjono

Chemistry Department, Faculty of Sciences and Mathematics, Diponegoro University, Semarang, Indonesia

Corresponding author: nor.basid.prasetya@live.undip.ac.id

**Abstract.** Synthesis of eugenol-divinylbenzene copolymers were carried out by reacting eugenol with various percent weight of divinylbenzene in a reactor at room temperature for 24 hours in the presence of sulfuric acid as a catalyst. Methanol was used to quench the copolymerization process. The effect of DVB mass on copolymer properties was studied based on molecular weight, thermal stability, surface morphology and swelling degree of the copolymers produced. The weight percent of the added DVB was responsible for the molecular weight of the copolymer by multiplying the site for propagation in the copolymerization process. In addition, the greater DVB used the better thermal resistance of polymer is obtained, which is possibly due to the higher number of DVB causing the larger cross-linked polymer network to increase the polymer bond thermal resistance. The swelling degree value was also affected by the number of crosslinkers used, in which make the polymer material become harder to expand. However, the influence of the weight percent of DVB was not seen on the copolymer morphology.

## 1. Introduction

The development of polymer industries is growing rapidly resulted in more widely utilization. Innovations have been created to produce new polymers or develop existing polymers with various modifications. Crosslink polymer is one of important engineering techniques for polymer materials[1]. Crosslinked polymers have been widely used in various fields, including in drug delivery, biomedical applications, ion exchange resins, membrane filtration and adsorbents [2-4]. Crosslinked polymeric material attracts a lot of attention because it generally has better properties than polymers without crosslinks, such as in swelling ratio, thermostability, number of pores, rigidity and mechanical strength[1, 5-7].

Eugenol (4-allyl-2-methoxyphenol) has high potency as a starting material in the polymerization process. This material is the main component in clove oil with a content of 70-90% and is easily isolated with high purity through separation using the acid-base principle[8]. Based on its chemical point of view, eugenol has allyl functional groups so that eugenol can be polymerized cationically in the presence of an acid catalyst, such as concentrated sulphuric acid or boron trifluoride. This polymerization leads to form a solid homopolymer called polyeugenol[9, 10]. In the presence of other compounds that have allyl group, a crosslinked copolymerization occurs to obtain a solid copolymer. Some crosslink agents have been successfully reacted with eugenol, including allyl eugenol[11], diallyl-4-allyloxy-5-methoxybenzene[12], or divinylbenzene (DVB)[4, 13].



DVB attracts attention because it has two allyl terminals which can be used in copolymerization to obtain polyeugenol-divinylbenzene (PEDVB), a net-like structure polymer[13]. This type of polymer becomes important because it is mechanically strong and resistant to heat and solvents attack. This material is widely used as a membrane carrier[3], antibacterial[13], and adsorbent[4].

So far, the effect of percent weight of divinylbenzene as crosslinking agent on the properties of PEDVB has not been widely reported in the literature. Thus, in this study, PEDVB with different percent weight of DVB were synthesized in the presence of sulphuric acid catalyst and the resulting polymers were investigated with respect to the functional groups, surface morphology and its size, swelling degree and thermostability.

## 2. Experimental

### 2.1. Materials

Eugenol, divinylbenzene (DVB), boron trifluoride etherate ( $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ), methanol, chloroform, anhydrous sodium sulfate were obtained from Merck and used as received without further purification. Aquadest was obtained from the Integrated Laboratory of Diponegoro University, Indonesia.

### 2.2. Instrumentation

The instrumentations used were set of laboratory glasswares, Ubbelohde viscometer, O'haus's digital balance sheet (Pioneer PA214), Fourier Transform Infra-Red (FTIR, Perkin Elmer Spectrum Version 10.03.06), Scanning Electron Microscopy (SEM, Phenom type Pro-X), and Thermogravimetry Analyzer (TGA, TG-DTA7300).

### 2.3. Procedures

2.3.1. *Synthesis of Eugenol-divinylbenzene copolymer (PEDVB)*. Eugenol (6 g, 36 mmol), DVB (with 5, 10, 15 and 20% relative weight to eugenol) and 5 mL chloroform were put into a three-neck flask while stirring. Then 2 ml of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  was added dropwise. During the reaction, the system was fed with nitrogen gas at room temperature. The reaction was allowed to take place overnight and end by adding 1 mL of methanol. The polymerization results were then dissolved in chloroform and then washed using distilled water until it reached neutral pH. Anhydrous  $\text{Na}_2\text{SO}_4$  was added to the organic layer and the solvent was evaporated. The residue obtained was then dried in a desiccator.

2.3.2. *Number-average molecular weight ( $M_n$ ) of copolymers*. The  $M_n$  of synthesized copolymers was determined using Ubbelohde capillary viscometer. Viscosity was measured at a concentration of about 1-5 mg/mL of the solvent. To obtain intrinsic viscosity values using "Least Square" method. From the least square equation, a straight line curve can be obtained, resulted in the intercept from the straight line called as intrinsic viscosity. Whereas the value of molecular weight can be obtained using the Mark-Kuhn-Houwink equation.

$$\eta = K.M^\alpha$$

Where K and  $\alpha$  are specific constants for the polymer, solvent, and temperature. The quantities K and  $\alpha$  are  $11 \times 10^{-3}$  mL/g and 0.725, respectively.

2.3.3. *Melting point analysis*. The melting point was measured using the Melting Point Apparatus (Fisher-Johns 220 VAC). The analysis of the functional groups produced was performed using Fourier Transform Infra-Red (FTIR, Perkin Elmer Spectrum Version 10.03.06), while surface morphology was analyzed by Scanning Electron Microscopy (SEM, Phenom type Pro-X).

2.3.4. *Thermal properties analysis*. Thermal analysis of polymeric materials was carried out using Thermogravimetry Analyzer (TGA, TG-DTA7300). The reference material used in the TGA analysis

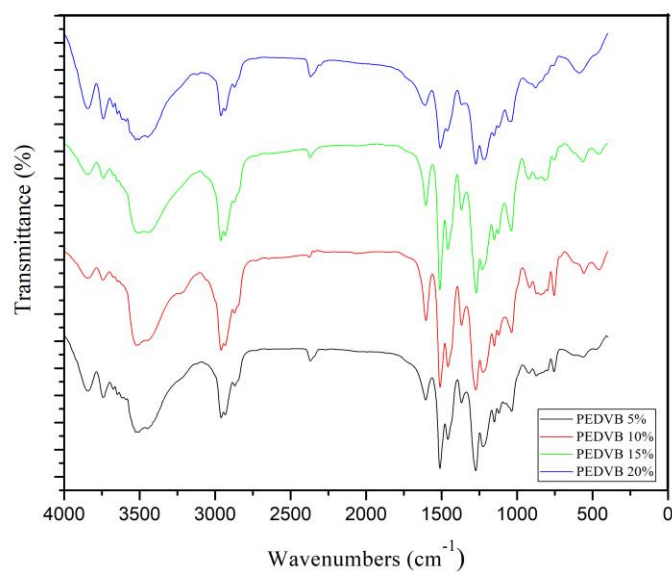
was platinum. TGA analyses were performed using temperature range of 50-500°C with a heating rate of 10°C per minute.

2.3.5. *Swelling ratio*. Swelling ratio measurements of the copolymers were carried out gravimetrically with the polymer material immerse in distilled water at room temperature for 24 hours.

### 3. Results and discussion

#### 3.1. Functional groups characterization

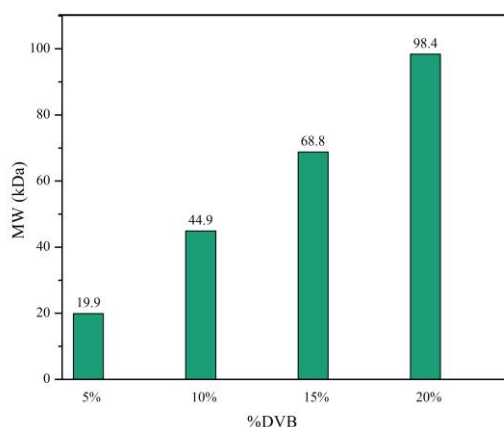
FTIR spectra of all synthesized PEDVBs is shown in Fig. 1. The spectra clearly show similar absorption at all wavenumbers. Eugenol has a typical absorption in the area of 1680-1620  $\text{cm}^{-1}$  from vinyl group absorption ( $-\text{C}=\text{C}-$ , stretching), as mentioned in the literature [9, 13, 14]. All synthesized PEDVBs do not show this absorption because the group has been used to form bonds with other monomers, eugenol or DVB, to form polymer bonds. Other absorptions that emerge show typical functional groups in PEDVB copolymers, such as absorption in the area of 3523.8  $\text{cm}^{-1}$  indicating the presence of hydroxyl groups,  $\text{C-H sp}^3$  at wavenumber of 2959.3  $\text{cm}^{-1}$ , and strain of  $\text{C-O}$  groups at wavenumbers of 1112.98 and 1152.3  $\text{cm}^{-1}$ . This evidence shows that the PEDVB copolymers have been successfully obtained.



**Figure 1.** FTIR spectra of synthesized PEDVBs

#### 3.2. Number-average molecular weight

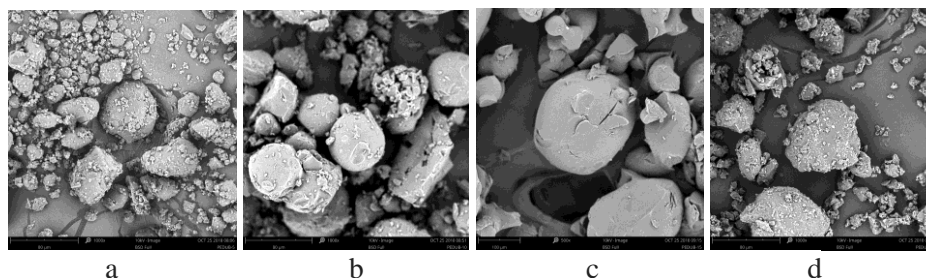
Molecular weight of polymer is important to analyze because it determines the polymers properties. Figure 2 shows that the molecular weight of the polymer is proportional to the percent weight of DVB used. The use of DVB by 5% produces PEDVB with  $M_n$  of 19.9 kDa, increasing DVB by 4 times also increases the molecular weight of the polymer by 4 times, which is 98.4 kDa. Clearly, the weight percent of the added DVB was responsible for the molecular weight of the copolymer by multiplying the site for propagation in the copolymerization process. As a result, the higher molecular weight of the copolymer is obtained.



**Figure 2.** The calculated molecular weight of PEDVBs

### 3.3. Surface morphology

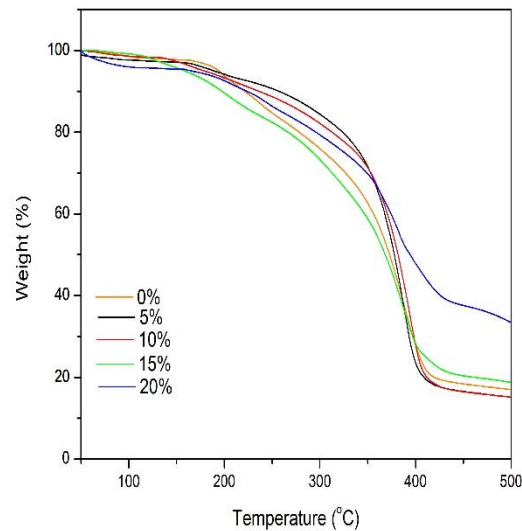
PEDVB materials obtained were analyzed using a Scanning Electron Microscope (SEM) with a magnification of 500 $\times$ . This analysis aims to determine the surface morphology of the material. The results of SEM analysis (Figure 3) show that the all PEDVB materials obtained have spherical morphology with a non-uniform size. Variations of DVB weight do not provide significant surface morphological differences.



**Figure 3.** Surface morphology of synthesized PEDVBs with DVB of (a) 5%, (b) 10%, (c) 15%, (d) 20%.

### 3.4. Thermal properties

The thermal resistance of synthesized PEDVBs was analyzed thermally using Thermogravimetry Analyzer (TGA). TGA analysis was performed to determine the weight loss of PEDVB material as a function of temperature. The analysis was carried out at a temperature range of 50-500 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C per minute under nitrogen atmosphere. Figure 4 presents the temperature dependence of the PEDVB copolymers with different %weight of DVB loading. The data shows the thermal degradation tendency of PEDVB shift towards higher temperature as the %DVB loading is increased. In other words, the greater DVB used the better thermal resistance of polymer is obtained. This is possibly due to the higher number of DVB causing the larger cross-linked polymer network to increase the polymer bond thermal resistance.



**Figure 4.** PEDVBs thermal resistance with DVB variation

### 3.5. Swelling degree

Swelling degree in polymeric material is one of the important parameters in determining compatible solvents primarily in the application of these polymers. Swelling degree data from PEDVB material (Table 1) shows that swelling degree polymer is a function of the amount of cross-linker content. The greater the cross-linker used, the lower the swelling degree value. This is probably due to more crosslinkers make it harder for the polymer material to expand.

**Tabel 1.** Swelling degree polymer values with variations in DVB

DVB variation	Swelling degree (%)
5%	42.7
10%	30.3
15%	19.6
20%	9.5

## 4. Conclusion

The results showed that PEDVB with different properties can be produced by variations of DVB as a crosslinking agent. The greater the DVB reacted produces a higher molecular weight polymer, swelling degree, and better thermal resistance. The weight percent of the added DVB was responsible for the molecular weight of the copolymer by multiplying the site for propagation in the copolymerization process. In addition, the greater DVB used the better thermal resistance of polymer is obtained, which is possibly due to the higher number of DVB causing the larger cross-linked polymer network to increase the polymer bond thermal resistance. The swelling degree value was also affected by the number of crosslinkers used, in which make the polymer material become harder to expand. However, the influence of the weight percent of DVB was not seen on the copolymer morphology.

## Acknowledgment

We gratefully acknowledge the Faculty of Sciences and Mathematics of Diponegoro University Semarang for the 2019 budget year Scheme funding with the contract number: 4843/UN7.5.8/PP/2019

**Reference**

- [1] Beveridge C, Sabiston A 1987 *Materials & Design* **8** 263-268
- [2] Chaiyasan W, Srinivas S P, Tiyaboonchai W 2015 *Mol Vis* **21** 1224-1234
- [3] Kiswandono A A, Siswanta D, Aprilita N H, Santosa S J, Hayashita T 2013 *Indonesian Journal of Chemistry* **13** 254-261
- [4] Silvianti F, Siswanta D, Aprilita N H, Kiswandono A A 2017 *Jurnal Natural* **17** 108-117
- [5] Bothe N, Döscher F, Klein J, Widdecke H 1979 *Polymer* **20** 850-854
- [6] Mane S, Ponrathnam S, Chavan N 2015 *Canadian Chemical Transactions* **3** 473-485
- [7] Uhl F M, Levchik G F, Levchik S V, Dick C, Liggat J J, Snape C E, Wilkie C A 2001 *Polymer Degradation and Stability* **71** 317-325
- [8] Cortés-Rojas D F, de Souza C R F, Oliveira W P 2014 *Asian Pacific Journal of Tropical Biomedicine* **4** 90-96
- [9] Prasetya N B A, Ngadiwiyanana, Ismiyanto, Sarjono P R 2019 *IOP Conference Series: Materials Science and Engineering* **509** 012101
- [10] Ngadiwiyanana N 2005 *Jurnal Kimia Sains dan Aplikasi* **8** 43-47
- [11] Ngadiwiyanana N, Ismiyanto, Gunawan, Sarjono P R, Adiwibawa Prasetya N B, Kusworo T D, Susanto H 2019 *IOP Conference Series: Materials Science and Engineering* **509** 012098
- [12] Yoshimura T, Shimasaki T, Teramoto N, Shibata M 2015 *European Polymer Journal* **67** 397-408
- [13] Prasetya N B A, Ngadiwiyanana, Ismiyanto, Sarjono P R 2019 *IOP Conference Series: Materials Science and Engineering* **509** 012102
- [14] Dhoot G, Auras R, Rubino M, Dolan K, Soto-Valdez H 2009 *Polymer* **50** 1470-1482