Synthesis of copoly-(eugenol−stearyl acrylate) via cationic polymerization

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Abstract. Synthesis of copoly-(eugenol−stearyl acrylate)/Eg-co-SA was carried out through cationic copolymerization. Copolymerization was conducted using H₂SO₄ initiator, at room temperature (28-30 °C) and under nitrogen atmosphere. Structure of Eg-co-SA was identified by FTIR and ¹H-NMR spectroscopy. Average molecular weight (Mᵥ) of Eg-co-SA was measured by Ostwald Viscometer at constant temperature 28 °C. Morphology and thermal properties of Eg-co-SA was characterized using SEM and DSC. Analysis of EG-CO-SA structure by using FTIR showed disappear of characteristics absorption of the vinyl group (−CH=CH₂) in 1638-1634 cm⁻¹ and 998-977 cm⁻¹ wave number. The success of synthesis was supported by the disappear of the ¹H-NMR vinyl proton signal at 5.7-6.39 ppm and the appearance of new proton signal of single bond carbon (C−C) at 1-2.6 ppm. The increasing the weight of SA in Eg-co-SA synthesis gives changes in average molecular weight (Mᵥ) and Degree of Polymerization (DP). The results of determining the average molecular weight of Eg-co-SA 2%, 4% and 5% were obtained 49812.10, 67709.25 and 75283.59 g/mol, respectively. Meanwhile, the degree of polymerization were 102, 139 and 154 for 2%, 4%, and 5% Eg-co-SA, respectively. Morphology of Eg-co-SA showed that increasing of SA weight resulted spongy surfaces with 0.35-10.46 µm diameter. Thermal analysis of Eg-co-SA showed that increasing of SA weight influenced thermal stability from 399 °C to 386 °C, when the SA content increase from 2% to 4%.

1. Introduction

Polymers have been perceived in all aspect of human life, due to many benefits offers including chemical and impact resistance, easy to be shaped, to be molded and also shiny. [1]. Currently, most of the polymers used are derived from petroleum and plastic so they are non-renewable, non-biodegradable, and pollute the environment [2]. This problem can be solved by utilizing natural material-based polymers. Eugenol which is a component of renewable natural resources can be explored further to be modified polymer material to produce an environmentally friendly polymer. Eugenol has several reactive groups i.e., allyl, methoxy, and hydroxy groups that can be converted into other more useful compounds [3]. Eugenol is widely used as a starting material for the manufacture of other compounds that have high economic value [4,5]. The modification of the active group on eugenol was carried out to increase applicability such as a polymer material [6,7]. Eugenol has a structure similar to styrene, which has a substituted vinyl (−CH=CH₂) group of aromatic compounds. Polymer synthesis with Styrene as a starting materials has been performed by previous investigators. Jang & Kim [8] has undertaken research on the synthesis of styrene with the second monomer of alkyl acrylate, such as Stearyl Acrylate (SA). The reason on using alkyl acrylate as a second monomer is its tendency to be in crystalline phase that cause decreasing of hydrophobic ability. The SA compound has a long alkyl chain (C18) and can produce the product in the amorphous phase so as
to enhance its hydrophobic capacity [9]. In addition, SA has a gel type structure and consists of elastic tissue and has a high degree of swelling to oil or non-polar solvents [10,11]. Judging from the similarity of the structure, the starting materials of styrene can be replaced with eugenol. Furthermore, there can be copolymerization between eugenol and SA. Copolymerization with an eugenol or SA starting may be proceeded through radical or cationic mechanisms. Copolymerization is radically a reactive and rapid method [12]. The use of radical copolymerization methods has been done by Jang & Kim [8] using AIBN initiator and Yang et al. [13] using BPO initiator. Nevertheless, according to Satoh et al. [14], phenolic compounds inhibit radical formation because of antioxidant activity. Kadoma et al. [15] explains that BPO initiators are less effective when used in eugenol and isoeugenol polymerization than in AIBN initiators.

Synthesis of polymers with eugenol or SA starting materials has different properties and characteristics. Therefore, the application of both polymers may be different whether for antibacterials, heavy metals absorbers, coating agents, or oil absorbents [11,16,17,18]. Jang & Kim [8] performed synthesis of styrene and lauryl acrylate with or without crosslinking agent of DVB obtained glass transition temperature (Tg) which difference was not so significant that in this study can be done without using crosslinking agent. Oil absorption test on CEMA/SA copolymer obtained result that higher SA content hence hydrophobicity ability will be higher. This is supported by the high average molecular weight [9]. Poly (eugenil methacrylate) has been successfully synthesized by Deng et al. [6] in the form of microsphere with a high absorption capacity, large absorption rate, and can be regenerated. Therefore, by utilizing the abundance of eugenol in nature as well as the high hydrophobic capability of stearyl acrylate, a study was conducted on the synthesis of copolymer (Eugenol-SA) to obtain a renewable and environmentally-friendly copolymer.

The synthesis of eugenol copolymers with SA can be carried out using a cationic copolymerization method. Previous studies have successfully conducted eugenol-based polymerization without solvent media at room temperature. The initiator used in this copolymerization was H$_2$SO$_4$. Sulfuric acid is a strong Bronsted acid initiator for cationic polymerization, so it can apply vinyl groups to eugenol or SA monomers. Both eugenol and SA have secondary C-atoms present in the vinyl group. However, when viewed from its structure, SA has a larger steric because of long aliphatic chain that allows H$^+$ from H$_2$SO$_4$ to initiate vinyl groups in eugenol first. Its initiates eugenol sprites to be attacked by vinyl in a nucleophilic SA monomer. The addition of SA at various eugenol composition may affect physical and chemical properties of the prepared copolymer (Eg-co-SA).

2. Experimental Methods

2.1. Materials
Eugenol (Eg) was obtained from PT. Indeso Aroma, Indonesia. Stearyl Acrylate (SA) was obtained from Aldrich Chemical Co., Germany. Sulphuric Acid (H$_2$SO$_4$), Chloroform, Sodium Chloride, and Na$_2$SO$_4$ were obtained from Merck. SA was purified by washing with 5% aqueous sodium hydroxide and aquadest.

2.2. Instruments
Fourier Tranform Infra Red (FT-IR, Shimadzu type FT-IR-8201 PC), NMR Spectrometer Agilent 400 Mhz, Scanning Electron Microscopy (SEM, Inspect-S50 EDAX), Differential Scanning Calorimetry (DSC, Linsesis tipe PT 1600).

2.3. Synthesis of Eg-co-SA
Eugenol 5 g was pured into a three-necked flask, then SA was added with a variation of 2%; 4%; and 6% (w/w) of eugenol weight. Polymerization was carried out at room temperature (28-30°C) and nitrogen atmosphere conditions. The copolymerization was conducted for 4 hours, in which every 1 hour 0.25 mL of H$_2$SO$_4$ initiator was added. Termination was done by adding 1 mL of methanol. The polymerization results were extracted with chloroform-distilled to neutral pH. The organic phase was
dried with anhydrous Na2SO4, then the solvent was evaporated using a rotary evaporator and was dried in a desiccator. Structural analysis was performed using FTIR and NMR, while characterization was performed with SEM and DSC. The average molecular weight of the polymer was determined by the viscometric method.

2.4. Determination of Molecular Weight Average of Eg-co-SA
Determination of molecular weight average of biopolymer was done by measurement of flow time with Ostwald Viscometer at room temperature with chloroform as blank. The variation concentration were 0.01 g/mL; 0.005 g/mL; 0.0025 g/mL and 0.00125 g/mL. From the time flow data of eugenol-alkyl acrylate solution and pure chloroform solvent, then calculated relative viscosity ($\eta_r$) and its specific viscosity ($\eta_s$). Thereafter, a graph $\eta_s$ vs C was obtained for obtaining an intrinsic viscosity [$\eta$]. The relative molecular mass was calculated by the Mark-Houwink equation (equation 1), with k value of $11 \times 10^{-3}$ and a = 0.725.

$$\log [\eta] = \log K + a \log M_v$$

\[\eta\] = intrinsic viscosity

$M_v$ = Molecular Weight Average

K = specific constants of polymer

a = specific constants of polymer solution in solvent (0<a<1)

3. Results and Discussion

3.1. Synthesis of Eg-co-SA
Synthesis Eg-co-SA on weight variation SA as much as 2%, 4% and 6% by weight of eugenol, obtained a solid product. The weight and % yield are presented in Table 1.

| Copolymer     | initial weight (g) | Product weight (g) | % yield |
|---------------|--------------------|--------------------|---------|
| Eg-co-SA 2%   | 5                  | 3.81               | 74.67   |
| Eg-co-SA 4%   | 5                  | 3.00               | 57.73   |
| Eg-co-SA 6%   | 5                  | 0.99               | 18.64   |

Eg-co-SA solubility was tested in several solvents. The test produces soluble Eg-co-SA in acetone, chloroform, ethanol, methanol; partially soluble in diethyl ether; as well as insoluble in aquades and hexane. This indicates that Eg-co-SA is semi-polar because in addition to having long alkyl chains, Eg-co-SA also has an O-H group on eugenol and -C=O on SA, so it can not dissolve in aquades (polar) and hexane (non polar).

Mechanism of cationic copolymerization through 3 steps; (1) initiation (2) propagation (3) termination [12]. The initiation stage occurs when concentrated H2SO4 is added to the mixture of eugenol and SA. Atoms H and O on H2SO4 have a high electronegativity difference so that the O atom can pull the electrons from the H atom which causes a positively charged partial H atom. This positive partial H causes electron phi in the nucleophilized vinyl group to become carbocation. Both eugenol and SA, both have C-secondary on their double bonds (-CH=CH2). Since both C atoms have the same reactivity, then initiation can occur in eugenol and SA. The initiation process of the two monomers is shown in Figure 1 (a) and (b). However, it is possible that eugenol is initiated first because the eugenol structure has a smaller steric than SA.
Figure 1. proposed initiation reaction on (a) Eugenol; (b) SA

Chain carrier was a carbocation, so stable carbocation was needed to increase the propagation rate [19]. The double bond on the SA will attack the carbocation and form a new carbocation. And so on until the extension of the copolymer chain. This process was called propagation (Figure 2). The termination of copolymerization was carried out by adding methanol. Methanol (CH\textsubscript{3}OH) had a free electron pair on the O atom, then the O atom will pull the electrons from the H atom so that the O atom is partially negative. Atom O with this negative partial charge was very nucleophilic in that it can attack the propagation carbocation. This makes the carbocation inactive and the copolymerization reaction stalled. Proposed termination reactions are shown in Figure 3.

Figure 2. One proposed propagation reaction on Eg-co-SA synthesis
3.2. Analysis structure of copolymer

Synthesis of Eg-co-SA was identified with FTIR. The functional group analysis of the copolymer product, the initial compound of eugenol and SA as shown in Table 2. Based on the FTIR analysis (Table 2) showed that the absorption loss of C = C from the vinyl group in the Eg-co-SA copolymer. This was indicated the success of Eg-co-SA synthesis.

| Functional groups       | Eugenol | SA   | Eg-co-SA 2% | Eg-co-SA 4% | Eg-co-SA 6% |
|-------------------------|---------|------|-------------|-------------|-------------|
| O-H stretch             | 3441    | -    | 3442        | 3440        | 3427        |
| –CH2— methylene         | 2974-2839 | 2849 | 2870, 2843  | 2870, 2849  | 2870, 2845  |
| C=O stretch             | -       | 1720 | 1708        | 1705        | 1710        |
| C=C stretch vinyl        | 1639; 995 | 998,977 | -          | -           | 989         |
| C=C bend aromatic       | 1610    | -    | 1602        | 1601        | 1601        |
| C-H stretch aromatic     | 3003    | -    | -           | -           | -           |
| C-H bend aromatic       | 853-817 | -    | 869-816     | 872-816     | 872-815     |
| C-O-C stretch           | 1264-1034 | 1298-1018 | 1271-1032  | 1273-1034  | 1278-1034   |
| –CH3 methyl             | 2974-2839 | 2916 | 2959,2930  | 2960, 2931  | 2965, 2930  |

Structural analysis using 1H-NMR was shown in Figure 4. Eg-co-SA proton signals do not show a chemical shift of 5.7-6.39 ppm which is the chemical shift of double bonds in eugenol and SA. This proves that eugenol and SA have reacted and the double bond has been converted into a single bond (C-C). This single bond is shown in a chemical shift of 1-2.6 ppm. In the chemical shear span, new proton signals appear which overlap each other due to the length of the copolymer chain formed. In addition, proton signals overlapping at 6.66-6.87 ppm chemical shifts indicate the presence of substituted aromatic groups. This shows that Eg-co-SA products have been formed.
Figure 4. Comparison of $^1$H-NMR spectra a) eugenol, b) SA and (c) Eg-co-SA

3.3. Influence of SA Addition to Eg-co-SA Characteristics

Determination of the average molecular weight of Eg-co-SA were using the viscomometric method. Measurement of viscosity using Ostwald viscometer and chloroform solvent. The result of determining the average molecular weight was shown in Table 3.

Table 3. Results of the average molecular weight determination of Eg-co-SA

| Copolymer   | Mv (g/mol) | DP  |
|-------------|------------|-----|
| Eg-co-SA 2% | 49812.10   | 102 |
| Eg-co-SA 4% | 67709.25   | 139 |
| Eg-co-SA 6% | 75283.59   | 154 |

$M_v =$ the average molecular weight  
$DP =$ degree of polymerization

Table 3 showed that the more SA weight was added, the average molecular weight of the copolymer (Mv) will be higher. Similarly, the degree of polymerization (DP) which had a linear relationship with Mv. The higher Mv of Eg-co-SA, the number of the degree of polymerization (DP) was also growing. The higher molecular weight of Eg-co-SA indicates that the longer the alkyl chain was attached to the copolymer. The length of the alkyl chain was one of the indicators for knowing the hydrophobic nature of the copolymer [8]. Based on the MV value in Table 3, it showed that 6% EG-CO-SA has the longest alkyl chain, so it had the highest hydrophobic properties.

The morphology of 2%, 4% and 6% Eg-co-SA were analyzed using SEM as presented in Figure 5. The addition of SA weight caused Eg-Co-SA morphology to be more hollow. Jang and Kim [8] states that
SA has a sponge-like structure so that the addition of SA can form a cavity on the resulting copolymer. The presence of a cavity in the copolymer may provide space for absorption (Rojo et al., 2006).

![Image](image1.png)

**Figure 5.** Morphology of (a) Eg-co-SA 2%, (b) Eg-co-SA 4% and (c) Eg-co-SA 6%

The thermal properties of Eg-co-SA of 2%, 4% and 6% were shown by the DSC curve in Figure 6. The results of the analysis with DSC resulted in melting point temperature (Tm) and crystallization temperature (Tc). The presence of Tm and Tc on the DSC spectra indicates that Eg-co-SA had a semicrystalline form.

The melting point (Tm) on the thermogram showed the endothermic properties. Eg-co-SA 2% thermogram showed the highest temperature, which was 399 °C, because Eg-co-SA 2% had a more rigid physical properties so it takes a high temperature to melt it. As for Eg-co-SA 4% and 6%, had the same Tm, that was equal to 386 °C. The thermal stability of Eg-co-SA 2% was higher than Eg-co-SA of 4% and 6%.

The temperature of crystallization of each variation indicates a temperature not much different. Thermogram of Eg-co-SA 2%, 4% and 6% respectively show a crystallization temperature of 486 °C, 486 °C and 482 °C.

![Image](image2.png)

**Figure 6.** Termogram of (a) Eg-co-SA 2%, (b) Eg-co-SA 4% and (c) Eg-co-SA 6%
4. Conclusion
The Eg-co-SA synthesis can be carried out through cationic copolymerization using H$_2$SO$_4$ initiator and without solvent, supported by loss of uptake at 1638-1634 cm$^{-1}$ by FTIR analysis and loss of $^1$H-NMR proton signal at 5.7-6.39 ppm of chemical shift of vinyl group. The addition of SA weight will increase the degree of polymerization, the surface was more hollow and will affect its thermal properties.

5. References

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